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Transition Metal-Catalyzed Living Radical Polymerization: Toward Perfection in Catalysis and Precision Polymer Synthesis

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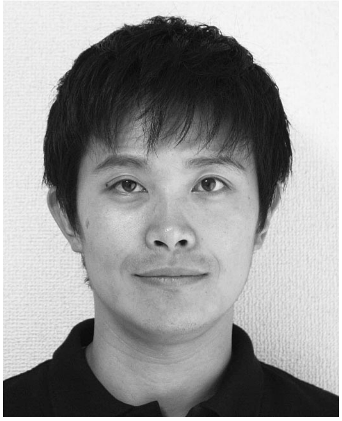
1. Introduction

Precision control of radical polymerization, or living radical polymerization, has been among the most important and long-waited subjects in polymer chemistry and macromolecular synthesis. Given the inherent nature of "free" radical species that tend to undergo bimolecular termination and disproportionation, along with their poor chemo- and regioselectivity in organic reactions, pessimistic views have prevailed for a long time. Since the 1980s and the 1990s, however, first gradually and then very rapidly, promising methods began to emerge, and in 2009, polymer chemists are certainly confident that one can now possess a variety of methodologies for precisely controlled and often living radical polymerizations. For these methods, numerous reviews and accounts are available (see below).[1−9]

In general, almost all of the current methods for living radical polymerization are based on a seemingly common concept, the reversible and dynamic equilibrium of a radical growing species with a dormant species (Scheme 1).[1] The dormant species in this context is defined as a covalent species (with an appropriate leaving group) that is stable enough to elude side reactions and thereby incapable of propagation but is capable of generating a true growth-active intermediate (propagating or growing species) by dissociating the leaving group upon chemical catalysis or physical stimuli (heat or light). In the authors' view, a considerable number of living or controlled polymerizations via ionic and other related mechanisms also rely on this concept.[1]

Typical dormant species for radical polymerization include alkyl halides with a conjugating and radical-stabilizing α-substituents such as 2-bromo-2-methylpropionates (bromoisobutyrates) [$(CH_3)_2CBrCO_2R$; R = alkyl, etc.], which is considered as a precursor of methacrylate radicals via dissociation of the bromine as a leaving group in the presence of a catalyst. Under selected conditions, a dormant species thus generates a growth-active radical species to initiate radical propagation, and a key to precision reaction control is the reversibility and dynamic equilibrium in this process assisted by catalysis or physical stimulus, namely, sooner or later the radical intermediates are, and should be, "capped" with the bromine and other leaving groups, to regenerate the dormant species. Equally important, the dormant-active species equilibrium is shifted to the former, retaining a low instantaneous concentration of the latter, while the exchange between the two is faster than the concurrent propagation. Combination of these conditions leads to fine control of radical polymerization to give macromolecules of well-defined molecular weights, main-chain structure, terminal groups, along with very narrow molecular weight distributions, though the mechanistic implication of the equilibrium stays outside of the scope of this article. As will be discussed in the following sections, the reversible generation of radicals involve metal catalysis,[1−6] stable radicals (as leaving groups),[7] addition−fragmentation chain transfer,[8] metal−carbon bonds,[9] among many others.



Makoto Ouchi, born in Osaka, Japan (1973), received his B.S. (1996), M.S. (1998), and Ph.D. degrees (2001) from Kyoto University. His doctoral study was on stereo- and regiospecific cationic polymerizations via designed Lewis acids and counteranions under the direction of Professor Mitsuo Sawamoto, during which he received a Research Fellowship for Young Scientist of the Japan Society for the Promotion of Scientists (1998−2001). In 2001−2004, he worked in Toyota Central R&D Laboratories, Inc., as a researcher to develop poly(lactic acid)-based materials for automobile parts. In 2004, he moved to the Graduate School of Engineering of Kyoto University as an Assistant Professor of the Department of Polymer Chemistry. He was a visiting associate at California Institute of Technology working with Professor David A. Tirrell (2007−2008). His current research interests include precision sequence control in chain-growth polymerizations through design of monomers, catalysts, and polymerization fields.

Takaya Terashima, born in Shiga, Japan (1978), received his B.S. (2002), M.S. (2004), and Ph.D. degrees (2007) from Kyoto University. His doctoral study was on development of multifunctional designer catalysts via living radical polymerization, especially focused on star polymer catalysis and tandem catalysis, under the direction of Professor Mitsuo Sawamoto, where he received a Research Fellowship for Young Scientist of the Japan Society for the Promotion of Scientists (2004−2007). He received Student Poster Board Award in SAS 2006 Kyoto. He joined the faculty of Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University in 2007 as an assistant professor. His research interests include functionalized catalysts toward precision polymer synthesis and organic reaction.

In the period of 1994−95, we found that a class of organometallic complexes of late transition metals, typically divalent ruthenium [Ru(II)], are excellent catalysts for such a dormant-active radical equilibria and thereby catalyze what we now call "transition metal-catalyzed living radical polymerization", which meets virtually all the phenomenological criteria for living polymerization.[1−3] Nearly the same time Wang and Matyjaszewski reported a similar process with copper catalysis and coined it as atom transfer radical polymerization or ATRP.[4−6] To summarize the discovery and

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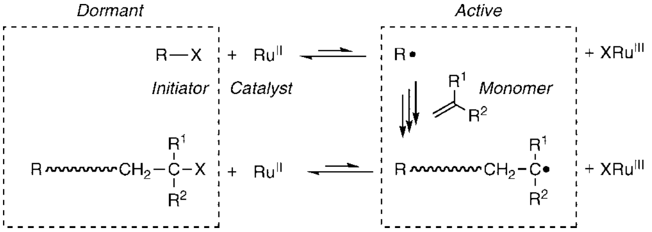
Scheme 1. Metal-Catalyzed Living Radical Polymerization



the early development of these metal-catalyzed polymerizations, in 2001, we published our first comprehensive review in this journal, and the current review may be considered as a sequel that covers the latest progress in the field after 2001.

Chronologically, the first review covers the period of 1994–2000, while the second covers 2001–2008. If we arbitrarily call these periods phase I and phase II, respectively, a comparison of our two reviews shows some notable and interesting trends in the metal-catalyzed living radical polymerizations: First, our phase I review involved 460 references, while the phase II article now comprises over 970 publications, indicating a fast and steady growth and extension of the field on going from phase I to phase II (the references herein do not include a considerable number of papers for copper-based catalysis). Second, in our view, research interest has also been shifting during the two periods. The major discovery and developments in these phases may be summarized as follows:

Phase I (1995–2001)

- Discovery of metal-catalyzed living radical polymerization
- Establishment of the dormant-active species concept
- Systematic development of metal catalysts
- Systematic development of initiators
- Living radical polymerization of common conjugated monomers
- Precision polymer synthesis for block, end-functionalized, star, and other polymers
- Aqueous-phase systems such as dispersion and emulsion living polymerizations

Phase II (2001–2008)

- Extension of catalysis into iron-based catalysts (abundant and safer)
- Extremely active catalysts (reduction of catalyst concentration)
- Removal, recovery, and recycling of metal catalysts
- Living radical polymerizations of functionalized monomers
- Precision synthesis of (multi)functional polymers
- Bidirectional interaction with organic and organometallic chemistry particularly in catalyst development
- Extended application in multidisciplinary areas notably in biology, biochemisty, medicine, and nanotechnology
- Combination with other controlled systems (polymerizations/ reactions)

These trend shifts would not necessarily be specific for metal-catalyzed living radical polymerizations but certainly for living and controlled radical polymerizations in general; however, for the former one can see that the shifts have certainly been driven by a few specific factors that include the following:

(a) A fast extension to the metal-catalyzed living radical polymerization of a wide variety of (nonprotected) functionalized monomers, while retaining the advantages inherited from free radical polymerization such as simplicity and versatility

(b) Establishment of reliable, reproducible, and robust living radical polymerizations via metal catalysis, now recognized as common "synthetic tools", so simple, versatile, and user-friendly as to prompt many researchers in disciplines outside polymer chemistry to use for their own purposes

(c) A fast expansion of interest and applications in biochemistry, chemical biology, biology, and medicinal science, along with nanotechnology, as seen in "bioconjugation" or "hybridization" of synthetic functional polymers with enzymes, proteins, etc., for medicine and diagnosis. It is particularly of importance, as implicated in item c, that these trends will encourage and promote new vistas and direction of future polymer chemistry and science, beyond its traditional disciplinary boundary for further development and deepening.

2. Design of the Initiating Systems

2.1. Required Initiating Systems

By around 2000, when we submitted a comprehensive review[1] about metal-catalyzed living radical polymerization to *Chemical Reviews*, the targeted subjects had been directed to fundamental ones, for example, improvement in control over molecular weight and its distribution, quantitative polymerization, block copolymerization, versatility of controllable monomer, clarification of the mechanism, etc. Although these are now still important and should be examined, interest or demands for living radical polymerization have shifted to more applicable and advanced ones, along with evolution of catalytic systems, Figure 1 summarizes general features required for the initiating systems of metal-catalyzed living radical polymerization from such viewpoints and the predicted strategies for these subjects. Before going into details, we will refer to these aspects.

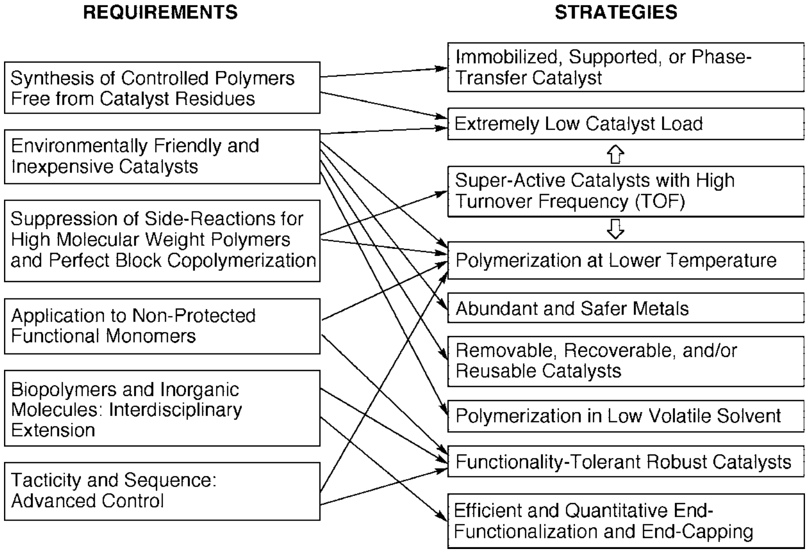


Figure 1. Requirements for initiating systems.

2.1.1. Synthesis of Controlled Polymers Free from Catalyst Residues

The synthesis of controlled polymer without catalyst contamination would be an important issue to be resolved toward actual applications of metal-catalyzed living radical polymerization, since metal residues are sometimes toxic and affect polymer functions. This problem would be more severe for biomedical and precision mechanical applications. Immobilization of catalysts could be a promising strategy as with polyolefins and in catalyst recycling. However, the heterogeneity of these catalysts might be disadvantageous in control over molecular weight, because such an immobilized catalyst causes difficulty in equal catalysis for generating polymer chains under dynamic catalysis. Phase-transfer catalysts would be also interesting for catalyst removal and recycling, though rather impractical in applications. Behind these trends, highly efficient catalytic systems have been focused, where the polymerization is controlled even with extremely small amount of catalyst (e.g., less than 10 ppm), because such a system possibly does not require catalyst removal if the catalyst concentration is low enough to be negligible for toxicity and polymer functions. For this, the catalytic cycle or the so-called turnover frequency should be fast (high) efficiently accelerated and rotated.

2.1.2. Environmentally Friendly and Inexpensive Catalysts

Environmentally friendly and less expensive systems are required in actual applications. For this issue, a decrease in catalyst amount or recycling without loss of catalytic functions would be desired, because metal catalysts are often expensive. Choice of the central metal is also significant for global environment: a precious or rare metal should be preferably replaced with an abundant one if similar performance is obtained. Among metals used in metal-catalyzed living radical polymerization, iron (Fe) would be ideal from this viewpoint. Polymerization at ambient temperature would be favorable if activity is not lost seriously, because it contributes to saving energy costs. For solution polymerization, use of low volatility solvent might be favored from environmentally consideration.

2.1.3. Suppression of Side Reactions for High Molecular Weight Polymers and Perfect Block Copolymerization

In living radical polymerizations, complete elimination of side reactions is difficult, distinguished from living anionic polymerizations, and it gets more severe for polymerization with lower concentration of initiator or at high monomer conversions in polymerization. This in turn causes difficulty in syntheses of high molecular-weight polymer (MW > 10^6) with low polydispersity and quantitative sequential block copolymerization. To overcome the difficulty, an efficient and fast catalytic cycle between dormant and active species is required, and therefore two antithetical processes, that is, "activation" to radical species and "deactivation" to dormant species, need to be catalytically promoted. Lowering the temperature would be useful for suppression of side reactions, if the catalytic activity is not seriously lowered.

2.1.4. Application to Nonprotected Functional Monomers

Radical species are inherently tolerance to functional groups, in contrast to ionic intermediates, and thus functional monomers can be directly polymerized, which is advantageous to living radical polymerization toward precision syntheses of functional polymers. However, in metal-catalyzed systems, functional groups are poisonous for some catalysts, and therefore polymerization control is sometimes difficult for functional monomers. This subject is rather specific to the metal-catalyzed system, relative to metal-free systems including nitroxide-mediated (NMP),[7,10] reversible addition−fragmentation chain transfer (RAFT),[8,11] and ogranotellurium-mediated (TERP)[9,12] polymerizations. The tolerance to functional groups is partly dependent on the central metal, while to be improved by ligand design.

2.1.5. Biopolymers and Inorganic Molecules: Interdisciplinary Extension

In living polymerization, all polymer chains carry an initiator moiety at the α-end because chain transfer is absent, thus lead to end-functionalized polymers from functionalized initiators. Due to tolerance against functional groups, living radical polymerization is now a powerful "tool" for incorporating controlled polymers into biomoleules and inorganic molecules, as seen in "bioconjugation"[13,14] or "organic/inorganic hybridization".[15] Metal-catalyzed living radical polymerization is mostly initiated from a ubiquitous carbon−halogen bond adjacent to a conjugating substituent, and its introduction is more facile than the initiating functionalities for other living radical polymerizations. Furthermore, the initiating efficiency is relatively high, and thus suitable for quantitative connection. This should be one of the reasons why the metal-catalyzed systems have been employed for variety of interdisciplinary applications. Efficient and quantitative incorporation of the initiating site without breaking the target molecule is essential for this purpose.

2.1.6. Tacticity and Sequence: Advanced Control

As reviewed by Kamigaito and Satoh in this issue,[16] stereospecific *and* living radical polymerization has received considerable attention over the years toward development of more advanced polymers of well-defined structures. As stereospecificity is usually drawn at lower temperature, active living polymerization systems even at low temperature are required for simultaneous control of molecular weight and tacticity. Inspired by perfectly controlled structures seen in natural polymers, advanced control over another class of selectivity is also getting targeted for polymerization: monomer sequence or the controlled sequence of repeat units, and thereby of functional groups along the main chains. For the untrodden control, some additional mechanisms might be combined with living polymerization, where polymerization would be performed at lower temperature to draw the selectivity for the next coming monomer.

As shown here, recent interests for metal-catalyzed living radical polymerizations have been certainly directed to more advanced control and practical applications. In focus on these aspects, initiating systems for the polymerization, mainly developed for the past 8 years from 2001−2008, will be reviewed below.

2.2. Transition Metal Catalysts

2.2.1. Overviews of Catalysts

As already established,[1−6] a catalyst in metal-catalyzed living radical polymerization contributes to catalysis for two antithetical processes (Scheme 1), that is, activation and deactivation of a dormant and a growing polymer terminal respectively, via a one-electron redox. A metal complex with a lower oxidation state first activates the carbon−halogen bond in an initiator, or the corresponding dormant terminal to generate a growth-active radical species. In the activation process, the catalyst is oxidized to a one-electron higher valence state upon abstracting the halogen, to form a new metal−halogen bond. While the catalyst remains the higher valence state of the catalyst, the radical species can propagate by repeating radical-addition to monomers. After propagation with some monomers, the oxidized catalyst returns the halogen to a radical intermediate by capping or giving a dormant species, in which it is reduced by one electron to regenerate the original complex of the lower oxidation state. The metal complex repeats such a one-electron redox catalytic cycle to mediate controlled polymerization, and because of the reversible and dynamic equilibrium between the dormant (carbon−halogen) and the active (carbon radical species), the concentration of the active growing species is consequently kept low (probably two orders magnitude lower than in a conventional radical polymerizations), leading to suppression of side reactions (e.g., coupling and disproportionation), as generalized for other living or controlled polymerizations. Importantly, this catalytic cycle in the metal-catalyzed radical polymerization consists of a "one-electron" transfer, distinguished from other oxidation/reduction catalysis via two-electrons transfer, typically as seen in some palladium-catalyzed coupling reactions involving an oxidative addition and subsequent reductive elimination.[17] Therefore, the central metal needs to take at least two states of valence with one electron difference, even though either state is unstable to be isolated, and also carry moderate a halogen-affinity to accept and release a halogen atom. From these requirements, most likely, late transition metals of group 8−11 have been employed for the metal-catalyzed living radical polymerization; most typically, these metals include iron, nickel, ruthenium, and copper.

2.2.2. Ruthenium

Ruthenium complexes are the first class of catalysts for metal-catalyzed living radical polymerization, as first reported in 1995.[18] The ruthenium catalyst employed therein is a divalent Ru(II) complex, typically carrying two anionic ligands, such as halogens, conjugated carbanions, and phenoxy anions, as well as some neutral ones as phosphines, amines, cymene, and carbenes. The large capacity of the coordination space and the inherent tolerance (low oxophilicity) to functional groups of the Ru(II) complexes allow coordination of various ligands, leading to a broad scope in catalyst design for the modulation of electron density and the steric environment in the ruthenium center. It is noteworthy that some ruthenium complexes allow the formation of ruthenium−carbon bonds, which enables the direct "communication" of the metal center with substituents and a wider range of "organic" design than other metal complexes mainly consisting of metal−heteroatom bonds.

Dichlorides. $RuCl_2(PPh_3)_3$ (Ru-**1**) is the first example of ruthenium complexes catalyzing living radical polymerization,[18] which was originally proved to catalyze Kharasch addition reactions,[19] a model of the polymerization (Figure 2). It certainly gives well-controlled polymers for some monomers in conjunction with cocatalysts (additives), such as aluminum isopropoxide and amines,[18,20−31] but usually a little higher amount is needed ($[Ru]_0/[Initiator]_0 = 1/2$) for sufficient catalytic activity than the later generation of Ru(II) complexes, for example, half-metallocene derivatives (see below). An ionic complex (Ru-**2**) was developed as a hydrophilic catalyst evolving from Ru-**1**, where one phenyl of the PPh_3 in Ru-**1** is replaced with that carrying a sulufonic acid sodium salt at the meta-position.[32] It is effective for catalyst removal in the polymerization of methyl methacrylate (MMA), as well as those of hydrophilic monomers, for example, 2-hydroxyethyl methacrylate (HEMA) in methanol. The triazol-5-ylidene complex (Ru-**3**) showed a high activity for MMA with the assistance of amine additive (n-Bu_2NH) to give narrow molecular weight distributions ($M_w/M_n < 1.3$) within 24 h.[33]

Half-Metallocenes. Half-metallocene-type ruthenium complexes with indenyl (Ru-**4**)[34−36] and pentamethylcyclopentadiene (Cp*, Ru-**5**)[35,37] ligands are representative of active catalysts for living radical polymerization giving quite narrow molecular weight distributions and well-defined block copolymers. Their superior catalysis supposedly originates from

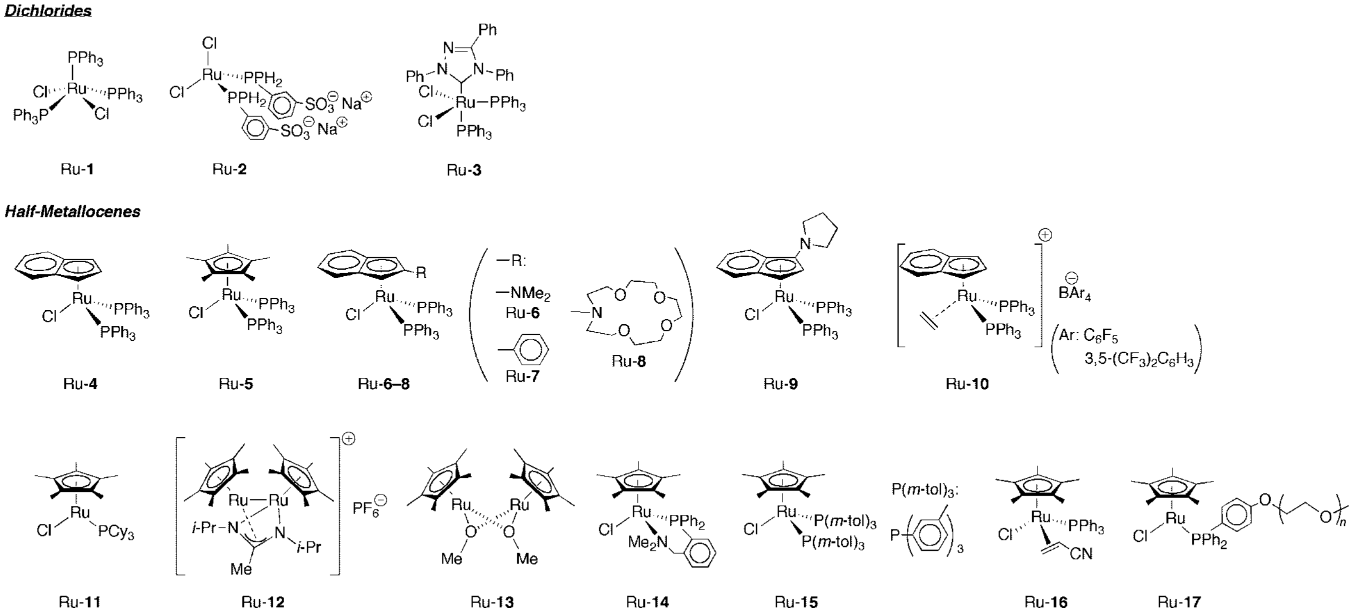


Figure 2. Ruthenium catalysts 1.

a fast halogen-exchange reaction, as supported by model reactions with an initiator or a model compound for the growing chain (dormant species), analyzed by ^{1}H NMR along with the low redox potential by cyclic voltammetry (CV).[35] Toward further enhancement of the catalytic activity for Ru-**4**, an electron-donating dimethylamino group was introduced onto the indenyl ring (Ru-**6**), and indeed this complex induced a faster polymerization (10 vs 16 h for >90% conversion) to give narrower molecular weight distributions ($M_w/M_n = 1.07$ vs 1.13) than does the nonsubstituted derivative (Ru-**4**).[38] Similarly, the introduction of other electron-donating groups, for example, phenyl (Ru-**7**) and aza-crown (Ru-**8**), was also effective to improve catalytic activity.[3] The position of these substituents seems to be important for polymerization control, as indicated by a poorer control with Ru-**9** with a pyrrolidinnyl group at the 1-position ($M_w/M_n > 1.30$).[3] A cationic complex with ethylene-ligand (Ru-**10**) is more active than Ru-**4** since the former easily gives a vacant site for acceptance of a transferred halogen by releasing the labile ethylene ligand.[39]

The Cp* complex Ru-**5** is potentially active enough to achieve fine control for three kinds of signature monomers, MMA, methyl acrylate (MA), and styrene (St) under the same conditions.[37] However, it had a drawback to take a long time for high conversion in the polymerizations, most likely because this complex is coodinatively saturated (an 18-electron complex), and so it would need to release at least one ligand to accept a halogen from the dormant terminal upon activation. So efforts have been addressed to accelerate polymerization without losing the fine control-ability. Thus, coordinatively unsaturated with a Cp* ligand were examined so as to achieve a more frequent activation. Ru(Cp*)Cl(PCy$_3$) (Ru-**11**), a 16-electron complex, induced a faster polymerization of MMA without a serious loss of the fine control ability as for Ru-**4**.[37] However, the control becomes worse for the polymerizations of MA and St. Similarly, coordinatively unsaturated dimers with amidinate (Ru-**12**)[40] and alkoxide (Ru-**13**)[41] were reported to induce controlled polymerization of MMA, but their activity were not sufficient, resulting in limited conversions (conv < ~50%). A P–N chelate complex (Ru-**14**) was developed from the finding that an amine compound works as a cocatalyst/additive for ruthenium complexes.[39] Also, nitrogen coordination is more labile than the phosphine counterpart for ruthenium, and thus such a hetero chelation is expected to promote the catalysis via a dynamic elimination/recoodination. Complex Ru-**14** exactly catalyzes a faster polymerization than Ru-**5** without loss of fine control, and the higher activity is supported by the lower redox potential (0.26 vs 0.46 V for Ag/AgCl).

Comprehensive study on steric/electronic effects of phosphine ligands for polymerization of MMA with a useful tetramer precursor ([RuCp*(μ_3-Cl)]$_4$) revealed that bulkiness is more critical for polymerization control than the electron-donating ability.[42] Within some range of bulkiness (cone angle, θ), the bulkier a ligand is, the narrower the molecular weight distribution of the produced polymers; thus, tri(*m*-tolyl)phosphine (Ru-**15**, $\theta = 165°$) gave narrower molecular weight distributions than triphenylphosphine derivative (Ru-**5**, $\theta = 145°$) under the same conditions (M_w/M_n, 1.07 vs 1.20). Combination of a primary mono- or diamine cocatalyst with Ru-**15** enhanced catalytic activity so as to decrease in catalyst concentration without loss of control ([catalyst]$_0$/[initiator]$_0$ = 1/40, $M_w/M_n = 1.11$, conversion = ~90%, in 4 h). According to ^{31}P NMR analysis, the added amine was exchanged with one of the phosphine, to form in situ a presumably reactive phosphine/amine-coordinated complex. The more labile and dynamic character of amine coordination would promote both activation and deactivation steps (see section 2.3.5). Hydrophilic aminoalcohols are also available as cocatalysts to enhance catalytic activity, and in this case the ruthenium residue was almost quantitatively removed (>97% removal) after the polymerization just by washing with water, since a hydrophilic catalyst carrying the alcohol is generated *in situ* via the ligand-exchange. A Cp*-ruthenium complex with π-coordinated acetonitrile (Ru-**16**) was employed for styrene polymerization, where combination with Et$_2$NH gave polystyrene fast with narrow MWDs ($M_w/M_n \approx 1.1-1.2$).[43]

The Cp*-based complex with poly(ethylene glycol) (PEG) phophine (Ru-**17**) shows an interesting thermosensitive and phase-transfer catalysis in suspension polymerization of MMA in toluene/water (~1/1 v/v).[44] Because of the thermosensitive character of PEG, the catalyst exists in the

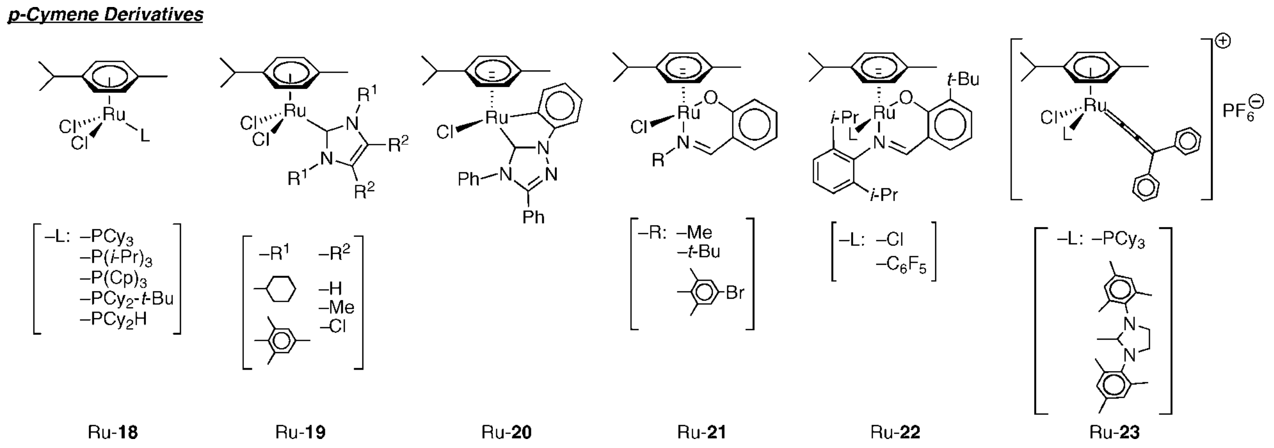


Figure 3. Ruthenium catalysts 2.

organic phase to catalyze the polymerization at 80 °C where the PEG moiety is hydrophobic, while it transfers to an aqueous phase at a lower temperature (~25 °C) where the reaction is quenched. Consequently, after the polymerization, the product polymers can be obtained from the upper organic phase, while the catalyst can be recovered from the lower aqueous phase, thus quantitatively providing colorless PMMAs of controlled molecular weights ($M_w/M_n \approx 1.1$; 93% removal of Ru). The recovered catalyst can be further employed in a second controlled polymerization of MMA, although MWDs become a little broader.

***p*-Cymene Derivatives.** *p*-Cymene (4-isopropyltoluene) complexes (Ru-**18**) with phosphine ligands [$RuCl_2$(*p*-cymene)(PR_3)] also catalyze living radical polymerization (Figure 3).[45] They can be easily prepared from [$RuCl_2$(*p*-cymene)]$_2$ and 2 equivalents of PR_3. Following previous results that such bulky ligands as tricyclohexylphosphine (PCy_3) and triisopropylphosphine [P(*i*-Pr)$_3$] are superior in terms of activity and controllability,[45−47] other bulky phosphines were employed for MMA in the presence of 2-bromo-2-methylpropanoate as an initiator. Tricyclopentylphosphine (PCp_3) and *tert*-butyldicyclohexylphosphine (PCp_2t-Bu) were also efficient ligands to give narrower MWDs ($M_w/M_n < 1.15$), while dicyclohexylphosphine (PCy_2H), less bulky and less basic, resulted in a slower and poorer controlled polymerization.[48]

Introduction of an N-heterocyclic carbene (NHC) into a *p*-cymene-based ruthenium complex in place of phosphine is also effective for living radical polymerization (Ru-**19**).[49] Substituents on the nitrogen (R^1) and the double bond (R^2) affect fundamental factors related to control ability in polymerization, such as competing side-reactions [e.g., metathesis (for styrene)], a one-electron redox, and a release of the arene ligand to give the active catalyst. Among the substituents examined, combination of 2,4,6-trimethylphenyl (R^1) and chlorine (R^2) gave narrowest molecular weight distributions ($M_w/M_n = 1.3-1.5$) for MMA. Orthometalated triazolinylidene (Ru-**20**),[48] Schiff bases (Ru-**21**[50] and Ru-**22**[51]), and cationic allenylidene complexes (Ru-**23**)[52] also demonstrated signs of catalytic activity for living radical polymerization, though the activities were still lower than those of original complexes with phosphine ligands (Ru-**18**).

Alkylidene Derivatives. Since the discovery with type of first generation Grubbs catalyst (Ru-**24**),[45,53] some ruthenium-benzilidinen complexes, known to catalyze metathesis and polymerization, have also been studied as catalysts for living radical polymerization (Figure 4), N-heterocyclic carbene (NHC)-based complexes (Ru-**25**), where the two phosphine ligands in Ru-**24** are replaced with NHCs, catalyze living radical polymerization of MMA, however the molecular weight distributions of the resultant PMMAs were broader than those with Ru-**24**.[54] Schiff base ruthenium-alkylidene complexes (Ru-**26**) also showed catalytic activity for the polymerization of MMA, MA, and St.[55] Among them, a catalyst with R = NO_2 and Ar = 2,6-Me-4-BrC_6H_2 showed the highest activity, but the activity was rather poor, giving low polymer yields. In contrast, the corresponding cationic species (Ru-**26**$^+$), prepared via reaction with silver salts, has a higher activity. Furthermore, the cationic complexes catalyzed controlled radical suspension polymerizations in water/toluene, in addition to homogeneous polymerizations in organic solvent. An alkylidene complex with NHC ligand and Schiff base ligand (Ru-**27**) and the cationic species (Ru-**27**$^+$) are also effective catalysts similar to Ru-**26** and Ru-**26**$^+$.[56]

Indelinidene (Ru-**28**,[57] -**30**,[57] and -**32**[57,58]) and ethyl vinilidene (Ru-**29**,[57] -**31**,[57] and -**33**[57,58]) complexes were also examined. These were superior to the benzilidinen counterparts (Ru-**24**−**27**) as catalysts in terms of the activity (polymerization rate) and control over molecular weights/MWDs. For example, the polymerizations of MMA with these complexes, coupled with a bromine initiator (ethyl-2-bromo-2-methylpropionate) in toluene, gave narrower molecular weight distributions ($M_w/M_n = 1.2-1.4$ vs $1.5-2.0$ with Ru-**24**−**27**). Among these, a complex (Ru-**33**) containing a NHC ligand, an electron-withdrawing Schiff base, and an ethyl vinilidene groups showed highest catalytic activity for MMA: almost quantitative conversion in 16 h; $M_w/M_n = 1.3$; initiation efficiency = 0.97. Cationic complexes (Ru-**28**$^+$-Ru-**33**$^+$), prepared by treating the neutral complexes with $AgBF_4$, were also active not only in organic solvent but also in suspension.

Other Ru(II) Complexes. A cyclometalated 2-phenylpyridine ruthenium complex (Ru-**34**) (Figure 5) also catalyzes controlled radical polymerizations of MMA, *n*-butyl acrylate (*n*BA), and St, with added Al(O*i*-Pr)$_3$ for generation of a vacant site and with $SnCl_2$ as a reducing agent for shifting the equilibrium to dormant species.[59]

Though smaller in number, a few bimetallic ruthenium complexes were examined in living radical polymerization. For example, a Cl-bridged bimetallic complex (Ru-**35**) with a benzilidene, a Schiff base ligand, and a *p*-cymene ligands catalyzes living radical polymerization of styrene, as well

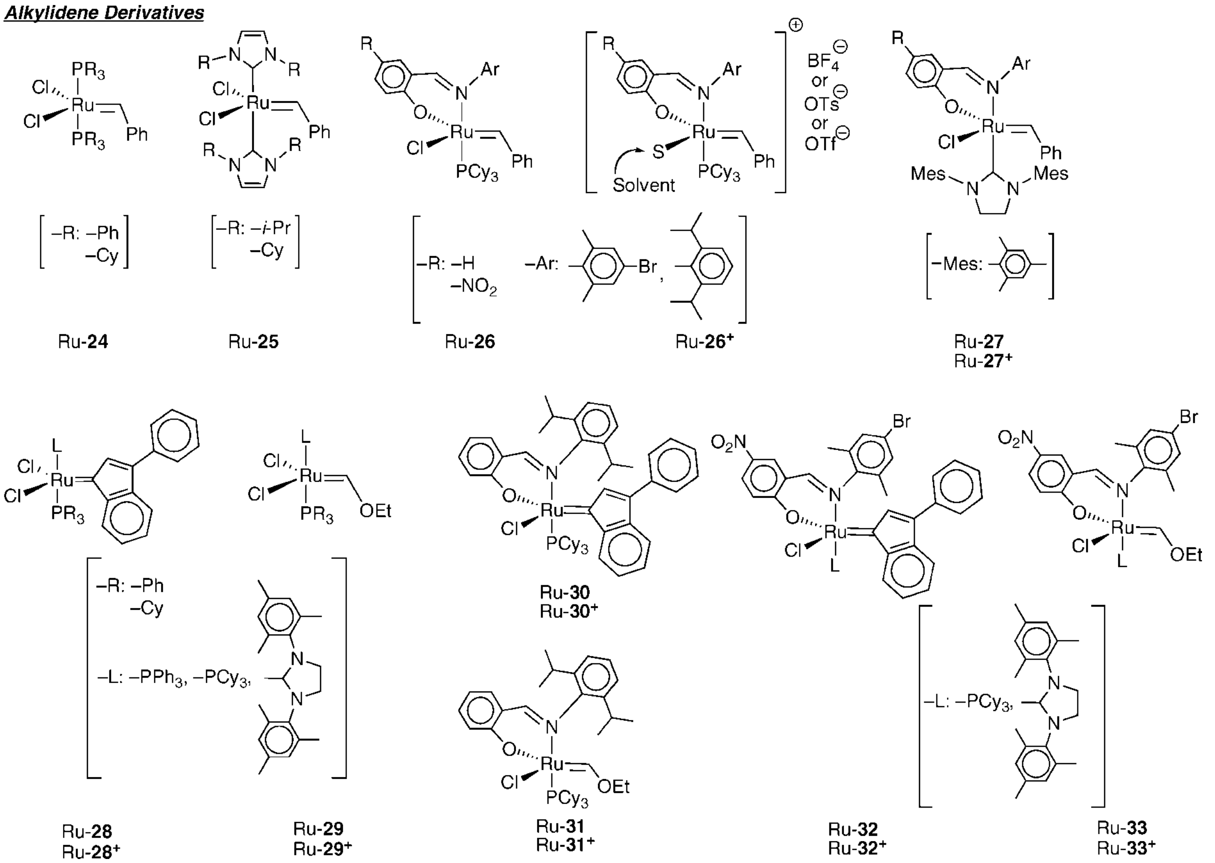


Figure 4. Ruthenium catalysts 3.

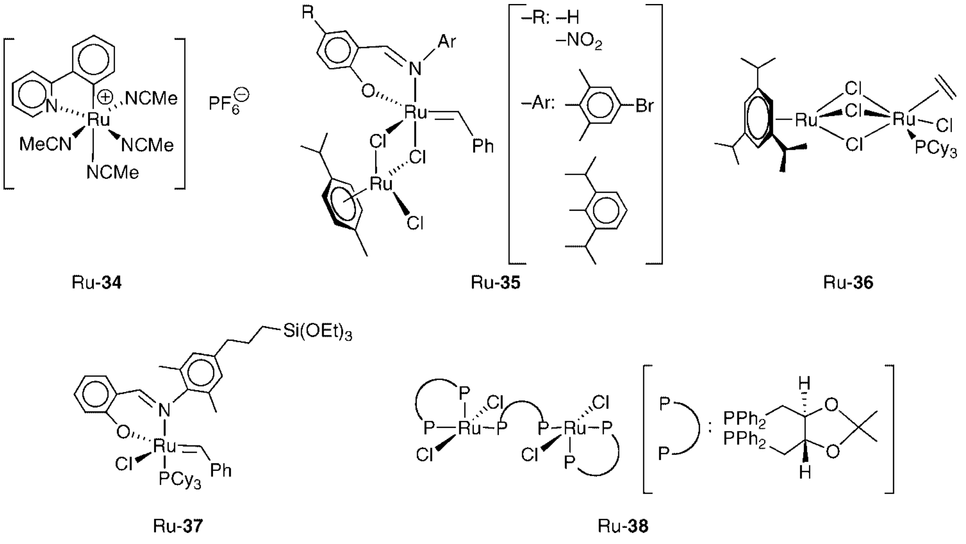


Figure 5. Ruthenium catalysts 4.

as atom transfer radical additions to various olefins.[60] Ru-**36** is another Cl-bridged bimetallic form, where one ruthenium carries 1,3,5-*i*-$Pr_3-C_6H_3$ and another ethylene and PCy_3.[61] This catalyst is active enough to give narrow molecular weight distributions ($M_w/M_n < 1.2$) for MMA even at ambient temperature (35 °C), although the true catalyst therein (mono- or bimetallic) is unknown.

Removal, separation, and recycling of catalysts after polymerization are problems on our hands, especially for ruthenium-based systems, because they are relatively expensive and hard to remove due to their high stability in organic solvents and tolerance to polar functional groups. Immobilization of catalyst would be a solution for such problems. For example, a ruthenium complex (Ru-**37**), carrying an alkoxy silane group [$-Si(OEt)_3$], was covalently anchored on mesoporous silica (MCM-41) and was employed for St.[62] The molecular weights of produced polystyrenes were increased with monomer-conversion, while the molecular weight distributions were broad ($M_w/M_n > 1.60$). In general, it is suspected that such heterogeneous catalysts are not uniformly available for dormant terminals.

Introduction of chirality into a ligand or an additive was attempted to give an optically active environment around the ruthenium center, aimed at advanced control such as stereospecificity and enantiospecificity. A chiral bimetallic ruthenium complex with DIOP-ligand [DIOP = 2,3-(iso-

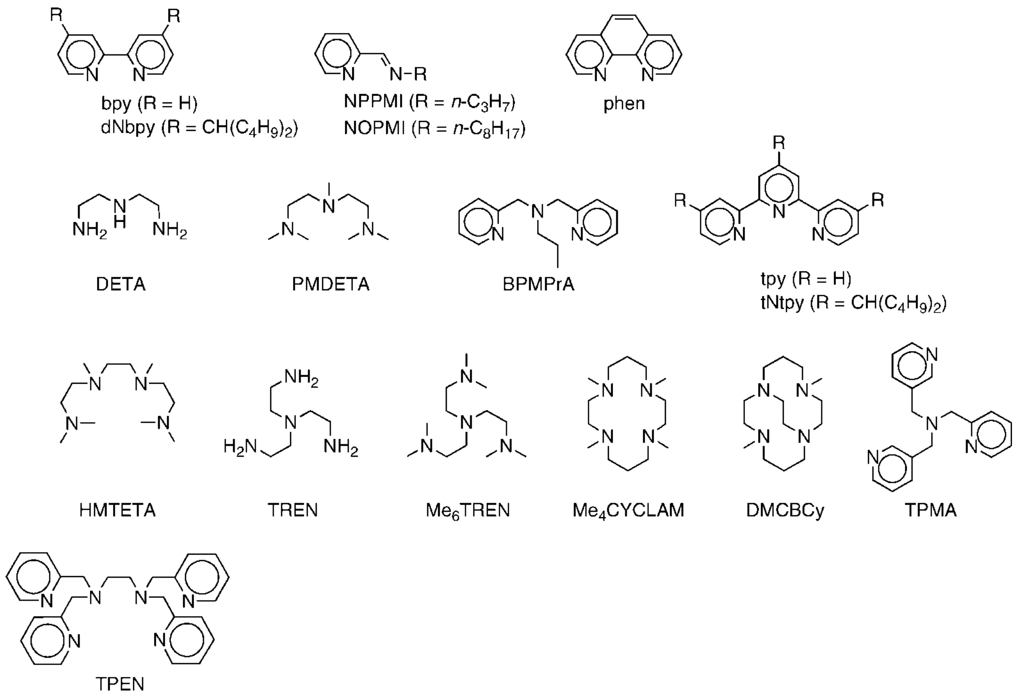


Figure 6. Ligands for copper catalysts.

propylidenedioxy)-2,3-dihydroxy-1,4-bis(diphenyl-phosphanyl)butane] (Ru-**38**) gave controlled polymers from styrene with Al(O*i*-Pr)$_3$ additive.[63] Unfortunately, the tacticity of the polystyrene was almost same as that in conventional radical polymerization. A chiral naphthol [(*S*)-1,1′-bi-2-naphthol] was similarly employed as an additive for Ru-**1** in an attempt for enantioselective radical polymerization of a racemic dimethacrylate (rac-2,4-pentanediyldimethacrylate). The RR-monomer was preferentially polymerized relative to the SS-derivative, independently of the chirality of the terminal repeat unit.[64]

2.2.3. Copper

In metal-catalyzed living radical polymerization, copper complexes have been most widely used for various applications due to not only the superior catalysis and the detailed understanding but also the low cost and the easy handling, that is, just mixing a copper halide with a ligand. Since the first discovery with CuCl/2,2′-bipyridyl (bpy),[65] a wide range of multidentate nitrogen-based ligands have been developed for copper catalysts. Figure 6 shows representatives of common and/or highly effective ligands employed for copper. Because a series of reviews[4−6,66,67] and articles[68−70] have already been published, however, this important subject is outside of the scope of this review, except for a brief general comment about active systems below.

Most ligands were developed before 2000, but recently some effective ones have been presented. For example, dimethyl cross-bridged cyclam (DMCBCy)[71] with CuCl showed 30-fold larger ATRP equilibrium constant than that for CuCl/Me$_6$TREN,[72] one of most active catalysts until then. Indeed, polymerization of *n*BA with this catalyst was fast even at 30 °C, though additional CuBr$_2$/DMCBCy was required for low polydispersity due to the slow deactivation. A hexadentate ligand, *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-ethylendiamin (TPEN)[73] with CuBr leads to more active systems available for MA, MMA, and St. Even with low concentration of the catalyst ($[CuBr]_0/[Initiator]_0 = 0.005$), the three monomers can be polymerized to yield controlled molecular weights and narrow MWDs. Structural analyses indicate that the complex is in equilibrium between binuclear and mononuclear state in solution, and the latter is presumed to be a “real” activator. Because of such dynamic structural change and the flexible coordination by the multidendate ligand, the complex is stabilized during polymerization without suffering from an extra coordination of solvents and monomers, which allows low does of the copper.

A notable progress in copper-catalyzed systems is the development of very efficient systems, where extremely a small amount of catalyst (<∼10 ppm) is required to achieve living polymerization without deteriorating reaction rate and fine control. As already pointed out, a decrease in catalyst dose is essential for actual applications with metal-catalyzed living radical polymerization. A crucial point is to efficiently accelerate the rotation of a catalytic cycle. Two methodologies have been reported so far. One is called as activators regenerated by electron transfer (ARGET) ATRP,[5,6,72,74−77] where a Cu(I) catalyst is considered to be continuously regenerated from the oxidized Cu(II) form by a reducing agent, such as Sn(Oct)$_2$ or vitamine-B. Another is as SET (single-electron transfer)-LRP,[78−85] where zerovalent copper [Cu(0)] triggers the activation step for generation of radical species and Cu(II) works as a deactivator to cap radical species. As shown below, Cu(I) is not an activator (catalyst), but a catalyst precursor that is spontaneously disproportionated into Cu(0) and Cu(II) by a specific solvent. Given their extremely high catalytic activity and resulting low dose, these efficient systems would lead to industrial applications of metal-catalyzed living radical polymerization.

Toward practical applications, a catalyst separation from produced polymers has been also examined in the normal copper catalyzed systems. A useful review article is presented focusing on separation of the copper catalysts.[86]

2.2.4. Iron

As ruthenium, iron belongs to group 8 series and is a promising central metal for catalysts in living radical polymerization. As mentioned above, the development of

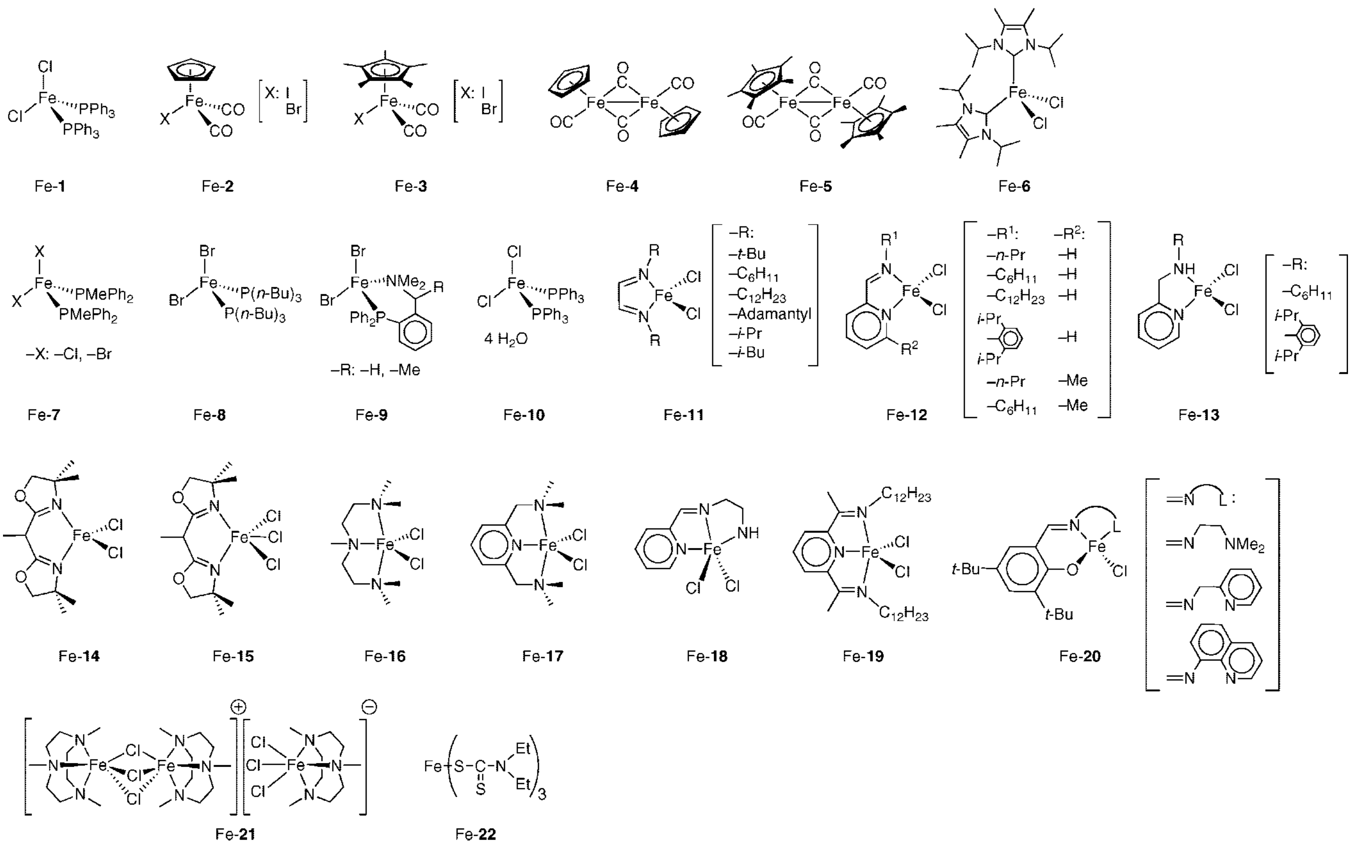


Figure 7. Iron catalysts.

iron-based catalysts is currently important, because of their potentially beneficial characters, safe, active, abundant, and inexpensive. In general, divalent iron complexes [Fe(II)] will be suitable, and polymerization proceeds under an equilibrium between Fe(II) and Fe(III). Earlier examples in fact follow this concept, but systems starting from more stable trivalent complexes [Fe(III)] have been attracted attention from the viewpoints of applications, like reverse ATRP[87] or AGET ATRP starting from Cu(II) (see sections 2.2.3 and 2.3.2)

The first example is the iron(II) chloride with triphenylphosphine [$FeCl_2(PPh_3)_2$; Fe-**1**],[88] inspired by a similar ruthenium complex [$RuCl_2(PPh_3)_3$; Ru-**1**][18] (Figure 7). Before the last review article (phase I),[1] some iron catalysts had been reported along with an Fe-**1**: a series of half-metallocene complexes with carbonyl and halogen (Fe-**2**-Fe-**5**)[89−92] and an imidazolidene (N-heterocyclic carbene) iron halide (Fe-**6**).[93] Fe-**2** and Fe-**3** are enough tolerance to functional groups and induce living polymerization not only in organic media but even in aqueous suspension.[94] In addition to their functionality tolerance, the binuclear complexes (Fe-**4** and Fe-**5**) are very active, and thereby useful for (co)polymerization of a nonconjugated monomer [e.g, vinyl acetate (section 2.6.3) and nonpolar olefins (section 3.5.2)] with functional monomers such as acrylamide (section 2.6.2).

The general problems of the iron complexes are the lower control ability in block copolymerization and the limited range of applicable monomers, relative to the ruthenium and copper counterparts. Most seriously, they are often sensitive to functional groups and thus less capable of catalyzing polymerization of functional monomers. Therefore, efforts are being focused on development of iron to circumvent these defects.

To increase catalytic activity, PPh_3 in Fe-**1** was replaced with more basic phosphine lingads (Fe-**7** and Fe-**8**).[95] The modified complexes indeed induced MMA polymerization faster than does Fe-**1** to give controlled PMMAs (M_w/M_n = 1.2−1.4). The activity of Fe-**8** was high enough to work even at low temperature (40 °C), and the controllability was supported by successful monomer-addition polymerization and block copolymerization of MMA with butyl methacrylate. With a P−N chelate complex (Fe-**9**), polymerization was further accelerated, and MWDs of the resultant PMMAs became narrower (M_w/M_n = 1.1−1.3).[96] Such an effect of the hetero bidentate chelation was demonstrated by comparative experiments with similar ligands, and the contribution to the control was attributed to be promotion of deactivation step by the doubly anchored ligand. Fe-**10**, a tetrahydrate complex of Fe-**1**, also allowed a controlled polymerization of *n*-butyl methacrylate (BMA), and especially the combination with $FeCl_3$ (10 wt %, relative to the divalent complex) made MWD narrower (M_w/M_n = 1.23 vs 1.40).[97]

A series of α-diimine-coordinated iron chlorides (Fe-**11**) showed catalytic activity for living radical polymerization.[98−101] They can be readily obtained just by mixing equimolar amounts of $FeCl_2$ and the α-diimine, and a variety of complexes with different substitutes on the nitrogens were isolated. The radical polymerization with Fe-**11** turned out very sensitive to the imine substituents: Alkyl groups gave polymers with controlled molecular weights, while aryl groups led to less controlled polymers with lower molecular weights, most likely caused by a catalytic chain transfer. Among the alkyl groups examined, cyclohexyl ($-C_6H_{11}$) and cyclododecyl ($-C_{12}H_{23}$) are superior in catalytic performances for MMA and styrene (M_w/M_n = 1.2−1.3). The cyclododecyl derivative was tested for MA with fairly good

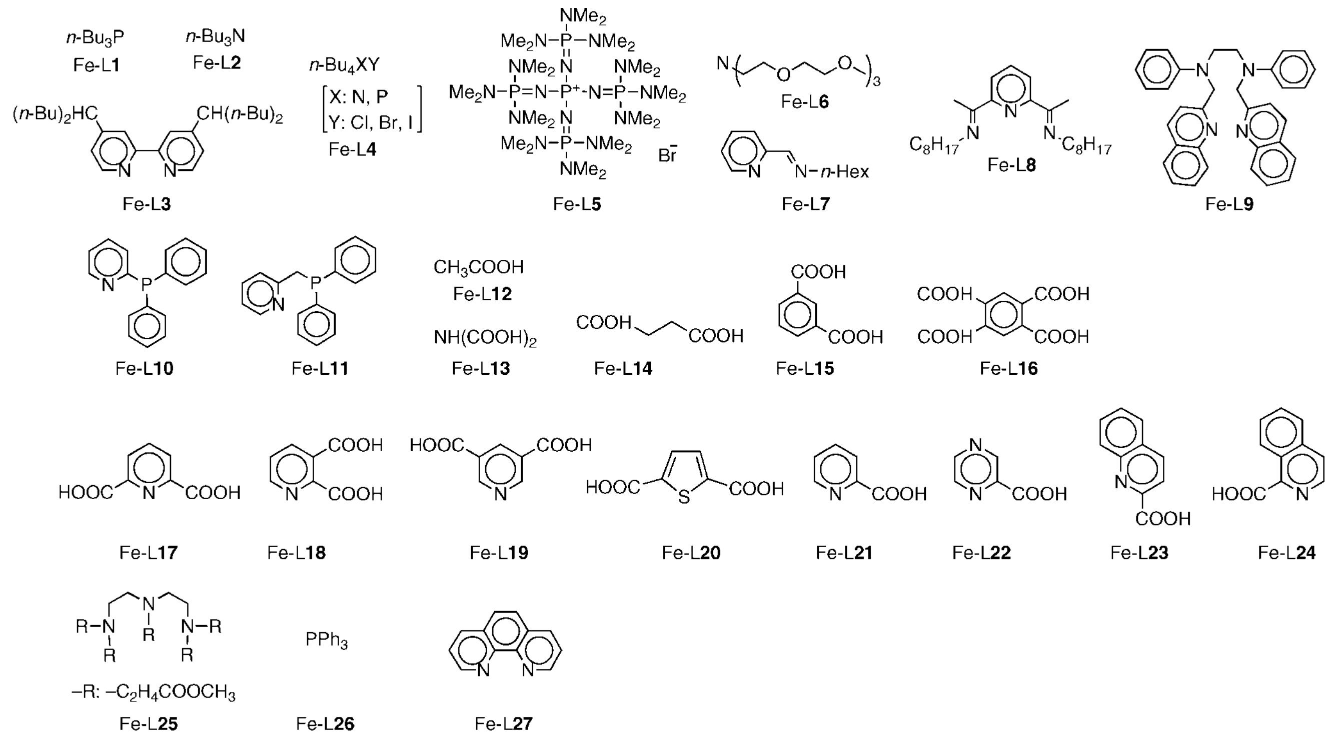


Figure 8. Ligands for iron catalysts.

results ($M_w/M_n = 1.53$). Such advantageous effects were rather specific to the diimine chelation, because other bidentate nitrogen and phosphorus ligands were less effective. Additionally, the α-diimine complexes seem tolerant to functional groups, and indeed the cyclohexyl derivative induces living polymerization even with HEMA in methanol ($M_w/M_n = 1.1-1.4$).[100] An important feature for the α-diimine complexes is that, despite the dichloride structure, they remain in a monomeric form, rather than bridged dimers often found in such complexes. The dimeric cyclohexyl derivative in fact shows a lower activity.[102]

Iron complexes bearing iminopyridine (Fe-**12**) and aminopyridine (Fe-**13**) were also employed.[103] Catalysts bearing alkyl substituents on the imino group in Fe-**12** or the amino group in Fe-**13** induce controlled polymerizations of St with reasonable molecular weight control ($M_w/M_n = 1.3-1.8$), while the aryl (2,6-diisopropylphenyl) derivatives of both series give molecular weights lower than predicted, suggesting chain transfer reaction. Such a different behavior was relative to a higher peak separation voltage of the former in cyclic voltammetry analyses. Fe-**12** with R^1 = cyclohexyl and R^2 = methyl catalyzes polymerizations of MMA as well as St. Single crystal X-ray analysis showed that only this particular complex is mononuclear, differing from the others in the series that take chlorine-bridged dinuclear forms.

Bis(oxazoline) is another type of bidentate nitrogen ligands for iron(II) chloride (Fe-**14**).[104] The polymerization of styrene gave controlled molecular weights in agreement with the calculated values based on the monomer-to-initiator ratio and monomer conversion, though the polymer MWD was rather broad ($M_w/M_n = 1.40-1.58$). On the contrary, the trivalent derivative (Fe-**15**), prepared from $FeCl_3$, was a useful catalyst for reverse ATRP of styrene (e.g., $M_w/M_n = 1.15$ at 70% conversion).

Five-coordinate complexes bearing tridentate nitrogen ligands (Fe-**16**-Fe-**19**) were also examined.[105] They catalyzed styrene polymerization, but the rate was slower and the MWD was totally broader ($M_w/M_n \approx 1.6$) than those with four-coordinate α-diimine derivatives (e.g., Fe-**11**). For an efficient halogen transfer in catalysis, the less sterically hindered four/five-coordinate equilibrium is presumably more favorable than five/six-counterpart because of less steric hindrance.

Tridentate salicylaldiminato iron complexes (Fe-**20**) provide highly active catalysts for living radical polymerization.[106] Molecular weights and MWDs are fairly controlled for styrene (typically $M_w/M_n \approx 1.10$). It is likely that the arm nitrogen-coordination contributes to lowering its oxidation potential and thereby stabilizes the reduced species.

An ionic trinuclear complex (Fe-**21**)[107] is active enough to catalyze not only living polymerization of styrene ($M_w/M_n = 1.2-1.4$) but also its block copolymerization with MMA. This catalyst possesses some additional properties for actual applications. First, it is readily soluble in methanol, and hence quantitative removal (>99%) of the iron residue from products is possible simply by precipitation into methanol. Second, the removed catalyst is reusable without an apparent loss of the catalytic activity, although careful recovery is required under inert atmosphere.

Dithiocarbamate iron complex [$Fe^{III}(SCSNEt_2)_3$, Fe-**22**] is available for reverse ATRP of styrene and MMA ($M_w/M_n = 1.1-1.3$).[108] Importantly, the dormant end is a dithiocarbamate, not a halide.

Variety of ligands has been developed for in situ generation of iron complexes right, similar to the preparation of copper catalysts (Figure 8). In some cases, this method would be more favorable especially for practical uses than the use of isolated catalysts incurring higher expense, though due care should be taken in identifying the catalysts.

Combination of $FeCl_2$ with tri*n*-butylphosphine [P(*n*-Bu)$_3$, Fe-L**1**], tri*n*-butylamine [N(*n*-Bu)$_3$: Fe-L**2**], and a bipyridine derivative (Fe-L**3**) was first reported for such an in situ preparation.[109] Although a large amount of catalyst was required (typically, $[Fe]_0/[initiator]_0 = 1$), the resulting

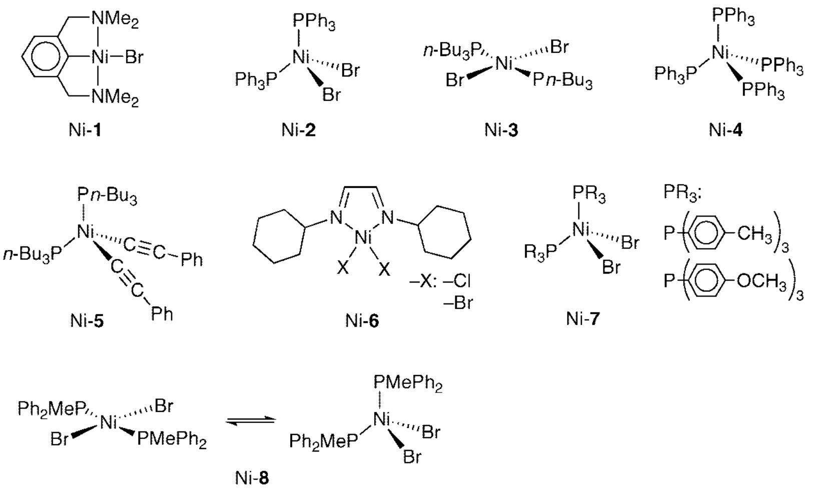


Figure 9. Nickel catalysts.

complexes apparently catalyze controlled polymerization for styrene ($M_w/M_n = 1.1-1.3$) and MMA ($M_w/M_n = 1.2-1.6$). Recently, even the combination of Fe-L**1** with $FeCl_3$ was found to be active for living radical polymerization of styrene ($M_w/M_n = 1.1-1.2$), although neither a reducing agent nor a conventional initiator was employed.[110]

Combinations of $FeBr_2$ with onium salts, such as ammonium and phosphonium (Fe-L**4**), were also demonstrated to catalyze living radical polymerization.[111] Some gave narrow molecular weight distributions, however, difficult to attain high conversion. Quite recently, phosphozenium bromide (Fe-L**5**) was reported for a ligand for $FeBr_2$.[112] This large and highly delocalized ion salt led to an active catalyst for MMA obviously more active than those with usual onium salts (Fe-L**4**). The high activity was demonstrated by successful monomer-addition experiment and the formation of high polymers with narrow MWD ($M_n = 91,000$; $M_w/M_n = 1.14$). Additionally, the $FeBr_2$/Fe-L**5** system was useful for a functional methacrylate carrying oligo ethylene glycol, and the catalyst can be removed almost quantitatively from hydrophobic polymers just by water-washing.

Some amine-based ligands are available for iron catalysts, as with copper. Among monodentate amines, tris(1,6-dioxaheptyl)amine (Fe-L**6**) works as a ligand for styrene polymerizations with FeX_2 (X = Cl, Br).[113] Although the polymerizations are under heterogeneous condition, monomer conversion reaches high with narrow MWDs ($M_w/M_n = 1.2-1.4$). The hydrophilicity of the amines further allows effective removal of the catalyst residue by water-washing. Followed by the success with *N*-alkyl-2-pyridylmethanimines complexes (Fe-**12**), the bidentate *n*-hexyl derivative ligand (Fe-L**7**) was employed as a ligand for iron complexes.[114,115] For MMA polymerization, the in situ formed Fe(II) catalyst was also combined with the oxidized salt ($FeCl_3$; 20 mol % for $FeBr_2$) to improve molecular weight control, where the use of Fe-L**7** equimolar to the total amount of iron ($[FeBr_2]_0 + [FeCl_3]_0$) gave best results ($M_w/M_n \approx 1.3$). A tridentate ligand, diiminopyridine (Fe-L**8**), was also employed for $FeBr_2$.[116] The equimolar combination ($[FeBr_2]_0/[\text{Fe-L}\mathbf{8}]_0 = 1$) showed catalytic activity for MMA, however the performance was inferior (lower rate, broader MWD) to the corresponding CuBr systems. A tetradentate ligand (Fe-L**9**) allowed controlled polymerization of MMA in conjunction with $FeCl_2$ (88%, $M_w/M_n = 1.35$), though less efficient than with CuCl.[117]

Recently, pyridylphosphine ligands (Fe-L**10**−L**11**) were found to generate active and efficient in situ generated iron catalysts.[118−120] The combination with iron dihalide (FeX_2, X = Cl, Br) induced living radical polymerization of MMA ($M_w/M_n = 1.2-1.3$) and styrene ($M_w/M_n = 1.4-1.5$). Interestingly, rather than the divalent precursor, trivalent halide (FeX_3, X = Cl, Br) was suited, even though any reducing agents and thermal radical initiators were not added. For instance, $FeBr_3$ combined with Fe-L**10** showed catalytic activity for various monomers including MMA, MA, *n*-butyl methacrylate (BMA), and St ($M_w/M_n = 1.1-1.3$), and the activity is especially high for MMA, thereby reducing the catalyst dose to 0.01 equiv to initiator.

Acids had been believed to be poisonous rather than beneficial to transition metal catalysts, but some carboxylic acids in fact act as ligands for iron halide catalysts. Those to be coupled with $FeCl_2$ include acetic (Fe-L**12**),[121,122] iminodiacetic (Fe-L**13**),[121,123] isophthalic (Fe-L**14**),[124] and succinic (Fe-L**15**)[121,124] acids. Generally, a slight excess over the initiator is needed to catalyze polymerizations of styrene or MMA. Though heterogeneous, the reactions led to high monomer-conversion (>80%) and controlled molecular weight ($M_w/M_n = 1.2-1.5$). Difunctional acids, Fe-L**13**,[125] Fe-L**14**,[126] and Fe-L**16**,[127] were also useful for reverse ATRP with $FeCl_3$. Importantly, Fe-L**13** and Fe-L**14** are applicable even for acrylonitrile. Fe-L**13** was also available for AGET with $FeCl_3$/reducing agent and the polymerizations were fairly controlled ($M_w/M_n = 1.1-1.3$).[128] Other carboxylic acids (mostly picolinic acid derivatives) (Fe-L**17**−**24**) are also useful for Fe(III)-mediated reverse ATRP of MMA ($M_w/M_n = 1.4-1.8$).[129] These acids are commercially available, and seemingly employed to develop simpler, less exotic, and inexpensive catalysts.

A mlltidentate aliphatic amine (Fe-L**25**), via Michael addition of methyl acrylate to diethylenetriamine (DETA), was applied for a mixture of hydrated metal halides, $SnCl_2 \cdot 2H_2O$ and $FeCl_3 \cdot 6H_2O$.[130] The real active catalyst is presumably some Fe(II) complex, generated via the redox reaction between the two precursors. Triphenylphosphine (PPh_3, Fe-L**26**) gives an AGET system for MMA with a bromide initiator, $FeCl_3 \cdot 6H_2O$, and a reducing agent (ascorbic acid).[131] At least half amount of catalyst relative to initiator is required for the fine control and high conversion ($M_w/M_n = 1.3-1.5$). Phosphine (Fe-L**26**) was utilized for reverse ATRP of MMA with $FeCl_3$ in the presence of a thermal initiator [dithiocarbamate disulfide ($Et_2NC(=S)$-S-$)_2$],[132] and was also combined with a mixture of $FeCl_3$ and $Fe^{III}(SCSNEt_2)_3$ (Fe-**22**).[133] In both systems, $FeCl_2(PPh_3)_2$ (Fe-**1**) and some Cl-based compounds are in situ generated during the early of reaction, and eventually the former leads to controlled polymerizations.

Importantly, Percec et al. reported that even zero valence iron [Fe(0)] catalyzes living radical polymerization.[134] Phenantrorine (Fe-L**27**) was coupled with Fe(0) as well as a bromide initiator for a controlled polymerization of vinyl chloride (VC). The polymerization was not quantitative (conversion <40%), but fairly controlled poly(VC)s with $M_n > 10^4$ of were obtained ($M_w/M_n = 1.5-2.0$). Note that most of metal-catalyzed and the other living polymerization are not applicable for nonconjugated monomers as VC (see section 2.6.3).

2.2.5. Nickel

Though attractive as potential catalyst, nickel complexes tend to undergo to a two-electron transfer reactions rather than a one-electron redox reaction,[135] and nickel catalysis usually works only a limited range of radical reactions as Kharasch reaction. Nevertheless, its utility for living radical polymerization was confirmed with some complexes at the earlier stage of the history; where examples include bis(ortho-chelated) arylnickel(II) (Ni-**1**),[136] nickel(II) bromide-phosphine (Ni-**2**[137] and Ni-**3**[138]), and zerovalent phosphine (Ni-**4**[139]) complexes (Figure 9). Typically, divalent derivatives [Ni(II)] are employed to catalyzed radical polymerization via an equilibrium with a trivalent intermediate [Ni(III)], except the specific case with Ni-**4**. Therein their activities are mostly milder than those of the ruthenium and copper counterparts, and their use for functional monomers had not been reported at the time when the last review article was published.

A mixture of $NiCl_2$ and PPh_3 ($[NiCl_2]_0/[PPh_3]_0 = 1/3$) induces a controlled polymerization of St, in conjunction with tetraethylthiuram disulfide (TD; $Et_2NC(=S)S$-$SC(=S)NEt_2$) as a thermal initiator.[140] The molecular weight was controlled up to 72,000 ($M_w/M_n = 1.34$). It is proposed that a trivalent form, $Ni(SC(=S)NEt_2)Cl_2$, is generated from $NiCl_2$ and TD, which in tern deactivates the growing polystyrene radical to give a Cl-capped dormant chain and the corresponding Ni(II) species, $Ni(SC(=S)NEt_2)Cl$. A neutral Ni(II) acetylide complex (Ni-**5**) induced living radical polymerization of MMA in conjunction with a simple organic halide such as $BrCCl_3$.[141] Although under some conditions a relatively fast polymerization occurs, the control was poorer than the previously reported simple catalysts (Ni-**1**−**4**). α-Diimine was examined as a ligand for nickel halide (NiX_2), as with a similar diimine iron catalyst (Fe-**11**).[142] The chloride derivative led to uncontrolled polymerization of styrene most likely because of the insolubility, while the bromide complex in conjunction with a bromide initiator gave controlled polymers ($M_w/M_n = 1.15-1.30$). However, it was ineffective for MMA.

An increase in electron donation from ligands is one of solutions to improve catalytic activity in metal-catalyzed living radical polymerization, in which one-electron release from the catalyst triggers radical generation. Indeed, introduction of more basic ligands, such as *para*-tolyl- and *para*-methoxyphosphine (Ni-**7**), onto a Ni(II) complex (Ni-**2**) gave better catalysis for MMA than the parent form in terms of polymerization rate and controllability.[3] However, even with these catalysts, polymerization rates were gradually decreased as conversion increased, which was presumably caused by their low thermal stability.[137,138] On the other hand, $NiBr_2(PMePh)_2$ (Ni-**8**) induced living polymerization of MMA without such retardation.[3] Furthermore, the improved catalyst was more versatile, applicable for not only MA and St but also functional monomers such as polyethylene glycol methacrylate (PEGMA) and dimethylaminoethyl methacrylate (DMAEMA). The long-lived catalytic activity allowed block copolymerization among these monomers. Such a superior catalysis is rationalized by a dynamic structural change of the complex between “pseudotetrahedral” and “square planar”.

Immobilization of Ni(II) catalysts has been attempted for catalyst removal and recycling. However, in general, such supported catalysts tend to deteriorate control due to the nonuniform catalysis for polymer chains. A $NiBr_2$-based complex imm*o*bilized on a diphenylphosphinopolystyrene resign (PS-PPh_3, 1% cross-linked resign) demonstrated not only the expected removal/reuse features but also fine control in MMA polymerization ($M_w/M_n \approx 1.15$).[143,144] The essential point is a combination with free PPh_3 ($[PPh_3]/[PS\text{-}PPh_3]/[NiBr_2]_0 = 6-12/6/1$), which reversibly ligates some of the supported $NiBr_2$ during polymerization. A cross-linked polyacrylate ion-exchange resin (HD resign) was also employed as a supporting ligand for $NiCl_2$.[145] The mixture ($NiCl_2$−HD) coupled with a chloride initiator was able to polymerize MMA, although control was poor. In contrast, an additional use of a small amount of $CuCl_2/Me_6TREN$ (1 mol % to $NiCl_2$) gave controlled molecular weights and MWDs ($M_w/M_n = 1.26$, for 90% conversion). It is proposed that the soluble Cu(II) complex facilitates the deactivation process by delivering its halogen, while the resulting Cu(I) form subsequently reduces the supported $NiCl_3$ into $NiCl_2$.

2.2.6. Molybdenum

Molybdenum complexes can be candidates as catalysts for living radical polymerization because the metal displays a wide range of oxidation states ranging from −2 to 6. However, their utility had been less known for not only living radical polymerization but also Kharash reactions. Among them (Figure 10), a lithium molybdate (V) complex (Mo-**1**) was first examined for living radical polymerization (Figure 10).[146] With a benzyl chloride initiator, it polymerized styrene with a benzyl chloride initiator, but the catalytic performances was rather poor: low activity, broad MWDs of products ($M_w/M_n = 1.5-1.7$), and low initiating efficiency (6−18%). Subsequently, half-sandwich Mo(III) complexes (Mo-**2**,[147] Mo-**3**,[148] Mo-**4**[149]) were examined for styrene. With a bromide initiator, a linear increase in molecular weights with conversion was observed, whereas the polymerizations were slow and MWDs of the products were still broad ($M_w/M_n = 1.5-1.7$). In these systems, along with the usual halogen-transfer activation mechanism on SFRP (stable free radical polymerization) process might accompany, giving dormant species containing a Mo(III)-polymer bond, as seen in cobalt-catalyzed systems.[149] In fact, polymerization control was possible even in the presence of a free radical polymerization initiator, not a halide-based initiator. Polymerization rate and controllability were improved with an alkyl iodide initiator and an aluminum cocatalyst [Al(O*i*-Pr)$_3$] in Mo-**4**-catalyzed system,[150] and controlled polymerization proceeds with alkyl acrylates, as well as St. Trimethylphosphine molybdenum(III) complexes (Mo-**5**) also show catalytic performances similar to the half-sandwich derivatives (Mo-**2**-**4**).[151,152] Mo-**5** showed

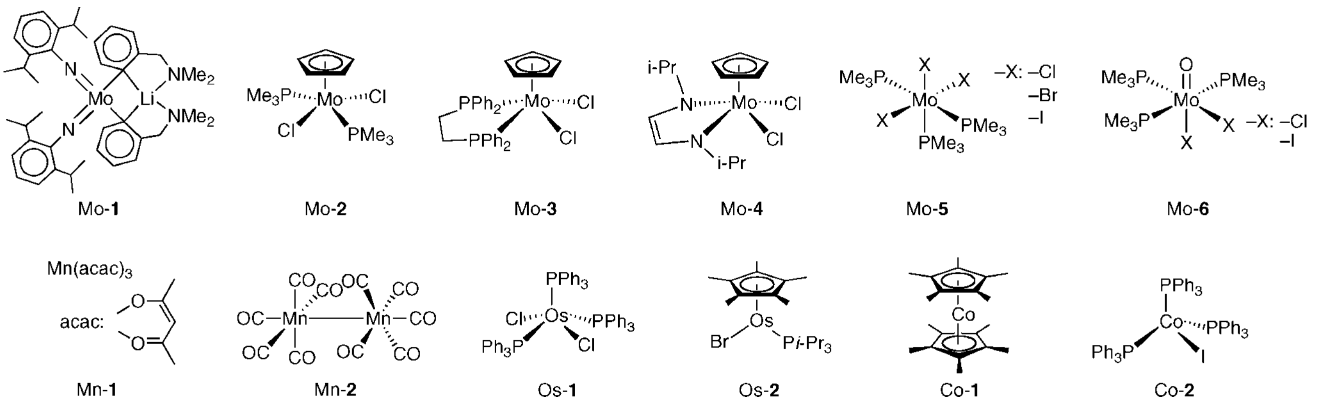


Figure 10. Other catalysts.

catalytic activity even for MA in an ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate).[153] These complexes are trivalent derivatives [Mo(III)], while use of a tetravalent complex [Mo(IV)] (Mo-**6**) was reported for styrene polymerization in conjunction with a bromide initiator and Al(O*i*-Pr)$_3$.[154] In this system, the catalysts should be oxidized to Mo(V) by abstracting a halogen during polymerization, but the oxidized species was not detected. Although the conversion and controllability is still insufficient, a similar MoO_2Cl_2/PPh_3 catalyst system was examined for controlled polymerization of butadiene.[155]

2.2.7. Manganese

Although manganese also takes wide range of oxidation states (from −3 to 7), just a few examples of catalysts for living radical polymerization have been reported so far. The acetylacetonate manganese(III) complex [Mn(acac)$_3$: Mn-**1**] induces styrene polymerization coupled with a benzyl bromide initiator.[156] The molecular weight was increased as monomer conversion, however the distributions were broad ($M_w/M_n > 2$). Recently, one of most common manganese complexes, a dinuclear carbonyl derivative [$Mn_2(CO)_{10}$, Mn-**2**] was found to show interesting catalysis for living radical polymerization.[157] Importantly, it is capable of catalyzing controlled polymerization of vinyl acetate in conjunction with an iodide initiator to give controlled molecular weight, and the activity was high enough to reach high conversion and to generate high molecular weight poly(VAc) (see section 2.6.3). The original dinucelar form is cleaved into a monomeric complex upon exposure to visible light to a generate manganese radical complex or a real catalyst. Hence, the catalysis is photosensitive for visible light and the polymerization-proceeding can be regulated by on/off of light keeping the controlled character. This system is also effective for control of not only homopolymerization of MA and St but also copolymerization of these with VAc.

2.2.8. Osmium

Osmium complexes were also targeted as catalysts for living radical polymerization because the metal belongs to group 8 same as ruthenium and iron. Dichloride complex [$Os^{II}Cl_2(PPh_3)_3$, Os-**1**] indeed catalyzed living radical polymerization of styrene with an alkyl bromide initiator to give narrow MWDs ($M_w/M_n = 1.11$).[158] This catalyst was also effective for MMA and *n*BA, however the MWDs were broader ($M_w/M_n \approx 1.6$). The addition of Al(O*i*-Pr)$_3$ is effective for acceleration of polymerization but not essential for polymerization-control, in contrast to $RuCl_2(PPh_3)_3$ (Ru-**1**). From analyses of K_{ATRP} (the equilibrium constant between dormant and active species) with UV/vis spectrometer, a pentamethylcycopentadien (Cp*) complexes (OsBrCp*P*i*-Pr$_3$: Os-**2**) proved to be potentially active catalysts for living radical polymerization.[159] It actually provided very narrow MWDs in styrene polymerization in the presence of a 1/10 amount of the trivalent complex (OsBr$_2$Cp*P*i*-Pr$_3$).

2.2.9. Cobalt

Some cobalt complexes are known to catalyze controlled polymerizations via a direct capping of a growing radical with a metal center (the so-called organometallic radical polymerization).[149] These systems are mechanically different from metal-catalyzed living radical polymerization, and thus, the details are not described here; this is also one of useful tools for controlled radical polymerization, especially for vinyl acetate.[160,161]

A few examples have been reported, however, that a cobalt catalyst works for the metal-catalyzed system with a halide initiator. A cobaltocene (Co-**1**) catalyzes polymerization of MMA with an alkyl bromide initiator to give narrow MWDs ($M_w/M_n = 1.1-1.2$).[162] However, the observed molecular weight is much higher than the calculated value, indicating a lower initiating efficiency ($f = 0.25$). Preheating the catalyst before mixing with the initiator led to an increase in the efficiency ($f = 0.63$). $CoI(PPh_3)_3$ (Co-**2**) is also active for MMA with a chlorine initiator.[163] Part of the initiator likely reacts with the catalyst via oxidative addition to give catalytically inactive trivalent complex, resulting in higher molecular weights.

2.2.10. Other Metals

Some complexes with rhodium (Rh), palladium (Pd), and rhenium (Re) had been reported for living radical polymerization before the last review article, but since then, there were few reports on the evolution of these complexes. Just a rhodium complex [$RhH_2(Ph_2N_3)(PPh_3)_2$] for styrene-polymerization was reported, with a poor performance ($M_w/M_n > 2$).[164] Rh(I) and Pd(0) are well-known to catalyze organic reactions, and usually the catalytic cycle involves an oxidative addition and a reductive elimination with two electrons transfer. For this reason, these complexes might be less suitable for metal-catalyzed living radical polymerization via one electron transfer.

2.3. Cocatalysts (Additives)

2.3.1. Overview of Cocatalysts

As described above, the acceleration of the catalytic cycle for the reversible activation/deactivation process should be most essential in metal-catalyzed living radical polymerization because it accelerates polymerization and enhance fine catalytic control but allows a decrease in required amount of the catalyst. In addition to design of metal complex catalysts as discussed above, an interesting feature is the use of additives or cocatalysts, mostly nonmetallic components that sometimes remarkably contributes to precision control of radical polymerization. The first example of cocatalysts have been reported for Ru(II) catalysts in the first original articles on metal-catalyzed living radical polymerization, where aluminum alkoxides[20] clearly accelerate polymerization and narrow MWDs. Since then, in phase II a variety of cocatalysts have been reported, extending their scope and, equally important, their "cocatalytic roles" including reducing agents, radical generators, alkylamines, and halogen donors.

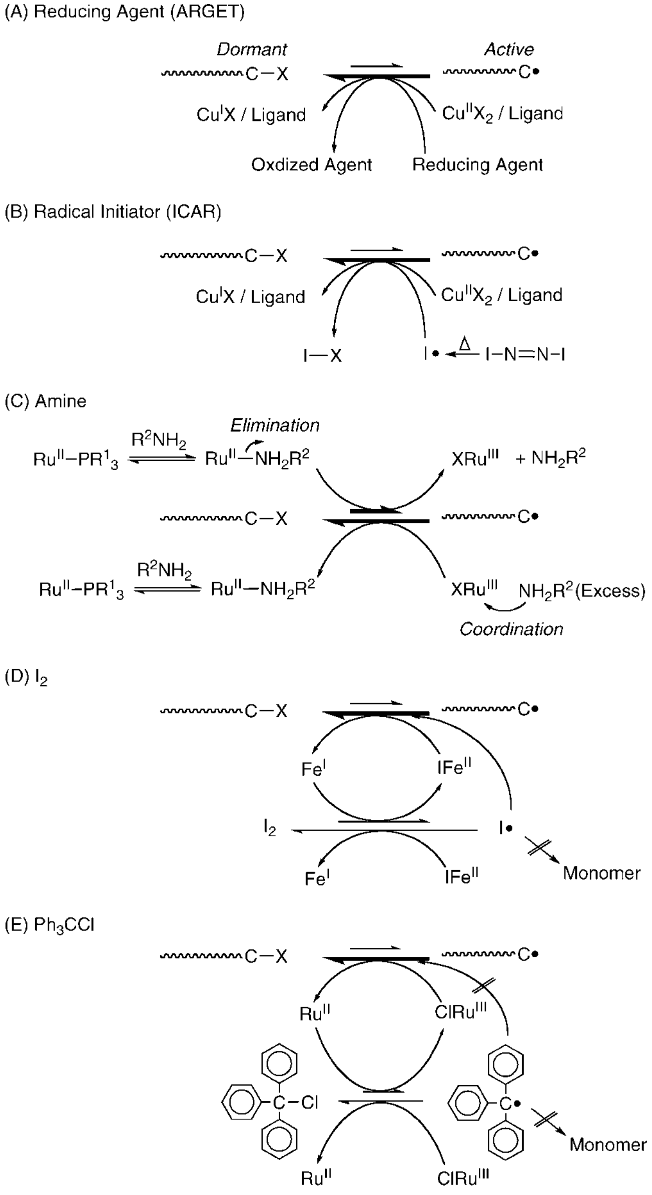
2.3.2. Reducing Agents

Matyjaszewski et al. have recently found that combination of a reducing agent for copper-catalyzed system is very effective to decrease the catalyst amount without affecting their catalytic functions.[5,6,72,74−77] Originally, the reducing agent was added for reduction of "injected" Cu(II) to generate active Cu(I) during polymerization (called activator generated by electron transfer or AGET), because the divalent complex is more stable and more preferable in catalyst handling.[165,166] In contrast, for normal copper-catalyzed systems, it had been recognized that Cu(II) species are accumulated because of unavoidable radical termination reactions during the polymerization. Accordingly, addition of a reducing agent was attempted to prevent such a gradual deactivation of the Cu(I) catalyst. The addition leads to continuous regeneration of Cu(I) from Cu(II), and a more efficient catalytic cycle emerges, requiring a minute amount catalyst so low that catalyst removal after polymerization is unnecessary. This system is called "activator re-generated by electron transfer" or "ARGET" (Scheme 2A), and now it attracts attention for practical uses, especially for biomedical applications. For example, when tin(II) 2-ethylhexanoate [$Sn(EH)_2$] is employed as a reducing agent for polymerization of styrene with EtBrIB/$CuCl_2$/Me_6TREN (EtBrIB, ethyl 2-broisobutyrate), even 10 ppm copper to monomer induces a well-controlled polymerization at a moderate rate [64% conversion in 1590 min, $M_n = 63\,000$ ($M_{n,theo} = 64\,000$), $M_w/M_n = 1.17$].[74] Besides $Sn(EH)_2$, some reducing agents have been reported for ARGET, including hydrazines (NH_2NH_2, $PhNH_2NH_2$),[75] glucose,[167] ascorbic acid,[76] phenol,[75] etc. It has been also reported that an excessively added nitrogen ligand works as a reducing agent.[168]

2.3.3. Free Radical Initiators

The addition of a small amount of free radical initiator is also effective for the reduction of Cu(II) to Cu(I), where the radical species therefrom can accept a halogen from Cu(II) to regenerate Cu(I) (Scheme 2B). Such a system is termed "initiators for continuous activator regeneration" or "ICAR",[75] and a similar decrease in catalyst amount is possible. For example, with azobuiisobuthyronitrile (AIBN), the polymerization of styrene with EtBrIB/$CuCl_2$/Me_6TREN needs only 50 ppm of copper to give controlled molecular weights and narrow MWDs [44% conversion in 2760 min, $M_n = 7900$ ($M_{n,theo} = 8700$), $M_w/M_n = 1.12$].[75] The rate enhancenent was lower than in ARGET and a small portion of undesired polymer chains form from the free radical initiator. Quite recently, this method has been demonstrated to be effective even for ruthenium catalyzed system with Ru(Cp*)Cl$(PPh_3)_2$ (Ru-**5**).[169]

Scheme 2. Contributions of Cocatalysts (Additives)



2.3.4. Metal Alkoxides

Aluminum isopropoxide [Al(O*i*-Pr)$_3$] has been widely used as a cocatalyst or an additive to accelerate polymerization or to allow the control of polymerization for many catalysts including ruthenium,[20−29] nickel,[136−138] iron,[88,89,92,94] rhenium,[170] molybdenum,[150,154] osmium,[158] and copper[171−173] complexes. An early study about their roles for $RuCl_2(PPh_3)_3$ (Ru-**1**) demonstrated that the added Al(O*i*-Pr)$_3$ stabilize the higher oxidation state (Ru^{III}) to facilitate radical generation, as judged from cyclic voltammetric analysis.[174] Later, a more detailed study was carried out with molybdenum catalysts by experimental and computational analyses, to reveal that the added alkoxide interacts with the higher oxidation complex via Lewis acid−base interaction and that the transferred halogen is charged to be more electropositive to catalyze the halide-exchange process.[175] Another study estimates that it serves to reduce an oxidized complex, similarly to reducing agents as described above.[171] Titanium isopropoxide [Ti(O*i*-Pr)$_4$] is also effective, particularly for iron-catalyzed polymerization of styrene or acrylate with cyclopentadiene-based iron catalysts (Fe-**2**−**5**).[88−92]

2.3.5. Amines

Amine compounds are typically cocatalysts first reported for Ru(II) to increase polymerization rate and precise control.[30,31,36,42] They are often employed for ruthenium catalyst with an excess amount (∼10 times), and some of these amines in situ convert the original metal catalysts into more active forms via dynamic ligand exchange (Scheme 2C). The amine coordination may enhance the electron density of the central metal, and the labile coordination would give a vacant site for halogen incorporation.

Further, the oversupplied amine would promote the deactivation process as well as the activation by dynamically repeating coordination and elimination. Such a facile ligand exchange was also utilized for catalyst removal: addition of hydrophilic amine (4-amino-1-butanol: $NH_2(CH_2)_4OH$) into ruthenium catalyzed polymerization of MMA with **Ru-15** led to not only a higher activity but also quantitative removal of the ruthenium residue with water-washing after polymerization.[42] Similar effects were seen in a copper catalyzed system with CuBr/TPEN.[73] The addition of tertiary amines, such as triethylamine or tributylamine, prevented precipitation of $CuBr_2$/TPEN complex and hence increased polymerization rate.

2.3.6. Halogen Source

Analogous to the common ion effects, addition of halogen source was proposed and verified to control the equilibrium between dormant and active species by external halogen delivery. An essential criterion for the donor is that it must not be an initiator nor a chain transfer, even though it is a halogen-based compound. For example, molecular iodine (I_2) was proven to serve as a radical scavenger to improve for MA polymerization catalyzed by dinuclear iron complex (Fe-**4**) (Scheme 2D).[176] In this system, the added iodine traps the growing radical to regenerate the carbon−iodine dormant species, which accordingly shifts the equilibrium to the dormant species. Importantly, the reactivity of the iodine radical toward a carbon−carbon double bond is too low to work as an initiator or a chain transfer agent. Added iodine also serves for control of the manganese-induced living radical copolymerization of 1-hexene and methyl acrylate with Mn-**2**.[177]

Addition of triphenylmethyl chloride (Ph_3CCl) was demonstrated to contribute to the equilibrium control in polymerization of MA (Scheme 2E).[178] A halogen-exchange study with Ph_3CBr and $RuCl(Ind)(PPh_3)_2$ (Ru-**4**) revealed that the carbon−halogen bond in Ph_3CBr is activated by the ruthenium complex much faster than the α-halo ester terminal in the dormant poly(MA) or a bromide-initiator. On the other hand, the resulting radical ($Ph_3C^\bullet$) was too bulky and too stable to initiate polymerization or to couple with the growing radical. Thus, the addition of Ph_3CCl clearly imposes an ill-controlled system with a high concentration of radical species by equilibrium shift to the dormant species.

2.4. Initiators

2.4.1. Overview of Initiators: Scope and Design

The leaving group or the transferred atom in dormant species is more or less exclusively a halogen in metal-catalyzed living radical polymerization, and thereby halogen-compounds (A−X, X = halogen) are widely employed as initiators. The component A should contain some conjugated or radical-stabilizing groups to facilitate radical generation, such as ester [−C(=O)OR], ketone [−C(=O)R], amide [$-C(=O)NR_2$], cyano (−C≡N), phenyl (−Ar), etc., similar to “conjugated” monomers for radical polymerization. Obviously, chlorine (Cl), bromine (Br), and iodine(I) are active as the halogen, while fluorine (F) is inactive for metal-catalyzed living radical polymerization. Simple alkyl halides, such as carbon tetrahalide (i.e., CCl_4 and CCl_3Br) are easily accessible and indeed work as initiators for some catalysts. However, their usage in catalyst screening is not recommended because of the poor initiation efficiencies and the possibility of multifunctional initiation or chain transfer as often seen in radical telomerization. Note that too a large radical-stabilizing effect from nearly substituents often results in no polymerization or a low initiation efficiency, as seen with triphenylmethyl halide (CPh_3X).[179]

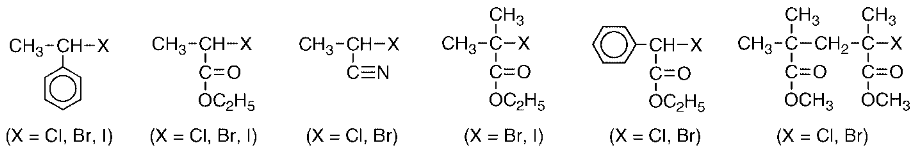
Because initiation needs to be faster than propagation to achieve fine molecular weight control, like classical living anionic polymerization, the structure A is further crucial and should judiciously be selected according to monomer. As a simple example, a styrene-like initiator (phenylethyl halide) is less favorable for MMA polymerization, as shown by difficulty in block copolymerization from styrene to more reactive MMA.

Selection of the halogen (X) mainly depends on the central metal of catalysts as well as monomers. For example, ruthenium-based catalysts tend to favor Cl-based initiators rather than Br-counterparts, whereas iron derivatives show an opposite preference, although both metals belong to the same group. This is likely due to difference in “halophilicity”: too high halophilicity would hinder halogen-release for deactivation, leading to worse control. The halophilicity may be accounted for by the hard−soft acid−base (HSAB) theory:[180] “soft” ruthenium is more compatible with bromine than chlorine (the former softer) and “hard” iron with harder Cl. In contrast, too low a halophicity is also unfavorable for control, as suggested by few examples of Cu catalyst/iodine initiator combinations because of the low stability of the Cu(II)−iodine bond. Thus, moderate halophilicity is required for the selection of halogen according to the central metal.

Halogen selection is also sensitive to monomer structure. As discussed later, the potential activity increases with the order I > Br > Cl, and thus, a suitable halogen is in part determined by the reactivity of monomer or the structure of the growing terminal therefrom. For example, the least dissociable chlorine is favored for MMA, which gives a highly stable and sterically conjugated tertiary carbon radical. In contrast, acrylates and styrenes favor Br- or I-initiators because of the less active secondary structure of their radicals with less activity.

2.4.2. Alkyl Halides

Figure 11 compares alkyl halides often employed as initiators in metal-catalyzed living radical polymerization in terms of their structural factors. Matyjaszewski et al. estimate activation rate constants (k_{act})[181] and overall equilibrium



	I-1	I-2	I-3	I-4	I-5	I-6
	(X = Cl, Br, I)	(X = Cl, Br, I)	(X = Cl, Br)	(X = Br, I)	(X = Cl, Br)	(X = Cl, Br)
Radical Stabilizaing Group	Phenyl	Ester	Nitrile	Ester	Phenyl/Ester	Ester
Monomer Model	Styrene	Acrylate	Acrylonitrile	Methacrylate	Styrene/Acrylate	Methacrylate
Carbon Radical	Secondary	Secondary	Secondary	Tertiary	Secondary	Tertiary
Structure	Monomeric	Monomeric	Monomeric	Monomeric	Monomeric	Dimeric

Figure 11. Initiators: alkyl halides.

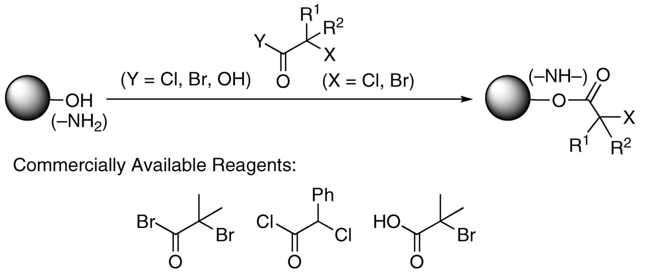
constants ($K_{ATRP} = k_{act}/k_{deact}$)[73] for various common initiators in conjunction with a copper catalyst ($Cu^{I}Br$/ligand), to discuss the effects of initiator structure on these constants. The estimation is helpful for studying structural aspects of not only initiators but also monomers. Larger values of these constants would mean more active initiators, although too fast initiation might cause the accumulation of oxidized complexes and side-reactions. The constant k_{act} increased with increasing substitution on the α-carbon adjacent to a leaving halogen, that is, primary < secondary (I-**1**−**3**, -**5**) < tertiary (I-**4**); the radical-stabilizing power increases in the order amide [−C(=O)NR$_2$] < ester [−C(=O)OR] (I-**2**, I-**4**) ≈ aryl (−Ar) (I-**2**) < cyano (−C≡N) (I-**3**) < ester [−C(=O)OR] + aryl (−Ar) (I-**5**) and for halogens (leaving groups) in the order Cl < Br < I. These tendencies are almost the same as the trends in K_{ATRP}, except that for halides (I < Br < Cl), and such a reversal is the result of too low of stability of the Cu^{II}−I bond. The preference for a particular halogen is therefore dependent on the central metal or the steric environment of a catalyst, but the effects of substitution and radical stabilizing groups would be almost common regardless the kind of catalysts or central metals. Initiators with synergistic phenyl and ester groups (I-**5**) have a higher initiating efficiency, and the aromatic group is additionally useful to characterize the terminal structure of produced polymers.[182] The halogen-capped MMA dimres (I-**6**), mainly employed with ruthenium and iron catalysts, are excellent initiators with high initiation efficiency and consequent control over polymerization, partially helped by the dimeric structure including the steric crowding around the radical-bearing α-carbon. Such a penultimate effect was more remarkable in a bulky structure, which was proven by comparison of k_{act} with other analogues.[183]

Halogen-based components initiation functions are easily incorporated into various compounds (frameworks) to give a variety of (multi)functional initiators; that sometimes allow conjugation with other molecules, oligomers, and biomolecules as shown below. Among frequently employed initiating units are α-halocarboxylic acids [haloisobutylates; −OCOC(Me)$_2$X, X = halogen] via the reactions with hydroxy (−OH) and amine (−NH$_2$) groups in the presence of a proton trap (e.g., triethylamine) or a condensation agent [e.g., dicyclohexylcarbodiimide/4-(*N*,*N*-dimethylamino)pyridine] (Scheme 3).

2.4.3. Arenesulfonyl Halides

Arenesulfonyl halides are a class of initiators different from alkyl halides [Figure 12A).[184] Their specific feature is a quantitative and fast addition of the sulfonyl radical to the "first" monomer in initiation probably because of its instability. Because of the fast addition and steric hindrance, they show low tendency to dimerization (radical coupling) on early stage relative to alkyl halides, leading to high initiating efficiency or good agreement of molecular weight with theoretical values. Originally, chlorine-based initiators (I-**7**) were examined, but later, bromine (I-**8**)[185] and iodine (I-**9**)[186] were also found to be effective.

Scheme 3. Introduction of Alkyl Halide Initiators



2.4.4. N-Chloro Compounds

Recently, N−Cl bond-containing compounds were found to give N-centered radical under metal catalysis to initiate living radical polymerization.[187] They carry some conjugated groups, such as ketone or phenyl, on the nitrogen to stabilize the radical, and the representative examples with high initiating efficiency are shown in Figure 12B (I-**10**−**13**). With a "self-regulating" catalyst, that is, Cu_2S/2,2′-bipyridine, MMA was almost quantitatively polymerized within 4 h to yield PMMA of narrow MWDs (M_w/M_n = 1.2−1.4). The structural environment around the nitrogen was very sensitive for initiating efficiency. For example, the initiation efficiency for I-**12** exceeds 80%, while only 50% for the crowded I-**14** though with the similar structure. Such a low efficiency is presumably caused by that the N-centered radicals are liable to radical coupling (dimerization) at the initial stage, because of the less hindrance around the N-radical, unlike the sulfonyl derivatives. *N*-Bromosuccinimide (NBS) was also employed as an initiator for St and MMA with CuBr/bpy. Molecular weight distributions of the obtained polymers were narrow (M_w/M_n = 1.15−1.40), though the initiator efficiencies were low (<40%), because of a side reaction specific for NBS.[188]

2.4.5. Halogen-Free Initiators

As mentioned above, the initiators in metal-catalyzed living radical polymerization involve almost exclusively a halogen as the leaving group, which is reversibly transferred into the catalyst. In contrast, Matyjaszewski et al. developed halogen-free initiating systems with alkyl diethyldithiocarbamates (I-**15**−**19**: R-S(C=S)NEt$_2$) in copper-catalyzed living radical polymerization [Figure 12 (C)].[189] Among them, I-**18** is the best initiators to give narrowest MWDs

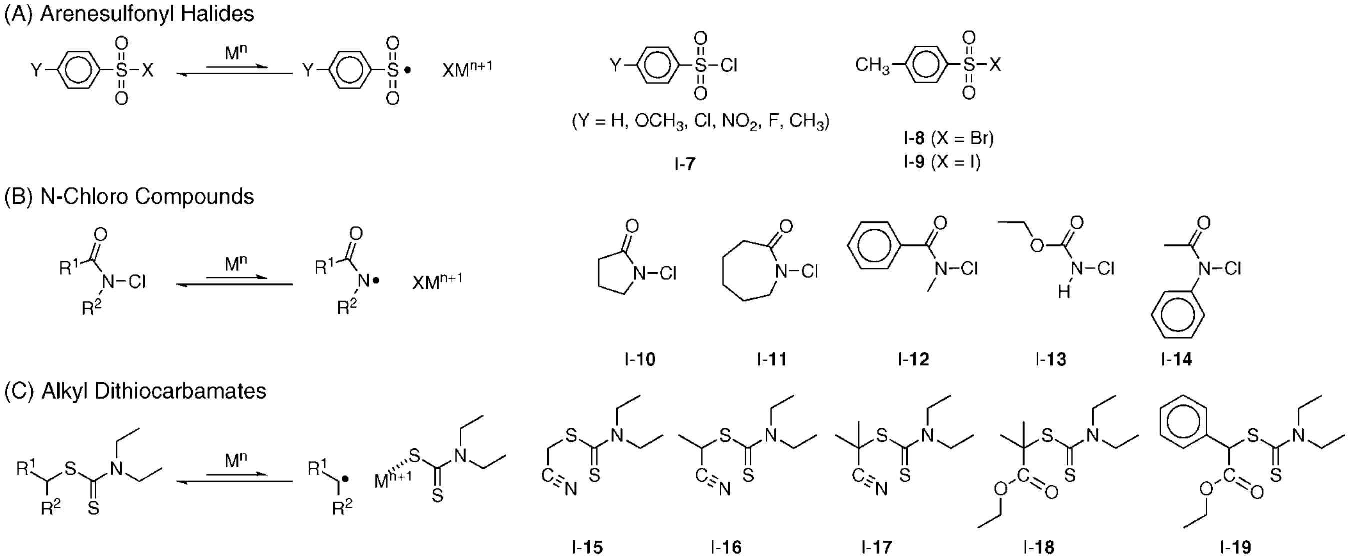
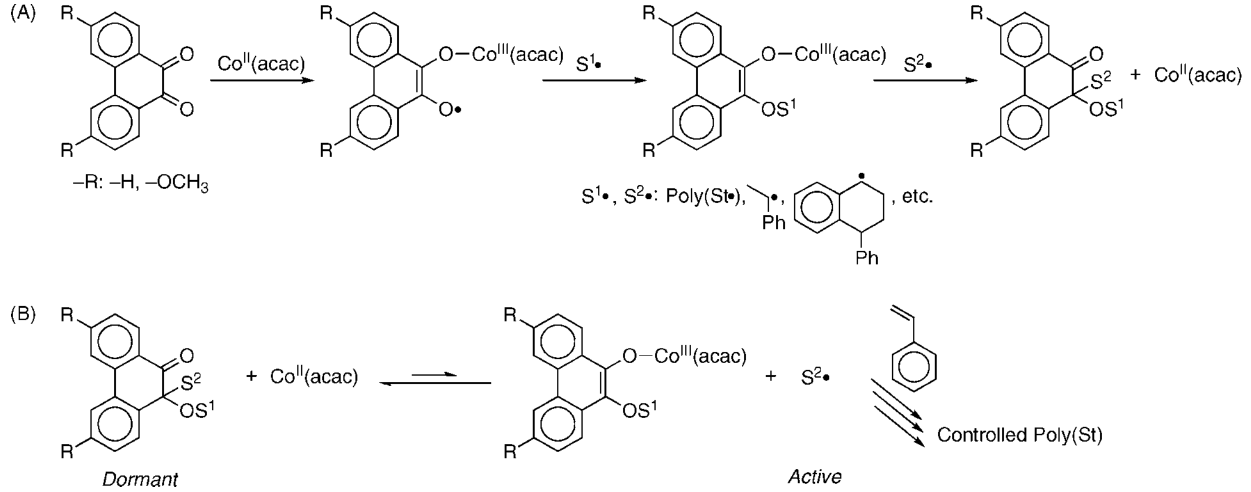


Figure 12. Initiators: arenesulfonyl halides, *N*-chloro compounds, and alkyl dithiocarbamates.

Scheme 4. Quinone Transfer Radical Polymerization



($M_w/M_n < 1.10$) with a tridentate ligand (PMDETA). **I-17** is rather specifically suitable for MMA in the presence of bipyridine. In these systems, the diethyldithiocarbamate group [$-S(C{=}S)NEt_2$] is likely exchanged between dormant and active species under copper catalysis, as with a halogen in the halide initiating systems. However, the exchange between the diethyldithiocarbamate and the bromine of the CuBr is almost negligible from analysis of the polymer chain end.

Jérôme et al. found another class of halogen-free systems with a quinone derivative as an initiator, and names the systems as quinone transfer radical polymerization (QTRP) (Scheme 4).[190−193] Examples include phenanthrenequinone and 3,6-dimethoxy-9,10-phenanthrenequinone, and they initiate a controlled radical polymerization of styrene with use of a catalytic amount of an acetylacetonate (acac) complex [e.g., $Co(acac)_2$ or $Al(acac)_3$]. Especially, the dimethoxy initiator gives a high initiating efficiency and narrower molecular weight distributions ($M_w/M_n < 1.2$).[191] In the proposed mechanism, a persistent radical centered on the oxygen atom of the quinone is first formed by the redox reaction with the acac-complex (Scheme 4A). The oxygen radical traps some styrene related radical, generated by autopolymerization, to form dormant species. Eventually, the polymerization is controlled via an equilibrium between the dormant and the growing polystyrene radical under the cobalt catalysis (Scheme 4B).

2.5. Solvents

2.5.1. Overview of Solvents

Polymerization control under bulk conditions is relatively less difficult in metal-catalyzed living radical polymerizations, since the so-called Trommsdorff (gel) effect is absent in contrast to conventional radical polymerization in solution.[194] Solvent-free systems are preferred in application, because they are simpler, inexpensive, and less energy intensive, and the reduction in volatile components. However, for precise control (e.g., quantitative block copolymerization), bulk systems are unfavorable because the increasing hinders diffusion of monomer and catalyst and therby causes side-reactions. Thus, most of living radical polymerizations have been studied in solutions, except for the synthesis of extremely high molecular weight polymers. Because of the inherent robustness of radical species, a wide range of solvents including water are applicable according to the solubility of monomers and polymers, in sharp contrast to controlled ionic intermediates. In the metal-catalyzed systems, however, due caution should be taken to solvent effects on metal catalysts, namely solubility, coordination of solvent, and solvent-related transformation in metal complexes.

2.5.2. Catalyst Solubility and Coordination of Solvent

Nonpolar aromatic solvents with high boiling point (>100 °C) are mostly employed for common hydrophobic monomers [e.g., alkyl (meth)acrylates and styrene] because of the low coordination abilities: benzene, toluene, xylene, anisole, etc. However, some catalysts, typically copper catalysts carrying aromatic nitrogen-based ligands (e.g., 2,2′-bipyridine, pyridineimine-based, terpyridine), are poorly soluble in these nonpolar solvents, and the poor solubility causes less controlled and slower polymerization. To improve catalyst solubility, long alkyl chains are introduced onto the ligands at the position far from the coordination site, which often contributes to making the medium homogeneous.[195−199]

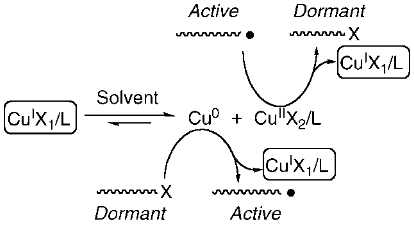
In some copper-catalyzed systems for hydrophobic monomers, solvent-induced positive effects (e.g., acceleration and improvement in controllability) were observed with specific polar solvents: ethylene carbonate,[200] dimethylformamide,[201] ethyl acetate,[202] acetonitrile,[202,203] 1,2-dimethoxybenzene,[204] diphenyl ether,[204] benzonitrile,[205] and pyridine.[206] The effects are likely attributable to coordination of the solvent or solubility change of the complex to improve the catalytic performances.

As shown in section 3.2, for functional monomers carrying polar groups, a polar solvent is needed for dissolution of the monomers and resulting polymers. In such a polymerization, multiple components (monomer, polymer, and solvent) potentially coordinate the catalyst to affect the catalysis, and thus tolerant catalysts with tight and flexible ligands are usually required to evade the additional coordination. For "normal" Cu^I-catalyzed systems, it was demonstrated that coordination of polar solvent to the Cu^{II}-center often induces a reversible dissociation of a halide from Cu^{II} complex to exacerbate polymerization control.[207] To suppress this, large amount of a Cu^{II}−halide complex is sometimes combined.

2.5.3. Environmentally Friendly Solvents

From the standpoint of environmentally friendly systems for practical uses, low-volatility solvents have drawn attention. Ionic liquid is such an example, and increasingly that is now more attractive due to their "green" properties (e.g., nonflammable and recyclable). The first successful example is the Cu^IBr-catalyzed living radical polymerization of MMA in an ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]), in conjunction with *N*-propyl-2-pyridylmethanimine (NPPMI) as a ligand.[208] The polymerization proceeded even at 30 °C at a high rate, though the MWDs were a little broader ($M_w/M_n \approx 1.3-1.4$). Simple extraction of the polymerization solution with toluene led to PMMA containing little copper residues because the ionic liquid is immiscible in toluene but dissolve the catalyst. [bmim][PF_6] was also applied for the Cu_2O/bpy-catalyzed polymerization of MMA to enhance the catalytic activity.[209] For *n*BA with CuBr/bpy, the some liquids enhances the terminal halogen efficiency relative to bulk systems.[210] Similar improvement in control was confirmed with CuBr-PMDETA system, where a quantitative block copolymerization of MA with *n*BA was feasible.[211,212] The particular polarity of ionic liquid affects even monomer reactivity ratio for copolymerization of styrene and *N*-hexylmaleimide, where a degree of alternating sequence is more favored in anisole.[213] Ionic liquids are also employed in iron-mediated polymerizations, and they often work as ligands or solubilizing agents for an iron halide (a precursor salt).[210,214]

Scheme 5. Solvent-Mediated Disproportionation of Cu(0) in SET-LRP



Poly(ethylene glycol)[215] or ethylen glycol[216] were also found to be considered as environmentally friendly solvents for copper-catalyzed living radical polymerization. These polyethers enable a fast polymerization, a polymerization at ambient temperature, and an efficient removal of copper residue, along with other advantages; inexpensive, low toxic, and low volatile.

2.5.4. Water

In sharp contrast to the ionic counterparts requiring rigorously dry conditions, radical polymerization not only tolerates a contamination by water but also welcomes the use of water for polymerization control and advanced products thereby. Now, the usage would be increasingly more significant for environmental aspects. In general, water-mediated radical polymerizations are classified into homogeneous and heterogeneous systems: the former is applied for aqueous monomers, while the latter, mainly involves emulsion and suspension processes. In the metal-catalyzed living radical polymerizations, copper catalysts are often employed in water, and a CuCl with bpy is a representative catalyst for fine control though insolubile in water. Some ruthenium and iron complexes are also reported for aqueous systems, where they are soluble in water or tolerance to water. Many useful and comprehensive reviews are available for these subjects.[5,217−221]

2.5.5. Catalytic Solvents: Catalyst Disproportionation

Recently, Percec et al. have found a very active copper-catalyzed systems, now coined as single-electron transfer living radical polymerization (SET-LRP), allowing very fast polymerizations, polymerizations at ambient temperature, the synthesis of ultrahigh molecular weight polymers ($M_n > 10^6$, $M_w/M_n < 1.2$), control for a nonconjugated monomer (vinyl chloride), and a dramatic reduction in catalyst concentration (~10 ppm).[78−85] The most accessible starting catalyst is an elemental Cu(0), not copper halides [Cu(I)X and Cu(II)X_2]. The zerovalent metal is potentially much more active than the later salts in the cleavage of the carbon-halide bond via outer-sphere electron transfer (OSET) between Cu(0) and Cu(I). SET-LRP is therefore fundamentally different from the Cu(I) catalysis with inner-sphere electron transfer (ISET). Another factor of consideration, perhaps specific to copper is the solvent-mediated dispropotionation of Cu(I) into Cu(0) and Cu(II) (Scheme 5). The workable solvents are highly polar ones involving DMSO, alcohols, ethylene/propylene carbonate, ionic liquids, and water. According to a UV−vis spectroscopy study, a certain nitrogen-based ligand (typically Me_6-TREN and TREN) is needed for the fast disproportionation.

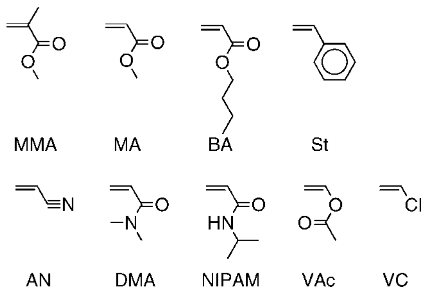


Figure 13. Common monomers.

2.6. Monomers

2.6.1. Overview of Monomers

Radical polymerizations are, in general, applicable to most of vinyl monomers, except for bulky or disubstituted monomers with low ceiling temperature. Even these monomers can be copolymerized with a less bulky and more reactive monomers, and it would be of interest to consider how the monomer structure affects the "controllability" of their metal-catalyzed polymerization. Since the metal-catalyzed living radical polymerization proceeds via reversible activation of the carbon-halide bond derived from monomer, the dissociation or bond energy of the terminal bond influences the reactivity of monomers. As indicated by the excellent correlation between the bond-dissociation energy of alkyl halide and the equilibrium constant (K_{ATRP}) with variety of halide-initiators,[70] the carbon−halogen bond dissociation energy of a dormant terminal will depend on the conjugation factor for a monomer's pendant group. Namely, with a more conjugating pendant, the resulting radical is more stable, or the carbon−halogen bond will be more dissociable and of less bond energy, and consequently affects controllability for polymerization. Thus, the equilibrium constant is dependent on the conjugation effect or the reactivity of monomer, causing difficulties in universal control for representative three conjugated monomers, MMA, MA (or *n*BA), and St using a single initiating system. To achieve fine control over variety of monomers, not only high activity but also flexibility according to monomer would be required for the catalysts. Combination with cocatalyst or higher oxidized complex would consequently contribute to such modulation for catalysis. In this section, only fundamental (nonfunctionalized) monomers for metal-catalyzed living radical polymerization are described.

2.6.2. Conjugated Monomers

Conjugated monomers, most widely used in metal-catalyzed living radical polymerization, are methyl methacrylate (MMA), methyl acryalate (MA), *n*-butyl acrylate (*n*BA), and styrene (St) (Figure 13). These fundamental monomers are usually employed for evaluating initiating systems, and quite naturally there are numerous studies dealing with their polymerizations. Therefore, the detailed discussion on these monomers will be omitted herein. For the controlled polymerizations of their derivative monomers with functional side groups, see section 3.2.

Acrylonitrile. Acrylonitrile (AN) is one of typical conjugated monomers, but the controlled radical polymerizations under metal catalysis were less advanced, which is likely caused by a coordination of the cyano group to a catalyst and a limitation in solvent to dissolve AN polymers (PAN). Additionally, a specific side-reaction is found in AN polymerization: a reduction of growing radical into a carbanion via outer-sphere electron transfer by Cu(I).[222] The use of alkylsulfonyl chlorides as initiators, coupled with bipyridine-based cuprous and cupric oxide catalysts, improves activity and controllability relative to the alkyl halide systems.[223] Recently, an ARGET system with $Cu^{II}Cl_2$/tris[(2-pyridyl)-methyl]amine (TPMA) in conjunction with tin(II) 2-ethylhexanoate in ethylene carbonate is found to form high molelecular weight PANs (M_n > 100 000) with narrow molecular weight distributions (M_w/M_n < 1.3).[224] The iron-based reverse ATRP with $FeCl_3$/isophthalic acid (**Fe-L14**) is also effective (>90% conversion, M_n > 80 000),[225] while reverse system with $CuCl_2$/bpy showed limited conversion (<50%).[226]

Acrylamides. Acrylamide polymers are widely employed in industry and of interest because of the potential functionality via the hydrogen bond, and hence development of the controlled polymerization has attracted attention toward more advanced applications. Polymerization control had been attempted for *N*,*N*-dimethylacrylamide (DMA) with ruthenium[27,28] and copper complexes,[227−229] though, for both cases, the catalysts were inefficient, either to give broader molecular weight distributions or to require an excess amount of catalyst relative to the initiator for a quantitative polymerization. Such an inadequate catalysis may stem from the following:[227] (1) deactivation of catalyst by the amide group in monomer or polymer, (2) nucleophilic displacement of terminal bromine by the penultimate amide chain, to form a terminal five-membered ring, inactive for the catalyst. Thus, the uses of polar solvents with hydrogen-bonding and a chlorine-initiator giving stronger growing terminal were found to be effective to prevent undesirable reactions. Indeed, when *N*-isopropylacrylamide (NIPAM) was polymerized with 2-chloropropionate (MCP) and $Cu^{I}Cl$/Me_6TREN as a catalyst in a mixed solvent of DMF/H_2O (1:1 v/v)[230] or in branched alcohol (e.g., isopropanol and *tert*-buthanol),[231] the polymerizations quantitatively proceeded even at ambient temperature to give controlled molecular weights and narrow MWDs. Independently, Fe-**4**, a highly active dinuclear Fe(I) catalyst catalyzes living radical polymerization of an acrylamide (DMA) in the presence of an iodide initiator.[176] The essence of the achievement is an addition of I_2 as a radical scavenger to control the equilibrium between dormant and active species (see section 2.3.6). The polymerization was almost quantitative within 2 h, and molecular weight and the distribution of produced poly(DMA)s were fairly controlled (M_w/M_n = 1.22).

2.6.3. Nonconjugated Monomers

Vinyl acetate (VAc) and vinyl chloride (VC) are representative monomers for radical polymerization. Their commercial polymers are manufactured virtually via only radical mechanism. They are easily polymerized once they encounter some radical source, however their highly reactive propagating radical species tend to undergo side reactions involving irregular propagations (e.g., head-to-head and tail-to-tail). Hence, the control for these monomers is more difficult than that for conjugated monomers.

Vinyl Acetate. Living radical polymerization of VAc has been one of challenging subjects for the metal-catalyzed systems. In contrast, other controlled radical polymerizations have achieved it, including iodine transfer,[232,233] MADIX/RAFT,[234−236] cobalt-mediated,[160,161] and organotellurium-mediated[9,237] polymerizations. Most

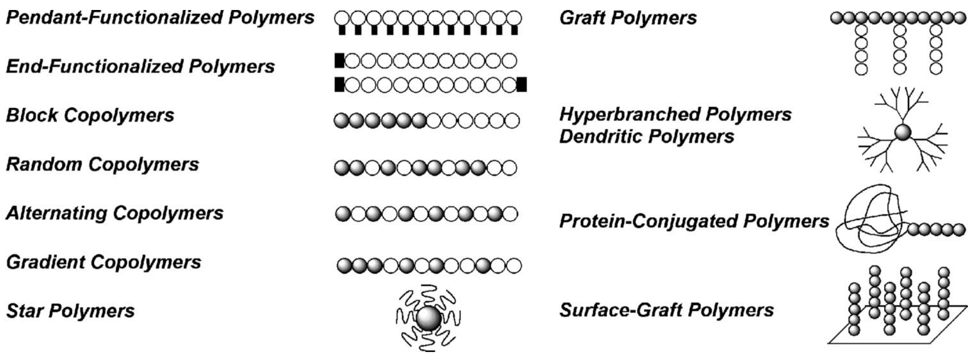


Figure 14. Precision polymer synthesis.

of them are controlled via degenerative chain transfer processes or radical-capping promotion, which might be favorable for control of the unstable propagating radical. On the other hand, metal catalysts need to activate the terminal carbon-halide bond derived from VAc. This bond is not so active for the homolytic cleavage under metal catalysis, and seriously tends to be decomposed into an aldehyde by water or in polar solvent. In spite of such disadvantages, the possibility of metal-catalyzed living radical polymerization of VAc was first demonstrated with a highly active dinuclear iron complex [$Fe_2Cp_2(CO)_4$, Fe-**4**], in conjunction with an iodine initiator and a cocatalyst (additive) such as $Al(O\textit{i}\text{-}Pr)_3$, $Ti(O\textit{i}\text{-}Pr)_4$, and $\textit{i}\text{-}Bu_3Al$.[238] The polymerizations proceeded up to ∼70%, and the molecular weights of the poly(VAc)s increased in direct proportion to monomer. Importantly, analyses of ^{1}H NMR showed that the polymers certainly carry an initiator moiety at the α-end and an iodine at the ω-end.

Quite recently, Kamigaito et al. have reported a more active controlled system for VAc with a dinuclear manganese complex [$Mn_2(CO)_{10}$, Mn-**2**] with an iodine initiator.[157] As described in section 2.2.6, the polymerization proceeds under visible light for photochemical homolysis of Mn-**2**, and is completed within a few hours even at low temperature (40 °C). Interestingly, molecular weight of produced poly(VAc) can be controlled up to 10^5.

Vinyl Chloride. Percec's group has extensively studied a metal-catalyzed living radical polymerization of vinyl chloride (VC). This polymerization should be worth challenging because no other categories of living radical processes thus far afford fine control. In 2002, they first presented a controlled radical polymerization of VC with a Cu(I) catalyst (Cu_2O, Cu_2Te, CuCl, and CuI) in H_2O/THF, initiated with CHI_3 and a nitrogen-based ligand [tris(2-aminoethyl)amine (TREN) and poly(ethylenimine)].[239] The water therein induces a disproportionation of Cu(I) to generate more reactive Cu(0), which presumably activates C−I bond for the initiator or growing terminal via outer-sphere single-electron transfer (SET). The molecular weights of the resultant poly(VC)s are well controlled to agree with the theoretical values, however, gradual retardation or limited conversion is observed. Such an insufficient catalysis is caused by that the degenerative chain transfer (DT) is also involved via the iodine-transfer system, along with usual metal-catalyzed halogen transfer process (later, they called the polymerization as SET-DTLRP). On the other hand, with a SET-LRP system in DMSO consisting of $CHBr_3$/Cu(0)/TREN, a controlled polymerization proceeds almost quantitatively up to 90% conversion.[78] Now, the SET-LRP is the only system to produce poly(VC)s with controlled high MWs and narrow MWDs.

3. Precision Polymer Synthesis

3.1. Overview of Precision Polymer Synthesis

One of the most prominent characteristics of metal-catalyzed living radical polymerization is that it allows the synthesis of polymers with precise architecture, well-controlled molecular weights, and narrow molecular weight distributions (MWDs) under relatively mild and convenient conditions, even in the presence of protic and/or polar functionality in monomers and solvents (Figure 14).[1−5,240,241] In particular, the tolerance against polar groups, originating from the neutral radical growing species, has opened a new scope to directly prepare functional polymers, in contrast to the less tolerant ionic living polymerizations that often require cumbersome protection and deprotection of monomer pendent groups. Especially, thanks to the recent evolution of metal catalysts as described in section 2,[3,5] one can obtain “designed” macromolecules with sophisticated and complex structures and functional groups to express specific functions. The molecular design of polymers has been further extended by the combination of other precision polymerization systems,[242−244] thereby possibilities are now virtually infinite.

With these backgrounds, this part deals with a wide variety of precision polymer synthesis via metal-catalyzed living radical polymerizations reported since 2001 (Phase II), categorized into the following 10 sections (Figure 14): pendant-functionalized polymers,[240] end-functionalized polymers,[240] block copolymers,[242−247] random copolymers,[248] alternating copolymers, gradient copolymers,[249] star polymers,[250,251] graft copolymers,[252−254] hyperbranched and dendritic polymers,[255] and advanced designer materials (protein−polymer conjugates[13,14] and surface-graft polymers[15,254,256−259]). Comprehensive reviews for precision polymer synthesis before early 2001 (Phase I) are also available.[1]

3.2. Pendant-Functionalized Polymers

The evolution of new and designed catalytic systems after 2001 (Phase II) has not only improved the controllability of metal-catalyzed living radical polymerization but also widened its scope of applicable monomers particularly to methacrylates, acrylates, styrenes, and acrylamides with polar functions. In addition to conventional hydroxyl, amino, and amide groups, the pendent functionalities include unique or complex structures, such as ionic salts, ionic liquids, sugars, amino acids, peptides, nucleic-acid bases, and liquid crystals. Functional groups that are potentially poisonous to metal catalysts but readily protected and deprotected via simple postprocess modifications have also been incorporated into monomers. Figures 15−17 present comprehensive lists of

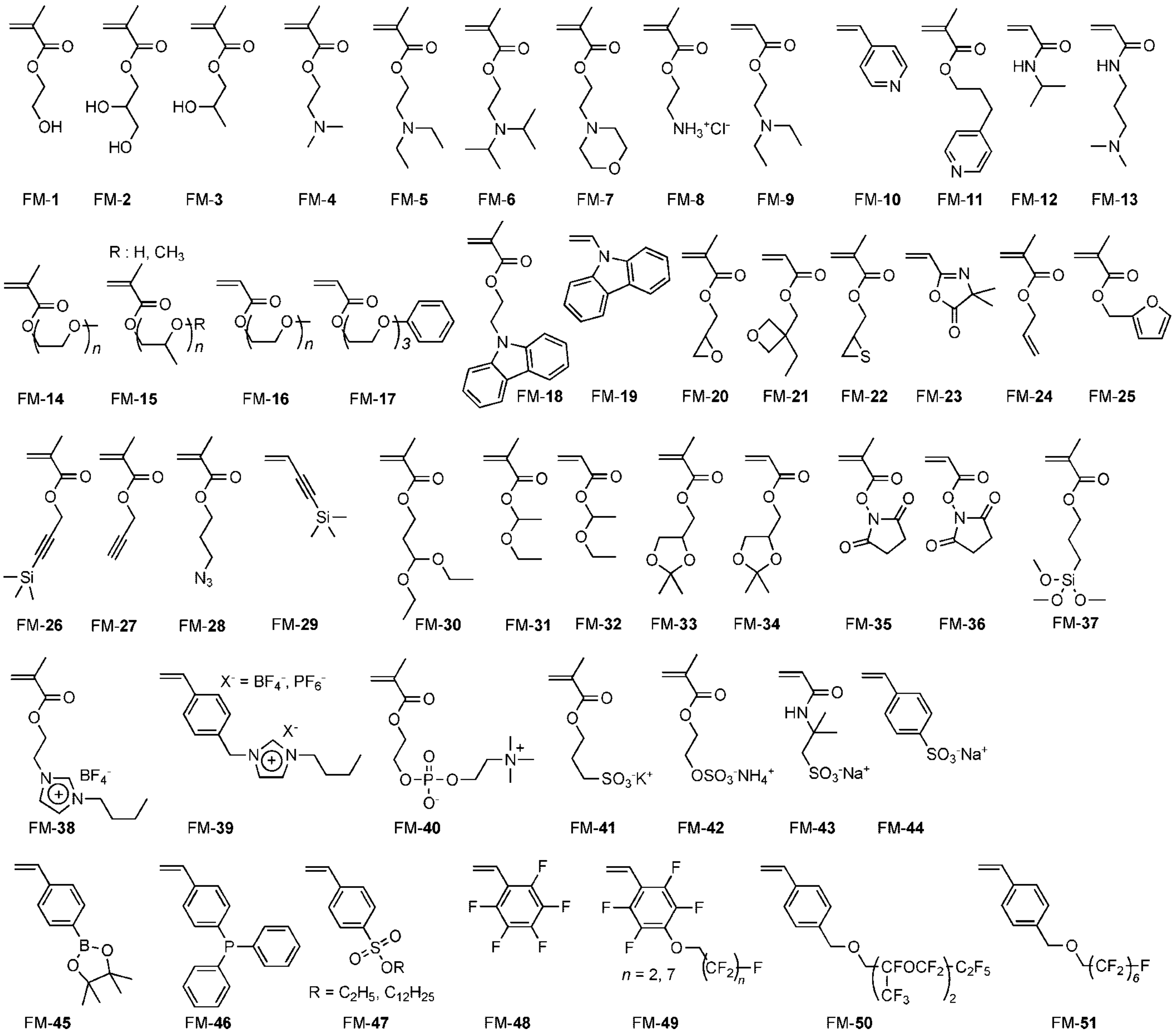


Figure 15. Functional monomers 1.

these functionalized monomers reported in phase II, and their metal-catalyzed living radical polymerizations are discussed herein.

Hereafter in this section, the cited examples of polymerizations and polymer syntheses imply, unless otherwise specified, that the product polymers are "well controlled" in terms of high conversion over 90−95% and narrow MWDs with $M_w/M_n = 1.1-1.3$.

3.2.1. Non-Protected Functional Monomers

Figure 15 shows "non-protected" functional monomers, which were newly reported or whose controllability was remarkably improved after 2001 (Phase II).

For example, though controlled polymerizations of 2-hydroxyethyl methacrylate (HEMA; FM-**1**) were already reported before 2001,[1,32,260] the polymer MWDs were relatively broad ($M_w/M_n = 1.3-1.8$) and the optimization of reaction conditions was necessary. Quite recently, a ruthenium Cp* catalyst (Ru-**15**, Cp* = pentamethyldicyclopentadienyl) with an amino alcohol additive allowed a fast and well-controlled polymerization of FM-**1** in ethanol at low temperature (ambient to 40 °C).[261] Polymer molecular weight was finely controlled ($M_w/M_n = 1.1-1.3$), and notably, the catalyst is active and efficient, thus working at a low catalyst/monomer feed ratio: [Ru-**15**]/[FM-**1**] = $1/10^4$ or 100 ppm. These systems give random and block copolymers with other functional monomers (sections 3.3.2 and 3.4.1).

In contrast to previous systems,[260] methanolic or aqueous systems coupled with a copper catalyst (CuBr/bpy) and a hydrophilic bromide initiator are now reported at ambient temperature (20 °C) in high yield (conversion >95%),[262,263] where the polymer molecular weights increased with increasing conversionersion, keeping narrow MWDs ($M_w/M_n = 1.1-1.3$). These systems also lead to **FM-1**-based block copolymers and random copolymers (section 3.3.2 and 3.4.1, respectively). Other hydroxyl-functionalized methacrylates (FM-**2**, FM-**3**)[264] can be polymerized faster than **FM-1** with a copper catalyst. The polymerizations of FM-**1**−**3** in aqueous media are clearly faster than those in pure MeOH.

Amino-functionalized (meth)acrylates (FM-**4** to FM-**9**) can be directly polymerized with metal catalysts. As well as a Ru(Ind) catalyst (Ru-**4**),[3,265] the RuCp* (Ru-**15**) catalyst with amino alcohols, the same as for FM-**1**, efficiently induces living radical polymerization of 2-(dimetylamino)-ethyl methacrylate (DMAEMA: FM-**4**) in EtOH at 40 °C to yield well-controlled poly(FM-**4**) with quite narrow MWDs ($M_w/M_n < 1.1$).[261] A nickel complex, $NiBr_2$ with a $PMePh_2$ ligand (Ni-**8**), also catalyzes a controlled polymerization of FM-**14**.[266] In addition to ruthenium and nickel catalysts, copper salts (CuBr or CuCl) coupled with appropriate multidentate amine ligands are effective. Actually, CuBr/HMTETA induces bulk polymerization of FM-**4** in high yield.[267,268] where a white powdery product was recovered by simple precipitation from an alkaline water solution.[268] As well as FM-**4**, a copper chloride catalyst in conjunction with HMTETA ligand is also effective for other tertiary amine-bearing methacrylates (FM-**5**−**7**),[269,270] leading to block copolymerization of FM-**4**−**7** and FM-**1** (section 3.3.2). 2-Aminoethyl methacrylate hydrochloric salt (FM-**8**) is polymerized with CuCl/bpy in 2-propanol/water (80/20), which also produce the random copolymers of FM-**8** with FM-**1**−**3** (section 3.4.1).[271] The polymerization of 2-(dimethylamino)ethyl acrylate was achieved with CuBr/Me_6TREN and a bromide initiator in bulk at 25 °C or in methanol at 50 °C.[272] However, the MWDs were relatively broad ($M_w/M_n = 1.4-1.7$) and further optimization seems necessary.

4-Vinylpyridine (FM-**10**)[273] and a pyridine-bearing methacrylate (FM-**11**)[274] are also polymerized with copper systems ($M_w/M_n < 1.25$), while a pyridine moiety often reacts with a dormant bromide terminal. Thus, the key for a better controlled and efficient polymerization of FM-**10** is to select a suitable copper chloride catalyst.

N-Isopropylacrylamide (NIPAM, FM-**12**), a typical thermosensitive amide monomer, can be polymerized with CuCl/Me_6TREN and a chloride initiator in DMF/water mixed solvent[230] or alcohol[231] at 20 °C to provide polymers with narrow MWDs. The poly(NIPAM) obtained from the alcoholic system ($M_w/M_n \approx 1.1$) exhibited thermosensitive functions, in which the lower critical solution temperature (LCST) gradually decreased as the molecular weight of the polymers increased from 1000 to over 30000. A controlled polymerization of an amino group-bearing acryl amide (FM-**13**)[275] was also catalyzed with CuBr/Me_4CYCLAM.

A series of methacrylates (FM-**14**) with poly- or oligo-(ethylene glycol) (PEG) methyl ether in the pendant [n = 4.5, 8.5, 23; M_n (monomer) = 300, 475, 1100] are attractive monomers: amphiphilic, thermosensitive, ion-conductive, and biocompatible.[276] They can be polymerized with ruthenium, iron, nickel, and copper catalysts. In particular, ruthenium systems with $RuCl_2(PPh_3)_3$ (Ru-**1**), Ru(Ind)Cl$(PPh_3)_2$ (Ru-**4**), Ru(Ph-Ind)Cl$(PPh_3)_2$ (Ru-**7**), and RuCp*Cl[P(m-tol)$_3$]$_2$ (Ru-**15**) efficiently induce living polymerizations in toluene at 80 °C.[261,265,277−279] Typically, $RuCl_2(PPh_3)_3$ (Ru-**1**)/n-Bu_3N with a chloride initiator efficiently produced poly(FM-**14**) (conversion ≈ 90%, $M_w/M_n \approx 1.4$).[277] With a high end-functionality, this system also produces amphiphilic and thermosensitive PEG-armed star polymers via an "arm-linking" reaction (section 3.8.2).[277] Additionally, block[278] and star[279] polymers with styrene (section 3.8.1) were also obtained by the Ru-**1**-catalyzed polymerization, where the products led to soft but tough transparent films that proved highly ion-conductive to function as novel solid polymer electrolytes for lithium battery. For FM-**14** (n = 8.5), Ru(Ind) and RuCp* catalysts (Ru-**4**, Ru-**7**, and Ru-**15**) showed controllability ($M_w/M_n < 1.2$) better than $RuCl_2(PPh_3)_3$ (Ru-**1**).[261,265] Especially, RuCp* catalyst (Ru-**15**) with an amino alcohol additive exhibits excellent controllability and efficiency in ethanol at 40 °C (conversion >98% in 24 h; $M_w/M_n = 1.07$),[261] also leading to various random and block copolymers.

Iron catalysts are generally less tolerant to polar functional groups than ruthenium. However, $FeBr_2$ coupled with a large, conjugated, and charge-delocalized phosphazenium salt (PZN-Br: Fe-**L5**) and a bromide initiator induced well-controlled polymerization of FM-**14** (n = 8.5) in toluene at 60 °C,[112] in sharp contrast to the near absence of polymerization with a conventional triphenylphosphine-bearing iron [$FeBr_2(PPh_3)_2$]. In addition, a nickel-phosphine complex, $NiBr_2(PMePh_2)_2$ (Ni-**8**), is recently found to induce the polymerization of FM-**14** ($M_w/M_n \approx 1.4$).[266]

In aqueous media at ambient temperature (20−25 °C), copper catalysts [CuCl/bpy[280] or CuCl(Br)/NPPMI or a hydrophilic pyridyl methanimine[281,282] with a bromide initiator efficiently induced a fast polymerization of FM-**14** (conversion >99%; 1 h). Recently, an aqueous AGET ATRP of the PEG monomer was reported in conjunction with a $CuBr_2$/TPMA catalyst and ascorbic acid (reducing agent).[283] Various organic solvents (THF, toluene, and anisole) are also applied to polymerization of FM-**14** with CuBr/bpy or CuBr/*N*-ethyl-2-pyridylmethanimine at 50−90 °C.[284,285] The products carrying a long PEG chain (23 units)[284] are, in fact, densely grafted PEO brushes obtained via "grafting through" method (section 3.9.2), and they are employed for bioconjugation.[285] The polymerization of poly(propylene oxide) methacrylate (FM-**15**)[280,286] was also catalyzed by CuBr/PMDETA.[286] Furthermore, PEG-bearing acrylates (FM-**16**[287] and FM-**17**[288]) are also polymerized with copper systems (CuBr/PMDETA, HMTETA, or CuCl/Me_6TREN).

A carbazole-bearing methacrylate (FM-**18**)[289] and 2-*N*-vinylcarbazole (FM-**19**)[290] were employed for CuBr/bpy-catalyzed polymerization ($M_w/M_n = 1.2-1.3$).

3.2.2. Protected Functional Monomers and Reactive Monomers

Metal-catalyzed living radical polymerization can apply to monomers carrying not only a functional but a reactive pendent group as well (FM-**20** to FM-**37**). Among monomers with a heterocyclic pendant for ring-opening polymerization (FM-**20** to FM-**23**), glycidyl methacrylate (FM-**20**) is polymerized with a ruthenium[265] or a copper catalyst.[291−293] Ru(Ind)Cl$(PPh_3)_2$ (Ru-**4**) with n-Bu_3N additive and a chloride initiator efficiently gave well-controlled polymers in toluene/anisole (1/1, v/v) at 80 °C without any gelation, also leading to block copolymers with MMA (section 3.4.2).[265] Controlled poly(FM-**20**) are also obtained with CuBr/NPPMI[291,292] (or PMDETA[293]) and a bromide initiator in diphenyl ether or in bulk. An oxetane-bearing acrylate (FM-**21**)[294] was polymerized with CuBr/HMTETA in p-xylene at 90 °C without any gelation, while the MWD was relatively broad ($M_w/M_n = 1.3-1.5$). The episulfide pendant in methacrylate FM-**22**[295] was fortunately tolerant to ring-opening reactions when treated with CuBr/HMTETA and a bromide initiator in acetone at 50 °C. The polymerization thereby proceeded up to conversion ∼50% to give non-cross-linked polymers with narrow MWDs, clearly superior to other cupper systems with different amine ligands. However, polymerization controllability seems to be better with RAFT than that with metal-catalyzed systems. Living radical polymerization of an oxazolone-based monomer (FM-**23**)[296] is also efficiently induced by CuBr/PMDETA and a bromide initiator.

Allyl methacrylate (FM-**24**), a typical cross-linkable monomer in free radical polymerization, was directly polymerized with CuCl/PMDETA and a chloride initiator in butyl acetate at 110 °C. The key to obtain noncross-linked products ($M_w/M_n \approx 1.5$) was to set the small degree of polymerization ([FM-**24**]/[initiator] = 12.5).[297] The system further yielded well-controlled random copolymers with St (section 3.4.2). The CuBr/HMTETA-mediated polymerization of furfuryl methacrylate (**FM-25**) successfully proceeded without gelation ($M_w/M_n = 1.5$), in sharp contrast to the gelation in conventional radical polymerization.[298]

Methacrylates with an alkyne (FM-**26**[299] and FM-**27**[300]) and an azide (FM-**28**)[301] groups can be applied to azide/alkyne cycloaddition, the so-called "click chemistry", toward convenient and selective macromolecular modification and functionalization.[302,303] A protected methacrylate carrying a trimetylsilyllated alkyne (FM-**26**) was efficiently and smoothly polymerized with CuBr/*N*-(*n*-ethyl)-2-pyridylmethanimine and a bromide initiator to yield well-controlled polymers (conversion ~90%; $M_w/M_n = 1.1-1.2$).[299] In the presence of azide compounds, interestingly, the same system catalyzed a simultaneous or sequential tandem reaction, first the azide–alkyne cycloaddition of a nonprotected alkyne methacrylate (FM-**27**) into the 1,2,3-triazole form and subsequently a living radical copolymerization of the coexisting two derivative.[300] The selection of a solvent considerably affected the kinetics of the cycloaddition and the polymerization. Toluene and DMF induced the cycloaddition faster than the polymerization to result in the sequential tandem catalysis, while DMSO simultaneously induced both processes. In the absence of an azide compound, however, gelation and chain transfer reaction occurred, though MWDs seem broader ($M_w/M_n > 1.5$).[300,301] Controlled polymerization of another azide methacrylate (FM-**28**) was also achieved with a copper catalyst,[301] leading to block copolymers with FM-**4** (DMAEMA). Quite recently, trimethylsilane-capped vinyl acetylene (FM-**29**) was employed for block copolymerization from a bromine-capped macroinitiator of MMA with CuBr/dNbpy (35–60% conversion; $M_w/M_n = 1.1-1.5$).[304]

Acetal and ketal are typical protecting groups for aldehyde (FM-**30**), (meth)acrylic acid (MAA and AA) (FM-**31** and FM-**32**), and diol (FM-**33** and FM-**34**). The acetal monomers (FM-**30** to FM-**32**) are efficiently polymerized with CuBr/bpy (FM-**30**)[305] or CuBr/PMDETA (FM-**31** and FM-**32**).[306] The ketal monomers (FM-**33** and FM-**34**) are also polymerized similarly.[307,308]

N-hydroxysuccinimide methacrylate (FM-**35**)[309,310] and acrylate (FM-**36**)[311] are versatile precursors of (meth)acrylamides. They were polymerized with a series of copper catalysts and a bromide initiator to give controlled homopolymers and block copolymers. The obtained polymers were actually converted into poly(methacrylamide)s and poly(acrylamide)s.

Living radical polymerization of 3-(trimethoxysilyl)propyl methacrylate (FM-**37**) was achieved with CuBr/PMDETA and a bromide initiator.[312] The products led to organic/inorganic nanocomposites via a sol–gel process.

3.2.3. Ionic Monomers and or Styrenic Functional Monomers

With the use of aqueous or alcoholic media, ionic or ionic liquid pendant monomers (FM-**38** to FM-**44**) can be directly polymerized with copper catalysts. For instance, the polymerization of an ionic liquid methacrylate (FM-**38**) with copper chloride ($CuCl/CuCl_2$/bpy + chloride initiator) was better controlled than with copper bromide,[313] whereas the styrene counterpart (FM-**39**) was apparently better suited for copper bromide.[314] A phosphorylcholine monomer (FM-**40**) can be polymerized in high yield with CuBr/bpy and a poly(oxyethylene) bromide initiator in water or methanol at 20 °C.[315,316] The aqueous system was faster and with a high controllability. This system is further applicable for a wide variety of FM-**40** block copolymers (section 3.4.2). Sulfonate monomers (FM-**41** to FM-**44**)[317−320] were also employed for living radical polymerization. The methacrylates (FM-**41**[317] and FM-**42**[318]) and the acrylamide (FM-**43**)[319] are efficiently polymerized with CuCl/bpy or Me_6TREN in the presence of a small amount of $CuCl_2$ in a water/DMF mixed solvent at 20 °C. Aqueous polymerization of a styrenesulfonic acid sodium salt (FM-**44**) proceeded with CuBr/bpy and a bromide initiator to high conversion (>95%) at 25 °C.[320]

Living radical polymerization of styrene derivatives (FM-**45** to FM-**47**) functionalized with boron,[321] phosphine,[277,322,323] and sulfonate[324] at the para-position was also investigated with copper and ruthenium catalysts. A boron-bearing styrene (FM-**45**)[321] was polymerized with CuBr/PMDETA in anisole at 90 °C to give controlled homopolymers at a medium conversion without any loss of the boron functionality (conversion ~60%, $M_w/M_n \approx 1.1$).

A phosphine-bearing styrene (FM-**46**) was employed in the synthesis of core-functionalized microgel star polymers:[277,322,323] Living poly(MMA) arms from a ruthenium catalyst (Ru-**1**) were combined into a microgel core, in which the core-forming polymer-linking reaction with a divinyl compound was carried out in the presence of FM-**46**, thereby introducing a large number of phosphine ligands to capture the Ru catalysts into the core (section 3). A sulfonate styrene (FM-**47**) was polymerized with a copper catalyst from a styrene-based multifunctional macroinitiator to prepare graft copolymers.[324] Additionally, fluorinated polystyrenes[325−327] with narrow MWDs ($M_w/M_n = 1.1-1.2$) were obtained from monomers FM-**48** to FM-**51** with CuBr/bpy and a bromide initiator in bulk or in xylene at 110 °C.

3.2.4. Designer Functional Monomers

With advanced catalysts, metal-catalyzed living radical polymerization of functional monomers has been extended to polymeric materials with novel functions. As shown in Figures 16 and 17, the pendant functional groups now include sugar, amino acid, peptide, and nucleic acid for bioconjugation,[13,14,328,329] as well as various rigid and bulky mesogens for liquid crystallinity.

Typically, the so-called glycopolymers[328,329] can be prepared with copper-catalyzed polymerizations of sugar-containing monomers (FM-**52** to FM-**59**)[330−335] without protection of the multiple hydroxyl groups. Similarly, monomers FM-**60** to FM-**62** are directly polymerized to give amino acid-functionalized polymers.[336−338] Metal-catalyzed system can be further applied to complicated monomers carrying peptides (FM-**63** to FM-**65**)[337,339,340] and cholic acid (FM-**66**).[341] Nucleic acid-containing monomers (FM-**67** to FM-**74**)[342−347] were used for specific interaction with a template so as to control free radical polymerization.[342] For example, copper-mediated living radical polymerization directly produce their polymers with narrow MWDs,[343−347] and the combination of FM-**71** and FM-**73** led to zipper-like block copolymers.[347]

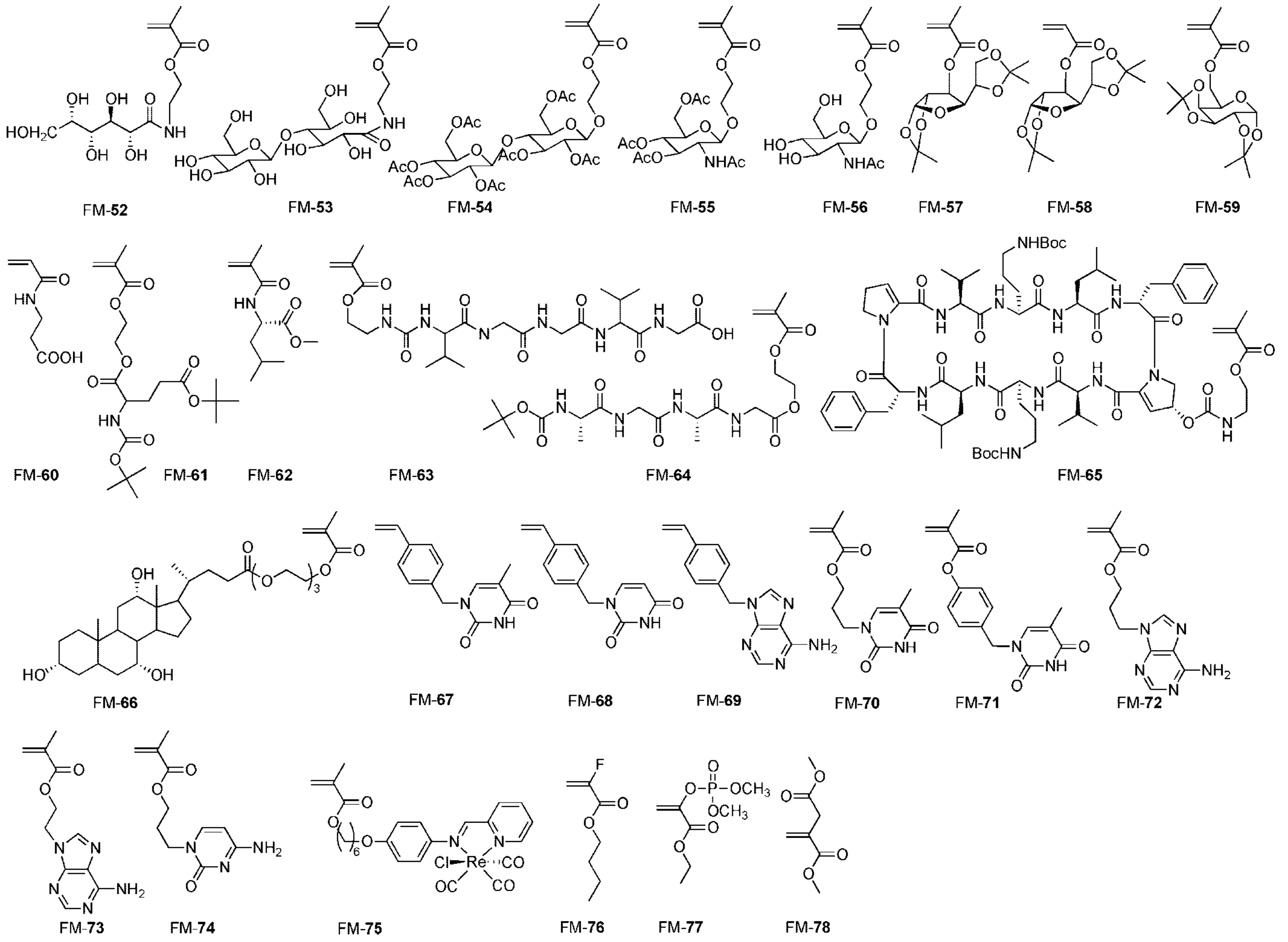


Figure 16. Functional monomers 2.

Placing metals onto organic polymers often develop attractive and unique properties.[348] For this purpose, metal-bearing monomers are directly polymerized with an appropriate catalyst as long as no side-reactions nor poisoning are induced by the pendent metals. For example, a rhenium-bearing methacrylate (FM-**75**)[349] gave photosensitizing polymers with CuBr/PMDETA in xylene or dioxane at 100 °C.

Metal-catalyzed living radical polymerization has also been extended to functional α,α-disubstituted acrylic and methacrylic derivatives (FM-**76** to FM-**78**)[350−352] in which one of the α-substituents are other than proton or methyl, respectively. For example, an α-fluoroacrylate (FM-**76**)[350] was efficiently polymerized with CuBr/HMTETA in anisole at 90 °C to yield well-controlled polymers with narrow MWDs. Silimarly, polymerizations of dimetyl(1-ethoxycarbonyl)vinyl phosphate (FM-**77**)[351] and dimethyl itaconate (FM-**78**)[352] successfully proceeded, while the former was incomplete and led to relatively broad MWDs (conversion ≈ 60%, $M_w/M_n = 1.4-1.9$),[351] and the latter was retarded at conversion below 50% but with $M_w/M_n = 1.1-1.3$.[352] Further optimization would therefore be necessary.

Figure 17 shows functional monomers (FM-**79** to FM-**99**),[353−374] all acrylates and methacrylates, thus far employed for liquid crystalline and optically active polymers via metal-mediated living radical polymerization with copper salts (CuBr or CuCl) and multidentate aliphatic amine ligands (PMDETA or HMTETA). Though monomer conversion is invariably at most about 50%, polymer molecular weights were generally controlled with $M_w/M_n < 1.3$, independent of the pendants structures. For example, FM-**79** is polymerized with CuBr/PMDETA in cyclohexanone at 80 °C to give controlled molecular weight polymers (50% conversion; $M_w/M_n = 1.1-1.3$).[353]

FM-**79,**[353,354] **80,**[355] **81,**[356−359] **82,**[360] **83,**[361] and **84**[362] are of azobenzene groups as pendent mesogens, among which chiral FM-**84**)[362] gave optically active polymers with photochromic properties. Additionally, most of them are further employed for block copolymerization to enhance the functions such as liquid crystallinity,[355,359] optical properties,[361] and micelle formation[357] (section 3.4.2). Another group carries rigid pendants, such as biphenyl (FM-**85**,[363] FM-**86**,[364] FM-**87**,[365] FM-**89**,[367] and FM-**90**[367]), cyanoterphenyl (FM-**88**),[366] and phenyl ester (FM-**91**),[363] can also be polymerized with copper catalysts. Homopolymers of FM-**88** and FM-**89** were insoluble in common organic solvents, whereas those of FM-**90** were soluble and with better controlled molecular weight ($M_w/M_n \approx 1.3$). More complex, buliker, and mostly branched (T-Shaped) structures are introduced in the acrylic derivatives beyond FM-**92** for the synthesis of liquid crystalline homo- and block polymers: FM-**92**,[368] **93**,[369] **94**,[370] **95**,[363] **96**,[371] **97**,[372] **98**,[373] and **99**.[374]

3.3. End-Functionalized Polymers

End-functionalized polymers can be synthesized by metal-catalyzed living radical polymerization, as with other systems, with the following two strategies: (a) from functional initiators for α-ends, (b) end-capping with functionalized

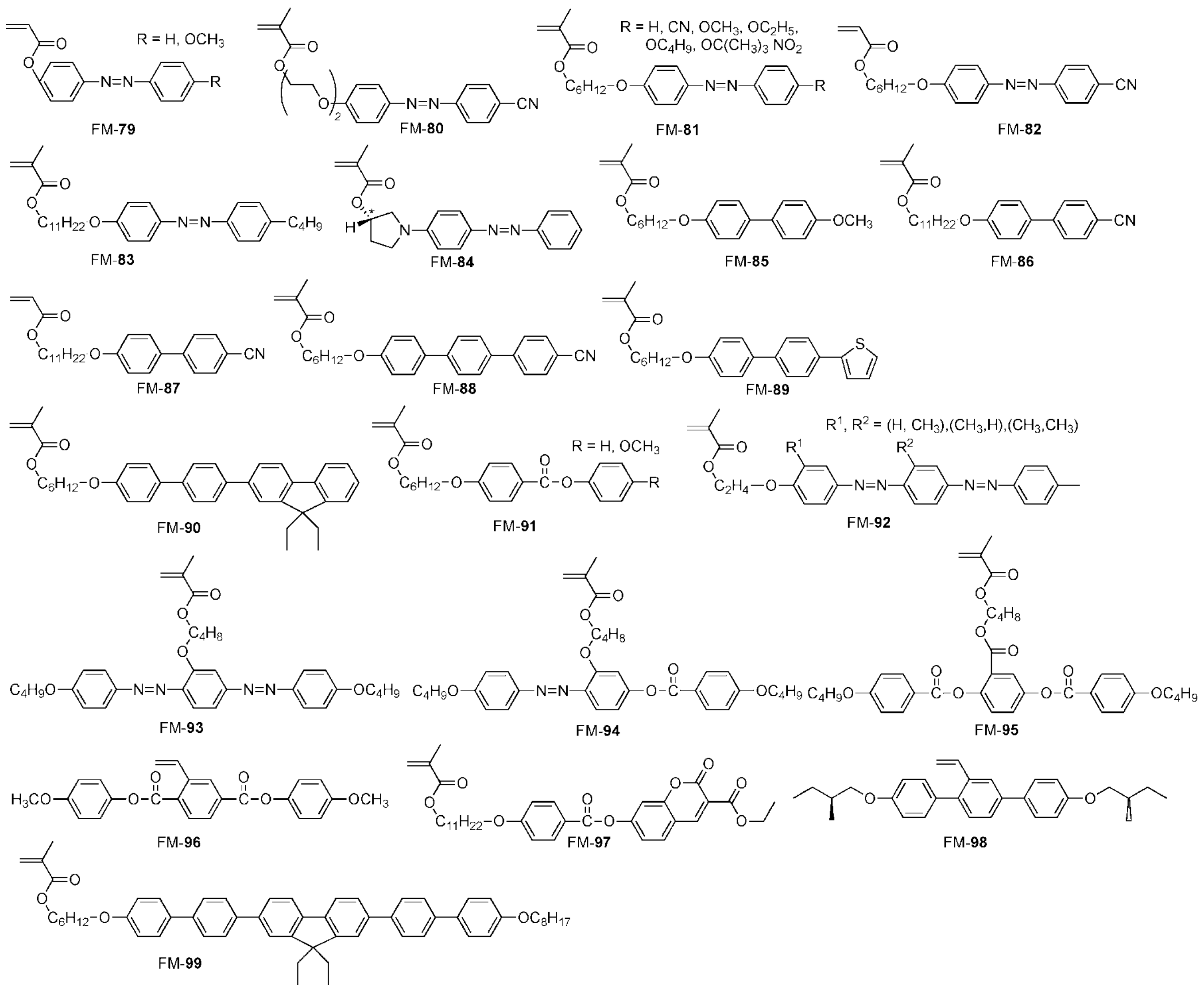


Figure 17. Functional monomers 3.

radical quenchers for ω-ends, and (c) transformation of the terminal halogens for ω-ends. Method a has been employed more frequently because a wide variety of functional groups can be easily introduced into a common initiator framework (typically 2-haloisobutyrate) that ensures near quantitative initiating efficiency and thus complete α-end functionalization. On the contrary, there were only few examples of functional capping agents other than silyl enol ethers[375,376] developed early 2001. More recently in phase II, alternative method c has been emerging for more versatile ω-end functionalization.

Thus, this section presents the recent evolution of functional initiators (method a) and the terminal-halogen transformation (method c), along with their combinations toward α,ω-telechelic polymers.

3.3.1. α-End Functionalization via Functional Initiators

Non-Protected Functional Initiators. Direct incorporation of polar functional groups into desired sites without any protection is one of the most attractive features in metal-catalyzed living radical polymerization. Figure 18 shows nonprotected functional initiators that have newly been reported or frequently employed since 2001.

Hydroxyl Group. Hydroxyl is one of the most popular functional groups that would not interfere radical propagation, and this seems particularly the case since 2001 in phase II. Thus, hydroxyl-functionalized initiators (FI-**1** to FI-**7**)[347,377−384] have been employed for methacrylates, acrylates, and styrenes with ruthenium,[377] copper,[347,378−383] and nickel[383] catalysts; almost quantitative α-end functionalization has invariably been achieved.

For example, FI-**1** (*n* = 1)[377−380] is often employed as a bifunctional initiator for the synthesis of block copolymers via metal-catalyzed living radical polymerization and ring-opening polymerization (ROP),[242−244] either sequentially or consecutively. Interestingly, when combined with CuBr/bpy and an immobilized enzyme (Novozyme-435) in supercritical carbon dioxide at 20 °C, FM-**1** simultaneously initiates living radical polymerization of MMA and enzymatic ROP of ε-caprolactone (ε-CL), to directly produce MMA-ε-CL block copolymers in one-pot.[378] Consecutive two-step approaches are examined with FI-**1**,[378,380] FI-**2**,[384] FI-**3**,[381] and FI-**5**.[382] The bipylidine unit in FI-**5** was employed for coordination of metal complexes.[382] The *o*-amidophenol in FI-**6** was for the recognition of nucleic acid monomers **FM-71** and FM-**73** in possible template polymerizations.[347]

Amino and Nitro Groups. Amine, (bi)pyridine, imidazolium salt, aniline, and nitro groups are also incorporated into haloester initiators. Tertiary amine initiator FI-**8**[377] was employed for the living polymerization of MMA with

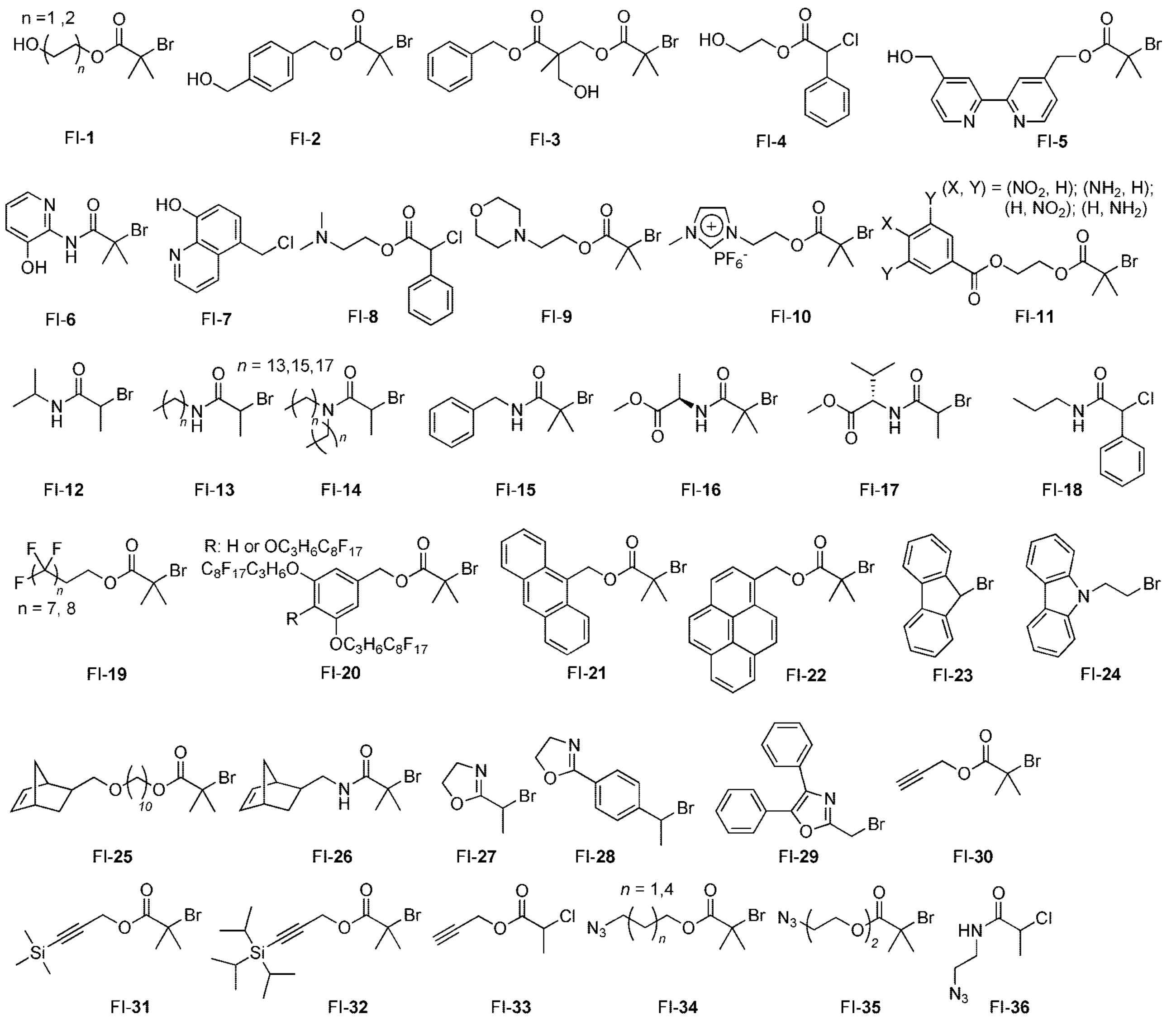


Figure 18. Functional initiators 1.

$RuCl_2(PPh_3)_3$ (Ru-**1**) in toluene at 80 °C: conversion ≈ 93%; M_w/M_n ≈ 1.3; near quantitative amino functionality by MALDI-TOF-MS. FI-**9**,[263] highly soluble in alcohols, is used in the homogeneous polymerization of HEMA (**FM-1**) with CuBr/bpy in methanol; the terminal morpholine moiety from FI-**9** provides a powerful NMR labeling for α-end group analysis.

Initiator FI-**10**[385] with CuBr/PMDETA induced MMA polymerization at a surprisingly wide range of temperature from −30 to 60 °C, probably via activation of the catalyst by the imidazolium salt (ionic liquid) moiety. Therein not only molecular weight but also tacticity were controlled to some extent (M_w/M_n ≈ 1.2; rr = 63−78%), resulting in varying glass transition temperatures of the products (T_g = 113−122 °C). Various nitrobenzene or aniline were introduced into the α-end of poly(MMA) with with FI-**11** and $NiBr_2(PPh_3)_2$ catalyst.[386]

Amides. N- or *N,N*-substituted haloamide initiators (FI-**12** to FI-**18**)[275,377,387,388] are effective for metal-catalyzed living radical polymerization.[1] For example, long alkyl initiators (FI-**13** and FI-**14**) efficiently initiate copper-catalyzed aqueous polymerization of acryl amides to give lipopolymers with unique self-assemble properties.[275] A phenyl group (FI-**15**)[387] and amino acids (L-alanine: FI-**16**;[387] L-valine: FI-**17**[388]) are quantitatively introduced into α-end. For FI-**15** and FI-**16**, high initiation efficiency and controllability were attained by controlling polymerization; namely, the CuCl/NOPMI-mediated polymerization of MMA is carried out initially at 25 °C for 30 min and subsequently at 90 °C.[387] Phenylamide FI-**18** is quite effective for MMA with $RuCl_2(PPh_3)_3$ (Ru-**1**) catalysts and n-Bu_3N additive (conversion > 90%; M_w/M_n ≈ 1.2).[377]

Fluorocarbon. Fluorocarbon-bearing α-bromoesters (FI-**19** and FI-**20**)[389−391] act as efficient initiators in copper-catalyzed polymerization of MMA,[389,391] BMA,[390] styrene,[390,391] and perfluoroalkylethyl methacrylate.[389] The perfluoroalkyl groups of the last monomers provide attractive properties to the end-functionalized polymers. For example, a blend of fluoride-capped poly(BMA) and polystyrene (1/1, w/w), both from FI-**19**, forms a transparent solid thin film, due to lamellar microphase separation via fluorophilic interaction as detected by TEM, whereas a mixture of fluoride-free poly(BMA) and polystyrene underwennt usual macrophase separation and thus turned white.[390] FI-**20** successfully modified the contact angle of solid film products therefrom against water and dodecane.[391]

Aromatic Groups. Functional initiators carrying anthracene (FI-**21**),[392−394] pyrene (FI-**21**),[395] fluorene (FI-**22**),[396] and carbazole (FI-**23**)[290] are employed for polymerization of MMA, HEMA (FM-**1**), St, FM-**19**, respectively. Anthracene

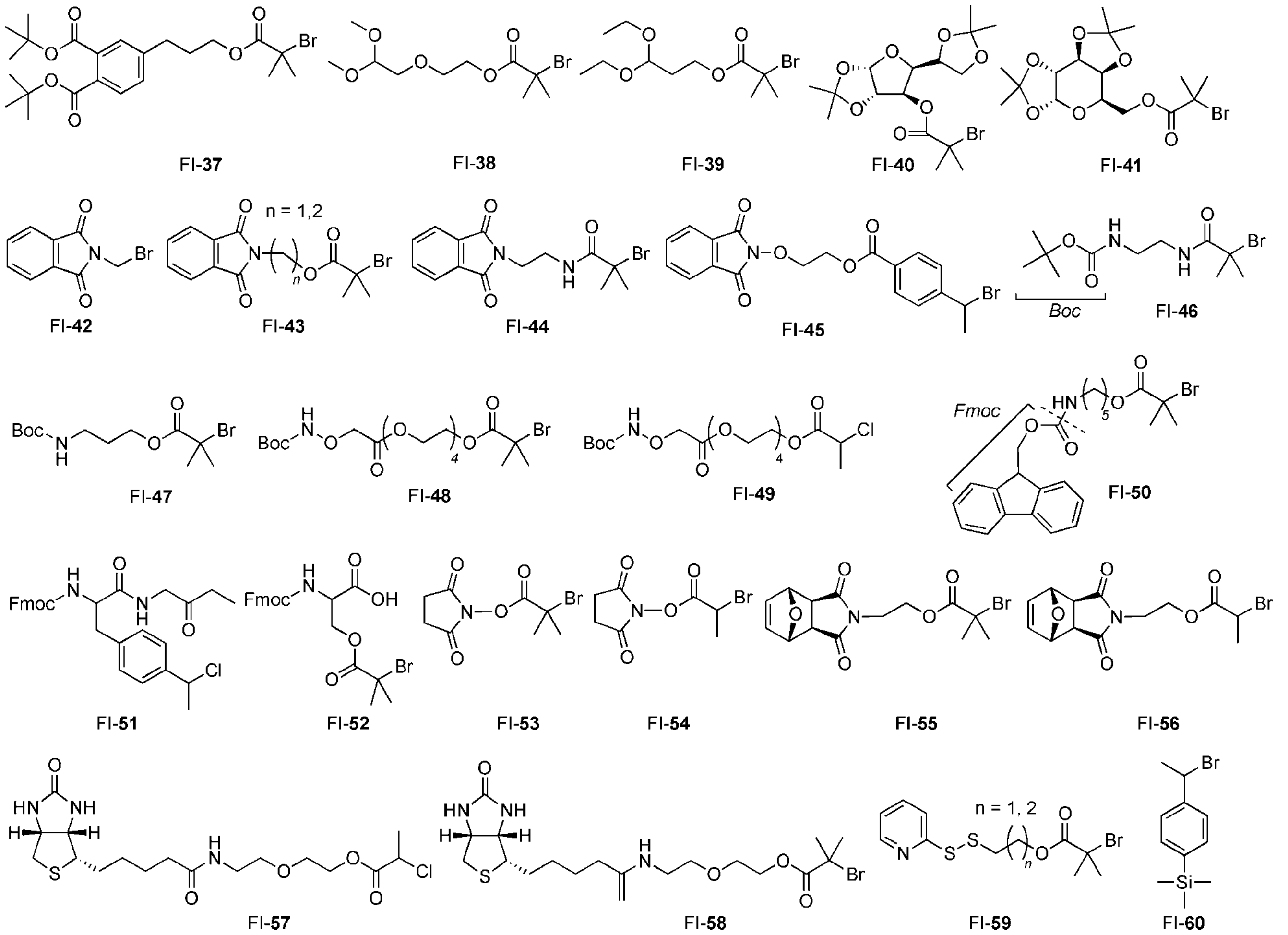


Figure 19. Functional initiators 2.

end groups were utilized for Diels−Alder reaction with a maleimide-capped polymers to obtain block copolymers (section 3.4.4).[393,394]

Macromonomers. Norbornene (FI-**25** and FI-**26**)[397,398] and oxazoline (FI-**27** to FI-**29**)[399,400] may directly be introduced into α-terminal without any protection. Polymerizations of methacrylates and styrene with FI-**25**[397] gave norbornene-capped polymers with very narrow MWDs (M_w/M_n <1.1), whereas acrylates gave bimodal products due to copolymerization of acrylate monomer and the terminal norbornene moiety. FI-**27** to FI-**29**[399,400] were also effective for styrene and MMA without any side-reactions. These macromonomers may be further employed for the synthesis of graft polymers (see below).

Alkyne and Azide. Initiators with an alkyne (FI-**30** to FI-**33**)[401−407] or an azide (FI-**34** to FI-**36**)[403,408−410] moiety are applied to copper-catalyzed polymerizations of styrene,[401,402,405,406] MMA,[405,408] DMAEMA (FM-**4**),[403,409] NIPAM (FM-**12**),[407,410] and FM-**32.**[404] The products were subsequently subject to chain extension by "click" cycloaddition of the alkyne and the azide terminals.[301,302] Typically, FI-**30**[401−404] with CuBr/PMDETA efficiently gave acetylene-functionalized polystyrene ($M_w/M_n = 1.1$);[401,403] the ω-bromine was then converted into an azide with NaN_3, giving AB-type telechelic polymers. Cycloaddition of these polymers led to self-chain-extension to high molecular weight[401] or to "cyclic" polystyrene.[402] An azide initiator (FI-**34**)[409] with CuBr/*N*-alkyl-2-pyridylmethanimine induced a sequential tandem reaction, that is, living radical polymerization of MMA, followed by click functionalization of the α-azide group with acetylene derivatives. The azide terminal in poly(FM-**12**) from FI-**36**[410] were subsequently transformed into various functional groups. A variety of block copolymers were also obtained by similar click reactions[403−406,409] (section 3.4.4).

Protected Functional Initiators. For highly reactive functional groups, protection is required in design of functionalized initiators, even in metal-mediated living radical polymerization, which are considered highly tolerant of polar functionality. Figure 19 compiles these protected or precursor functional initiators for α-end functionalization.

Protected Phthalic Anhydride, Aldehyde, and Diol. 2-Bromoisobtyrates carrying di-*tert*-butyl phthalate (FI-**37**),[411] acetal (FI-**38**),[412] and cyclic ketal (FI-**40** and FI-**41**)[413] are used in copper-mediated polymerization as protected initiators of the following functional groups: phthalic anhydride, aldehyde, and diol, respectively. With CuBr/bpy, FI-**37** efficiently gave end-functionalized poly(MMA) and polystyrene with narrow MWDs (M_w/M_n <1.2). Treated at around 200 °C, the α-end di-*tert*-butyl phthalate were quantitatively deprotected into α-phthalic anhydride, in sharp contrast to some loss of the anhydride functionality in direct polymerizations with a phthalic anhydride initiator.[414] The acetal terminal in poly(FM-**14**) from FI-**38**[412] was transformed into an aldehyde via the simple treatment with CF_3COOH, and the products are empoyed for protein conjugation. Similar deprotection was also effective for protected sugar initiators FI-**40** and FI-**41**.[413] Interestingly, an acetal-bearing isobutyrate (FI-**39**)[415] works as a dual-functional initiator for living radical polymerization of *t*BA and living cationic polymer-

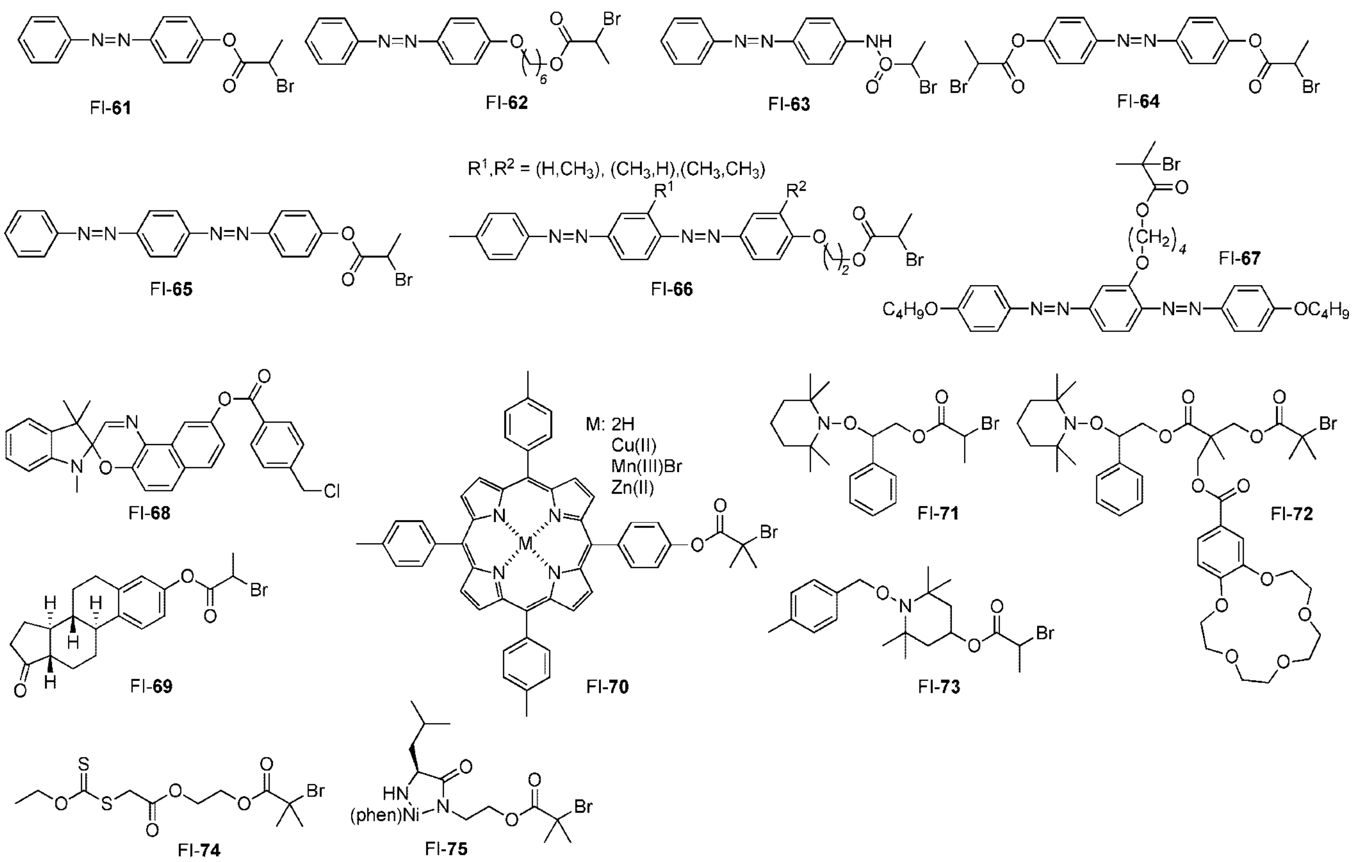


Figure 20. Functional initiators 3.

ization of methyl vinyl ether in tandem, to give, in one step, acrylate-vinyl ether AB-block copolymers (section 3.4.3).

Protected Primary Amine. Phthalimide, *tert*-butoxy carbonyl (Boc), and 9-fluorenylmethyl chloroformate (Fmoc) are often utilized as protecting groups for primary amines. Thus, phthalimide initiators (FI-**42** to FI-**45**)[416−418] efficiently initiate copper-catalyzed polymerization of styrene[416,418] and *t*BA[417] to give α-phthalimide-capped polymers (M_w/M_n = 1.1−1.2) that are effectively deprotected into α-primary amine derivative by usual hydrazinolysis. Boc-protected (FI-**46** to FI-**49**)[419−423] and Fmoc-protected (FI-**50** to FI-**52**)[424,425] initiators are also effective for α-primary amine functionalized polymers; the deprotected forms are often applied to peptide conjugation.[423,425]

Amide Precursors. N-succinimide can be easily transformed into amide by treatment with a primary amine, and when the deprotecting agent is a protein N-terminal, for instance, this transformation leads to polymer-protein conjugation. Thus, *N*-succinimidyl initiators (FI-**53** and FI-**54**)[333,426,427] are utilized for copper-catalyzed polymerizations of PEGMA (FM-**14**; $n = 9$)[426,427] and sugar-pendant monomers (FM-**57** and FM-**59**)[333] aimed at polymer−peptide conjugation.

Maleimide Precursors. Isobutyrate initiators with the *exo*-adduct of furan and maleimide (FI-**55** and **FI-56**)[285,393,394,428,429] were employed for the synthesis of α-maleimide polymers,[285,428,429] with which retro-Diels−Alder deprotection was quantitative upon simple reflux in toluene. The products were then conjugated with bovine serum albumin (BSA) via the latter's thiol terminal. The deprotected terminals from FI-**55** (or **FI-56**) and FI-**21** are subject to a Diels−Alder reaction for block polymer synthesis.[393,394]

Initiators for Protein Conjugation. In addition to the classical conjugation as described above, more specific endfucntionalization has been utilized for protein conjugation. Thus, with designed initiators FI-**57** and FI-**58**,[332,430−433] biotin-tagged polymers were synthesized from *t*BA,[430] MMA,[430] NIPAM (FM-**12**),[431−433] and sugar methacrylates FM-**55** and FM-**56**[332] (conversion >80%; M_w/M_n < 1.2; quantitative end function). The biotin parts efficiently serve as a tag linker to connect streptavidin (SAv).[431,432] Alternatively, FI-**57** was first attached to SAv, and the modified initiator was allowed to polymerize NIPAM to realize a one-pot protein conjugation (section 3.11.1).[433] Pyridyl disulfide initiators (FI-**59**)[434−436] are also utilized in block copolymer synthesis including protein conjugations (section 3.4.4).[435,436]

Borane and Bronic Acid Precursors. A trimethysilyl group (TMS) in initiator FI-**60**[437] is an efficient precursor of borate and bronic acid. In a typical example, the terminal TMS group was first transformed into BBr_2 with BBr_3, from which dithiophene-borane or boronic acid was obtained. Additionally, BBr_2-telechelics were chain-extended with 4,4-dipyridyl via donor−acceptor complex.

Designer Functional Initiators. Figure 20 compiles functional initiators especially designed for specific functions including liquid crystallinity, photochromism, and dual initiation functionality.

Azobenzene Derivatives. As already described in section 3.2.4, azobenzene-based (co)polymers are now attracting attention because of their unique photochemical properties and possible liquid crystallinity. Though slightly different in cotext, initiators carrying an azobenzene unit (FI-**61** to FI-**67**)[368,369,438,439] successfully provide α-end functionalized polymers of MMA[438,439] and styrene,[439] as well as azobenzene-bearing methacrylates (FM-**92**[368] and FM-**93**[369]).

Function-Oriented Initiators. Initiators FI-**68** through FI-**70** are designed for the following specific functions: FI-**68** (spirooxazine), photochromism;[440] FI-**69** (Estron), optically active polymers;[441] and FI-**70** (porphyrin), metal complexation and self-assembling.[442] All of the polymerizations thereby were controlled to form the corresponding end-functionalized polymers.

Hetero-Bifunctional Initiators. In these initiators (FI-**71** to FI-**75**), two initiating sites are incorporated for living polymerizations via different mechanisms (or system combination, section 3.4.3) to synthesize block copolymers that would not be feasible via a single mechanism. Typically, FI-**71**,[443] FI-**72**,[444] and FI-**73**[445] are with a nitroxide moiety for another living radical polymerization of styrene[443,444] and 4-VP (FM-**10**).[445] In FI-**71**[443] and FI-**72**,[444] the order of two living processes does not affect controllability, where the monomer pairs include *t*BA and styrene[443] or MMA and styrene.[444] FI-**74**[446] and FI-**75**[447] efficiently initiated a reversible addition−fragmentation chain transfer (RAFT) polymerization of vinyl actetate (VAc) and a nickel-initiated polymerization of γ-benzyl-L-glutamate *N*-carboxy anhydride (NCA), to give VAc-peptide block polymers.

3.3.2. ω-End Functionalization via Terminal Transformation

Metal-catalyzed living radical polymerization involves a reversible and homolytic cleavage of a terminal carbon−halogen bond with a transition metal catalyst, but carbon−halogen bonds are, in general, stable and "dormant", thus rendering them rather inactive in further transformation into a useful ω-end functionality. In addition, the propagating carbon radical is by definition neutral and thus hardly reacts with polar compounds; their very low instantaneous concentration further hampers end-group transformation under metal-catalyzed living polymerization conditions. In one hand, these characteristics are of course advantageous in that the polymerization is not disturbed by functional groups in monomers and solvents. On the other, rather ironically, the relative stability of both dormant and radical terminals make their end-capping reactions almost unfeasible.[375,376] This is the very reason why ω-end-functionalization is developed much less extensively than α-end-functionalization in metal-catalyzed living radical polymerization.

ω-End transformation is basically achieved by two pathways: (A) In Situ Functionalization: End-capping of living and dormant polymers in situ with a functional terminator (Figure 21). (B) Post-Functionalization: Terminal transformation on isolated polymers (Figure 22). In the metal-catalyzed systems, the two methods are more or less similar, to be directed toward selective and clean reactions on dormant carbon−halogen bonds, because dormant species predominate in situ and are also isolable. In spite of the potential difficulty reviewed above, novel ω-end-transformations have been developed in phase II (Figures 21 and 22), typically including an in situ tandem catalysis (Scheme 6), in situ ionic reactions via terminal umpolung (Scheme 7), and postpolymerization azide-attachments, followed by "click" reactions (Figure 22).

In Situ Functionalization. *In Situ Hydrogenation.* Because, though not versatile in chemical reactions, the terminal halogens in radically obtained polymers ($\sim\sim CH_2-CRR'-X$; X = halogen, R = H or methyl, R' = substituent) are thermally unstable, releasing noxious hydrogen halides, their removal is quite important to stabilize products especially in industry. Perhaps the best way is hydrogenation, but before 2001, there was only one report with a hazardous tin reagent.[448] Thus, the development of more efficient and convenient methodologies has strongly been desired.

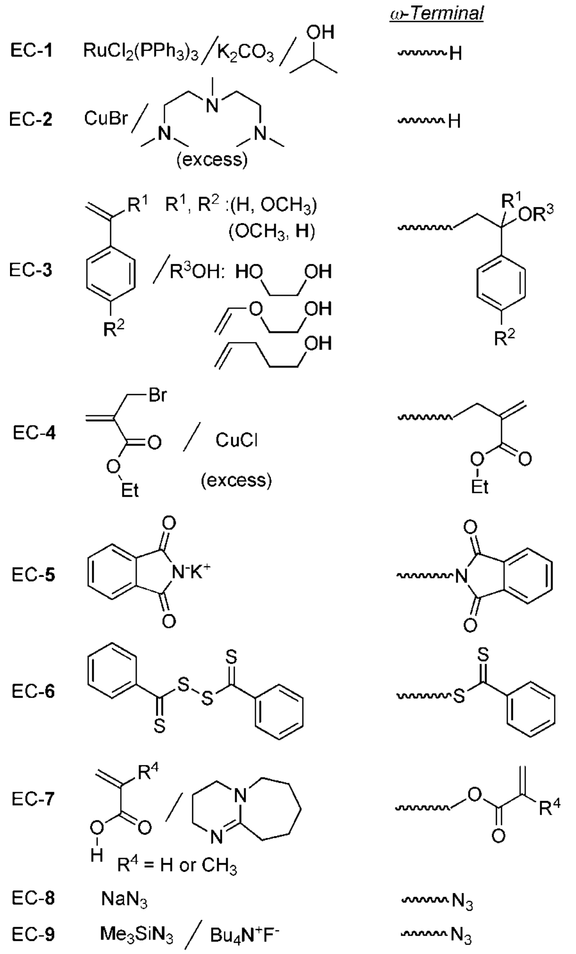


Figure 21. End transformation of carbon−halogen terminals.

Tandem Catalysis. Recently, a tandem sequential hydrogenation has been discovered in ruthenium-catalyzed living radical polymerization,[182] where the catalysts are in situ converted into hydrogenation-active hydride forms (Scheme 6). In a typical example, at the end of the MMA polymerization, the ruthenium catalyst [$RuCl_2(PPh_3)_3$ (Ru-**1**)] was transformed into hydrides [RuHCl and RuH_2 with phosphine ligands] upon addition of K_2CO_3 (base) and excess 2-propanol (hydrogen source) (EC-**1**; Figure 21). During this treatment, the reaction mixture changes in color from red-brown ($RuCl_2$) through red-purple (RuHCl) to yellow (RuH_2). The polymerization was completely terminated, and the terminal chlorine was quantitatively hydrogenated without side-reactions.

Chain Transfer. Another in situ hydrogenation was achieved in CuBr-catalyzed polymerizations of *n*BA, *t*BA,[449] and MMA[419,420] with the use of a large excess of PMDETA (EC-**2**), which acts not only as a ligand for the catalyst but as a chain-transfer agent on depletion of monomer, to give ω-hydrogenated polymers. Probably depending on the extent of chain transfer relative to propagation, the MWD was narrow with acrylates but broader with MMA (M_w/M_n = 1.2 vs >2.0).

End-Capping via Terminal Umpolung. In sharp contrast to metal-meidated living radical polymerization, living cationic polymerization is readily terminated with methanol, to give methoxy-capped polymers via nucleophilic substitution. Also a variety of nucleophiles are available for selective

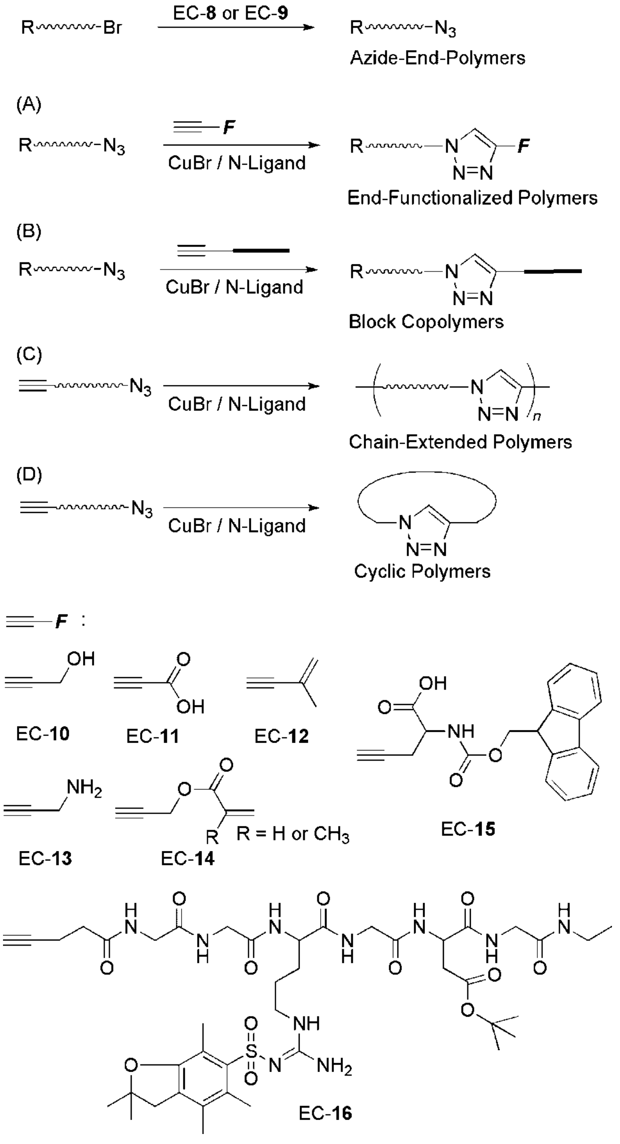
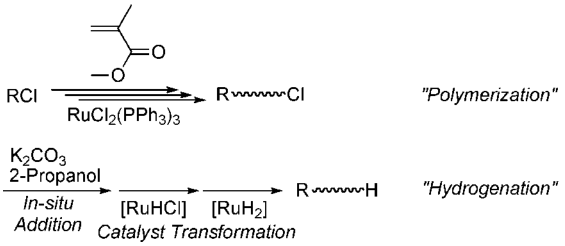
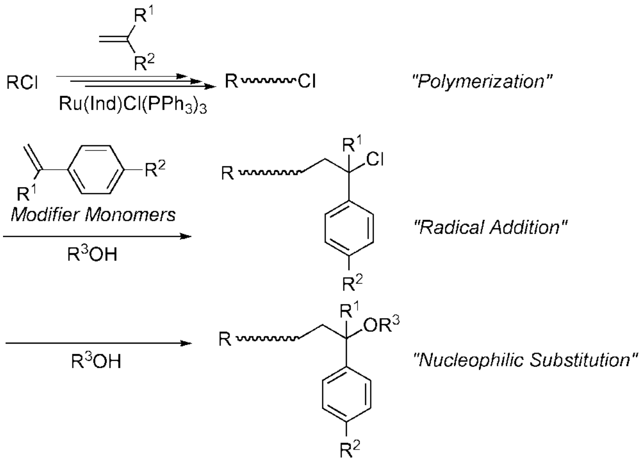


Figure 22. End functionalization via click chemistry.

Scheme 6. In Situ End-Hydrogenation of Living Polymers via Sequential Tandem Catalysis



Scheme 7. In Situ End-Functionalization of Living Polymers via Terminal Umpolung



end-capping upon growing carbocations. Noting these aspects, we employed styrene derivatives carrying electron-donating groups as "terminal modifiers" for "terminal umpolung", namely, in situ conversion of the dormant carbon−halogen bond, originally designed for homolytic dissociation, into a more polarized, better suited for ionic dissociation via the assistance of neighboring electron-donating substituent (Scheme 7). Once this umpolung is done, it s straightforward to proceed to the well-established end-capping with alcohols (EC-**3**) (Scheme 7).[450] By definition the modifiers should be eligible not onlyt to radical addition but to carbocation formation via its electron-donating substituents. Typical modifiers are *p*-methoxystyrene (pMOS, R^1 = H, R^2 = OCH_3) and α-methoxystyrene (αMOS, R^1 = OCH_3, R^2 = H).

In an example, chlorine-capped polymers [poly(MMA)-Cl], obtained from $Ru(Ind)Cl(PPh_3)_2$ (Ru-**4**), were sequentially treated with αMOS and methanol to give methoxy-capped polymers [poly(MMA)-(αMOS)-OCH_3] through a single αMOS unit. First, αMOS (molar equivalent to the growing end or initiator) radically added onto poly(MMA)-Cl to give poly(MMA)-αMOS-Cl. The chloride is now attached to a more or less electron-rich carbon and highly subject to nucleophilic substitution via a carbocationic intermediate into a methoxy group via nucleophilic substitution with methanol. Additionally, various functional alcohols (with diol, olefin, vinyl ether) can be applied to this methodology for end-functionalized polymers.

Dehydrobromination into Olefins. The terminal halogens in living/dormant poly(MA) or poly(*n*BA) is almost quantitatively transformed into an olefin upon addition of excess 2-bromomethylacrylate and CuCl (EC-**4**)[451] in a copper-mediated polymerization. The key is to employ excess CuCl for inducing radical hydrobromination.

Post-Functionalization. *Functional Groups.* Halogen-capped polymers are converted into end-functionalized polymers via postmodification. A phthalimide group is quantitatively introduced into ω-terminal of poly(*t*BA)s via nucleophilic substitution with phthalimide potassium (EC-**5**),[452] where the terminal phthalimide is further deprotected into a primary amine. The process is confirmed by IR, ^1H NMR, and MALDI-TOF-MS. A RAFT agent (EC-**6**)[453] is radically incorporated into a poly(MMA) terminal in the presence of zerovalent Cu(0) and CuBr/*N*-n-pentyl-2-pyridilmethanimine. *n*BA-based macromonomers are obtained from the treatment of bromine-capped poly(*n*BA)s and EC-**7**,[454] applying to graft copolymers.

"Click" Cycloaddition. As already reported before 2001,[1] terminal halogens of living polymers are efficiently transformed into an azide group in conjunction with sodium azide (EC-**8**)[455] or trimethylsilyl azide and tetrabutylammonium fluoride (EC-**9**).[456,457] Based on this transformation, copper-catalyzed cycloaddition ("click reaction")[302,303] with azide end-functionalized polymers[394,401,402,404−407,458−463] have been frequently employed for ω-terminal functionalization due to the selectivity, efficiency, and convenience.

As shown in Figure 22, various functional groups can be introduced into the ω-terminal through 1,2,3-triazole linkage by the treatment of azide-ω-end polymers and functional

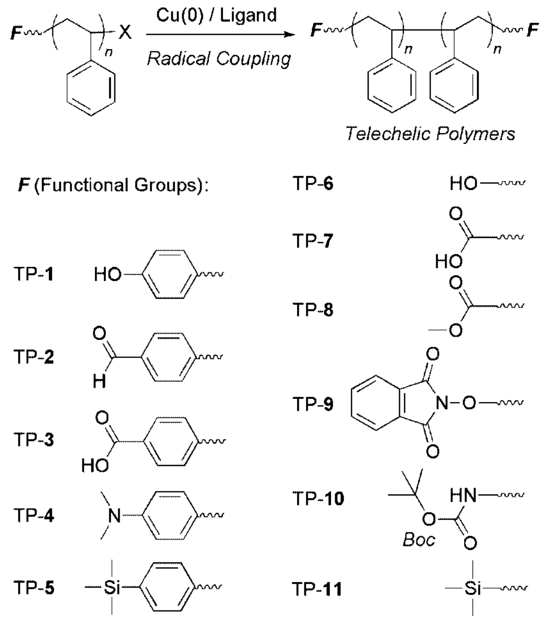


Figure 23. Telechelic polymers via radical coupling.

groups-carrying alkynes such as propargyl alcohol (EC-**10**),[458–460] propiolic acid (EC-**11**),[458] 2-methyl-1-butene-3-yne (EC-**12**),[458] propargyl amine (EC-**13**),[460] propargyl (meth)acrylate (EC-**14**),[461,462] a Fmoc-bearing alkyne (EC-**15**),[460] and an oligopeptide bearing alkyne (EC-**16**).[460] All cases demonstrated quantitative functionalization. Various block copolymers are obtained from the combination of azide-ω-end polymers and alkyne-α-end polymers[394,404–406,463] (Figure 22B, see Section 3.4.4). Additionally, telechelic polymers with α-alkyne end and ω-azide counterpart lead to self-chain-extended products[401] with high molecular weight in high polymer concentration (Figure 22C), while they, in turn, selectively yield cyclic counterparts in the low concentration (Figure 22D).[402,406] Therefore, it concludes that cycloaddition of alkyne or azide-end functionalized polymers is new, efficient, and powerful tool for design of functionalized materials with precise architecture.

3.3.3. α,ω-Telechelics via Polymer Reaction

Telechelic functionalized polymers are synthesized by the following three methods: (1) living radical polymerization with a functional initiator to give α-end-functionalized polymers, followed by ω-end-capping reaction with a functionalized quencher for α,ω-difunctionalized polymers, (2) living radical polymerization with a bifunctional initiator to give ω,ω-dihalogen-bearing polymers, followed by ω-end-capping reaction with a functionalized quencher for ω,ω-difunctionalized polymers, and (3) living radical polymerization with a functional initiator to give α-end-functionalized polymers, followed by the ω-end-coupling reaction for α,α-difunctionalized polymers. Recently, atom transfer radical coupling (ATRC)[418,422,437,464–469] has been often examined as the third method (Figure 23).

Atom Transfer Radical Coupling (ATRC). As shown in Figure 23, α-end-functionalized ω-bromide-poly(St)s[418,422,437,464–468] are efficiently and radically coupled in the presence of CuBr, a suitable *N*-ligand, and a zerovalent copper [Cu(0)], to produce α,α-difunctionalized telechelic poly(St)s with narrow MWDs ($M_w/M_n \approx 1.2$) in almost quantitative yield. The molecular weight of the products is almost twice as much as that of the ω-bromide precursors. The key for efficient coupling reaction is to employ Cu(0) as a reducing agent. The radical coupling is robust enough to produce telechelic polymers with various functional groups: phenol (TP-**1**),[466] aldehyde (TP-**2**),[466] carboxylic acid (TP-**3**, TP-**7**),[466,467] aniline (TP-**4**),[466] trimethylsilil groups (TP-**5**, TP-**11**),[437,467] hydroxyl groups (TP-**6**),[467,468] ester (TP-**8**),[469] phthalimide (TP-**9**),[418] and *N*-Boc (TP-**10**).[422] Some of the ω-functional groups are further modified into other groups: a trimethylsilil group of TP-**5** into $-BBr_2$, phthalimide of TP-**9** into primary amine ($-NH_2$), and *N*-Boc of TP-**10** into trimethylammonium salt ($-Me_3N^+I^-$). ATRC was further applied to end-functionalized poly(butyl α-fluoroacrylate: FM-**76**) with copper catalysts,[469] while the coupling yield was lower (~80%) than that of poly(St) counterparts because of inevitable disproportionation (~20%).

Difunctional Initiator with Click Cycloaddition. Another efficient pathway for telechelic polymers is to combine a bifunctional initiator and a post terminal transformation via click cycloaddition. Typically, ω,ω-dibromo-poly(St)s, obtained from a bifunctional bromide initiator, were treated with EC-**8** to give ω,ω-diazide-functionalized poly(St)s with narrow MWDs ($M_w/M_n \approx 1.1$), followed by the cycloaddition with a propargyl alcohol (EC-**10**).[459] The final product owned hydroxyl groups in the both terminal over 97% yield, analyzed by gradient polymer elution chromatography. Catalyst performance was also evaluated in copper-mediated cycloaddition of ω,ω-diazide-functionalized poly(St)s and propargyl ether for chain extension, especially focused on multidentate amine ligands originally designed for living radical polymerization.[470]

3.4. Block Copolymers

Block copolymers is one of the most attractive products obtained from living polymerization due to the unique properties such as microphase separation and micellization.[242–247] Among them, recent advance of metal-catalyzed living radical polymerization has successfully enlarged monomer combination for block copolymers. Basically, the block copolymers can be prepared by the two methodologies: (1) sequential polymerization of second monomers via the direct fresh feed into the prepolymer solutions and (2) living radical polymerization of second monomers from isolated macroinitiators. The former is a simple and convenient method without any isolation and purification but fundamentally include some contamination of first monomers in a second block. On the other hand, the latter gives pure block copolymers, however bothersome isolation is necessary. Now, commercially available polymers and other kind of polymerization are often combined with metal-catalyzed living radical polymerization to prepare block copolymers with features, functions, and productivity superior to those via metal-catalyzed system alone. Furthermore, postpolymer reaction is also efficient for block copolymerization.

In this section, we comprehensively describe the recent evolution of block copolymers, categorized in the four sections: (1) system design in metal-catalyzed living radical polymerization, (2) functional block copolymers via metal-catalyzed system alone, (3) system combination with other kind of polymerization including commercially available polymers, and (4) polymer reaction with end-functionalized polymers (Figure 24−38).

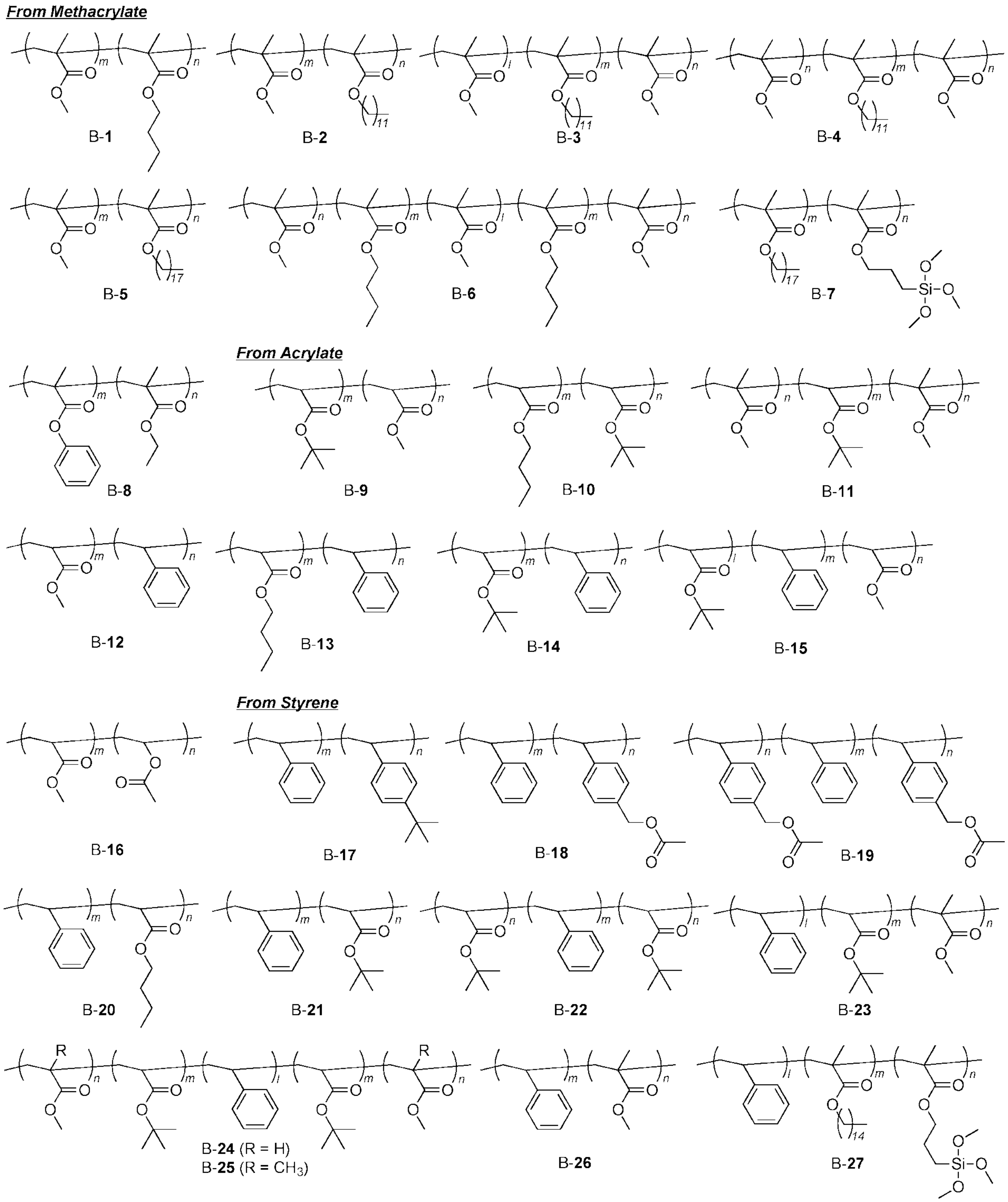


Figure 24. Block copolymers.

3.4.1. System Design

Efficient block copolymerization essentially requires selection of catalytic systems and terminal (initiator) halogens suitable for respective monomers. High-end functionality in prepolymers (1st block) is especially indispensable for high blocking efficiency. Therefore, sequential block copolymerization without isolation is realized by a catalytic system giving almost quantitative halogen end-capped polymers even in high monomer conversion (~90%). Additionally, in contrast to same monomer families with similar reactivity, combination of different monomer ones sometimes needs transformation of terminal halogen species for efficient cross-propagation. Herein, we describe system design for hydrophobic (nonfunctionalized) block copolymers of methacrylates, acrylates, and styrenes (Figure 24).

Block Copolymers from Methacrylates. Methacrylate-based block copolymers (B-**1** to B-**8**) have been prepared with ruthenium, copper, and iron catalysts after 2001. Among them, combination of ruthenium catalysts and chloride initiators is quite effective for sequential block copolymerization via direct feed of second monomers. Typically, $\mathrm{Ru(Ind)Cl(PPh_3)_2}$ (Ru-**4**)/*n*-$\mathrm{Bu_3N}$ and a chloride initiator efficiently gives diand triblock copolymers (B-**2** to B-**4**) of MMA and dodecyl methacrylate (DMA) with very narrow MWDs (M_w/M_n = 1.1−1.2), high blocking efficiency (>97%), high molecular weight (M_n = 20 000−500 000), and controlled MMA contents (10−40%).[2,3,265] Though triblock copolymers between B-**3** and B-**4** contain the same composition of MMA and DMA, the synthetic procedure is different. Namely, B-**4** is obtained from the two step procedure: DMA polymerization with a bifunctional initiator (dichloroacetophenone), followed by direct feed of MMA, while B-**3** is prepared by the three steps: MMA polymerization with a monofunctional initiator [$(MMA)_2$-Cl], followed by sequential addition of DMA and MMA twice. Thus, B-**4** is faster and more efficiently synthesized than B-**3**. For B-**2** and B-**4**, ruthenium catalyst (Ru-**4**) performs controllability superior to copper catalysts.[471,472] Additionally, B-**4** behaves thermoplastic elastomers. Thanks to high functionality-tolerance of ruthenium catalysts, Ru-**4** achieved dispersion block copolymerization for B-**4** in the presence of water without any retardation of blocking efficiency, clearly faster than that in toluene,[3] and also succeeded in functionalization of block copolymers (see section 3.5.1).

Now, iron catalysts also perform controllability and stability suitable for sequential block copolymerization of MMA and *n*BMA in spite of slightly broad MWDs (B-**1**, $M_w/M_n = 1.4$).[95] The key is to select active and stable iron bromide catalysts carrying a relatively highly basic alkyl phosphine ligand [$FeBr_2(PBu_3)_2$ (Fe-**8**)] and a bromide initiator.

Other hydrophobic methacrylate block copolymers (B-**5**,[166] B-**6**,[473] B-**7**,[474] B-**8**[475]) can be synthesized with copper catalysts and isolated macroinitiators. Particularly, AGET system coupled with $CuCl_2$/dNbpy and tin(II) 2-ethylhexanoate [$Sn(EH)_2$] smoothly induced MMA polymerization from the macroinitiator of octadecyl methacrylate (ODMA) to give B-**5** with narrow MWDs ($M_w/M_n \approx 1.1$).[166] Noted that the copper(II)-based system performs efficient block copolymerization in sharp contrast to that of reverse ATRP.

Block Copolymers from Acrylates. Copper and iron catalysts are suitable for the synthesis of acrylate-based block copolymers (B-**9** to B-**16**). Block copolymers from acrylates to acrylates and/or styrenes (B-**9**, B-**14**, B-**15**) are efficiently prepared with CuBr/PMDETA and a bromine-capped poly(*t*BA) macroinitiator (M_w/M_n <1.2),[476,477] where slight amount of $Cu^{II}Br_2$ or diluted conditions are key factors to enhance chain-end functionality (decrease termination) for high blocking efficiency. Importantly, the bromine-capped acrylate macroinitiators are effective for even cross-propagation to styrene. On the contrary, cross-propagation from a bromine-capped poly(acrylate) to a methacrylate (B-**11**) requires halogen exchange reaction via copper chloride catalysts to realize high initiating (blocking) efficiency and narrow MWDs ($M_w/M_n \approx 1.1$).[477] This is because bromide-capped methacrylate terminals induce propagation faster and more preferentially than remaining acrylate terminals to cause termination and low blocking efficiency.

Combination of a high oxidation state copper catalyst [Cu(II)] and a reducing agent, aqueous AGET ATRP with $CuBr_2$ and ascorbic acid[165] and ARGET one with $CuBr_2$ and $Sn(EH)_2$,[167] is also quite effective for block copolymerization from bromide-acrylate macroinitiators to styrene (B-**12**, $M_w/M_n \approx 1.3$; B-**13**, $M_w/M_n \approx 1.2$). By 2D chromatography analyses with SEC and HPLC, the AGET system apparently exhibited higher blocking efficiency (>99%) than SR&NI counterparts with the same $CuBr_2$ (∼90%).[165]

In sharp contrast to copper catalysts, iron catalysts with iodide initiators can sequentially produce block copolymers from acrylates to acrylates (B-**10**), styrene (B-**12** to B-**14**), and vinyl acetate (VAc) (B-**16**) in one-pot. Because of the high catalyst-tolerance to water, $FeCpI(CO)_2$ (Fe-**2**) with an iodide initiator efficiently performs block copolymerization in aqueous media to give B-**10**, B-**13**, and B-**14**,[94] in addition to B-**12** and B-**13** in toluene ($M_w/M_n \approx 1.2$).[92] B-**16** requires fresh feed of another iron catalyst $[FeCp(CO)_2]_2$ (Fe-**4**) along with VAc into Fe-**2**/Al(O*i*-Pr)$_3$-catalyzed living radical polymerization of MA ($M_w/M_n \approx 1.3$).[478]

Block Copolymers from Styrene. Block copolymers (B-**17** to B-**27**) are efficiently synthesized with copper or iron catalysts and bromine-capped poly(St) macroinitiators. B-**17** is obtained from $FeBr_3$/*n*-Bu_3N (Fe-L**2**)/$Sn(EH)_2$ [tin(II)2-ethylhexanoate]-catalyzed AGET ATRP of 4-tert butyl styrene (4*t*BuSt) with a poly(St) macroinitiator ($M_w/M_n \approx 1.2$).[479] Uniquely, block copolymers of St and acetoxy styrene (AcSt) (B-**18**,**19**) are directly prepared with a copper catalyst without isolation of prepoly(St) due to preferential consumption of AcSt against St.[480] In contrast to cross propagation from styrene to acrylates (B-**20**,[167] B-**21**,[481] B-**22**,[476,481] B-**23**,[481] B-**24**,[476] B-**25**[476,481]), terminal halogen exchange from bromine to chlorine with CuCl is essential for efficient block copolymerization from MA (acrylate) to MMA (methacrylate) (B-**23** and B-**25**). Furthermore, ionic iron catalysts (Fe-**21**) with a chloride initiator and CuBr/PMDETA with a bromide initiator smoothly achieved cross propagation from styrene to methacrylates for B-**26**[107] and B-**27**,[482] respectively.

3.4.2. Functionalized Block Copolymers

Metal-catalyzed living radical polymerization allows us to selectively introduce the functional monomers into the each segments of block copolymers toward the functionalization performing reversible micellization[246] and self-assembly properties.[244] This section reviews wide variety of functionalized block copolymers via metal-catalyzed living radical polymerization and the interesting functions (Figures 25−29).

Hydroxyl, Amine, and Pyridine. Hydroxyl- or amine-functionalized block copolymers (FB-**1** to FB-**15**) are prepared with ruthenium, copper, and nickel catalysts (Figure 25). A typical hydroxy-functionalized block copolymer (FB-**1**)[267] is efficiently obtained from CuCl/bpy-catalyzed living radical polymerization of HEMA (FM-**1**) with a hydrophilic bromide initiator (FI-**9**) in methanol at 20 °C, directly treated with MMA at over 90% conversion of HEMA to give narrow MWDs (M_w/M_n <1.3). This CuCl-based system showed high end-functionality applicable to the sequential procedure without any isolation of prepolymers.

A simple amine-functionalized block copolymer (FB-**2**) of MMA and DMAEMA (FM-**4**) is also obtained from sequential addition method with a $NiBr(PMePh_2)_2$ (Ni-**8**)/excess $PMePh_2$ catalyst and a bromide initiator.[266] Among other amine-bearing block copolymers via copper catalysts (FB-**3**,[483] FB-**4**,[483,484] FB-**5**,[485] FB-**6**,[485] FB-**7**,[486] FB-**8**,[270] FB-**9**,[270] FB-**10** to FB-**13**,[269] FB-**14** and FB-**15**[487]), dual-functionalized block copolymers with amino and hydroxyl groups (FB-**10** to FB-**13**,[269] FB-**14** and FB-**15**[487]) are synthesized by sequential procedure with copper chloride catalysts (CuCl/HMTETA[269] or CuCl/bpy[487]) and a bromide initiator ($M_w/M_n \approx 1.3$). The products and their derivatives showed unique pH responsible micellization[269] and gelation.[487] Pyridine segment (FM-**10**) is also incorporated into block copolymers (FB-**16**,[488] FB-**17**,[489] FB-**18**[476]) in conjunction with copper chloride catalysts and macroinitiators.

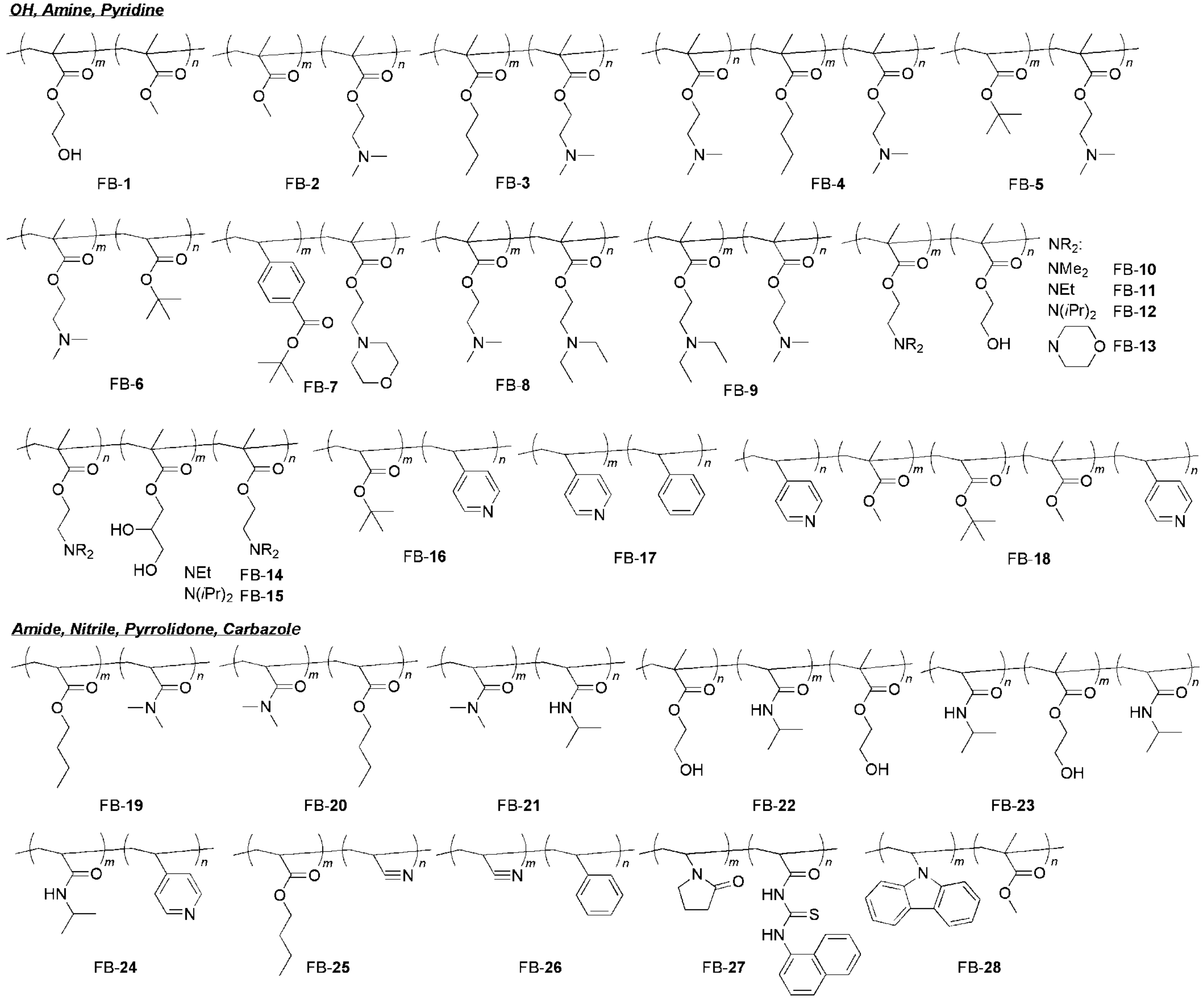


Figure 25. Functionalized block copolymers 1.

Amide, Nitrile, Pyrrolidone, and Carbazole. Amide, nitrile, pyrrolidone, and carbazole-functionalized block copolymers (FB-**19** to FB-**28**) are obtained from copper-catalyzed living radical polymerization with macroinitiators (Figure 25). As well as those of *N*,*N*-dimethylacrylamide (DMAA) (FB-**19**,**20**, $M_w/M_n < 1.3$),[490] block copolymers containing a NIPAM (FM-**12**) (FB-**21**,[230] FB-**22**,[491] FB-**23**,[491] FB-**24**[492]) are also controlled ($M_w/M_n < 1.5$). FB-**22-24** performed thermo- or pH-responsive behaviors.[491,492] Acrylonitrile (AN), vinylpyrrolidone (VP), and *N*-vinylcarbazole (FM-**19**) are also employed as functional monomers for block copolymers (FB-**25**,[493] FB-**26**,[494] FB-**27**,[495] and FB-**28**[290]).

PEG. Hydrophilic, amphiphilic, and thermosensitive poly(ethyleneglycol) (PEG)-functionalized block copolymers (FB-**29** to FB-**41**) are obtained from poly(ethyleneglycol) methyl ether (meth)acrylate (PEGMA, FM-**14**; PEGA, FM-**16**) in conjunction with ruthenium, iron, nickel, and copper catalysts (Figure 26). FB-**29** from MMA to PEGMA can be prepared by various catalytic system [$FeBr_2PZN$ (Fe-L**5**),[496] $NiBr_2(PMePh_2)_2$ (Ni-**8**),[266] CuBr/PMDETA[497]] in conjunction with a bromide initiator ($M_w/M_n = 1.2-1.3$), where the iron and nickel catalysts conveniently permit a sequential method without isolation in contrast to the copper one with isolation of prepoly(MMA)s. Furthermore, FePZN (Fe-L**5**) with a bromide initiator,[496] as well as $RuCl_2(PPh_3)_3$ (Ru-**1**)/*n*-Bu_3N (additive) with a chloride initiator,[277] is also effective for block copolymerization from PEGMA to MMA (FB-**30**), inverse version of FB-**29**. HEMA (FM-**1**) and DMAEMA (FM-**4**) are also introduced into PEGMA (FM-**14**)-based block copolymers (FB-**37**,[261,262] FB-**38**[261]) with a RuCp*(**Ru-15**) catalyst[261] or CuBr/bpy[262] ($M_w/M_n < 1.2$). All of other PEG-carrying block copolymers (FB-**31**,[497] FB-**32**,[497] FB-**33**,[412] FB-**34**,[498] FB-**35**,[498] FB-**36**,[499] FB-**39**,[497] FB-**40**,[286] FB-**41**[500]) were obtained with copper catalysts and macroinitiators.

Reactive or Protected Functional Groups. Reactive or protected functional groups are incorporated into block copolymers (FB-**42** to FB-**61**) using their corresponding macroinitiators (Figure 26). Though epoxy or oxazolone-bearing monomers (FM-**20** or FM-**23**) with copper or ruthenium catalysts efficiently gave functionalized block copolymers (FB-**42**,[501] FB-**43**,[265] FB-**44**,[293] FB-**45**,[263] and FB-**46** to FB-**49**[296]) in high yield without any side reaction such as the ring-opening reaction, allyl methacrylate inevitably induced cross-linking reaction in block copolymerization (FB-**50** to FB-**52**).[502] Alkyne pendant-bearing block copolymers (FB-**53**)[303] are prepared by copper-catalyzed polymerization of FM-**29** with bromine-capped poly(MMA) macroinitiators, where the deprotection of the trimethylsilyl group

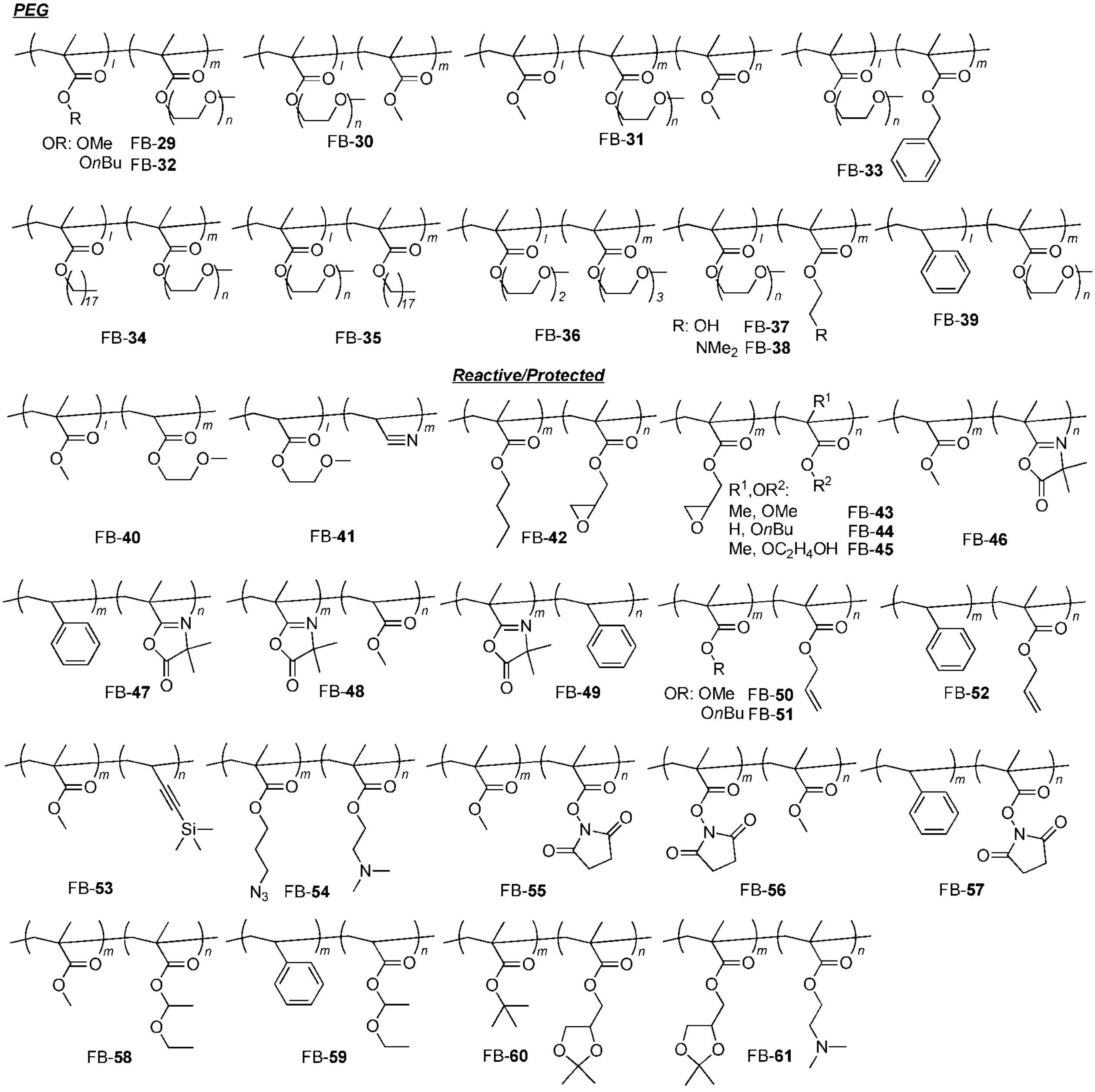


Figure 26. Functionalized block copolymers 2.

efficiently yield MMA and vinylacetylene-based block copolymers. Copper catalysts succeed in introduction of azide and succinimide groups into block copolymers (FB-**54**,[301] FB-**55**,[310] FB-**56**,[309] FB-**57**[310]) without any side reaction. The azide-bearing FB-**54** is efficiently functionalized with alkyne-containing agents to produce various functionalized block copolymers.[301] The pendant succinimide groups in FB-**55** to FB-**57** are efficiently transformed into amide linkages with primary amine-containing compounds for functionalization of block copolymers.[309,310] Acetal and solketal groups are also employed as protecting groups in FB-**58**,[306] FB-**59**,[306] FB-**60**,[308] FB-**61**,[307] where the deprotection is also successful.[306,308]

***p*-Functionalized Styrene Derivatives.** *para*-Functionalized styrene derivatives with silicon, boron, and fluorine are employed for functionalized block copolymers (FB-**62**,[321] FB-**63**,[321] FB-**64**,[503] FB-**65**[503]) in copper-catalyzed living radical polymerization (Figure 27). After hydrolysis of the poly(MA) block segment in FB-**64**, the resulting amphiphilic block copolymers formed micelles in aqueous media, which were further converted into shell-cross-linked nanoparticles.[503]

Ionic Groups. In sharp contrast to ionic living polymerization, metal-catalyzed living radical polymerization can directly produce ionic pendant-functionalized block copolymers (FB-**66** to FB-**82**) without any protection, including phosphorylcholine, ammonium salt, and potassium and sodium sulfonate (Figure 27). Focused on the biocompatibility and the biomedical applications, lots of phosphorylcholine-functionalized block copolymers (FB-**66** to FB-**77**,[315,424,504] FB-**78**[505]) are synthesized by methanolic or aqueous CuBr/bpy-catalyzed living radical polymerization of FM-**40** with a hydrophilic bromide initiator at ambient temperature (20 °C), followed by direct and sequential addition of second block monomers into the prepoly(FM-**40**) solution. However, B-**79**[506] is, in turn, synthesized with NIPAM (FM-**12**) and macroinitiator of FM-**40** because of the difference of effective catalysts in the respective segments. All FM-**40**-based block

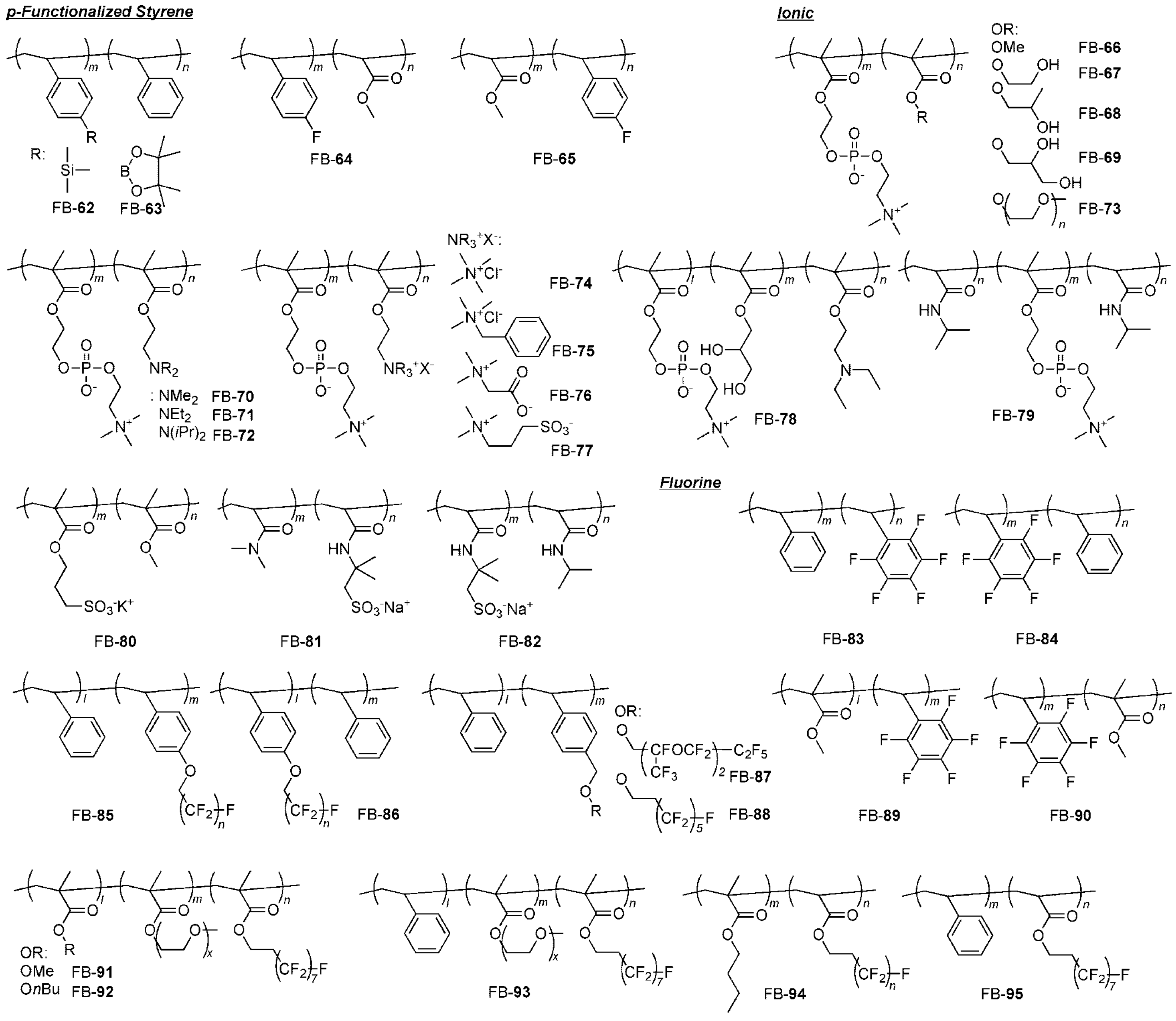


Figure 27. Functionalized block copolymers 3.

copolymers (FB-**66** to FB-**79**) had well-controlled molecular weight and narrow MWDs ($M_w/M_n = 1.1-1.4$). Some of them indicated unique stimuli-responsible micellization by solvent, pH, and temperature.[314,423,504−506] Other ionic pendant-functionalized block copolymers (FB-**80**,[317] FB-**81**,**82**[319]) are also successfully obtained with CuCl/bpy[317] or Me_6TREN[319] in water/DMF mixed solvent at ambient temperature .

Fluorine Groups. Fluorinated polymers have unique properties such as high thermal stability, oil and water repellency, and good resistance to chemical and physical treatment. Thus, various fluorinated block copolymers (FB-**83**,**84**,[325] FB-**85**,**86**,[326] FB-**87**,**88**,[327] FB-**89**,**90**,[507] FB-**91** to FB-**93**,[497] FB-**94**,[508] and FB-**95**[509]) are also prepared by copper-catalyzed living radical polymerization with their corresponding macroinitiators (Figure 27). Typically, 2,3,4,5,6-pentafluorostyrene (FM-**48**) is polymerized with CuBr/bpy and a bromide-capped poly(St) in bulk at 110 °C to efficiently give FB-**83** with narrow MWDs.[325]

Unique Functional Groups. DNA-base (FB-**96**),[347] cholesteryl groups (FB-**97**),[510] and metal complexes (FB-**98**)[349]-functionalized block copolymers are also synthesized via copper-catalyzed system in conjunction with macroinitiator method (Figure 28). Particularly, FB-**96** was obtained from the following template polymerization:[347] (1) copper-catalyzed living radical polymerization of FM-**71** with a hydroxyl group-functionalized initiator (FI-**6**) ($M_w/M_n \approx 1.3$), (2) synthesis of a template macroinitiator via the esterification of the α-end hydroxyl group, (3) copper-mediated template living radical polymerization of FM-**73** from the template macroinitiator via selective interaction of their side chains between FM-**71** and FM-**73** to give zipper-like diblock copolymers. Block copolymerization of α-substituted monomer (FM-**77**) is also achieved with a copper catalyst and poly(MMA) or poly(St) macroinitiators (FB-**99** and FB-**100**, $M_w/M_n < 1.3$).[351]

Liquid Crystalline Polymers. Various liquid crystalline block copolymers (FB-**101** to FB-**120**) are efficiently obtained from copper-catalyzed living radical polymerization with the corresponding macroinitiators (Figure 29). Pendant functional groups include p-substituted azobenzene, terphenyl and biphenyl derivatives, in addition to quite bulky groups like FB-**119**. For example, *para*-cyano-azobenzene carrying methacrylate (FM-**80**) was efficiently polymerized with CuBr or CuCl/HMTETA and a poly(*n*BA) macroinitiator to give FB-**101** and **102** with narrow MWDs ($M_w/M_n = 1.1-1.2$).[355] Other block copolymers (FB-**103**,[511] FB-**104**,[357] FB-**105**,[512,513]

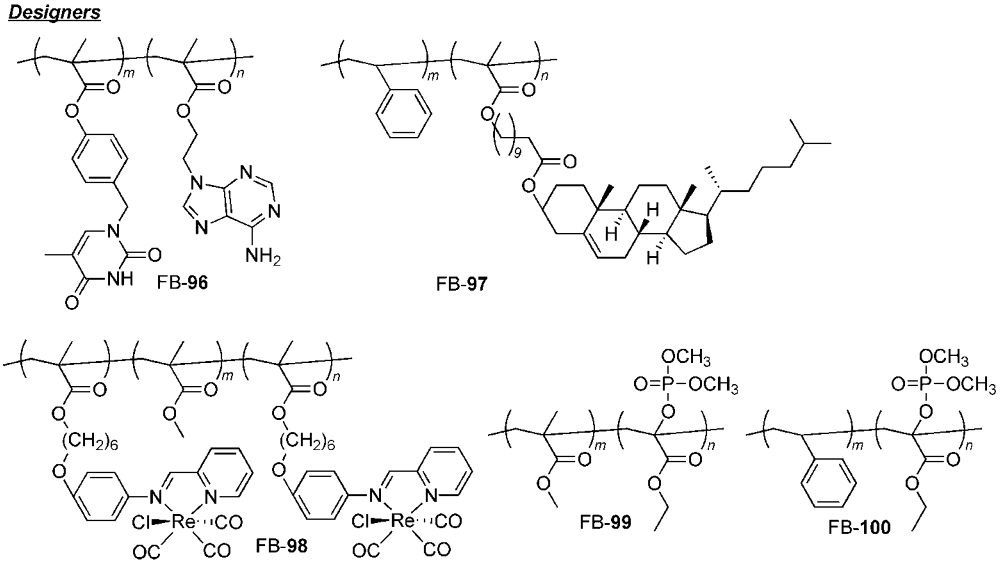


Figure 28. Functionalized block copolymers 4.

FB-**106**,[514] FB-**107** to FB-**110**,[356,359] FB-**111**,[361] FB-**112**,[366] FB-**113**,**114**,[367] FB-**115**,[369] FB-**116**,**117**,[370] FB-**118**,[515] FB-**119**,[374] and FB-**120**[372]) were also prepared as the similar procedures. All examples actually show liquid crystalline properties. Additionally, introduction of well-soluble segments succeeds in the solubility modification of the liquid crystalline block copolymers. Typically, DMAEMA (FM-**4**)-functionalized block copolymers of azobenzene-carrying monomers (FB-**107** to FB-**110**) turned water-soluble and exhibited unique miceller aggregates.[356,359] FB-**112** and FB-**113** carrying a poly(St) segment are also well soluble,[366,367] in sharp contrast to low solubility of homopolymers of FM-**88** and FM-**89**.

3.4.3. System Combination

Combination of commercially available polymers or other polymerization in metal-catalyzed living radical polymerization can widely expand the variation of block copolymers.[242−244] The synthetic procedures are categorized in the following four groups: (1) metal-catalyzed polymerization with a macroinitiator based on commercially available polymers, (2) metal-catalyzed polymerization with a macroinitiator prepared by other polymerization and postintroduction of initiating groups, (3) metal-catalyzed polymerization with a bifunctional initiator carrying a radical initiator and others, followed by the other polymerization, vice versa, and (4) metal-catalyzed polymerization from a macroinitiator carrying a carbon−halogen bond terminal which directly obtained from other polymerization, vice versa. Figures 30−37 comprehensively show block copolymers synthesized by system combination in metal-catalyzed living radical polymerization since early 2001.

Commercially Available PEG and PPO Macroinitiators. Poly(ethylene glycol) (PEG) and poly(propylene oxide) (PPO) with one hydroxyl terminal are often employed as commercially available precursors for PEG or PPO-based macroinitiators in metal-catalyzed living radical polymerization, where the hydroxyl groups are efficiently esterified with appropriate acyl halides (Scheme 3). Thanks to the high solubility, PEG or PPO-based macroinitiators efficiently induced homogeneous polymerization of wide variety of monomers. Additionally, PEG-macroinitiators can provide attractive functions such as hydrophilicity, amphiphilicity, thermosensitivity, biocompatibility, and low toxicity onto the block copolymers. On the basis of these features, this section presents block copolymers synthesized with PEO- or PPO-based macroinitiators and various monomers (Figure 30, 31).

Hydrophobic Segment. PEG- or PPO-based block copolymers with a hydrophobic segment (PB-**1**,[516] PB-**2**,[517−519] PB-**3**,**4**[516] PB-**5**,[519] PB-**6**,[520] PB-**7**,[516] PB-**8**,[521] PB-**9**,[522] PB-**10**[312]) are obtained from copper,[312,516−518,521,522] iron,[519] and nickel[520]-catalyzed polymerization of MMA, EMA, *t*BMA, *n*BMA, hexyl methacrylate, ethyl acrylate (EA), nitrophenyl methacrylate, FM-**33**, and FM-**37**, in conjunction with PEG or PPO-based macroinitiators (Figure 30). Some of the resulting products exhibit micelle formation in aqueous solution[517,521,522] and unique morphologies in the solid state.[520] PB-**10** afforded organic/inorganic hybrid materials.[312]

Functional Groups. Various functional groups such as hydroxyl, amine, amide, PEG, ionic, and fluorine groups can be incorporated into PEG and PPO-based block copolymers in metal-catalyzed living radical polymerization (Figure 30). Among them, hydroxyl functionalization is achieved with copper-catalyzed polymerization of HEMA (FM-**1**), FM-**2**, and FM-**3** (PB-**11**,[523,524] PB-**12**,[524] PB-**13**,[525] PB-**14**,**15**,[264] PB-**16**,[263] and PB-**17**[264]). Especially, controlled PB-**11** and PB-**12** ($M_w/M_n \approx 1.3$) were obtained from inverse miniemulsion AGET ATRP of HEMA with a PEG-macroinitiator, where PB-**12** turned a core [poly(HEMA)]-shell (PEG) miceller nanoparticle in water.[524] Copper-based metanolic system at ambient temperature was also effective for PB-**14** to PB-**17** ($M_w/M_n = 1.1-1.2$).[263,264]

Amine and amide-functionalized block copolymers with a PEG segment (PB-**18**,**19**,**20**,[526] PB-**21**,[527] PB-**22**,[528] PB-**23**,[529] PB-**24**,[263] PB-**25**,[530] PB-**26**,[531,532] and PB-**27**[533]) are prepared with copper catalysts. The triblock copolymers (PB-**21**, PB-**24**, PB-**25**, PB-**26**) formed pH-responsible micelles in water,[263,527,530−532] where PB-**21** and PB-**26** further worked as precursors of shell cross-linked micelles.[527,531,532] Additionally, PB-**27** was uniquely dual responsive to pH and temperature.

PEG, PPO, and ionic pendant block copolymers (PB-**28**,**29**,[534] PB-**30**,[535] PB-**31**,[536] PB-**32**,**33**,[504] PB-**34**,[506] and PB-**35**[537]) are efficiently synthesized by aqueous and/or alcoholic copper-catalyzed polymerization of PEGMA (FM-**14**), PPOMA (FM-**15**), and ionic pendant monomers (FM-**38**, FM-

Liquid Crystal

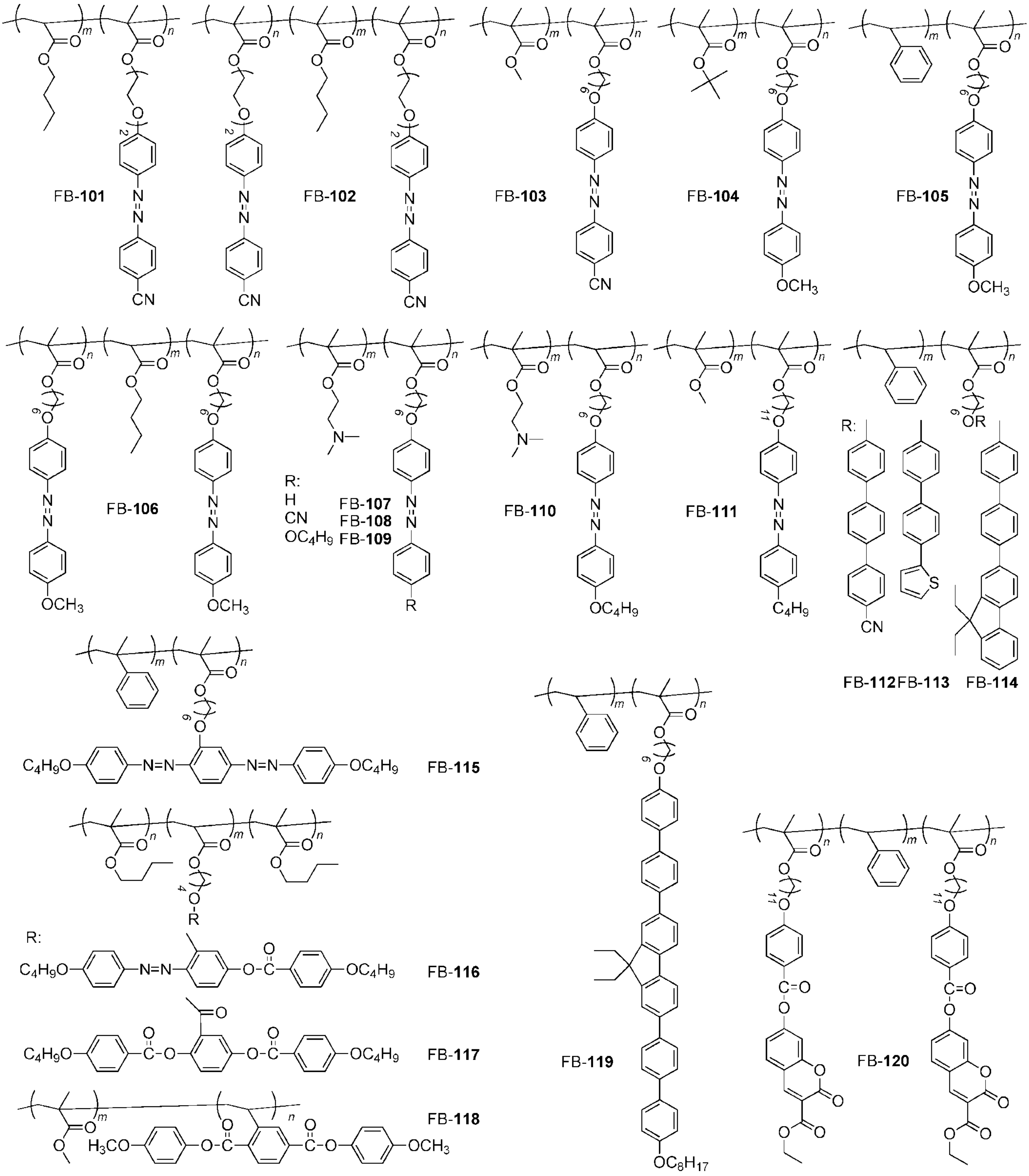


Figure 29. Functionalized block copolymers 5.

40) in the presence of PEG or PPO-macroinitiators. PEG-based di(tri)block copolymers with a fluorinated segment (PB-**36**,[538] PB-**37**[539,540]) uniquely show microphase separation in bulk and association in solution.

Sugar, Peptide, Nucleobase, and Liquid Crsytal. As shown in Figure 31, sugar, peptide, nucleobase, and liquid crystalinity-monomers are successfully combined with PEO and PPO-based macroinitiators (PB-**38** to PB-**57**). Typically, sugar pendant-containing block copolymers with a PEG or PPO segment (PB-**38**[330,331] and PB-**39** to PB-**44**[331]) were obtained from aqueous and/or alcoholic copper-catalyzed living radical polymerization of FM-**50** and FM-**51** in high yield ($M_w/M_n = 1.1-1.3$). Introduction of peptide or nucleobase-carrying segments is suitable for copper-mediated polymerization in DMSO (PB-**45**,[337] PB-**46**,[344,345] PB-**47**[345]). Additionally, PEG-macroinitiators are effective for copper-catalyzed polymerization of azobenzene-containing monomers (FM-**81**, FM-**83**), biphenyl and ter-

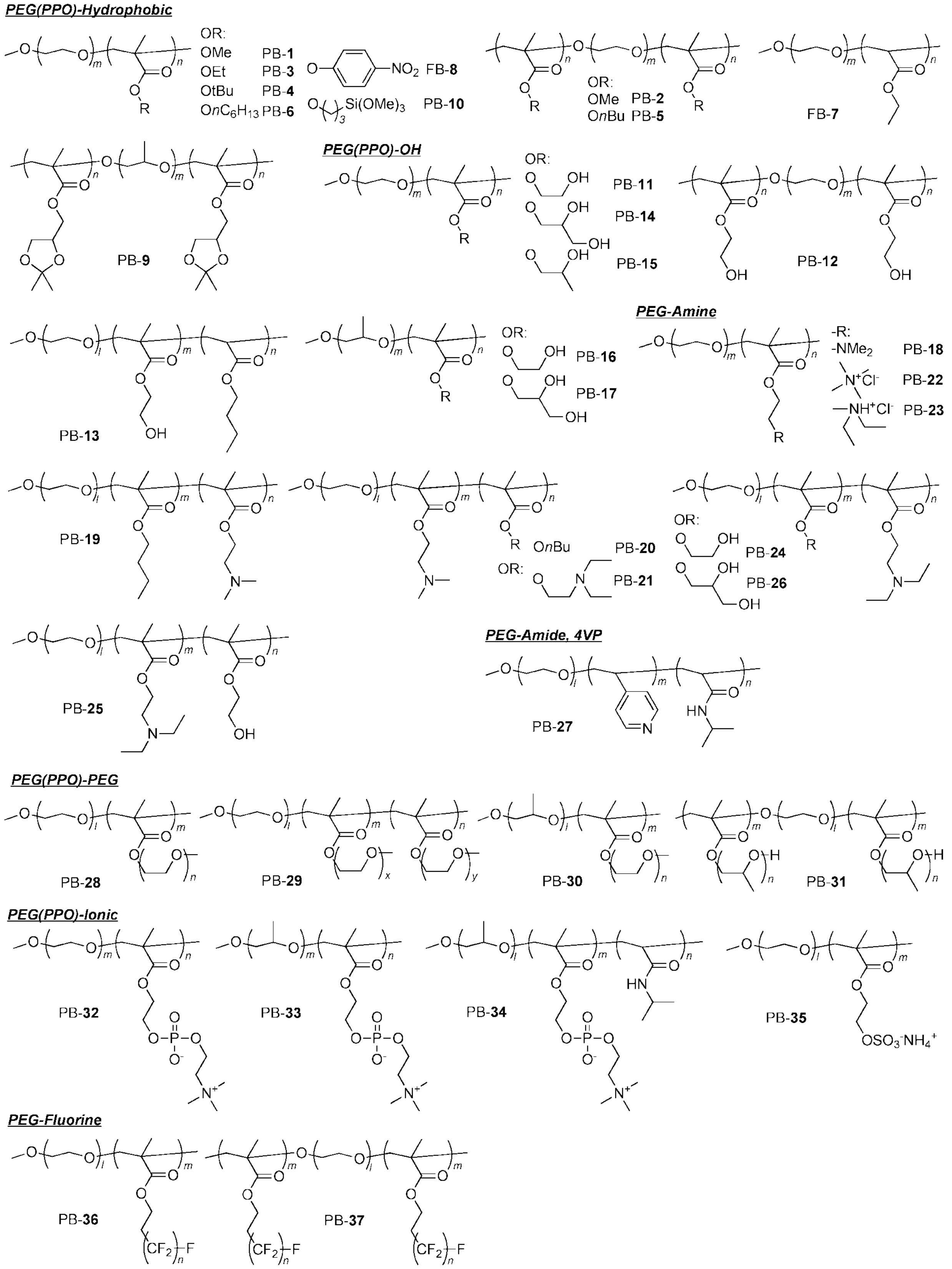


Figure 30. Block copolymers prepared from commercially available polymers 1.

phenyl pendant monomers (FM-**86**, FM-**88**), and bulky pendant ones (FM-**96**, FM-**98**), to give well-controlled amphiphilic liquid crystal block copolymers (PB-**48**,[541] PB-**49**,[358,542] PB-**50**,[358,543] PB-**51**,[358] PB-**52**,**53**,[364] PB-**54**,**55**,[366] PB-**56**,[373] PB-**57**[544]).

Other Living Addition Polymerization. Figure 32 shows block copolymers synthesized by combination of metal-catalyzed system and other kind of living addition polymerization such as nitroxide-mediated radical polymerization (NMP),[7] cobalt-mediated living radical polymerization (CoLRP),[148] reversible addition−fragmentation chain transfer (RAFT),[8] single electron transfer/degenerative chain transfer mediated living radical polymerization (SET-DTLRP),[239] and living cationic polymerization.[545]

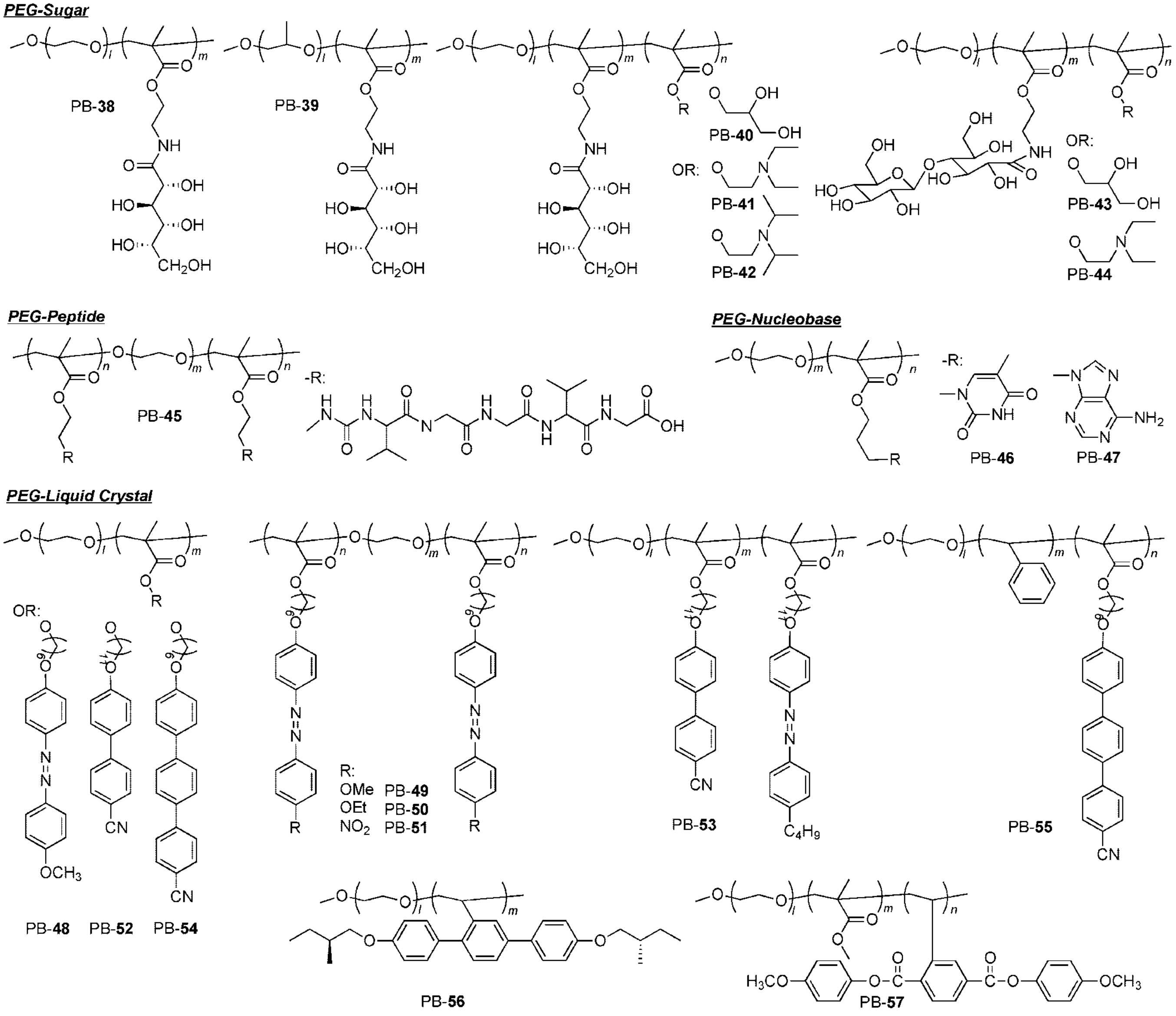


Figure 31. Block copolymers prepared from commercially available polymers 2.

NMP. Dual functional initiators (FI-**71**, FI-**72**, FI-**73**) carrying a α-halo ester and a 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) moiety are especially designed for block copolymerization combined with metal-catalyzed system and NMP. Actually, FI-**71** and FI-**72** give CB-**1**,[444] CB-**4**,[443] CB-**5**,**6**[546] via copper-catalyzed polymerization of the corresponding monomers and NMP of St, where the controllability is independent of their polymerization order because the nitroxide radical is capped and stable in the condition of metal-catalyzed polymerization. However, a dual functional initiator with a naked nitroxide radical naturally just allow us to first employ NMP of styrene and subsequently copper-catalyzed polymerization for well-controlled CB-**2**,**3**,**4**.[547] Quite recently, vinylpyridine-based block copolymers (CB-**7**) have been also synthesized by copper-catalyzed living radical polymerization of MMA and subsequent NMP of 4-VP (FM-**10**) with FI-**73**.[445]

Co-LRP and RAFT. Cobalt-LRP is now quite effective for VAc polymerization at ambient temperature.[160] Thus, treated with a nitroxide radical-bearing α-halo ester, Co(acac)$_2$-terminal poly(VAc)s are transformed into haloester-terminal poly(VAc)-macroinitiators. They efficiently initiate copper-catalyzed living radical polymerization of MMA, EA, St, for VAc-based block copolymers (CB-**8**, CB-**9**, CB-**10**) (Figure 32).[548] After methanolysis of CB-**10**, the resulting amphiphilic block copolymers with a hydrophilic poly(vinyl alcohol) segment uniquely forms large vesicles (average diameter, ∼1 μm) in water/THF. Additionally, CB-**10** is also obtained form the combination of RAFT polymerization of VAc and copper-catalyzed polymerization of styrene with a dual functional initiator (FI-**74**).[446]

SET-DTLRP. Single electron transfer/degenerative chain transfer mediated living radical polymerization (SET-DTLRP) gives well-controlled poly(vinyl chloride) carrying α,ω-iodide terminals (I-PVC-I).[239] The I-PVC-I efficiently worked as a bifunctional macroinitiator for copper-catalyzed living radical polymerization of MMA and MA, leading to the corresponding poly(VC)-based block copolymers (CB-**11**,[549−551] CB-**12**[552]) (Figure 32).

Living Cationic Polymerization. Lewis acid-catalyzed living cationic polymerization of vinyl ether (VE) and isobutylene (IB) are combined with metal-catalyzed system to produce block copolymers (Figure 32) according to the following two methods: (1) living radical polymerization with a radical/cationic bifunctional initiator, followed by living cationic polymerization, vice versa, and (2) living radical

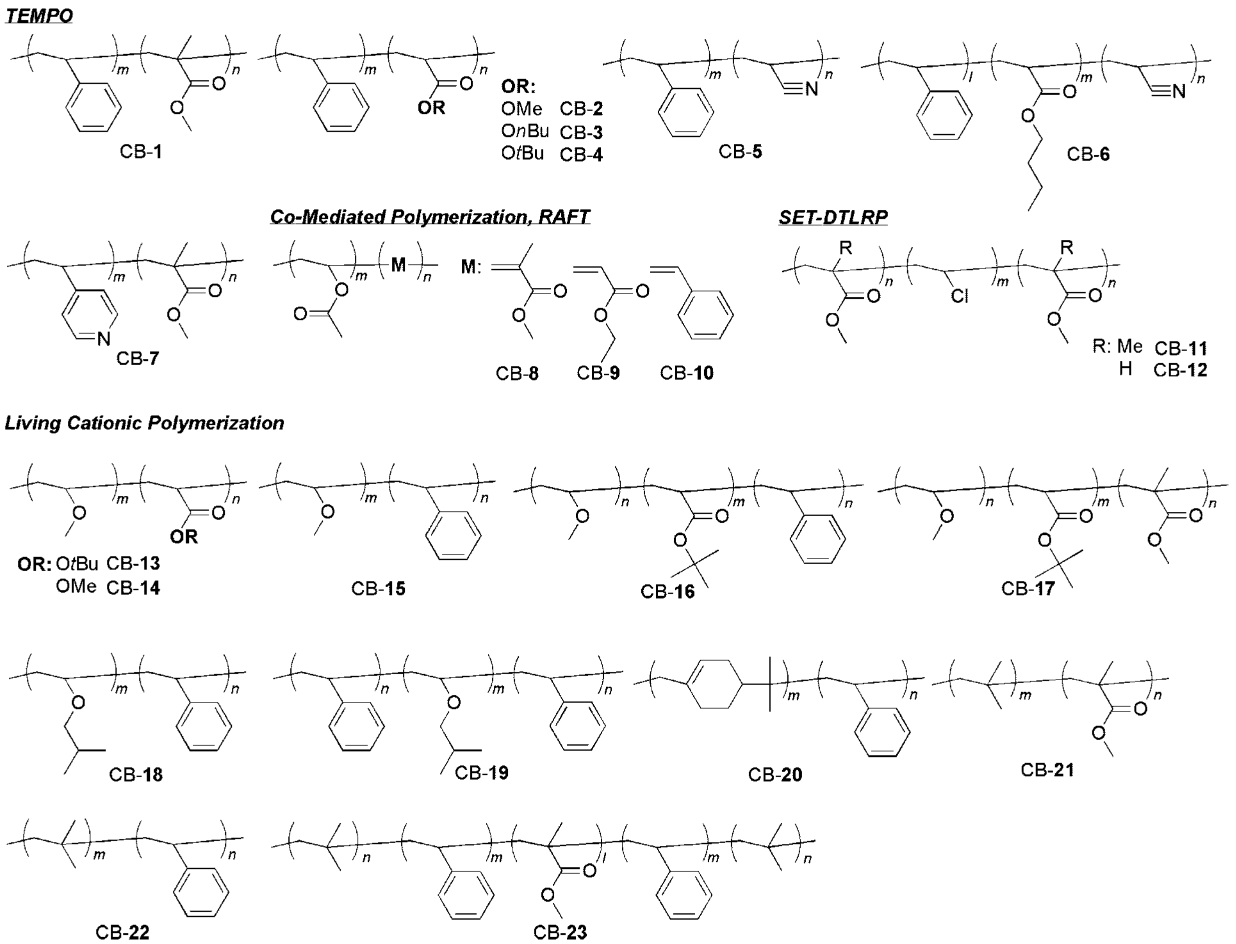


Figure 32. Block copolymers prepared via living radical and cationic polymerization

polymerization with a halogen-capped macroinitiator obtained from living cationic polymerization, vice versa, which include mechanism transformation of halogen terminals.

Based on the former method, an acetal-bearing α-halo ester initiator (FI-**39**) gives well-controlled block copolymers (CB-**13**,**14**,**15**) via ZnI_2-catalyzed living cationic polymerization of methyl vinyl ether (MVE) and CuBr/PMDETA-catalyzed living radical polymerization of *t*BA, MA, St, where the controllability is independent of the polymerization order (M_w/M_n <1.2).[415] This procedure is further extended to MVE-based triblock copolymers (CB-**16**, CB-**17**).[415]

In contrast, block copolymers from CB-**18** to CB-**23** are obtained from the latter method. For CB-**19**, isobutyl vinyl ether (IBVE) is first cationically polymerized with $SnCl_4$ and a bifunctional chloride initiator (ClRCl) in the presence of styrene (St) at −78 °C to lead to well-defined poly(IBVE)s with a chlorine-capped short poly(St) segment in the both terminals, in which the styrene are almost remained in the solution. Subsequent addition of $RuCp^*Cl(PPh_3)_2$ (Ru-**5**) and *n*-Bu_2NH into the solution initiates living radical polymerization of styrene from the both chlorine terminals, giving well-defined CB-**19**.[553] The similar mechanism transformation from cationic polymerization to radical counterpart is applied to CB-**18**[553] and CB-**20**.[554] For CB-**21**, **22**,[555] an ally halide-bearing poly(IB) via living cationic polymerization was employed as a macroinitiator for copper-catalyzed living radical polymerization of St and MMA, while for CB-**23**,[556,557] a chlorine-capped St-MMA-St triblock macroinitiator via metal-catalyzed system was applied to living cationic polymerization of IB.

Ring-Opening Polymerization (ROP). Ring-opening polymerization (ROP) combined with metal-catalyzed system includes the following five systems (Figure 33, 34): (1) ring-opening cationic polymerization (ROCP), (2) ROP with enzyme, (3) ring-opening anionic polymerization (ROAP), (4) ring-opening metathesis polymerization (ROMP), and (5) polymerization of amino-acid *N*-carboxy anhydrides (NCA). These combinations contribute expansion of species and functions in block copolymers.

ROCP. Well-controlled polyether, polyester, and polyoxazoline are obtained from ring-opening cationic polymerization (ROCP) of tetrahydrofuran (THF),[558] trimethylene oxide (oxetane),[559] ε-caprolactone (ε-CL),[382,560−565] and L-lactide (LLA)[566−568] with Lewis Acid catalysts and alcohol initiators and ROCP of oxazoline[569] with an acyl halide initiator. Thus, they are often combined with copper-catalyzed living radical polymerization to produce block copolymers with polyether, polyester, and polyoxazoline segments (CB-**24** to CB-**40**) (Figure 33). There are two procedures to introduce poly(ether) or poly(ester) segments: (1) metal-catalyzed living radical polymerization with dual functional initiators carrying a α-haloester (or benzene) and a hydroxyl group such as FI-**1**[558,559,567] and FI-**5**,[382] followed by Lewis Acid-catalyzed ROCP, and ROCP with the initiators vice versa; (2) terminal transformation of hydroxyl groups in ROCP products with an acyl halide into α-haloester-bearing macroinitiators, followed by metal-catalyzed polymerization. The former methods are applied to CB-**24**,**25**,**26**,[558] CB-**27**,[559] CB-**28**,[382] CB-**30**,[382] CB-**34**,[565] CB-**36**,[566,567] and CB-**37**,[567] and the latter ones are, in turn, done to CB-

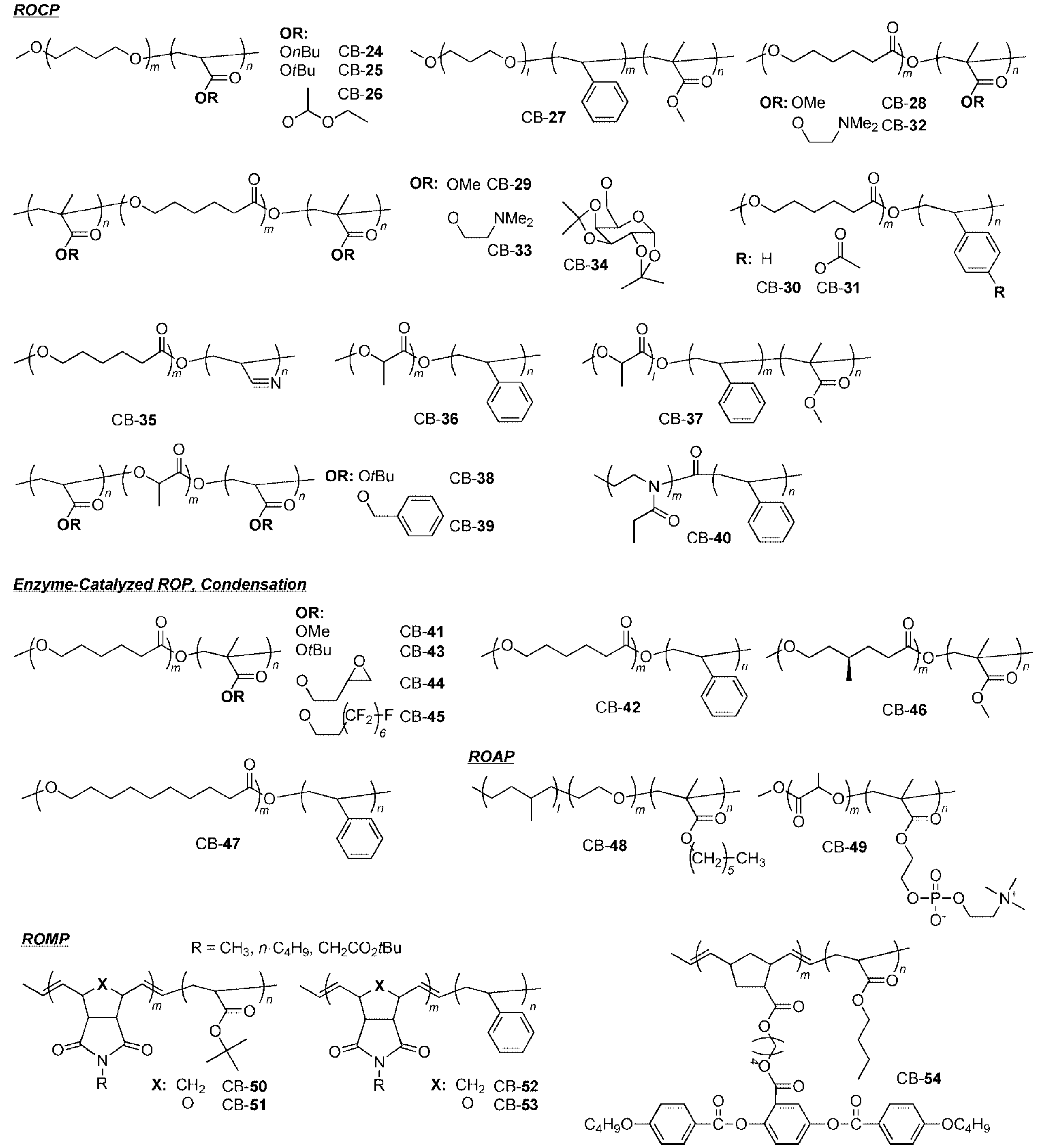


Figure 33. Block copolymers prepared via ring-opening polymerization 1.

29,[327] CB-**30**,[328] CB-**32**,[562] CB-**33**,[563] CB-**35**,[564] and CB-**38**,**39**.[568] The products are well-controlled ($M_w/M_n = 1.1-1.4$) and often exhibit unique morphology[560,564] and micellar aggregation in aqueous media.[562] CB-**40** ($M_w/M_n \approx 1.2$) is prepared by ROCP of an oxazoline monomer with α-bromoisobutylbromide, followed by copper-catalyzed polymerization of styrene.[569]

ROP with Enzyme. ROP of ε-caprolactone (ε-CL) and (R)-4-methylcaprolactone ((R)-4MeCL), catalyzed by Novozyme-435 (enzyme), Lipase B from *Candida antarctica* (CALB) immobilized on an acrylic macroporous resin, is often coupled with copper- or nickel-catalyzed living radical polymerization to give block copolymers carrying a poly(ester) segment (CB-**41** to CB-**46**) (Figure 33). Most of them (CB-**41**,[378] CB-**42**,[381,570,571] CB-**43**,[380] CB-**45**,[379] and CB-**46**[384]) are first prepared by enzyme-catalyzed ROP with a bifunctional initiator with a α-haloester and a hydroxyl group such as FI-**1**,[378−380] FI-**2**,[384] and FI-**3**,[381] subsequently followed by living radical polymerization. In contrast, CB-**44**[572] is prepared by the latter method described in Lewis Acid-catalyzed ROCP.

More importantly, CB-**41**,[378] CB-**43**,[579] and CB-**46**[384] are obtained from concurrent or sequential tandem block polymerization using metal catalysts and enzyme catalysts without any bothersome isolation of prepolymers (macroinitiators), respectively. Typically, CuBr/bpy-catalyzed living radical polymerization of styrene and Novozyme-435-catalzyed ROP of ε-CL were simultaneously carried out in the presence of FI-**1** in supercritical carbon dioxide at 35 °C, directly, one-pot, leading to the related block copolymers

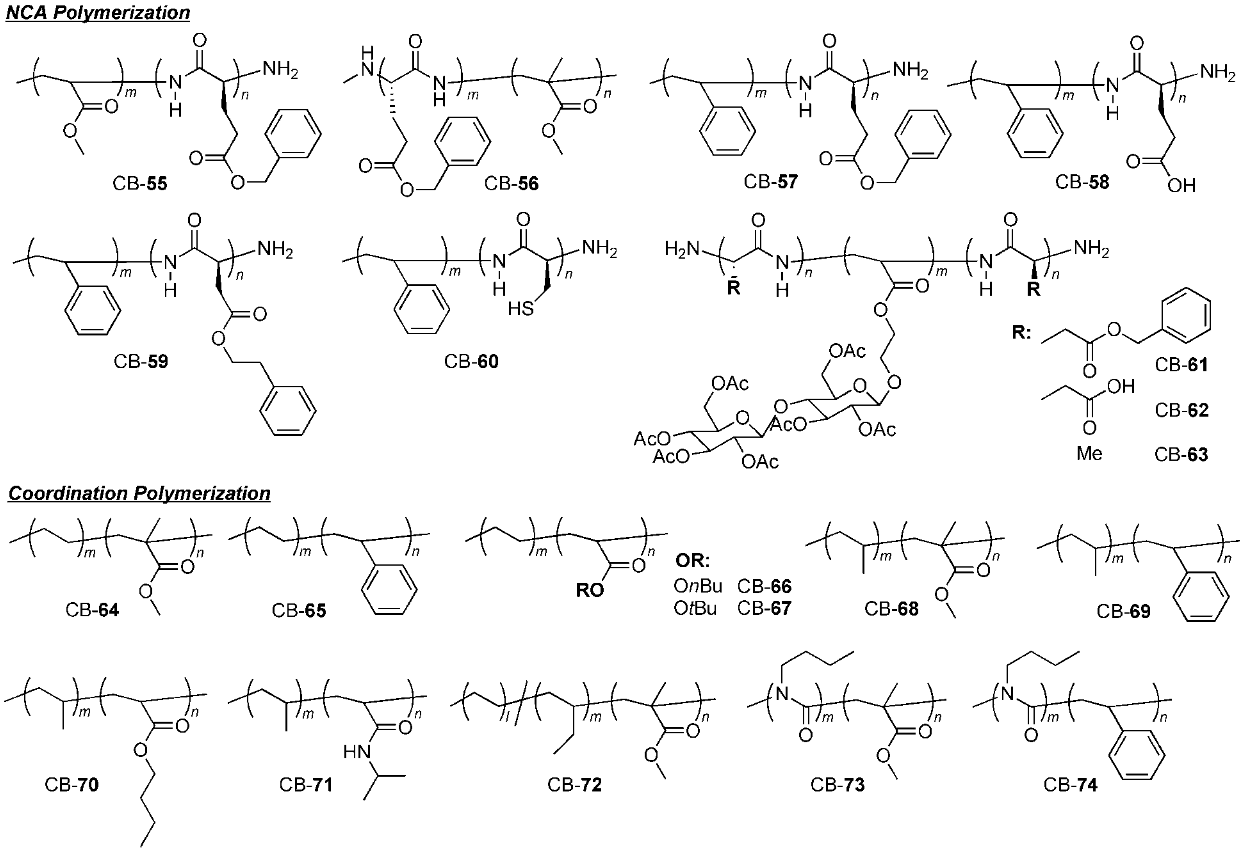


Figure 34. Block copolymers prepared via ring-opening polymerization (part 2) and coordination polymerization.

(CB-**41**) with controlled molecular weight and narrow MWDs ($M_w/M_n \approx 1.2$),[378] as well as the isolated methods of their respective polymerization steps. Additionally, Novozyme-435 enzyme effectively worked as a catalyst not only for ROP but also self-condensation polymerization to yield the novel block copolymers (CB-**47**).[573]

ROAP. Ring-opening anionic polymerization (ROAP) of ethylene oxide[574] and D,L-lactide (DLLA)[575] are coupled with metal-catalyzed system for block copolymers carrying a poly(ethylene oxide) or poly(DLLA) segment (CB-**48**,[574] CB-**49**:[575] $M_w/M_n = 1.1-1.5$) (Figure 33). In CB-**48**,[574] ROAP of ethylene oxide and the subsequent quenching with an alcohol is first carried out for poly(ethylene oxide) with a hydroxyl terminal, which is further transformed into a bromoester-bearing polyethylene macroinitiator with an acyl bromide. The initiator is applied to nickel-catalyzed living radical polymerization of hexyl methacrylate, leading to the final product (CB-**48**).

ROMP. Block copolymers (CB-**50** to CB-**53**[576] and CB-**54**[577]) are also synthesized by ring-opening metathesis polymerization (ROMP) of norbornene derivatives and copper-catalyzed living radical polymerization (Figure 33). The block copolymers were obtained from the following three steps: (1) ruthenium-mediated ROMP of the corresponding norbornene, (2) subsequent addition of excess of a vinyl ether-bearing α-bromoester, giving a poly(norbornene)-based macroinitiator, and (3) copper-catalyzed polymerization with the macroinitiator. The obtained polymers were well controlled ($M_w/M_n = 1.1-1.3$), and CB-**54**[577] clearly exhibited liquid crystalline properties.

ROP of NCA. Nickel-catalyzed ROP of α-amino acid-*N*-carboxyanhydride (NCA) gives a well-controlled polypeptide. Thus, the combination of metal-catalyzed polymerization and ROP of NCA efficiently achieved polypeptide conjugation onto (meth)acrylate and styrene-based block copolymers (CB-**55**,[578] CB-**56**,[447] CB-**57**,**58**[579] CB-**59**,[580] CB-**60**,[581] CB-**61**,**62**[582] and CB-**63**[334]) with relatively narrow MWDs ($M_w/M_n = 1.1-1.4$) (Figure 34). Here, γ-benzyl-L-glutamate NCA, β-phenetyl-L-aspartate NCA, carbobenzoxy-L-cysteine NCA, and L-alanine NCA are typically employed as NCA monomers. The γ-benzyl groups in CB-**57** and CB-**61** are easily transformed into carboxylic acid groups (CB-**58** and CB-**62**) via hydrolysis and hydrogenation, respectively.[579,582]

Coordination Polymerization. Polyolefins are widely produced as commercial polymers via coordination polymerization and exhibit excellent properties such as high mechanical strength and flexibility, chemical stability, and good corrosion resistance. However, they fundamentally indicate poor adhesion or incompatibility with other materials because of the low polarization. On the basis of these backgrounds, block copolymers containing polyolefin segments via coordination polymerization and polar polymer segments via metal-catalyzed counterpart are developed (CB-**64** to CB-**72**) (Figure 34).[583-592]

For example, polyethylene and polypropylene via coordination polymerization mediated by Zieglar/Natta catalysts, metallocene catalysts, etc., or commercially available ones, are often introduced into block copolymers based on copper or ruthenium-catalyzed living radical polymerization of MMA (CB-**64**,[583] CB-**68**,[586,587,589] CB-**72**[591]), styrene (CB-**65**,[584] CB-**69**[588,589]), *n*BA (CB-**66**,[585] CB-**70**[589]), *t*BA (CB-**67**),[585] and NIPAM (FM-**12**) (CB-**71**[590]). Here, vinyl or hydroxyl end group-bearing polyolefins are utilized as precursors of macroinitiators: a vinyl terminal-carrying polypropylene by the treatment with *N*-bromosuccinimide (NBS) turns an allyl bromide terminal-carrying poly(propy-

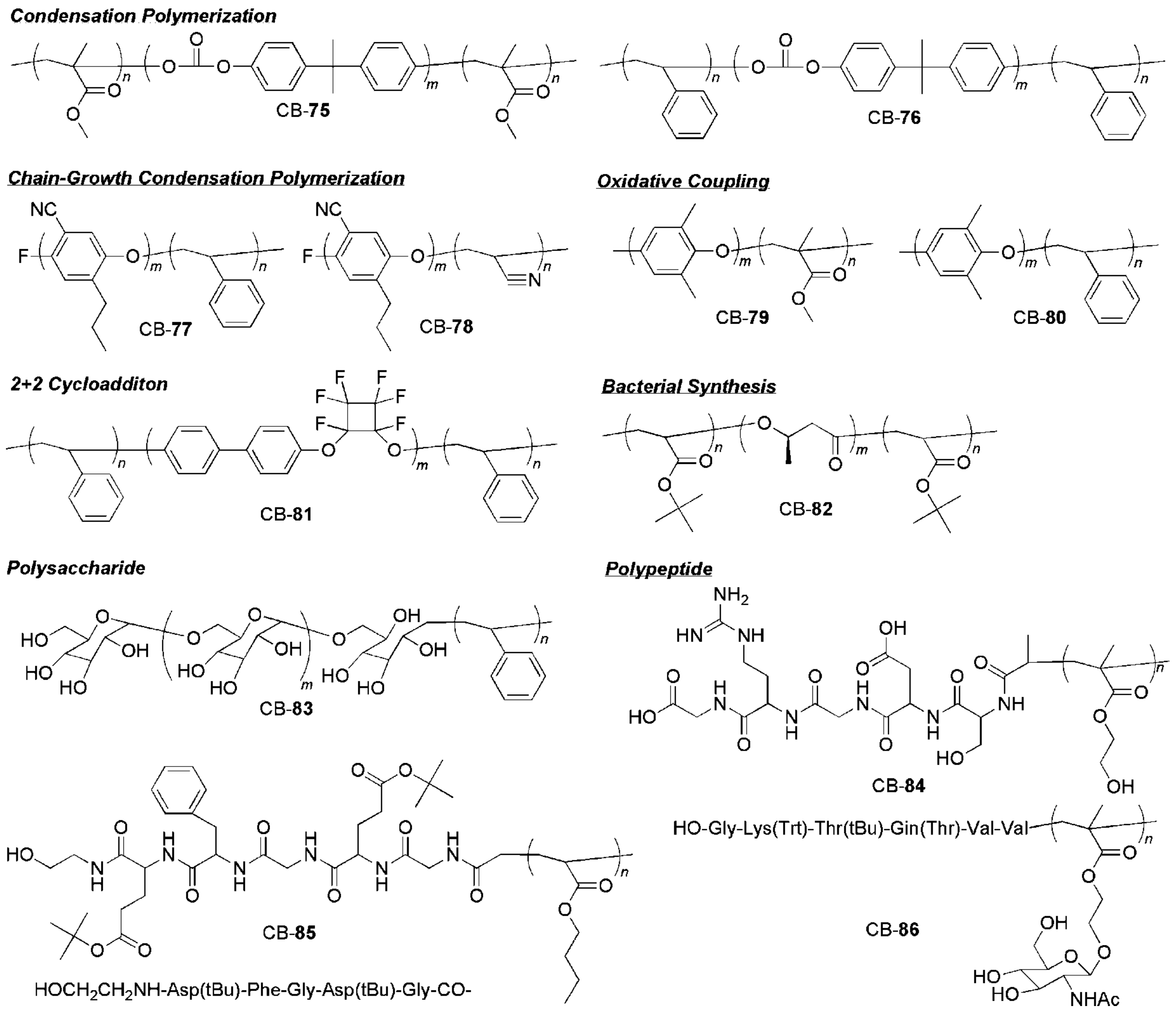


Figure 35. Block copolymers prepared from polycarbonates, polyesters, polyethers, polysaccharides, and polypeptides.

lene) macroinitiator in high yield. The initiator with CuBr/PMDETA is effective for MMA, styrene, and *n*BA (CB-**68**, CB-**69**, CB-**70**).[589] Polyethylene- and polypropylene-based block copolymers often show microphase separation,[583,588−590] and a block copolymer of ethylene and MMA (CB-**64**) further works as a compatibilizer for poly(MMA) and polyethylene blend.[583] Additionally, polyisocyanate via titanium-catalyzed coordination polymerization is also combined with copper-catalyzed polymerization of MMA or styrene to lead to the rod−coil block copolymers with narrow MWDs (CB-**73**, CB-**74**, $M_w/M_n \approx 1.2$).[592]

Other Combinations. As other polymer species, polycarbonates, polyethers, polyesters, polysaccharides, polypeptides, conjugated polymers, and inorganic silicon-based polymers are also incorporated into block copolymers in conjunction with metal-catalyzed living radical polymerization.

Polycarbonate, Polyether, and Polyester. A bis(hydroxy)-telechelic bisphenol A polycarbonate, obtained from melt polycondensation of bisphenol A and diphenyl carbonate, is employed as a precursor for a polycarbonate-based bifunctional macroinitiator, which efficiently initiates copper-catalyzed living radical polymerization of MMA and St (CB-**75**, CB-**76**) (Figure 35).[593,594] Chain-growth condensation polymerization (CGCP) now achieves precise control of molecular weight in polyether with potassium 5-cyano-4-fluoro-2-propylphenolate.[595] A 4-fluorophenyl-terminal prepoly(St), synthesized by copper-catalyzed living radical polymerization of styrene with 4-fluorophenyl sulfonyl chloride, efficiently initiate CGCP of 5-cyano-4-fluoro-2-propylphenolate to give well-controlled CB-**77**.[596] On the contrary, CGCP for CB-**78**[597] was followed by copper-catalyzed living radical polymerization of AN, to prevent the decomposition of poly(AN) segments. The resulting rod−coil block copolymers (CB-**77**, CB-**78**), cast on glass plate, performed unique self-assembly. Other polyether- or polyester-based block copolymers are obtained from oxidative coupling polymerization of 2,6-dimethylphenol (CB-**79**, CB-**80**),[598] intermolecular [2 + 2]-cycloaddition of the bifunctional trifluorovinyl ether monomer (CB-**81**),[599] and bacterial polymerization of (*R*)-3-hydroxybutyrate (CB-**82**).[600]

Polysaccharides and Polypeptides. Sugar- or amino acid-based polymers such as commercially produced polysaccharides (dextran) or precision sequence-regulated polypeptides via solid-phase supported synthesis also efficiently work as macroinitiators for copper-catalyzed living radical polymerization of styrene, HEMA (FM-**1**), *n*BA, and FM-**56**, even in the presence of lots of the polar functional groups. The products (CB-**83**,[601] CB-**84**,[602] CB-**85**,[603] and CB-**86**[425]) have well-controlled molecular weight and narrow MWDs (Figure 35). CB-**83** exhibited self-assembly in water, and the polymer cast from the aqueous solution gave stable spherical morphologies.[601]

π-Conjugated Polymers. Since Π-conjugated polymers not only show unique electronic and photonic properties but also form rod-like structures due to the rigidity, rod−coil block copolymers with π-conjugated segments would become quite

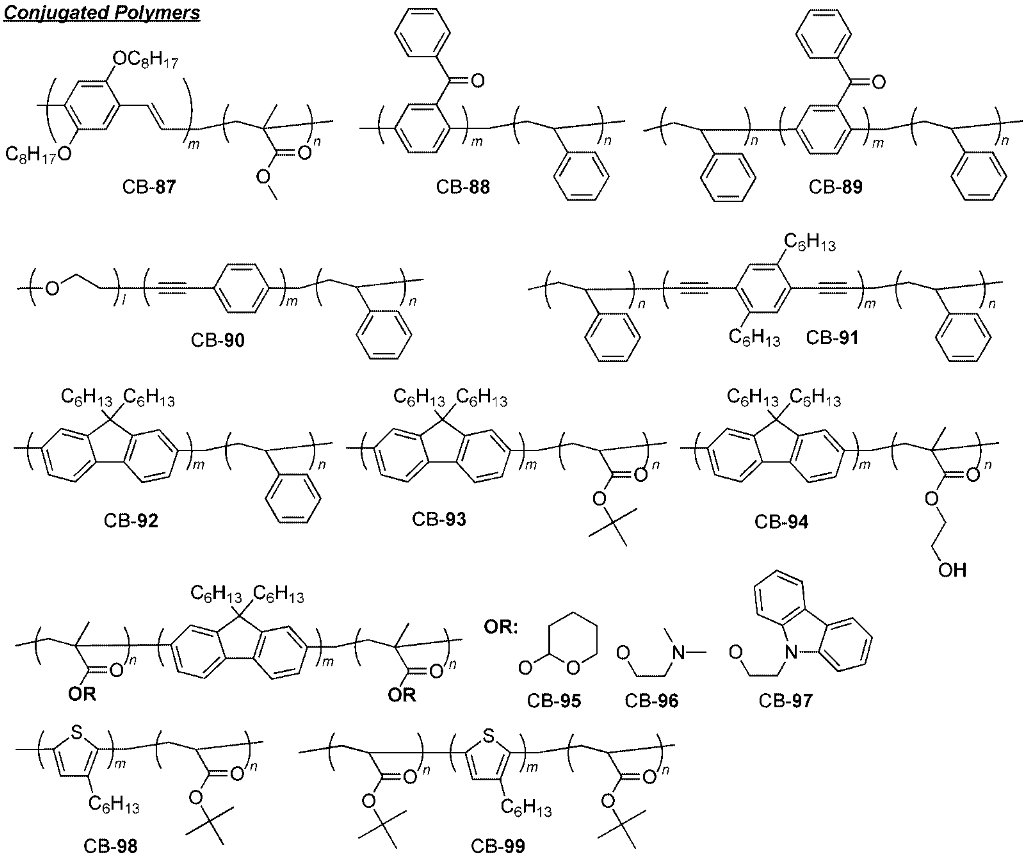


Figure 36. Block copolymers prepared from conjugated polymers.

attractive materials. As shown in Figure 36, several π-conjugated polymers are actually utilized as macroinitiators for copper-catalyzed living radical polymerization to yield the corresponding rod−coil block copolymers (CB-**87** to CB-**99**). The π-conjugated segements include poly(*p*-phenylene vinylene) (CB-**87**),[604] poly(2,5-benzophenone) (CB-**88**,**89**),[605] oligo(*p*-phenyleneethynylene) (CB-**90**,[606] CB-**91**[607]), polyfluorene (CB-**92**,**93**,[608] CB-**94**,[609] CB-**95**,[610] CB-**96**,[611] CB-**97**[289]), and polythiophene (CB-**98**,**99**[612]), prepared by coupling reactions with nickel, palladium, and iron catalysts. The morphologies[289,605] and luminescent properties[607−611] are also evaluated.

Silicon Hybrid Polymers. Inorganic silicon-containing block copolymers (CB-**100**,[613] CB-**101**,[614] CB-**102**,[615] CB-**103**,[614] CB-**104**,[616] CB-**105**,[617] CB-**106**,**107**,[618] CB-**108**,[619] and CB-**109**[620]) are obtained from silane- or siloxane-based macroinitiators in copper-, nickel-, ruthenium-catalyzed living radical polymerization of MMA, DMAEMA (FM-**4**), FM-**96**, *t*BA, styrene (Figure 37).

3.4.4. Polymer Reaction

Block copolymers are now synthesized by efficient coupling reactions of end-functionalized polymers obtained from metal-catalyzed living radical polymerization. The coupling reaction includes copper-catalyzed cycloaddition of an azide and an alkyne, Diels−Alder reaction, and disulfide coupling reaction (Scheme 8).

Alkyne/Azide Cycloaddition. Block copolymers are prepared with alkyne/azide cycloaddition via the following three methods (Scheme 8, part 1):[302,303] (A) postpolymer coupling reaction via cycloaddition of azide end-functionalized polymers and alkyne end-counterparts, (B) polymerization of 2 nd monomers with a macroinitiator obtained from cycloaddition of azide end-functionalized polymers and haloester-bearing alkyne compounds and alkyne end-functionalized counterparts, vice versa, and (C) one-pot tandem reaction of cycloaddition and polymerization.

As shown in Figure 38, method A efficiently provides block copolymers of PEG, MMA, and St (TB-**1** to **4**).[405] Namely, they are combined with alkyne end-functionalized prepolymers obtained from copper-catalyzed living radical polymerization with alkyne-bearing initiator (FI-**31**), and azide end-functionalized prepolymers obtained from sequential transformation of the ω-end halogen of living prepolymers with Me_3SiN_3 and tetrabutylammonium fluoride (TBAF), leading to narrow MWDs ($M_w/M_n = 1.1-1.2$) in high yields. The similar procedure is applied to various block copolymers [TB-**5**,**6**,[406] TB-**7**,[404] TB-**8**,[463] TB-**9**,[409] TB-**10**,**11**,[403] TB-**13**,[621] EC-**16**-capped poly(FM-**14**)[460]] including polyester via tin-catalyzed ring-opening cationic polymerization (ROCP) of ε-caprolactone (ε-CL),[409] polypeptide via nickel-catalyzed ring-opening polymerization (ROP) of γ-benzyl-L-glutamate *N*-carboxyanhydride (NCA),[403] and sequence-regulated oligopeptide.[460]

In contrast, TB-**12**[622] is efficiently synthesized by nickel-catalyzed ROP of L-valine NCA with a poly(*t*BA)-based macroinitiator obtained via halogen-terminal transformation (method B). More importantly, one-pot tandem synthesis (method C) of TB-**9** is also achieved to give narrow MWDs ($M_w/M_n \approx 1.3$), as well as method A and also method B.[409]

Diels−Alder Reaction, S−S Coupling. Diels−Alder reaction of maleimide end-functionalized polymers from FI-**55**, FI-**56**, and anthracene end-counterparts from FI-**21** successfully gives well-controlled block copolymers (TB-**14** to TB-**17**) ($M_w/M_n = 1.1-1.3$) (Figure 38).[393] A triblock copolymer (TB-**18**) is also synthesized by in situ

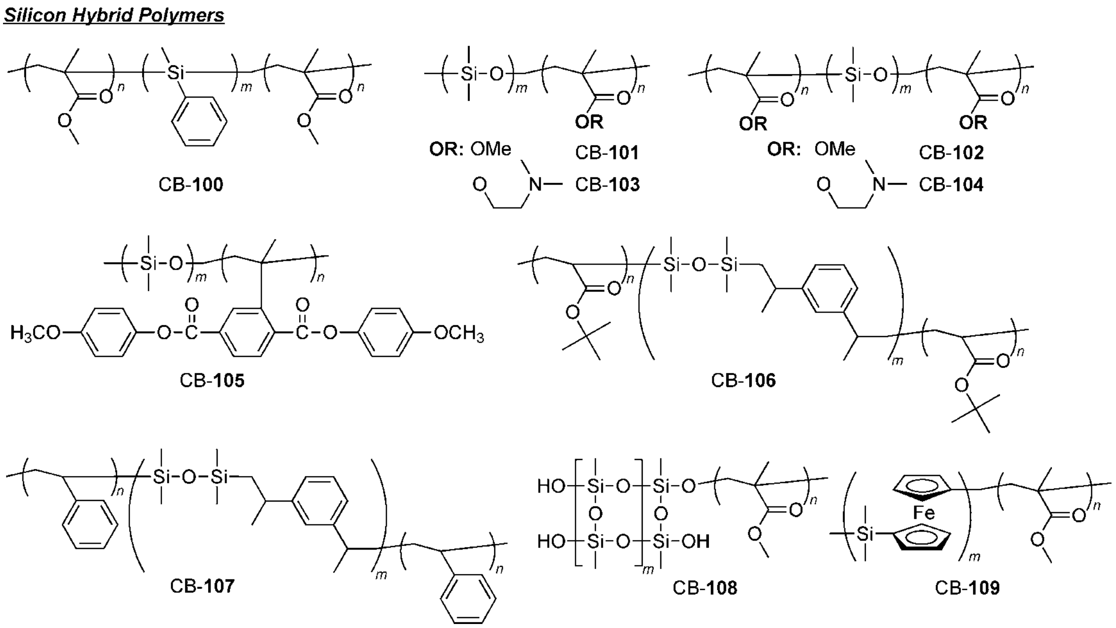
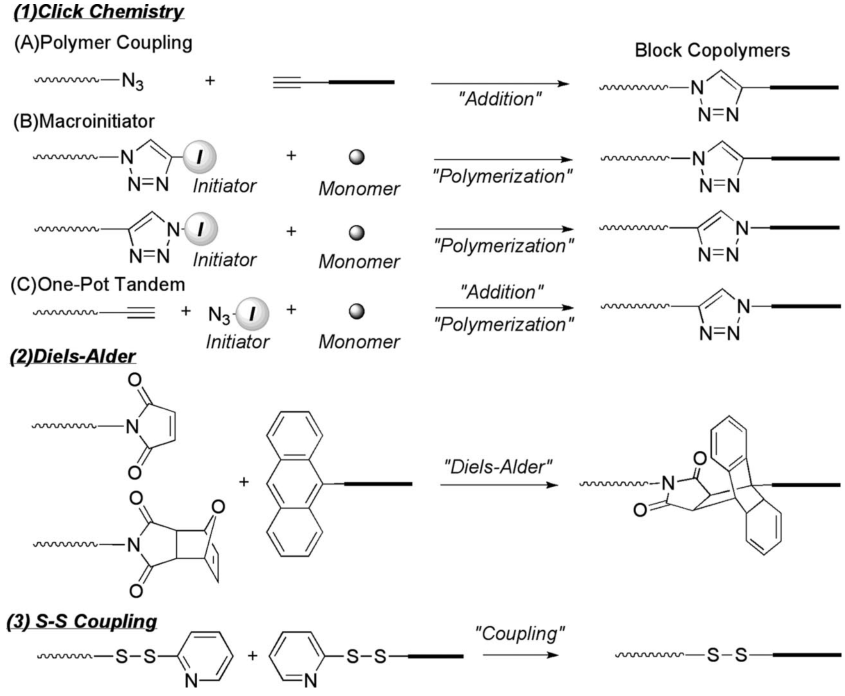


Figure 37. Block copolymers prepared from inorganic polymers.

Scheme 8. Block Copolymers Prepared from End-Functionalized Polymers



"click" cycloaddition and Diels–Alder reaction.[394] Additionally, reversible redox cleavage and coupling reaction with disulfide and thiol groups[623] are also effective for TB-**19** to TB-**22**.[434]

3.5. Random Copolymers

Thanks to neutral propagating species and a wide variety of applicable monomers, radical polymerization potentially, efficiently induces random/statistical copolymerization of over two kinds of monomers. Metal-catalyzed living radical polymerization also fortunately inherits this attractive feature, in fact, to produce random copolymers of methacrylates, acrylates, styrene, and so on, with controlled molecular weight and narrow MWDs. The key for the efficient random copolymerization is to select catalytic and initiating systems suitable for the respective monomers. Especially, this is quite important for different comonomer families because of the cross-propagation including the different monomer reactivity and the terminal radical and/or carbon–halogen bond reactivity.

Another advantage of radical copolymerization is that one monomer never performing radical homopolymerization, such as nonpolar olefins, for example, ethylene, 1-hexene, is also radically copolymerized with other monomers carrying a highly radical reactivity and generating a highly reactive radical like methyl acrylate (MA).[248] Importantly, metal-catalyzed system, because of the living nature, leads to a single copolymer sample with the uniform compositional distribution in each copolymer chain, in sharp contrast to

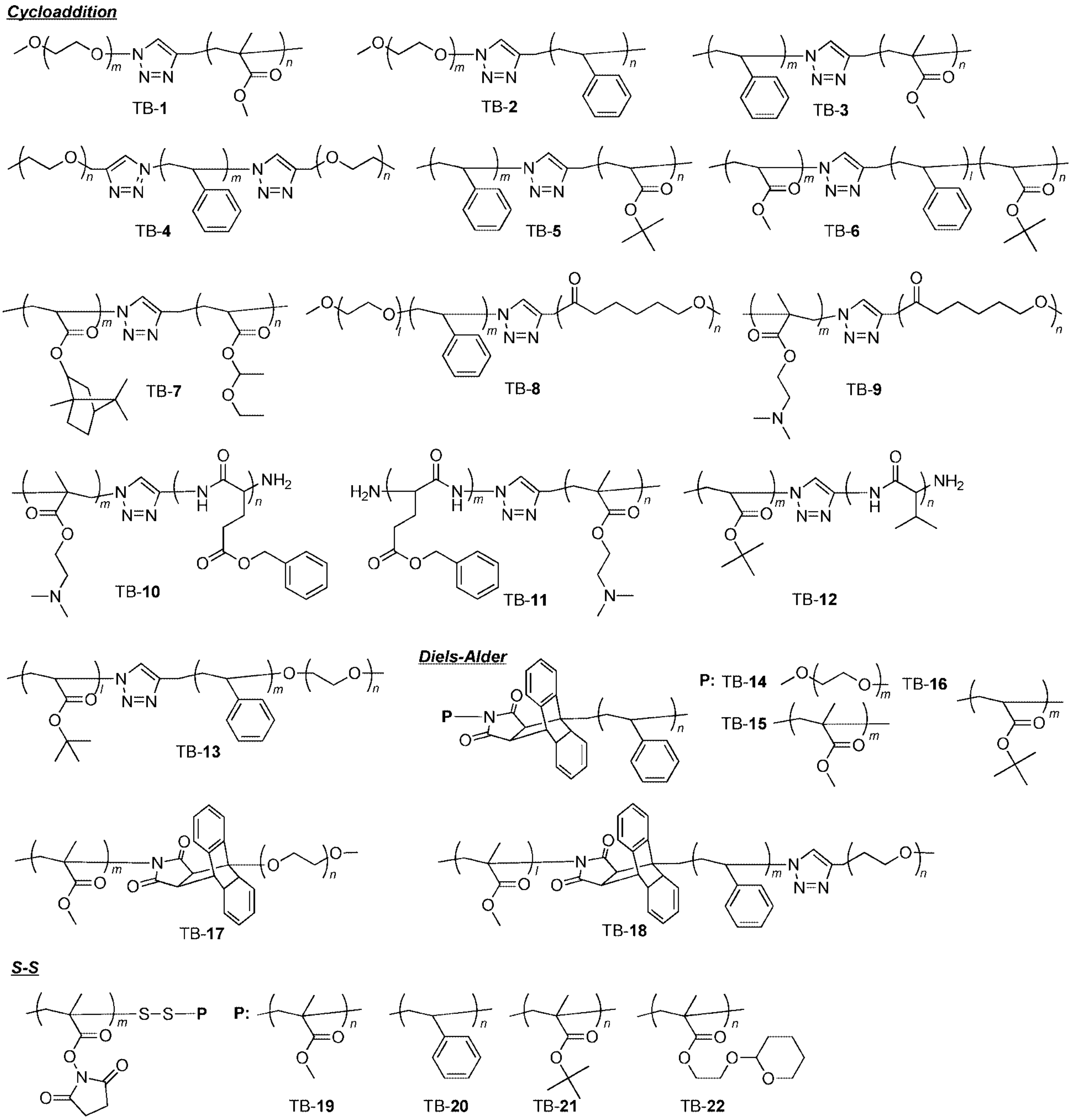


Figure 38. Block copolymers prepared via postpolymer reaction.

the conventional free-radical system affording copolymers with considerable composition distribution from chain to chain.

This section comprehensively deals with random copolymers prepared by metal-catalyzed living radical polymerization, including (functionalized) random copolymers, random block copolymers, and random copolymers of polar olefins and nonpolar olefins (Figures 39−42).

3.5.1. Conjugated Monomers

Non-Functionalized Random Copolymers. Random copolymers with nonpolar functional pendants (R-**1** to R-**10**) are efficiently synthesized by ruthenium-, copper-, and iron-catalyzed living radical polymerization (Figure 39). In methacrylate-based random copolymers (R-**1** to R-**5**), random copolymers of ethyl methacrylate (EMA)/benzyl methacrylate (BzMA) (R-**1**),[624] EMA/phenyl methacrylate (PhMA) (R-**2**)[475] are obtained with a copper catalyst (CuBr/bpy) and a bromide initiator, but the MWDs are relatively broad (M_w/M_n = 1.4−1.8). On the contrary, ruthenium-catalyzed system [Ru(Ind)Cl(PPh_3)$_2$ (Ru-**4**)/*n*-Bu_3N] with a chloride initiator smoothly copolymerize butyl methacrylate (BMA)/BzMA (R-**3**), BMA/2-ethylhexyl methacrylate (2EHMA) (R-**4**), and 2EHMA/BzMA (R-**5**), where the respective two comonomers are almost simultaneously consumed, to give their well-controlled random/statistical copolymers with narrow MWDs (M_w/M_n < 1.2).[3]

As already discussed, iron catalysts coupled with a iodide initiator are quite effective for acrylates, styrene, and vinyl acetate. Actually, iron-mediated system [FeCpI(CO)$_2$ (Fe-**2**)/metal alkoxide (cocatalyst)] gives well-controlled random copolymers of MA/BA (R-**6**),[92] BA/tBA (R-**7**),[94] MA/St (R-**8**),[92] and BA/St (R-**9**)[94] (M_w/M_n = 1.2−1.7), even in the case of cross propagation of acryrate and styrene. Thanks to the water tolerance of the iron catalysts, suspension polymeri-

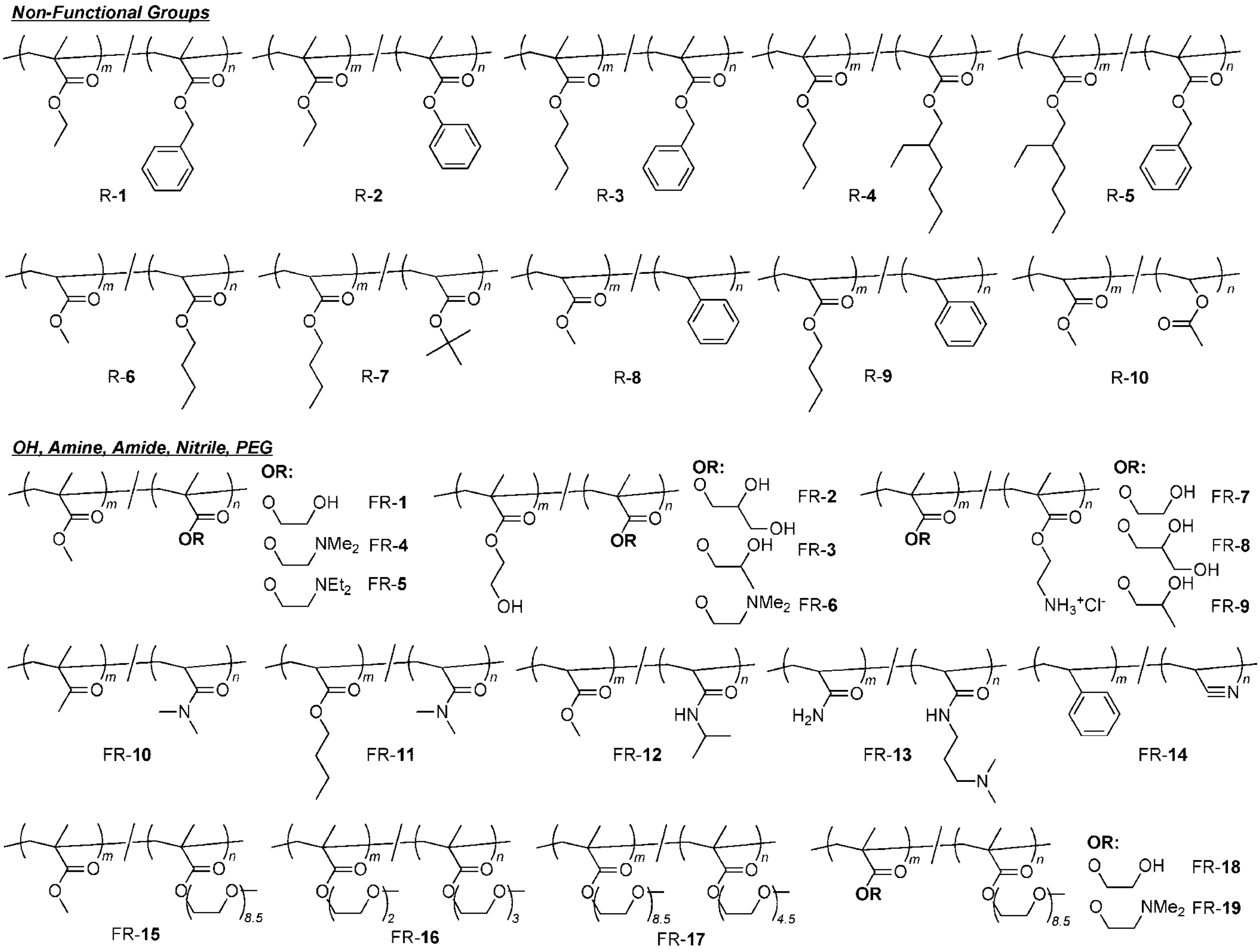


Figure 39. Random copolymers 1.

zation with water can be also applicable for the random copolymerization.[94]

Functionalized Random Copolymers. Thanks to functionality-tolerance of metal-catalyzed system, functionalization of random copolymers is simply achieved by direct copolymerization of functional monomers (FR-**1** to FR-**36**) without any bothersome protection and deprotection of the functional groups (Figure 39). Hydroxyl-functionalized random copolymers (FR-**1**,[32] FR-**2**,**3**[263]) can be obtained with ruthenium or copper catalysts. Typically, HEMA (FM-**1**) and MMA are smoothly copolymerized with a hydrophilic $RuCl_2[P(m\mathrm{NaSPh})Ph_2]_2$ (Ru-**2**) and a chloride initiator in methanol at 80 °C.[32] Here, HEMA was consumed slightly faster than MMA [conv. 90% (FM-**1**), 80% (MMA), 10 h], independent of feed ratio of HEMA and MMA (3/1, 1/1, 1/3, mol/mol), finally to lead to controlled FR-**1** ($M_w/M_n \approx 1.5$). Functionalization of random copolymers with amines (FR-**4**,**5**,[3,265] FR-**6**,[261,625] FR-**7**,**8**,**9**,[271]) are efficiently achieved with copper or ruthenium catalysts. Acrylamides are also randomly copolymerized with methacrylates, acrylates, and another acrylamide (FR-**10**,[265] FR-**11**,[490] FR-**12**,[2] FR-**13**[275]) by ruthenium, copper, and iron catalysts. Copolymerization of acryronitrile and styrene efficiently performed by a copper catalyst ($M_w/M_n < 1.2$).[626,627] Poly(ethylene glycol) groups are randomly introduced into the polymer pendant by ruthenium-, nickel-, and copper-catalyzed living radical copolymerization of PEGMA (FM-**14**)/MMA (FR-**15**),[3,265] two kinds of FM-**14** with a different PEG length (FR-**16**,[499] FR-**17**[282]), FM-**14**/HEMA (FM-**1**) (FR-**18**),[261,262] and FM-**14**/DMAEMA (FM-**4**) (FR-**19**).[261,266] The respective two monomers are simultaneously consumed in spite of the bulkiness of the relatively long side PEG chains to realize their random distribution along the main chain.

Reactive functional groups such as olefins (FR-**20**,[265] FR-**21**,[297] FR-**22**[265]), epoxide (FR-**23**, **24**),[3,265] furfuryl group (FR-**25**),[298] and oxazolone (FR-**26**)[297] can be randomly introduced into the side chains of linear polymers via ruthenium- and copper-catalyzed living radical copolymerization of allyl methacrylate (FM-**24**), vinyl methacrylate, FM-**25**, and FM-**23** (Figure 40). However, introduction of vinyl group pendant was more difficult than that of the other reactive functional groups because of the cross-linking reaction through the side chain olefins. *N*-methacryloxysuccinimide (FM-**35**) is also copolymerized with MMA, BMA, PEGMA (FM-**14**), and St in conjunction with a copper catalyst (FR-**27** to FR-**30**) ($M_w/M_n = 1.1-1.3$), respectively.[310] By the treatment of FR-**30** with a amine-bearing terpyridine compound, the succinimide in FM-**30** was converted into a terpyridine-carrying amide for the ligands of lanthanide ions, working as unique emissive materials.

Fluorinated segments is statistically incorporated into the side chains of linear polymers via copper-catalyzed polymerization of a pendant-fluorinated methacrylate and MMA (FR-**31**)[389,628] or St (FR-**32**)[389] (Figure 40). Additionally, copper-catalyzed system efficiently performs statistical copolymerization of bulky pendant-bearing monomers includ-

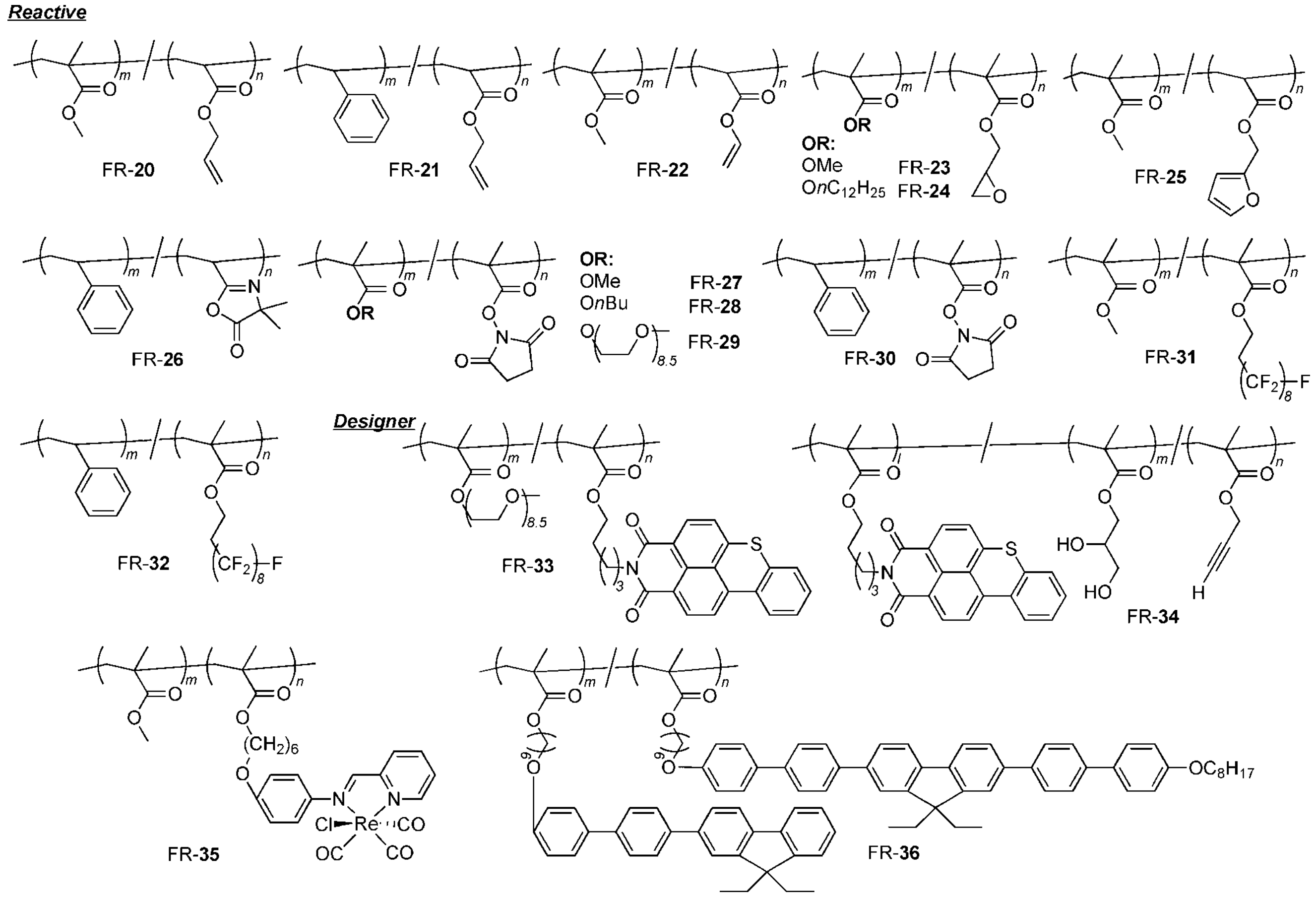


Figure 40. Random copolymers 2.

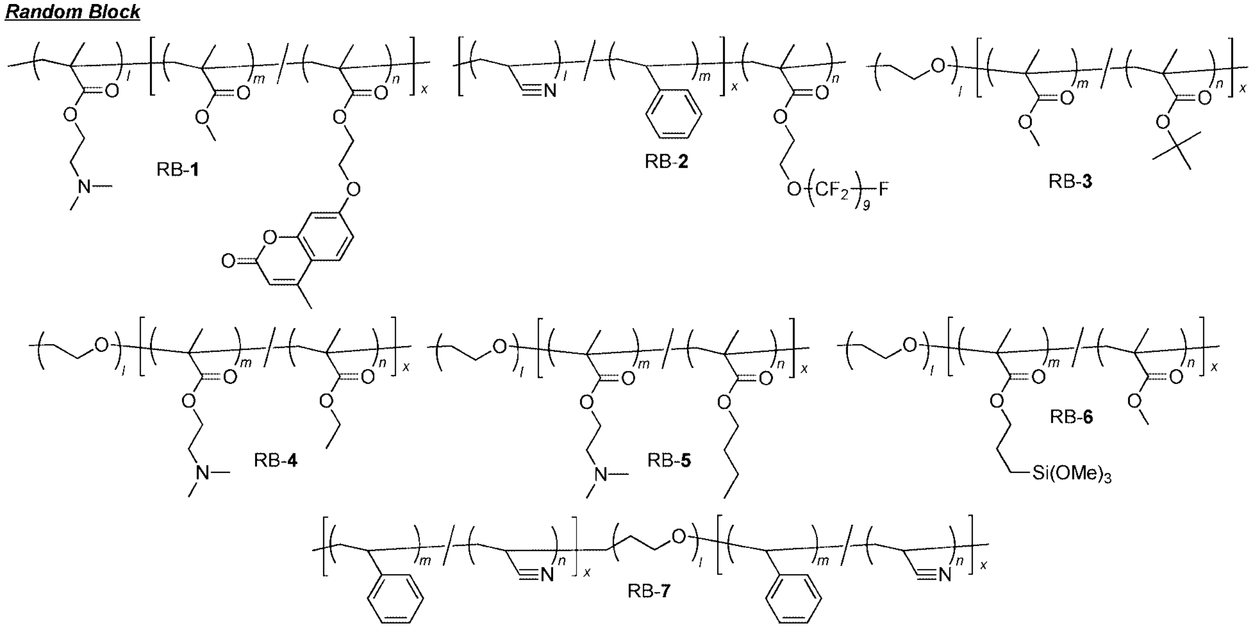


Figure 41. Random block copolymers.

ing a bulky hostasol moiety for FR-**33**,[427] FR-**34**,[428] a metal complex (FM-**75**) for FB-**35**,[349] and bulky/rigid biphenyl fluorine-bearing methacrylates (FM-**90**/FM-**99**) for FB-**36**.[374] The hostasol-tagged polymers (FR-**33**,[427] FR-**34**[428]) obtained with FI-**54** or FI-**55** are applied to bioconjugation to efficiently work as fluorescently labeled polymers.

Random Block Copolymers. Random block copolymers are also conveniently and directly prepared by metal-catalyzed system (Figure 41). Copper catalysts with bromide initiators including α-bromo ester-capped poly(ethylene glycol) macroinitiators are effective for random block copolymers (RB-**1**,[629] RB-**2**,[630] RB-**3**,**4**,[516] RB-**5**,[526] RB-**6**,[312] RB-**7**[631]). All the products exhibit unique self-assemble properties in the solution and solid state. Typically, RB-**1**, treated with HCl, efficiently formed a reverse micell in organic solvents, and the further photoinduced dimerization of the coumarin groups in the outer shell produced the shell cross-linked micelles.[629] Additionally, a ruthenium catalyst

[$Ru(Ind)Cl(PPh_3)_2$ (Ru-**4**)/n-Bu_3N] with a chloride initiator succeeds in selective and direct functionalization of the respective segments in ABA-triblock copolymers (B-**4**) with various functional monomers (FM-**1**, FM-**4**, FM-**5**, DMAA, FM-**24**), keeping high controllability and high blocking efficiency ($M_w/M_n < 1.2$; blocking efficiency: >97%).[3,265]

3.5.2. Non-Conjugated Monomers

Copolymerization of polar vinyl monomers and α-olefins is attractive for modification of the properties of their homopolymers. However, the synthesis seems to be rather difficult because the former is originally suitable for ionic or radical polymerization and the latter is, in turn, for coordination polymerization. Radical polymerization is generally quite useful for wide variety of polar monomers under mild conditions, while the system can never achieve the smooth polymerization of nonpolar olefins due to the low stability of the generating radicals without any stabilizing conjugation, except for under such an extreme condition as quite high temperature and pressure. Among them, metal-catalyzed living radical polymerization has been recently employed for copolymerization of α-olefins coupled with polar vinyl monomers,[248] as well as late transition metal-catalyzed coordination polymerization.[632,633] The living radical polymerization has fundamentally no bimolecular termination reaction, thus can afford valuable copolymers with uniform composition on the respective chains, in sharp contrast to the conventional free radical polymerization giving mixtures of copolymer chains with different compositions because of the termination reaction during the copolymerization.

Olefins Copolymers. Copolymerization of polar monomers and various nonpolar olefins are examined with copper, iron, ruthenium, and manganese catalysts in the presence of the suitable initiator (Figure 42). Methyl acrylate (MA) or MMA are copolymerized with the following olefins: primary olefins, such as ethylene (OR-**1**, OR-**12**),[3,265,634] propene (OR-**2**),[634] 1-butene (OR-**3**),[634] 1-hexene (OR-**4**, OR-**13**),[3,177,265,634,635] 1-octene (OR-**5**, OR-**7**, OR-**14**),[265,636−638] a secondary olefin of 2-methyl-1-pentene (OR-**6**, OR-**15**, OR-**16**);[3,265] cyclic olefins of norbornene derivatives (OR-**8** to OR-**10**),[639] and cyclopentene (OR-**11**).[3]

Typically, methyl acrylate (MA) and 1-hexene is efficiently copolymerized by CuBr/PMDETA with a bromide initiator at 90 °C,[634] $[FeCp(CO)_2]_2$ (Fe-**4**)/$Al(O$-$i$$Pr)_3$ with a iodide initiator at 60 °C,[3,265] and $Mn_2(CO)_{10}$ (Mn-**2**)/I_2 with a iodide initiator and visible light at 40 °C[177] to produce a controlled random copolymer OR-**4** ($M_n = 5000−25000$, $M_w/M_n = 1.3−2.0$). Introduction of 1-hexene is fully confirmed by ^1H NMR, ^{13}C NMR, ^{13}C DEPT NMR, MALDI-TOF MS, HPLC, and DSC analyses. Olefin contents are controlled from 5 to 25% by the feed ratio of MA and 1-hexene in bulk or toluene without any loss of the controllability independent of the catalytic system.[3,177,265,634] Uniquely, manganese (Mn-**2**)-mediated system coupled with fluoroalcohol solvents dramatically increased the olefin contents into the copolymers up to 50% in the high olefin feed ratio ([MA]/[1-hexene] = 400/3600 mM), in which the monomer sequence of the obtained products is predominantly alternating.[177] This is because the fluoroalcohols form hydrogen-bonding interaction with the carbonyl moieties of the acryl monomer (MA) units to efficiently enhance the reactivity of the MA-radical to the 1-hexene monomers. Copolymerization of other primary olefins and the contents are also successfully controlled with iron and copper catalysts (OR-**1**,**2**,**3**,**5**,**7**, $M_w/M_n = 1.4−1.8$; olefin content, 5.0−20 mol %).[3,265,634,636,637]

2-Methyl-1-pentene, a secondary olefin, is more efficiently copolymerized with MA via an iron catalyst ($[FeCp(CO)_2]_2$ (Fe-**4**)/$Al(O$$i$-$Pr)_3$) and a iodide initiator to lead to the controlled random copolymers (OR-**6**) with higher olefin contents than primary olefin copolymers in the similar conditions (olefin content, 5.0−34 mol %) because of the relatively high stability of the secondary radicals derived from 2-methyl-1-pentene.[3,265] Random block copolymerization of MA/2-methyl-1-pentene and BA/2-methyl-1-pentene (OR-**16**) is also successfully achieved by the direct addition of BA into OR-**6** at the final stage in the presence of remaining 2-methyl-1-pentene [conversion. 83% (MA), 25% (2-methyl-1-pentene)], suggesting that the first random copolymer (OR-**6**) owns high end-functionality of the terminal iodide. Furthermore, the addition of a Lewis Acid (BF_3OEt_2) into the iron-catalyzed system efficiently increases the 2-methyl-1-pentene contents in the random copolymers, as well as that for 1-hexene, probably because electron poor acrylic radicals carrying the carbonyl groups coordinated by BF_3OEt_2 effectively react onto electron rich nonpolar olefins. More importantly, the compositional distribution of the olefin is homogeneous through all the copolymer chains, in sharp contrast to that in the conventional free radical copolymerization of MA and 1-hexene with azobisisobutyronitrile (AIBN): the olefin contents decrease with increasing the molecular weight.

Cyclic olefins, such as norbornene derivatives and cyclopentene, was copolymerized with MA via copper- or iron-mediated system, while cyclohexene was, in turn, hardly done.[3] The contents of norbornene derivatives were higher than those of cyclopentene [olefin contents, 20−40 mol % (OR-**8** to OR-**10**);[639] ∼7.0 mol % (OR-**11**)[33]]. The strain of the cyclic olefins seems to be driving force for the efficient incorporation into the copolymers. The MWDs in OR-**8** to OR-**11** were slightly broad ($M_w/M_n = 1.4−1.8$).

MMA is effective as another polar monomer for copper-, ruthenium-, and iron-catalyzed living radical copolymerization of olefins (OR-**12** to OR-**15**).[3,638] A copper catalyst ($CuCl/CuCl_2$/PMDETA) with a chloride initiator actually induce copolymerization of MMA and 1-octene to give OR-**14** with narrow MWDs ($M_w/M_n = 1.1−1.3$),[638] in which the olefin contents are controlled from 2 to 26 mol % by the feed ratio of the two comonomers. An iron catalyst {$[FeCp(CO)_2]_2$ (Fe-**4**)/$Al(O$$i$-$Pr)_3$} with an iodide initiator and a ruthenium catalyst {$Ru(Ind)Cl(PPh_3)_2$ (Ru-**4**)/$Al(O$$i$-$Pr)_3$} with a chloride initiator is also effective for MMA and 1-hexene (OR-**13**).[3] The olefin content in the iron-based system is controlled from 7 to 16 mol % via the monomer feed ratio, which is smaller than those with MA and 1-hexene, because of the lower activity of the radicals generated from the methacrylate (MMA) toward 1-hexene than that from the acrylate (MA). Additionally, ethylene and 2-methyl-1-pentene are also successfully copolymerized with MMA via the iron catalyst [olefin contents, 14 mol % (OR-**12**), 7 mol % (OR-**15**)].

Functionalized Olefin Copolymers. Functionalization of olefin-containing random copolymers is achieved with functionalized polar monomers or functionalized nonpolar olefins in copper- or iron-catalyzed living radical copolymerization (Figure 42), including the functionalized nonpolar olefins, DMAA (OR-**20**,**21**),[3] PEGA (FM-**16**) (OR-**22**, OR-**29**),[3] acrylonitrile (AN) (OR-**28**),[640] the functionalized nonpolar

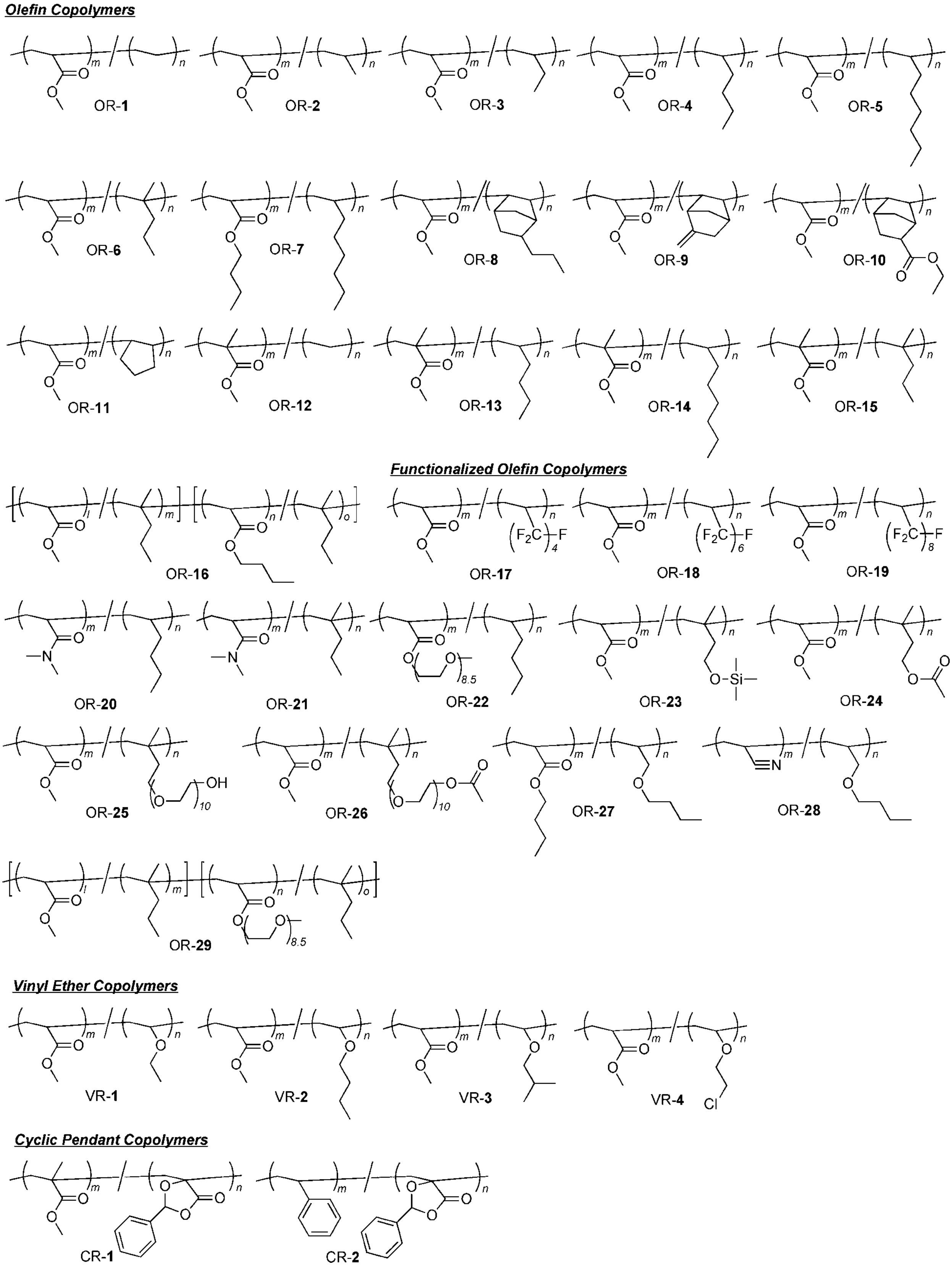


Figure 42. Random copolymers of nonpolar/nonconjugated monomers and cyclic monomers.

olefins fluorine (OR-**17** to OR-**19**),[641] trimethyl- or acetyl-protected groups (OR-**23**,**24**),[3] hydroxy- or acetyl-capped poly(ethylene glycol) (OR-**25**,**26**),[3] and ether (OR-**27**,**28**).[640,642]

Three kinds of fluoroalkenes are copolymerized with MA via CuBr/PMDETA with a bromide initiator to give narrow MWDs and appropriate olefin contents (OR-**17** to OR-**19**, M_w/M_n = 1.2−1.3, olefin contents = 5.0−12 mol %).[641] Under the same reaction condition, fluorinated olefins performed faster polymerization and gave higher olefin contents than nonfluorinated counterparts. The iron system {$[FeCp(CO)_2]_2$ (Fe-**4**)/Al(O*i*-Pr)$_3$} with an iodide initiator is widely employed for functionalized olefin copolymers (OR-

20 to OR-**26**, OR-**29**). Olefin contents with DMAA were smaller than those with PEGA (OR-**20**,**21**, $M_w/M_n \approx 1.7$, olefin contents ≈ 6 mol %; OR-**22**, $M_w/M_n \approx 1.6$, olefin contents 11−14 mol %). Functionalized secondary olefins are also efficiently introduced into the corresponding copolymers (OR-**23** to OR-**26**, $M_w/M_n = 1.3-2.2$, olefin contents 21−30 mol %), as well as nonfunctionalized 2-methyl-1-pentene.[3] Additionally, a random block copolymer (OR-**29**) is successfully obtained from direct addition of PEGA (FM-**16**) into the OR-**6** solution with a remaining 2-methyl-1-pentene. Allyl butyl ether are also copolymerized with BA or AN in the presence of copper catalysts (OR-**27**,**28**, $M_w/M_n \approx 1.3$).[640,642]

Vinyl Ethers. Vinyl ethers (VE)s are typically employed as monomers for cationic polymerization and hardly polymerized in radical process because of the no substituent to stabilize the generating radical. However, various vinyl ethers, such as ethyl vinyl ether, *n*-butyl vinyl ether, *i*-butyl vinyl ether, and chloroethyl vinyl ether, can be copolymerized with MA in the ruthenium-mediated living radical polymerization with RuCp*Cl(PPh_3)$_2$ (Ru-**5**)/*n*-Bu_3N and a bromide initiator (VR-**1** to VR-**4**, Figure 42).[3] The key to achieve efficient radical copolymerization is essentially to suppress cationic polymerization of VEs and decomposition of a halogen-capped VE terminal because the Lewis acidic metal catalysts employed would potentially induce cationic cleavage or β-hydrogen elimination of the halogen-capped VE terminals carrying an electron-rich substituent. Thus, the ruthenium-catalyzed system is more suitable than the more acidic iron counterpart with a iodide initiator. In terms of the leaving halogen of the initiator, bromine seems to be more suitable than chloride or iodide because of the activity for the radical generation and suppression of the β-hydrogen elimination. Typically, the copolymers of MA and ethyl vinyl ether own the following results ($M_n = 15\,000$, $M_w/M_n \approx 1.4$, VE content ≈ 5 mol %).

3.5.3. Cyclic Monomers

A cyclic monomer, 5-metylene-2-phenyl-1,3-dioxolan-4-one, is efficiently copolymerized with MMA or St in copper-mediated system with a bromide initiator to produce CR-**1** and CR-**2** with relatively narrow MWDs ($M_w/M_n = 1.1-1.5$) (Figure 42),[643] where the cyclic acrylate selectively introduced via 1,2-vinyl addition. The contents are controlled from 5 to 58 mol % by the feed ratio of the cyclic acrylate to MMA or St. On the contrary, copper-mediated copolymerization of other cyclic monomer, 5,6-benzo-2-methylene-1,3-dioxepane, and MMA proceeds by ring-opening radical mechanism of the cyclic monomer, leading to various monomer sequence products.[644]

3.6. Alternating Copolymers

Alternating copolymers are often obtained from the monomers that can be never or less polymerized alone but can be copolymerized in the presence of the other suitable monomers. Typically, *N*-substituted maleimides are employed for alternating copolymerization with styrene, resulting in narrow MWDs ($M_w/M_n = 1.1-1.3$). The substituted groups include phenyl, cyclohexyle, and fluorobutyl groups.[645,646] Furthermore, sequential multistep addition of a small amount of different *N*-substituted maleimides into copper-catalyzed copolymerization of styrene gives unique tetra block copolymers that carry four different blocks consisting of a N-substituted maleimide/styrene alternating part and the following homopolystyrene part.[647] As already described, an alternating copolymer of MA and 1-hexene is also obtained with a manganese complex, an iodide initiator and a fluoroalcohol solvent in the large excess feed ratio of 1-hexene to MA.[177]

3.7. Gradient Copolymers

Gradient copolymers are another class of copolymers with controlled monomer composition and sequence distribution,[249] in which the monomer A in the two monomers (A, B) is preferentially near the initiating terminal (α-end) and the monomer B is, in turn, mainly near the halogen terminal (ω-end) and the monomer sequence is gradually changing along the main chain. Thus, unique and attractive physical properties would be expected in comparison to those of random, alternating, and block copolymers. So far, gradient copolymers are synthesized by metal-catalyzed living radical polymerization coupled with the following two strategies (Figure 43). One method is according to the spontaneous formation of gradient composition because of the differences of the original monomer reactivity, and the other is according to the continuous change of the monomer composition via sequential second monomer addition into the polymerization solution at the controlled rate.

3.7.1. Monomer Reactivity

To achieve spontaneous gradient formation along main chain, two monomers with different reactivity should be used, where methacrylates/acrylates (G-**1** to G-**6**)[288,648−652] are typical monomer combinations, in addition to vinyl acetate/methyl acrylate (G-**7**)[177,653] and hydroxyl methacrylate (HEMA: FM-**1**)/*tert*-butyl-dimethyl- silil-capped HEMA (G-**8**).[654] G-**1** is obtained from copper-catalyzed living radical copolymerization of *n*BMA and *n*BA in bulk or miniemulsion,[648] in which the gradient composition varies from *n*BMA rich to *n*BA rich along with the α-end to ω-end. The gradient slope can be further controlled by feed ratio of the two monomers. Other gradient copolymers of methacrylates and acrylates (G-**2**,**3**,[649] G-**4**,[650] G-**5**,[288] G-**6**,[651,652]) are also prepared by copper-catalyzed system.

Gradient block copolymers of VAc and MA (G-**7**) are obtained from a manganese complex [$Mn_2(CO)_{10}$] with an iodide initiator in the presence of visible light in bulk or fluoroalcohols.[653] Herein, MA was preferentially consumed in comparison to VAc at the initial stage, followed by homopolymerization of VAc from the gradient copolymer segment after the complete consumption of MA, to finally give gradient block copolymers with a gradient segment from MA to VAc and homopoly(VAc) segment (M_w/M_n = 1.5−2.3). After saponification of the VAc units in G-**7** uniquely gave the corresponding poly(MA-co-g-lactone)-block-poly(vinyl alcohol) because of the intermolecular cyclization between the hydroxyl groups and the neighboring carboxyl groups of MA in the gradient segment.

Hydroxyl methacrylate (HEMA, FM-**1**) and *tert*-butyl-dimethyl-silil-capped HEMA (SiHEMA) is copolymerized with RuCp*Cl(PPh_3)$_2$ (Ru-**5**) and a chloride initiator in the presence of fluoroalcohol solvent. Interestingly, this leads to well-controlled dual gradient copolymers (G-**8**) with composition gradient from HEMA to SiHEMA and tacticity gradient from atactic units to syndiotactic ones ($M_w/M_n \approx$ 1.3).[654]

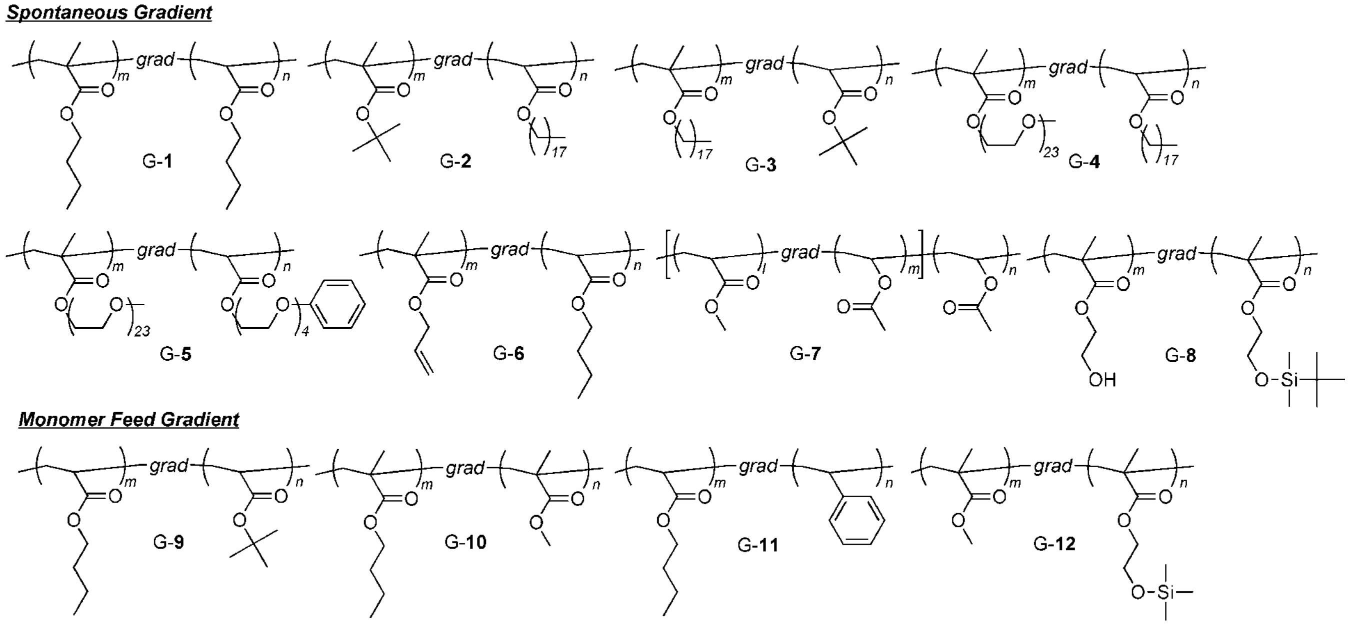


Figure 43. Gradient copolymers.

3.7.2. Monomer Addition

Radical copolymerization of the same family monomers, for example, methacrylate each other, usually provides random copolymers because of the similar reactivity, except for some special cases such as G-**8**. Thus, gradient copolymers composed of the same family monomers with similar reactivity are obtained from monomer addition, naturally applicable to those of the different families (G-**9** to G-**12**). AGET miniemulsion system with a copper catalyst, ascorbic acid, and a bromide initiator is effective for G-**9** to G-**11** with narrow MWDs ($M_w/M_n \approx 1.2$).[655] G-**12**, synthesized with a copper catalyst, is employed as a macroinitiator for graft copolymers in metal-catalyzed living radical polymerization after the transformation of the silyl groups.[656]

3.8. Star Polymers

Star polymers,[250,251,657,658] typical branched polymers prepared by living polymerization, have a globular three-dimensional structure consisting of multiple linear polymers (arms) radiating from the central moiety (core) with a certain statistical distribution of the molecular weight. In detail, the structural density gradually decreases from core to surface area along with the arms, in contrast to that of dendrimers[659] with completely uniform structure and the inverse density change from the core to the surface. Importantly, star polymers are more easily synthesized than dendrimers that are obtained from difficult, bothersome multistep synthesis and purification, in addition to the unique physical properties different from linear ones.

Needless to say, metal-catalyzed living radical polymerization is applicable to star polymers.[250,251] The synthesis via living polymerization is fundamentally followed by the three strategies: (1) "initiator method" living polymerization of monomers (arms) from a multifunctional initiator (core), (2) "quencher method" coupling reaction of living linear polymers (arms) with a multifunctional quencher (core), and (3) "linking method" cross-linking reaction of living linear polymers (arms) with a bifunctional linking agent (core). Though methods 1 and 3 were usually employed in metal-catalyzed system before 2001 because of little examples of efficient multifunctional coupling agents, method 2, coupled with efficient coupling reactions, has been sometimes reported since 2001. Thanks to recent advance of catalytic system, functional groups are now selectively introduced into the desired site in star polymers. Additionally, combination with other precision polymerizations or macromolecules has been also utilized as novel synthetic pathway of star block copolymers and hetero(mikto)arm star polymers. Herein, this section comprehensively presents star polymers obtained from metal-catalyzed living radical polymerization since 2001 (Figures 44−51).

3.8.1. Multifunctional Initiators

Metal-Catalyzed Living Radical Polymerization. Various multifunctional initiators carrying more than two reactive carbon−halogen bonds (MI-**1** to MI-**36**) are designed for star polymers with method 1, where the arm number is precisely defined by the number of the initiating site. The multifunctional initiators successfully produce various star polymers with precise arm numbers: 3 (MI-**1** to MI-**7**), 4 (MI-**8** to MI-**15**) (Figure 44), 5 (MI-**16** to MI-**19**), 6 (MI-**20** to MI-**25**) (Figure 45), 8 (MI-**26** to MI-**32**), 10 (MI-**33**), 12 (MI-**34**), 18 (MI-**35**), 21 (MI-**36**), 24 (MI-**37**), and 64 arms (MI-**38**) (Figure 46).

3 Arms. Haloester-type trifunctinal initiators (MI-**1** to MI-**7**) are prepared with the corresponding triols and acyl halides (Figure 44). MI-**1** is examined in various copper-based living radical polymerization, including, so-called, "normal ATRP", "SR&NI ATRP", and "AGET ATRP". The normal ATRP of *n*BA and St with MI-**1** gives well-controlled 3-armed star poly(*n*BA) and poly(St) with narrow MWDs (M_w/M_n = 1.1−1.2),[660] which are further utilized as macroinitiators for 3-armed star block copolymers [poly(*n*BA)-b-poly(St),[660] poly(St)-b-poly(*n*BA),[660] poly(*n*BA)-b-poly(AN)[661]]. 3-Armed star polymers with MI-**1**-cores are also effectively obtained from the copper(II) systems: "SR&NI ATRP" of St or MA with MI-**1** and AIBN;[662] "AGET ATRP" of MA with MI-**1** and a reducing agent.[663] Importantly, the blocking efficiency of styrene from the 3-armed star poly(MA) via the AGET system (~100%) is superior to that via SR&NI system

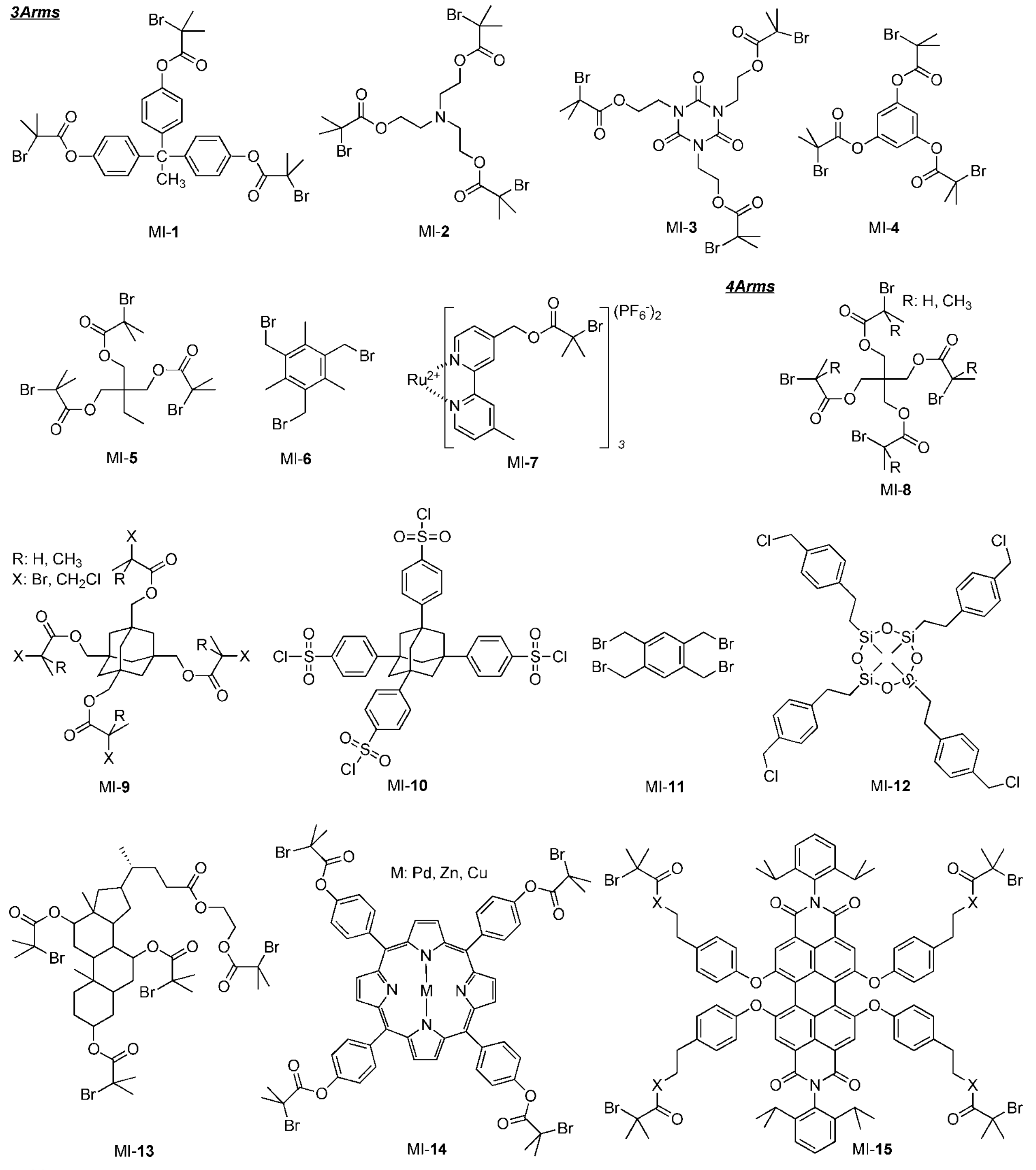


Figure 44. Multifunctional initiators 1.

(~90%), because the AGET system never induces homopolymerization of second block monomer (St) and SR&NI slightly produce the homopolymerization because of AIBN.

A triethanol amine-based initiator, MI-**2**, is successfully employed for alcoholic copper-catalyzed living radical polymerization of phosphorylcholine-bearing monomer (FM-**40**), sequentially followed by addition of amine or poly(propylene oxide)-bearing monomers (FM-**4**, FM-**5**, FM-**15**) without any isolation of the star macroinitiator, to efficiently give the corresponding star block copolymers.[664] These star polymers demonstrated thermoresponsive gelation in aqueous solution. MI-**2** is also effective for HEMA (FM-**1**) arms and FM-**1**/NIPAM (FM-**12**) block arms.[665]

Other haloester initiators (MI-**3**,[666−668] MI-**4**,[669−671] MI-**5**,[672] MI-**7**[673]) and a benzyl bromide-type initiator (MI-**6**)[365] are also utilized for star polymers, some of which perform unique functions. Typically, MI-**3**-star poly(St)s are employed as macroinitiators for ring-opening polymerization of α-amino acid-*N*-carboxyanhydride (NCA), giving a St/NCA block star polymer,[667] and as precursors for palladium surface-bearing star polymer catalysts in ethylene oligomerization.[668] Copper-catalyzed polymerization of FM-**84** with MI-**4** interestingly led to optically active photochromic star polymers.[669]

4 Arms. Tetrafunctional haloester (MI-**8**, MI-**9**, MI-**13** to MI-**15**), sulfonyl chloride (MI-**10**), and, halomethyl benzene (MI-**11**, MI-**12**)-based initiators are employed for the synthesis of 4-armed star polymers in copper-catalyzed living radical polymerization (Figure 44). Typical tetra-functionalized initiator, MI-**8**, prepared by pentaerythritol, is ap-

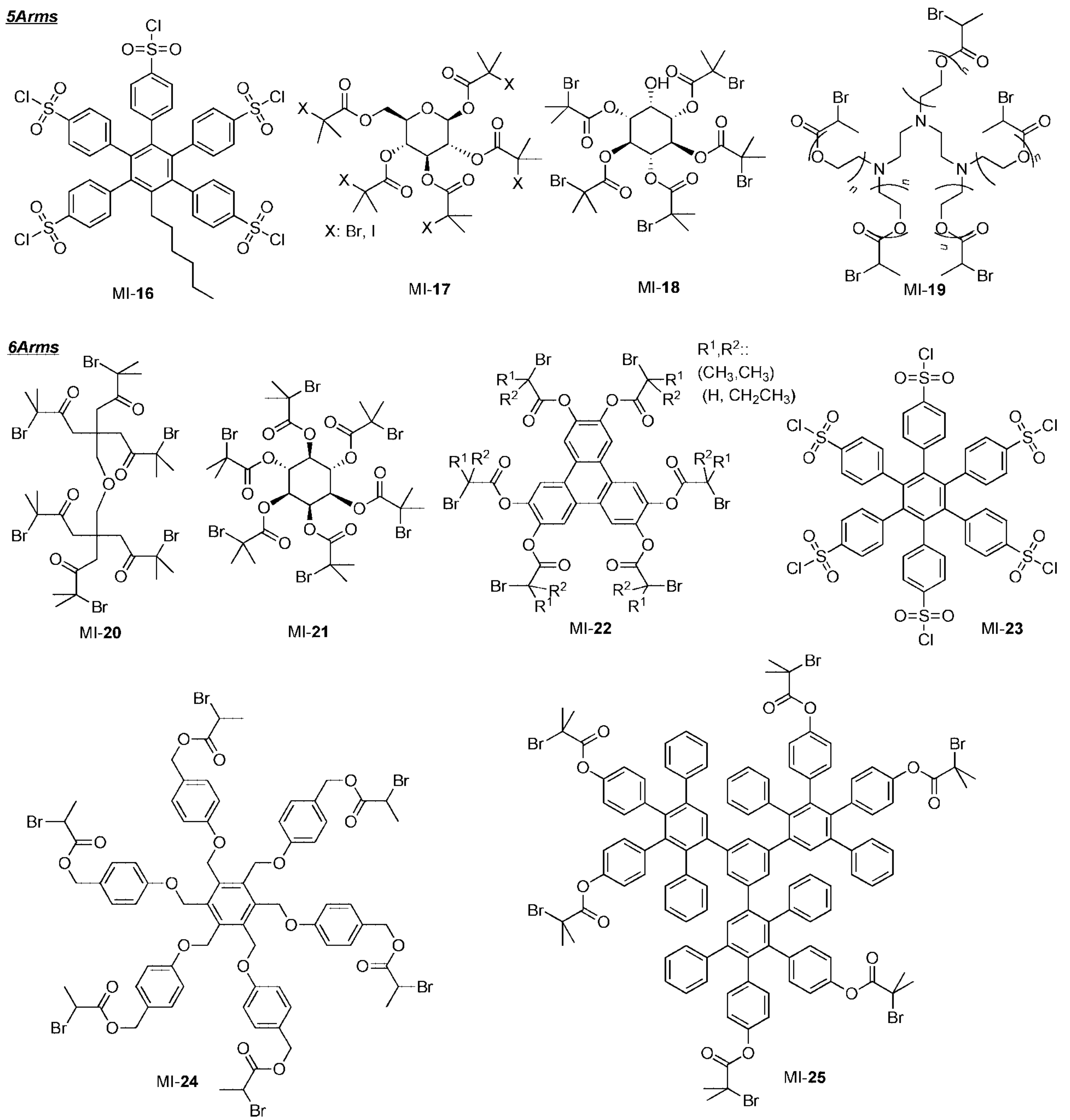


Figure 45. Multifunctional initiators 2.

plicable to AN,[672] FM-**16** ($n = 1$),[674] FM-**20**,[675] and FM-**81**.[676] Star polymers of FM-**20** are hydrolyzed into glycerol-bearing counterparts, whose micelles can efficiently extract hydrophilic dye from water into dichloromethane.[675] Adamantane-based initiators (MI-**9**,[677] MI-**10**[678]), tetra(bromomethyl)benzene (MI-**11**),[679] and a four chloromethylbenzene-bearing siloxane (MI-**12**)[680] are also effective for MMA, *t*BA, St. Cholic acid (MI-**13**),[681] porphyrin (MI-**14**),[682] and perylene (MI-**15**)[683] moieties are also successfully introduced into the cores of 4-armed star polymers.

5 Arms. Pentafunctional sulfonyl chloride (MI-**16**)[678] and haloester (MI-**17**, MI-**18**, MI-**19**)[671,675,684−688] are applied to five-armed star polymers in copper- or iron-catalyzed system (Figure 45). Though MI-**16** with a copper catalyst is used for MMA, *t*BMA, MA, and St, the initiator seems to be suitable for the methacrylates, leading to narrow MWDs ($M_w/M_n \approx 1.2$). MI-**17**[671,675,685,686] and MI-**18**[687] are efficiently obtained from simple esterification of α-D-glucose and meso-inositol with acyl halides, respectively. Typically, the iodide-based MI-**17** is effective for iron [FeCpI(CO)$_2$ (Fe-**4**)/Ti(O*i*-Pr)$_4$]-catalyzed polymerization of St.[685,686] Poly(ethylene oxide) (PEO)-pentafunctional macroinitiator (MI-**19**)[688] directly gives block armed well-controlled star block copolymers of PEO and poly(*t*BA) ($M_w/M_n \approx 1.3$). After the poly(*t*BA) segments are hydrolyzed into poly(acrylic acid), the resultant double hydrophilic star polymers encapsulate and release a hydrophilic dye in dichloromethane water by changing the pH.[688]

6 Arms. Haloester or sulfonyl chloride-based hexafunctional initiators (MI-**20** to MI-**25**)[672,675,678,689−693] with copper catalysts induced polymerization of various monomers to give 6-armed star polymers (Figure 45). The central core parts include ester, sugar, and multiple phenyl groups. For example, MI-**20**[672,689] and MI-**21**[675] are efficiently obtained from esterification of dipentaerythritol and myoinositol with acyl halides, respectively.

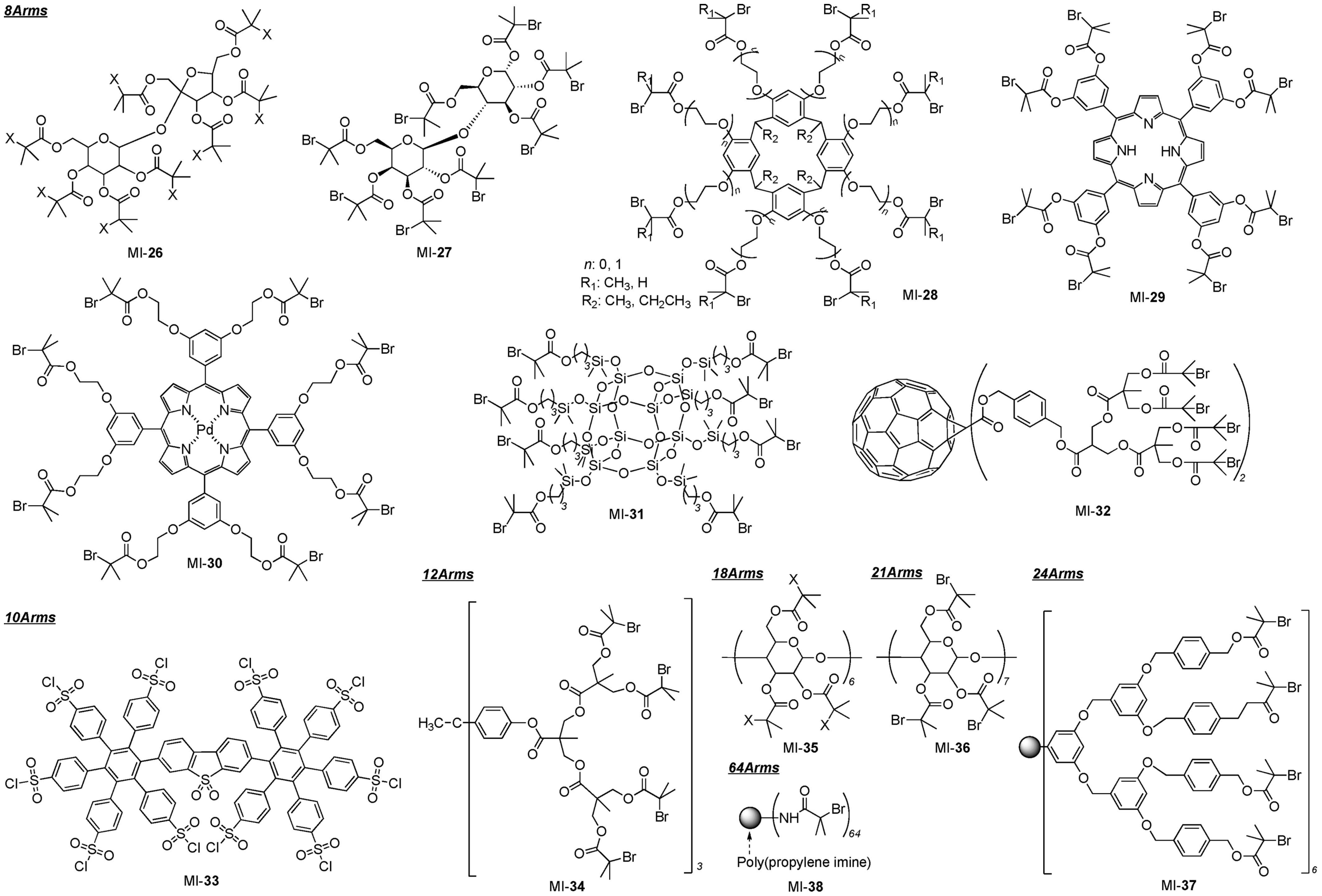


Figure 46. Multifunctional initiators 3.

8 Arms. Various octafunctional initiators (MI-**26** to MI-**32**) are designed for 8-armed star polymers in living radical polymerization (Figure 46). MI-**26**[685] and MI-**27**[671] are obtained from the esterification of sucrose and lactose with the corresponding acyl bromide, where iodide type-MI-**26** is further followed by halogen exchange reaction of a bromide MI-**26** with NaI. The iodide type-MI-**26** with $FeCpI(CO)_2$ (Fe-**2**)/Ti(O*i*-Pr)$_4$ typically gives well-controlled star poly(St) with the 8 arm numbers though monomer conversion is low (Conv. <25%).[685] Resorcinarene-based initiators (MI-**28**) with or without an ethylene oxide (EO) spacer between the resorcinarene core and the initiating group ($n = 0$[694] or 1[695]) are examined in copper-catalyzed living radical polymerization of MMA and *t*BA for 8-armed star polymers. The EO spacer-bearing MI-**28** efficiently initiated to give 8-armed star polymers, while no EO spacer-MI-**28** led to 4-armed star polymers due to the steric hindrance around the initiating site. Additionally, porphyrin (MI-**29**),[696] palladium-porphyrin (MI-**30**),[697] silsesquioxane (MI-**31**),[698,699] and C60 (MI-**32**)[700] are also successfully introduced into the core of 8-armed star polymers. Interestingly, shell cross-linked star polymers were prepared by copper-catalyzed living radical copolymerization of St and 4-butenylstyrene with MI-**29**, followed by cross-linking reaction of the pendant olefins with a ruthenium-based metathesis catalyst. Finally, the porphyrin core was removed from the shell cross-linked star polymers to give shell cross-linked star polymers with an empty-core.[696] Additionally, palladium-bearing 8-arm star polymers, obtained from MI-**30**, work as photooxidation catalysts.[697]

Multiarms. Multiarmed star polymers with precise arm numbers (10, 12, 18, 21, 24, 64) can be synthesized with multifunctional initiators (MI-**33** to MI-**38**)[678,685,693,701−708] in copper- or iron-mediated living radical polymerization (Figure 46). All multifunctional initiators, even dendrimers (MI-**34**,[701,702] MI-**37**,[707] MI-**38**[708]) and α- or β-cyclodextrin (MI-**35**,[685] MI-**36**[703−706]), showed high controllability and efficient initiation. Additionally, hyperbranched polymers with multiple bromide groups, obtained from copper-catalyzed living radical copolymerization of a maleimide-bearing bromoester initiator and excess styrene were subsequently and directly employed as a multifunctional initiator for multi poly(styrene)-armed star polymers.[709]

System Combination for Heteroarm Star Polymers. Hetero(Mikto)arm star polymers,[710] which have at least two kinds of different arm chains, can be prepared with hetero-multifunctional initiators via combination of metal-catalyzed living radical polymerization and other kind of polymerization or polymers, such as ring-opening cationic polymerization (ROCP) and nitroxide-mediated radical polymerization (NMP), ring-opening anionic polymerization (ROAP), commercially available polymers, and dendrons (Figure 47).

ROCP and ROAP. Heteromultifunctional initiators carrying ROCP initiating groups such as hydroxyl, acetal, acyl chloride groups in addition to haloester groups (CMI-**1** to CMI-**10**)[711−720] are designed for combination of ROCP and metal-catalyzed living radical polymerization (Figure 47). The initiators efficiently provide heteroarm star polymers with the following ROCP monomers: CMI-**1** to CMI-**7** for ε-caprolactone (εCL),[711−717] CMI-**8**,[718] CMI-**9**[719] for THF, and CMI-**10**[720] for 1,3-dioxepene.

Heteroarm star polymers carrying poly(εCL) arm chains (CMI-**1**,[711,712] **2**,[713] **3**,[712] **4**,[714,715] **5**,[716] **6**,**7**[717]) are prepared by copper-catalyzed polymerization and Lewis Acid [Sn(Oct)$_2$][711−717]

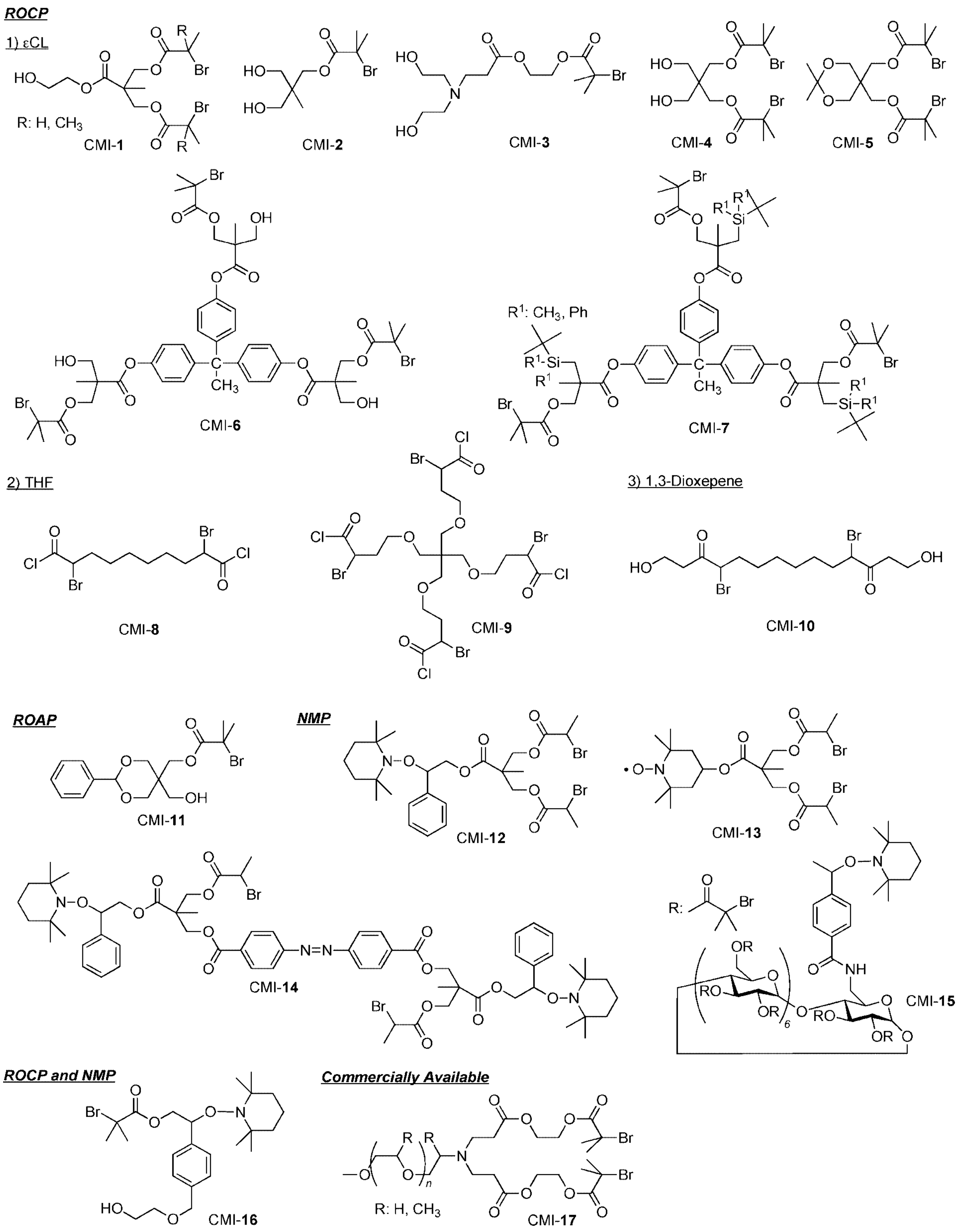


Figure 47. Hetero-multifunctional initiators.

or Al(Et)$_2$[713]]-catalyzed ROCP (M_w/M_n = 1.1−1.4). Selection of suitable copper catalysts and ligands affords the introduction of various monomers including methacrylates, acrylates, and styrene, into the radical segment. The respective arm numbers for metal-catalyzed system and ROCP are precisely controlled with the number of hydroxyl groups and halogens in the initiators, respectively. Importantly, the controllability is independent of the polymerization order because of high tolerance of the metal-catalyzed system against hydroxyl or acetal groups in the initiators. On the contrary, poly(THF)-heteroarm star polymers are first synthesized by ROCP of THF with AgClO$_4$ and CMI-**8**[718] or CMI-**9**[719] and subsequently done by copper-catalyzed living radical polymerization of St, to prevent a side reaction between acyl chloride moieties in the initiators and copper-based catalysts.

Additionally, ROAP of ethylene oxide (EO) with CMI-**11**[721] is also applied to 4-heteroarm star polymers with 3 poly(EO) segments and 1 poly(St) counterparts.

NMP and Others. NMP is quite useful for introduction of poly(styrene) segments into heteroarm star polymers with poly[(meth)acrylate]s in metal-catalyzed living radical polymerization. For this, heteromultifunctional initiators containing 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO) and haloester groups (CMI-**12** to CMI-**16**)[722−726] are designed (Figure 47), where CMI-**12**,[722] **14**,[724] **15**,[725] **16**[726] include styrene-capped TEMPO and CMI-**13**[723] does, in turn, a naked nitroxide radical. The former demonstrates high controllability independent of the polymerization order because the initiating groups are stable in the respective polymerization. However, the latter (CMI-**13**) must first undergo NMP, followed by copper-catalyzed living radical polymerization,[723] to prevent bimolecular terminations between naked radicals in the CMI-**13** and growing radicals derived from metal-catalyzed system.

According to these methodologies, CMI-**12** and CMI-**13** actually provide well-controlled heteroarm star polymers with a single polystyrene arm and two poly[(meth)acrylate] ones ($M_w/M_n = 1.1-1.3$). CMI-**14**[724] efficiently gave four heteroarm star polymers with an azobenzene core, performing trans−cis isomerization slower than the original CMI-**14**. β-cyclodextrin-based CMI-**15**[725] with one TEMPO moiety and 20 haloester were also effective for heteroarm star polymers with one linear poly(styrene) and 20 linear poly-[(meth)acrylate]s. Additionally, a trifunctional initiator with a haloester, TEMPO, and a hydroxyl group (CBI-**16**)[726] is designed for a 3-heteroarm star polymer. The star polymer was actually synthesized by the following: (1) ROCP of εCL at r.t.; 2) copper-catalyzed living radical polymerization of MMA at 75 °C, followed by terminal hydrogenation with Bu_3SnH; 3) NMP of styrene at 120 °C, leading to narrow MWDs ($M_w/M_n \approx 1.3$).

CMI-**17**[727] carrying one commercially available poly(ethylene oxide) or poly(propylene oxide) chain and two haloesters is employed for CuBr/bpy-catalyzed living radical polymerization of various functional monomers (FM-**1**, FM-**2**, FM-**4**, FM-**5**, FM-**7**, FM-**40**) in MeOH at 20 °C, to give well-controlled heteroarm star polymers ($M_w/M_n = 1.1-1.3$). The products exhibited unique thermoresponsible micellization. Furthermore, a polyester dendritic segment was also coupled with a linear poly(MMA) or poly(BzMA) for heteroarm star polymers in metal-catalyzed living radical polymerization.[728]

System Combination for Star Block Copolymers. Star block copolymers are obtained from combination of metal-catalyzed living radical polymerization and other polymerization such as various ring-opening polymerization (ROP)s or macromolecules like a dendrimer and a hyperbranched polymers.

ROP, Commercially Available Polymers. Ring-opening cationic polymerization (ROCP) of ε-caprolactone (εCL),[729,730] L-lactide (LLA),[731,732] and THF[733] is often combined with metal-catalyzed system for star block copolymers. Star polymers with poly(εCL) or poly(LLA)-based block arms are synthesized by the following three steps: (1) ROCP with a multi-hydroxyl-functional initiator to give hydroxyl-terminal (surface) star polymers, (2) synthesis of multi-haloester-bearing star polymer initiators via the esterification of the terminal hydroxyl groups with acyl halides, and (3) metal-catalyzed living radical polymerization with the initiator.[729−732] This pathway efficiently provides star polymers with 3-poly(εCL)-*b*-poly(FM-**96**) arms,[729] those with 6-poly(εCL or LLA)-*b*-poly(MMA or *t*BA) arms and an iron tris(bipyridine) core,[730] those with 6-poly(LLA)-*b*-poly(St-ran-FM-**36**) arms and a triphenylene core,[731] and dendrimer-like triblock (St-*b*-LLA-*b*-St) star copolymers.[732]

On the contrary, star polymers with 3-block arms [poly-(THF)-*b*-poly(*t*BA)][733] is, in turn, obtained from the following steps: (1) ROCP of THF with a bifunctional initiator carrying a haloester and a hydroxyl group (FI-**1**, $n = 2$), (2) the coupling reaction with a multifunctional quencher for a tribromo-functional star poly(THF) macroinitiator, and (3) thr copper-catalyzed living radical polymerization of *t*BA to give the final star block copolymers. Additionally, ring-opening anionic polymerization (ROAP) of ethylene oxide,[734] ROP of γ-benzyl-L-glutamate *N*-carboxyanhydride (NCA),[735] and commercially available Pentaerythritol ethoxylate[736] are also applicable to block arms.

Dendrimer, Dendrimer-like Core. Dendrimers and dendrimer-like spherically radiating polymers are employed as a central (core) segment of star block copolymers with precise, plenty of arm numbers.[737] Typically, polyaryl ether dendrimers with 24 hydroxyl groups around the surface are used as an initiator for $Sn(Oct)_2$-catalyzed ROCP of LLA to give well-controlled 24 hydroxyl surface-functionalized star block poly(LLA)s. The resulting star polymers are quantitatively converted into 24-bromoester poly(LLA)-star macroinitiators, which efficiently initiate copper-catalyzed living radical polymerization of St or MMA, finally giving triple layer star copolymers with polyaryl ether (core), poly(LLA) (middle), and poly(St) or poly(MMA) (outer) ($M_w/M_n < 1.1$).[738,739]

Dendrimer-like star block copolymers are also efficiently obtained from metal-catalyzed living radical polymerization (outer layer) with dendrimer-like radiating macroinitiators (central core) via ROCP[740,741] or living anionic polymerization.[279,742] Figure 48 shows one example of well-defined dendrimer-like star block copolymers of St and FM-**14** with quite narrow MWDs ($M_w/M_n < 1.05$),[279] which are prepared by combination of living anionic and radical polymerization. Interestingly, the star polymers perform high ion conductivity with high mechanical strength as solid polymer electrolytes, in comparison to the corresponding block copolymers.[278,279]

Hyperbranched Core. Hyperbranched polymers are utilized as multifunctional macroinitiators in copper-catalyzed living radical polymerization, leading to various star block copolymers with a statistical distribution of arm numbers.[743−748] Hyperbranched segments are composed of the followings: multiple hydroxyl groups-bearing poly(ester) via oxyanionic vinyl polymerization of HEMA (FM-**1**) [average numbers of OH groups (N_{OH}) = 18],[743] condensation reaction (N_{OH} = 24),[744] commercial source (N_{OH} = 32),[745] multiple hydroxyl groups-bearing polyether via ring-opening anionic copolymerization of ethylene oxide (EO) and acetal-bearing EO (N_{OH} = 16, 44, 114),[746] and ring-opening anionic polymerization of 3-ethyl-3-(hydroxymethyl)oxetane (N_{OH} = 37, 25).[747,748] These hydroxyl groups are efficiently transformed into haloester initiating groups via esterification (Scheme 3).

3.8.2. Cross-Linked Microgel Cores

As well as living ionic polymerization, metal-catalyzed living radical polymerization conveniently affords microgel-core star polymers[250,251] via linking reaction of linear arm polymers with divinyl compounds or polymerization of vinyl monomers from living microgel cores. The star polymers have microgel cores with cross-linked structure in nano-order

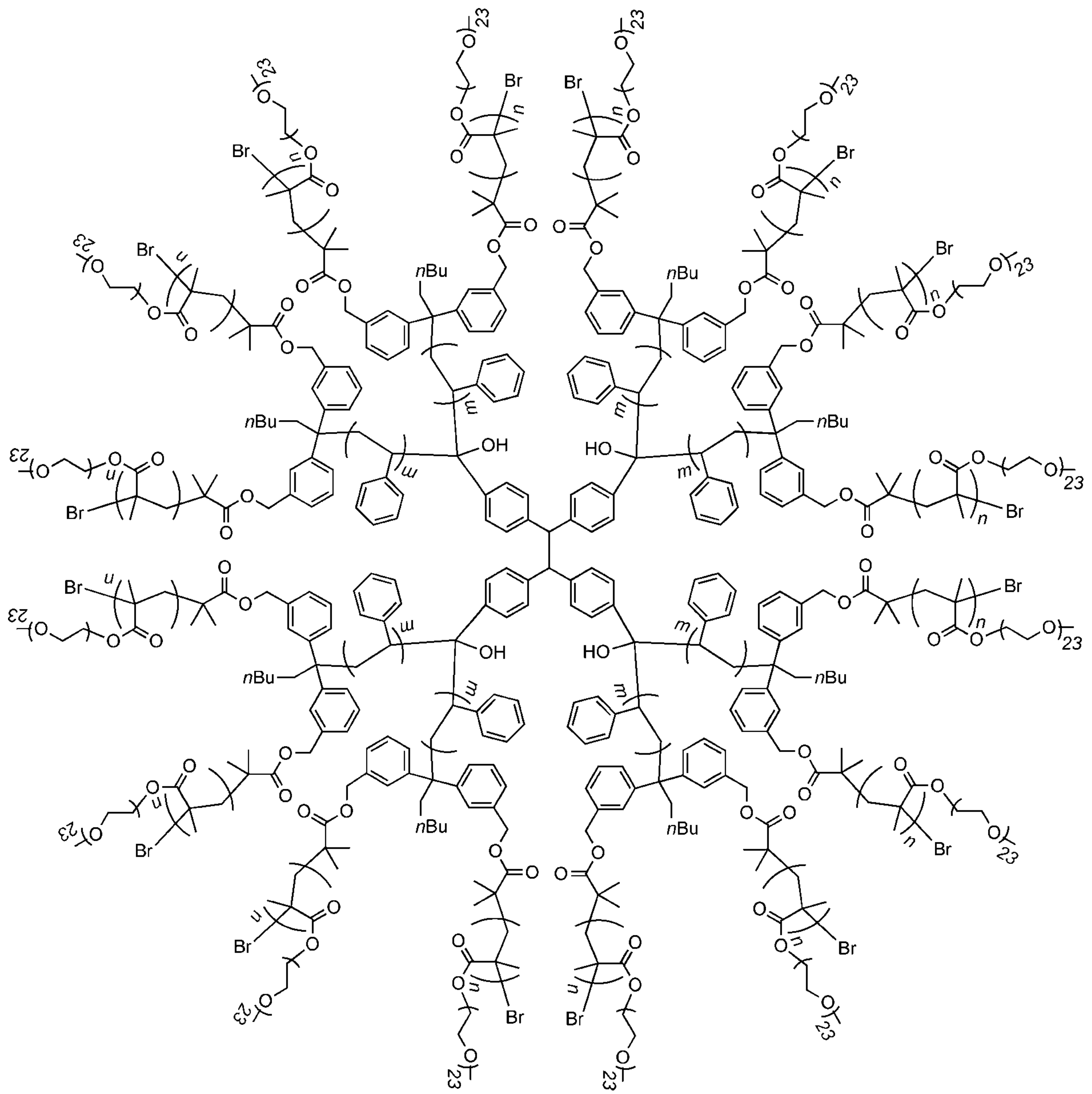


Figure 48. Dendrimer-like star block copolymers.

size and lots of linear arms radiating from the core, where the core is therefore separated from outer environment with the arms.

System Design. Microgel-core star polymers are prepared by the following three methods: (A) linking reaction of living linear arms with a divinyl compound,[749−751] (B) linking reaction of olefin end-functionalized polymers (macromonomers) with an initiator and a divinyl compound,[752] and (C) polymerization of a vinyl monomer with living microgel cores obtained from an initiator and a divinyl compound[753,754] (Scheme 9). Method A is the most popular pathway for microgel-core star polymers to give relatively narrow MWDs and high yield ($M_w/M_n < 1.5$, yield >90%) via the optimization of linking agents and reaction conditions such as concentration of linear arm polymers and the molar ratio of a divinyl compound to the linear polymers. This method is coupled with either in situ linking reaction of living prepolymers via sequential addition of a linking agent into the prepolymer solution or linking reaction of isolated prepolymers with a linking agent. The latter is especially useful for heteroarm star polymers as described later.

Scheme 9. Syntheses of Microgel-Core Star Polymers

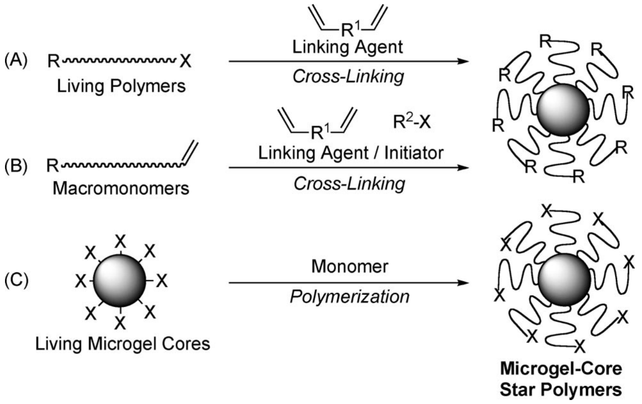


Figure 49 and 50 shows the arm polymers (A-**1** to A-**12**, MA-**1** to MA-**11**), linking agents (L-**1** to L-**15**), and functional comonomers (FC-**1**, **2**), employed for the synthesis of microgel-core star polymers in metal-catalyzed living radical polymerization. System design and reaction condition of method (A) are systematically discussed in the sequential

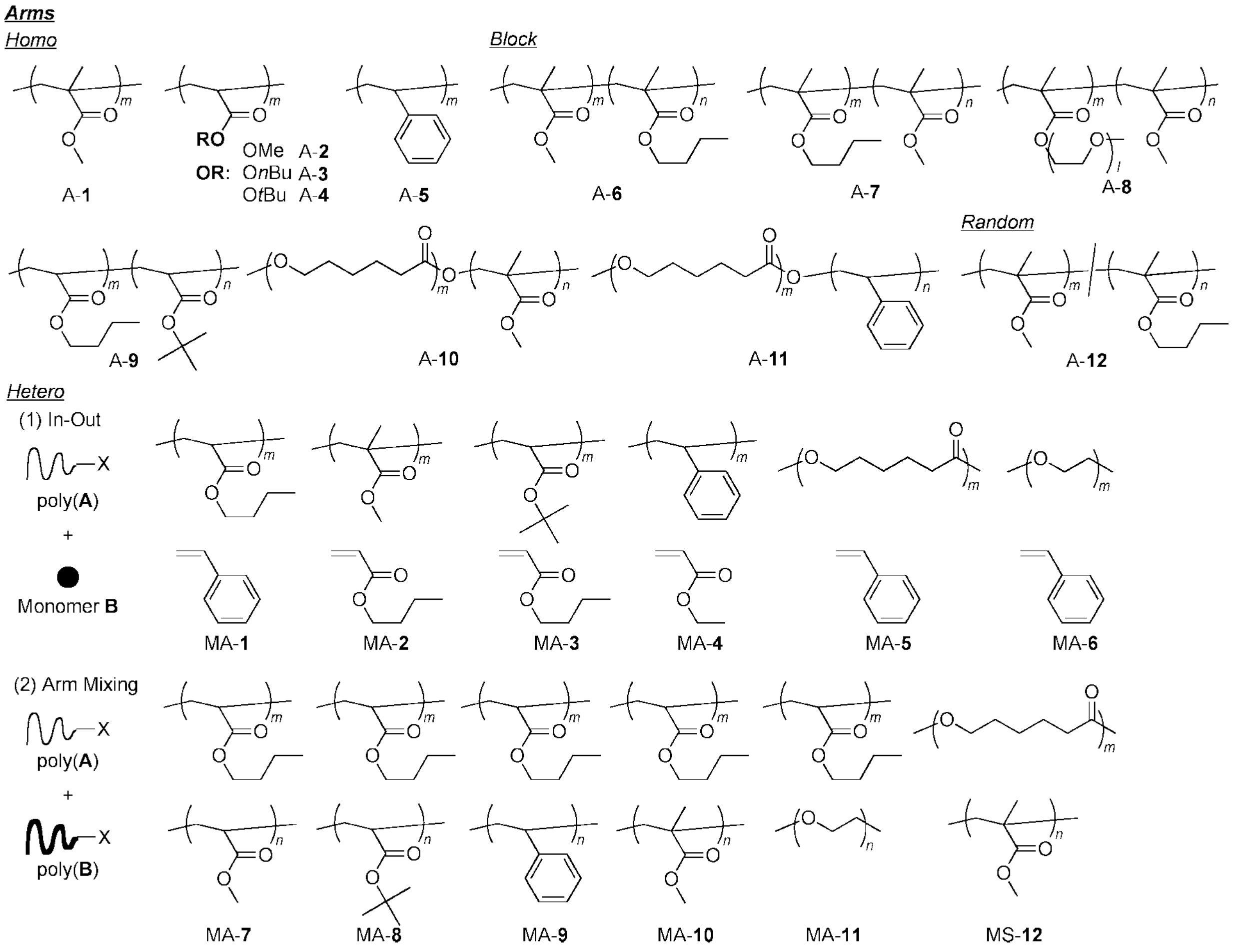


Figure 49. Arm polymers for microgel-core star polymers.

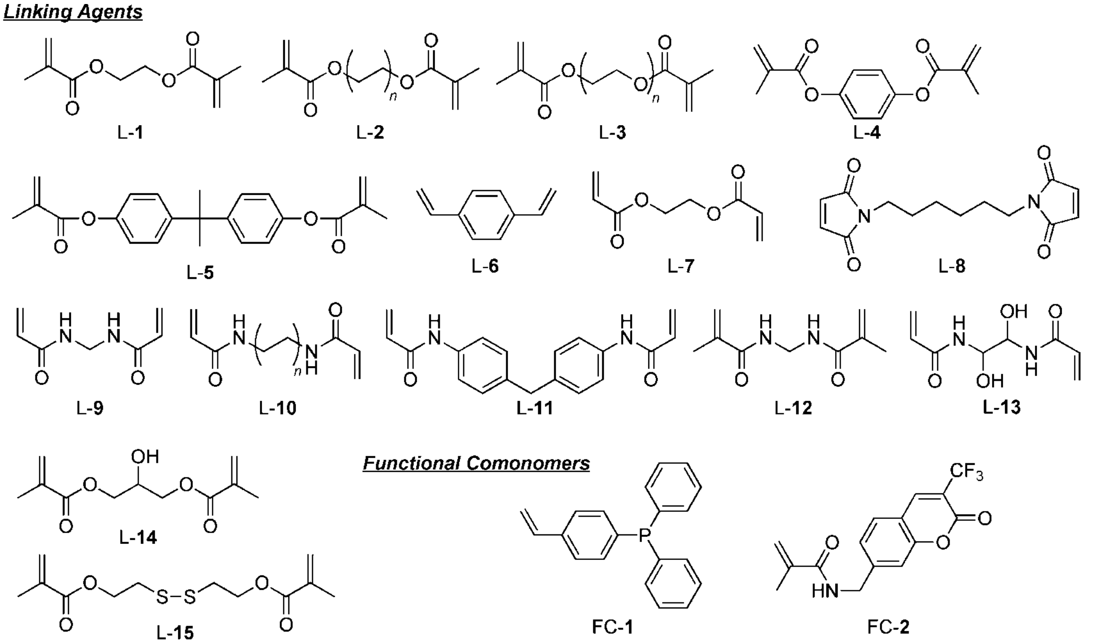


Figure 50. Linking agents and comonomers for microgel-core star polymers.

addition of dimethacrylates linking agents (L-**1** to L-**5**) into ruthenium [$RuCl_2(PPh_3)_3$(Ru-**1**)/Al(O*i*-Pr)$_3$]-catalyzed living radical polymerization of MMA with a chloride initiator.[749,750] L-**1**, L-**2** ($n = 2, 3$: aliphatic spacer) and L-**5** (bisphenol spacer) is effective for the linking reaction of PMMA arms (A-**1**), while L-**3** ($n = 3$: trioxyethylene spacer) and L-**4** (hydroquinone spacer) is in turn ineffective.[749] Here, L-**3** ($n = 3$) would probably form intramolecular cyclization because of the stable structure that the two olefins are close to each other via the trioxyethylene spacer. Thus, the design of linking agents is important for efficient preparation of microgel-core star polymers.

The star polymer yield, arm numbers (f), absolute weight average molecular weight (M_w), and gyration radius (R_g) are controlled by the feed ratio of a linking agent to linear arm polymers (P) (r = [divinyl compound]/[P]), concentration of arm polymers ([P]), degree of polymerization (DP = [monomer]/[initiator]), and species of divinyl compounds.[750] Especially, the feed ratio of a linking agent to arms (r) is quite important for the efficient star formation. For example, the linking reaction of a living poly(MMA)Cl ([P: arms] = 20 mM; $DP = 100$; $M_n = 10\,000$; $M_w/M_n = 1.31$; MMA conversion ∼90%) with a linking agent (L-**5**) in 10 of r led to higher star yield (90%) than that with L-**5** in 5 of r (star yield: 74%). Absolute weight average molecular weight (M_w) and gyration radius (R_g) of star polymers are evaluated by multiangle laser light scattering coupled with SEC (SEC-MALLS). Dependent on the parameters of DP, r, a star poly(MMA) with a L-**5** core has the following molecular weight (M_w), arm numbers (f), and gyration radius (R_g) [$M_w = 141\,000-1\,477\,000$; $f = 6-63$; R_g (nm) $= 8.0-22$], keeping over 80% star yield.

Poly(tBA) (A-**4**)-armed star polymers are obtained in high yield (∼90%) from copper (CuBr/PMDETA)-catalyzed living radical polymerization of tBA with a bromide initiator, sequentially treated with divinylbenzene (L-**6**) in 80% tBA conversion (r = [L-**6**]/[poly(tBA)] = 10).[751] However, the MWDs ($M_w/M_n \approx 2.0$) were fairly broader than those from linking reaction of isolated poly(tBA)s with L-**6** ($M_w/M_n \approx 1.3$), indicating that the linking reaction of isolated polymers would be more suitable for the copper system than in situ counterparts.

Method B also efficiently produces well-defined star polymers ($M_w/M_n < 1.2$, yield > 90%),[752] while the MWDs seem to be narrower than those of method A. Though method A inevitably provides the same numbers of arm chains and the terminal halogens in the core, the method (B) can identically control the number of arms and core-bound halogens. Thus, decrease of core-bound halogen (radical) concentration efficiently contributes suppression of star−star coupling to lead to narrow MWDs of star polymers.[752] Acrylate end-functionalized poly(nBA)s [A-**3**: $M_n = 5{,}300$; $M_w/M_n = 1.05$; commercially available from Kaneka (Japan)] and divinybenzene are copolymerized with (L-**6**) in the presence of a bromide initiator (EA-Br) and CuBr/Me$_6$TREN catalyst in the following feed ratio ([A-**3**]/[EA-Br]/[L-**6**] = 1/0.2/3: $r = 3$), to lead to star polymers with quite narrow MWDs and appropriate yields ($M_w/M_n = 1.15$, 77%). The yields increased up to over 98% by using multistep addition of an initiator (EA-Br) and a linking agent (L-**6**) with keeping narrow MWDs ($M_w/M_n < 1.2$). Additionally, the copper system coupled with long poly(ethylene oxide) (PEO)-carrying macromonomer (FM-**14**, $n = 23$), a linking agent (L-**1**), and a bromide initiator, efficiently leads to PEO-arms star polymers with narrow MWDs in high yield ($M_w/M_n \approx 1.2$).

On the contrary, though method (C) gives star polymers in high yield, the MWDs tend to be broad ($M_w/M_n \approx 2.0$, yield >80%). Typically, an acrylate-based linking agent (L-**7**) was cross-linked with a bromide initiator and a copper catalyst in diluted condition to in situ form multi bromide-functional microgel initiators (L-**7**, 97% conv.).[753] The subsequent treatment with MA resulted in high yield of the corresponding star polymers, while the MWDs were actually broad in comparison to those of methods A and B ($M_w/M_n \approx 2.0$, yield ≈ 80%).[753] Copolymerization of excess styrene and a bismaleimide linking agent (L-**8**) in the presence of a bromide initiator is also effective for star polymers with A-**5** chains.[754]

Block, Random, and Heteroarm Star Polymers. *Block or Random.* Block or random arm polymer chains can be introduced into microgel-core star polymers via metal-catalyzed living radical polymerization in conjunction with method A and method C. Typically, star polymers with block or random arms of MMA and BMA (A-**6**, A-**7**, A-**12**) are efficiently synthesized by method (A) with in situ addition of monomers (MMA or BMA) and/or linking agents (L-**1** or L-**5**) in ruthenium [RuCl$_2$(PPh$_3$)$_3$ (Ru-**1**)/Al(Oi-Pr)$_3$]-based system (star yield = 80−90%).[755] Method A is further extended to star polymers with PEGMA and MMA-block arms (A-**8**, $m = 50$, $n = 10$) via the in situ linking reaction with L-**1** and Ru-**1**/n-Bu$_3$N. Thanks to the amphiphilic, hydrophilic, and thermosensitive poly(ethylene oxide) (PEO) pendant, the star polymers are completely soluble in various solvents such as toluene, CHCl$_3$, DMF, MeOH, and water, and uniquely exhibit upper critical solution temperature (UCST ≈ 30 °C) in 2-propanol.[277] Method C with a copper catalyst was applicable to star polymers carrying nBA/tBA block arms (A-**9**).[753]

Polyester-based block copolymers of MMA/ε-CL (A-**10**) and styrene/ε-CL (A-**11**) can be incorporated into star polymers via combination of metal-catalyzed living radical polymerization and ROCP.[756] For this, telechelic block copolymers (A-**10**) of a bromine-capped poly(MMA) and a hydroxyl-capped poly(ε-CL) was first prepared by combination of copper-catalyzed polymerization of MMA and ROCP of ε-CL with FI-**1** ($n = 1$). The subsequent linking reaction with L-**1** gave star block copolymers carrying poly(MMA) inner shell and poly(ε-CL) outer shell with hydroxyl groups surface. Similar star block copolymers with bromide surface are also obtained from the other pathway: (1) linking reaction of a bromester end-functionalized poly(ε-CL)OH with [4,4′]-bioxepanyl-7.7′-dione (BOD) for bromine surface-functionalized star poly(ε-CL) and (2) copper-catalyzed polymerization of MMA with the star macroinitiator to give star block copolymers carrying poly(ε-CL) inner shell and poly(MMA) outer shell with bromide surface. This combination method was further extended to A-**11**-armed star polymers.

Hetero(Mikto) Arms. Hetero(mikto)arm star polymers, that carry at least two kinds of different arm chains, are obtained from the following two pathways: (1) "in−out method" linking reaction of a linear arms with a divinyl compound, followed by living radical polymerization of monomers from the halogen terminal-containing star polymer core and (2) "arm-mixing method" linking reaction of different arms mixture with a divinyl compound. The arm combination for heteroarm star polymers (MA-**1** to MA-**12**) is listed in Figure 49. According to the in−out method,[757−761] MA-**1**-heteroarm star polymers[757] are synthesized. First, bromine-capped poly(nBA)s are cross-linked with L-**6** in the presence of a copper catalyst (CuBr/PMDETA). The resultant star poly(n-BA)s with core-bound bromines ($M_w = 279\,000$) work as multifunctional initiators for styrene polymerization to lead to MA-**1** star polymers ($M_w = 444\,000$). Though the molecular weight was clearly larger than that of the original star poly(nBA)s, the styrene conversion retarded around 15% because of the intrastar arm−arm coupling reaction.[757] This copper-mediated system is also effective for MA-**2** heteroarms and a degradable core with a disulfide-bearing L-**15**. Importantly, the core cleavage with a reducing agent revealed that the initiation efficiency from L-**15** core-bound bromines in the *n*BA polymerization was estimated as just 19%, probably due to the steric hindrance around the initiating site and the imcompatibility of the original poly(MMA) arms and the generating poly(*n*BA) arms. Additionally, the copper-based in−out method is applied to various heteroarm star polymers of MA-**3**,[758] MA-**4**,[759] MA-**5**,[760] and MA-**6**.[761]

Another arm-mixing method[762−764] also successfully provide various arm combinations (MA-**7** to MA-**12**).[762,763] All of the arm mixtures (MA-**7** to MA-**11**) are efficiently and homogeneously cross-linked with L-**6** in copper systems to give the corresponding heteroarm star polymers with relatively narrow MWDs in high yield ($M_w/M_n \approx 1.4$, yield ≈ 90%).[762] Liquid adsorption chromatography analysis of the products strongly supports that all of the star polymers consist of the corresponding two arm species. This arm-mixing technique is further extended to method C with two kinds of olefin end-functionalized macromonomers and a linking agent (L-**6**).[764]

Functionalized Star Polymers. Metal-catalyzed living radical polymerization affords selective introduction of various functional groups into desired sites of star polymers such as arm, surface, and core. This section especially deals with functionalization of the surface and the microgel-core.

Surface. Hydroxyl, amine, and amide surface-functionalized star polymers are obtained from linking reaction of end-functionalized polymers in ruthenium-catalyzed living radical polymerizaton.[765] End-functionalized poly(MMA)s derived from hydroxyl, amine, and amide-bearing initiators (FI-**4**, FI-**8**, FI-**18**)[377] are sequentially cross-linked with a divinyl compound (L-**1**), to result in the corresponding star polymers in high yield (75−90%).[765] Another hydroxyl surface-functionalized star poly(*n*BA)s are also prepared by copper-catalyzed linking reaction of hydroxyl end-functionalized poly(*n*BA) with L-**6**.[766] After the esterification of the hydroxyl groups with an acyl chloride into methacryloyl groups, the olefin-surface functionalized star polymers were further cross-linked inter- or intramolecularly under heating or UV irradiation. Bulky dendrons are also successfully introduced into the surface of star poly(styrene) via the arm-linking with L-**6**.[767] Additionally, benzophenone or benzoic acid-surface functionalized star poly(styrene)[768] were employed as supporting beds of trimethylaluminum (cocatalyst) for iron-catalyzed polymerization of ethylene.

Core. Core-functionalized star polymers are synthesized by arm-linking reaction with functional divinyl compounds (L-**9** to L-**15**) or with divinyl compounds and functional comonomers (FC-**1**, **2**). Especially, in situ linking reaction of living poly(MMA)Cl (A-**1**) with amide or hydroxyl-containing linking agents [L-**9**, L-**10** ($n = 1, 2$), L-**11**, L-**12**, L-**14**][769] is effective for amide or hydroxyl-functionalized microgel star polymers in ruthenium-catalyzed living radical polymerization, respectively ($M_w = 670\,000-13\,300\,000$, 23−637 arms, $R_g = 12-42$ nm), where the core confines a large number (up to 51 000) of polar functional groups in the nano-order size space. These core-functionalized star polymers selectively interacted with protic guest compounds such as benzoic acid, benzyl alcohol, and benzylamine via the hydrogen bond.[770]

Metal-bearing microgel core star polymers are directly synthesized by linking reaction of living poly(MMA)Cl (A-**1**) with a dimethacrylate (L-**1** or L-**5**) and a phosphine ligand-bearing styrene derivative (FC-**1**) in ruthenium [$RuCl_2(PPh_3)_3$ (Ru-**1**)/*n*-Bu_3N]-catalyzed living radical polymerization,[322,323] where the ligand monomers (FC-**1** = FM-**43**) efficiently entrap the polymerization catalysts (Ru-**1**) into the microgel core via ligand exchange reaction during the copolymerization. This strategy is represented as "direct transformation of polymerization catalysts into star polymer catalysts". The obtained polymers exhibited dark red-brown close to the original Ru-**1** and the core-bound ruthenium was estimated as 31−74 μmol per g of polymer by UV−vis and inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses. The ruthenium contents increased with increasing the feed ratio of a ligand monomer (FC-**1**) to poly(MMA)Cl (r_{ligand} = [FC-**1**]/[poly(MMA)Cl]) from 1.25 to 5. The molecular weight, arm numbers, and gyration radius were well controlled as the following: $M_w = 170\,000-1\,720\,000$, 11−92 arms, $R_g = 7.9-19$ nm (SEC-MALLS). The star polymers cast on a glass plate can be directly observed as darkened dots (2 − 3 nm) by transmission electron microscopy (TEM)[322,323,771] even without the staining, and as semicircular images (diameter ≈ 30 nm, height ≈ 6 nm) by atomic force microscopy (AFM).

Amphiphilic, thermosensitive polyethylene glycol (PEG)-carrying-arm chains (A-**8**) are successfully introduced into ruthenium-bearing microgel star polymers by the linking reaction with L-**1** in the presence of a phosphine-ligand monomer (CF-**1**) (∼75%).[277] This star polymer actually showed amphiphilic solubility (soluble in toluene, $CHCl_3$, DMF, MeOH, and water) and thermosensitive properties (UCST, ∼31 °C in 2-propanol). Interchange of core-bound metals in the star polymers is also achieved by the two steps: (1) removal of the core-bound ruthenium with a hydrophilic, highly basic phosphine compound [$P(CH_2OH)_3$], followed by precipitation into methanol, giving multiple phosphine-ligand bearing star polymers and (2) introduction of iron or nickel counterpart salts or complexes.[3]

The metal-bearing star polymers are regarded as unique polymer-supported catalysts that are totally homogeneous because of the soluble arms and, in turn, partially heterogeneous due to the cross-linked microgel. For example, ruthenium-bearing microgel star polymers with PMMA arms efficiently, homogeneously catalyzed oxidation of 1-phenylethanol into acetophenone in acetone in high yield [conversion ≈ 90% (3 h), TOF (turn over frequency, h^{-1}) ≈ 300],[3,322] where the high catalyst load into the core adversely affected the activity. The star catalysts are easily recyclable without any loss of activities. Additionally, ruthenium-bearing star polymers with PEG-carrying arms are effective as catalysts for homogeneous hydrogenation of various ketones into sec-alcohols in 2-propanol and further perform thermoregulated phase-transfer catalysis in aqueous hydrogenation of a hydrophobic alkyl ketone (2-octanone).[3]

As other functionalization, a fluorescence compound[772] and pyrene[773] are successfully incorporated into microgel-cores of star polymers via copper-catalyzed living radical polymerization. The former is achieved by the linking reaction of poly(MMA)Cl macroinitiator with L-**6** in the presence of FC-**2**, and the latter is done by copolymerization [method (C)] of poly(*n*BA) macromonomer and L-**6** with a pyrene-bearing initiator. Star polymers with cores cross-linked by thermally exchangeable, dynamic covalent bonds are also obtained from mixture of two kinds of block copolymers carrying an alkoxyamine pendant segment.[774]

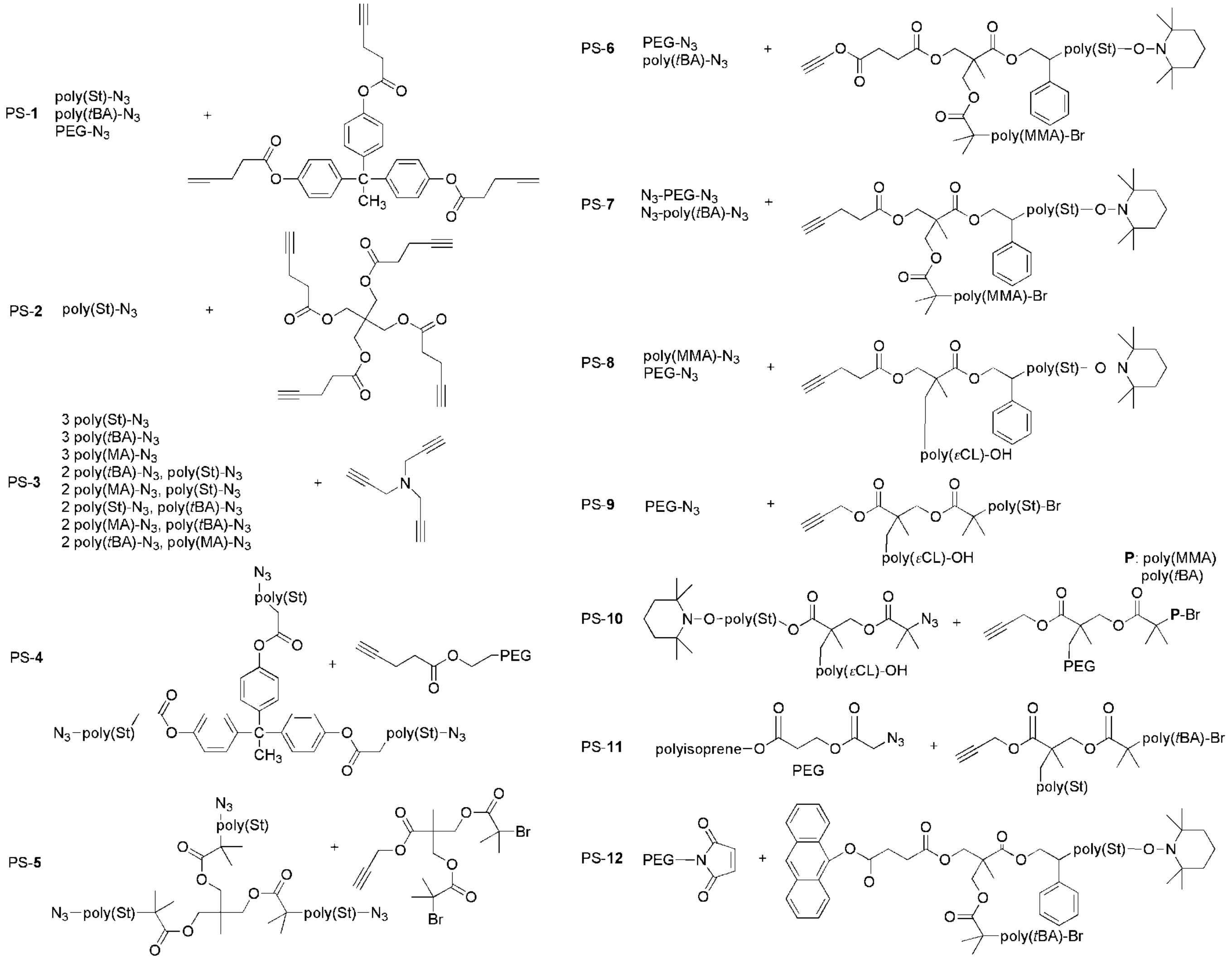


Figure 51. Star polymers via click chemistry.

3.8.3. Polymer Reaction

Selective and robust "click" coupling reactions such as cycloaddition of an alkyne and an azide (PS-**1** to PS-**11**) and Diels−Alder reaction (PS-**12**) are now available for synthesis of star polymers coupled with metal-catalyzed living radical polymerization, as well as for block copolymers (Figure 51). These reactions can produce various arm structures such as homo, block, dendrimer-like, and hetero(mikto) arms, and are especially effective for dendrimer-like and heteroarm star polymers due to the selective, efficient reactivity and the convenience.

As already described, azide end-functionalized polystyrenes and polyacrylates are efficiently obtained from the corresponding halogen-end polymers and azide compounds (EC-**8** or **9**) (see section 3.3.2). Therefore, the resultant azide-end polymers, in addition to azide end-functionalized poly(ethylene glycol) (PEG), are linked with multi-alkyne-functionalized coupling agents (PS-**1**,[775] PS-**2**,[776] PS-**3**[777,778]) via copper (CuBr/PMDETA)-catalyzed cycloaddition, to lead to 3- or 4-arm star polymers in high yield (>80%). Various heteroarm star polymers are conveniently, efficiently synthesized by the precision control of the feed ratio of an azide-terminal polymer to an alkyne-coupling agent.[777,778] Typically, three alkyne-bearing PS-**3** is treated with one equivalent of azide-bearing poly(St) and subsequent two equivalent of azide-bearing poly(*t*BA) to give well-controlled (St)(*t*BA)$_2$-heteroarm star polymers with quite narrow MWDs (M_w/M_n = 1.03).[777] This strategy was further extended to the synthesis of dendrimer-like macromolecules.[777−781] In contrast, star polymers are also obtained from cycloaddition of alkyne-end functionalized polymers and multi azide-bearing coupling agents (PS-**4**,[782] PS-**5**[783]). Among them, an alkyne-bearing bifunctional bromoester (PS-**5**) efficiently and conveniently led to well-defined dendrimer-like star polymers with narrow MWDs (M_w/M_n < 1.16) via repeating the polymerization of styrene and the multiplication of haloester initiating sites.

Additionally, various heteroarm star polymers (PS-**6**,[784] PS-**7**,[785] PS-**8**,[786] PS-**9**,[787] PS-**10**,[788] PS-**11**,[789] PS-**12**,[790]) are obtained from alkyne/azide cycloaddition[784−789] or Diels−Alder reaction[790] in conjunction with not only metal-catalyzed living radical polymerization but also other polymerization system including nitroxide-mediated radical polymerization (NMP),[784−786,788,790] living anionic polymerization,[789] ring-opening cationic polymerization (ROCP),[786−788] and ring-opening anionic polymerization (ROAP).[789] All cases demonstrated high controllability. Other halogen terminal transformation in bromine-capped polystyrenes is also employed for heteroarm star polymers and dendrimer-like polymers. Here, living polystyrenes are treated with 2-amino-1,3-propanediol (serinol) to almost quantitatively lead to ω,ω-bishydroxy-bearing polystyrenes, whose hydroxyl groups are further converted into bifunctional haloester initiators for copper-mediated living radical polymerization of styrene or *t*BA.[791,792]

3.9. Graft Copolymers

Graft copolymers including polymer brushes[252−254] are one of the branched macromolecules as well as star polymers, hyperbranched polymers, and dendrimers. In contrast to their globular structures, graft copolymers consist of a linear main chain attaching multiple long pendant chains. Thus, they often lead to the unique brush structure and physical properties. Graft copolymers are obtained from living polymerization via the following three pathways: (1) “grafting from”, living polymerization of monomers (side) from pendant-multifunctional linear macroinitiators (main), (2) “grafting through”, living (co)polymerization (main) of macromonomers (side); and (3) “grafting onto”, coupling reaction of living polymers or end-functionalized polymers (side) onto pendant-multifunctional linear quenchers or pendant-reactive linear polymers (main), respectively.

Thanks to the high controllability and high tolerance to polar functional groups, metal-catalyzed living radical polymerization is quite effective for functionalized graft copolymers. Grafting from or grafting through methods are especially popular for the synthetic procedures, which are frequently combined with other polymerization system or polymers: nitroxide-mediated radical polymerization (NMP), reversible addition−fragmentation chain transfer (RAFT); cobalt-mediated living radical polymerization (Co-LRP), ring-opening cationic polymerization (ROCP), ring-opening anionic polymerization (ROAP); ring-opening metathesis polymerization (ROMP), acyclic diene metathesis polymerization (ADMET), coordination polymerization, polycondensation, conjugated polymers, commercially available polymers, and so on. The combination effectively expands varieties of graft copolymers, thereby successfully enhance the physical properties and functions. Recently, the grafting onto method, coupled with selective, efficient, and convenient reactions, has been also employed for preparation of graft copolymers, as well as that for end or pendant-functionalized, block, star polymers. Additionally, direct observation and analysis of one molecule of graft copolymers has been also achieved with atomic force microscopy (AFM), which would contribute to open new vistas in one molecules analysis of polymers.

This section comprehensively presents graft copolymers via metal-catalyzed living radical polymerization, especially categorized into the follows: (1) Grafting from, (2) grafting through, and (3) grafting onto (Figures 52−58).

3.9.1. Grafting From

Graft copolymers are prepared by the two grafting from methods using metal-catalyzed living radical polymerization: (1) living polymerization or polymer reaction (side chain) from a pendant multifunctional macroinitiator obtained from metal-catalyzed living radical polymerization and (2) metal-catalyzed living radical polymerization (side chain) from a pendant multifunctional macroinitiator obtained from other polymerization (non metal-catalyzed system). In other words, the former consists of main chain via metal-catalyzed system and the latter does of that via none metal-catalyzed system (side chain: metal-catalyzed system).

Main Chain via Metal-Catalyzed Living Radical Polymerization. Graft copolymers with main chains via metal-catalyzed living radical polymerization (GF-**1** to GF-**15**) are listed in Figure 52. The side chains are also mainly prepared by the metal-catalyzed polymerization, in addition to ROCP and NMP. Pendant initiators for metal-catalyzed graft polymerization mainly consist of haloesters, which are introduced by the esterification of pendant trimethylsilyl or hydroxyl groups originated from 2-(trimethylsilyl)ethyl (meth)acrylate [TMSHE(M)A: TMS-protected HE(M)A, HEMA (FM-**1**)] or the esterification of α-carbon of polyacrylates. As a result, almost all the backbones result in methacrylates or acrylates, in sharp contrast to graft copolymers via system combination [see section 3.9.1]. The grafting density and position can be efficiently controlled as follows: (1) brush (GF-**1** to GF-**5**)[354,793−800] that bears grafting pendants in all main chain monomer units, (2) block (GF-**6** to GF-**9**)[801−804] that consists of densely grafting segments and non grafting counterparts, (3) random (GF-**10** to GF-**13**)[805−808] that statistically places grafting segments along the main chain, and (4) gradient (GF-**14**, GF-**15**)[809] that has grafting pendants with the gradual density change along the main chain.

Brush. GF-**1** and GF-**2** are typical brush polymers obtained from copper-catalyzed living radical polymerization. To prepare pendant-multifunctional linear macroinitiators in GF-**1**,[793] TMSHEMA was first polymerized with CuBr/bpy and a chloride initiator to give well-controlled poly(TMSHEMA)s with high molecular weight and narrow MWDs (M_n = 101 000, $M_w/M_n \sim 1.1$). The TMS groups were quantitatively deprotected with potassium fluoride (KF) and tetrabutylammonium fluoride (TBAF), which were subsequently treated with 2-bromopropionyl bromide, resulting in bromoester-bearing multifunctional polymethacrylate initiators [poly(EABrMA)] with narrow MWDs (SEC-MALLS, M_n = 136 000, $M_w/M_n \approx 1.16$, Br/one polymer chain ≈ 514).[793] The densely multifunctional macroinitiator was effective for *n*BA to lead to well-controlled poly(EABrMA)-*graft*-poly(*n*BA) (M_n = 1 180 000, $M_w/M_n \approx 1.22$), though *n*BA conversion is quite low (∼4%).

The resultant *n*BA-based graft polymers were further applied to block copolymerization of styrene with copper catalysts for poly(EABrMA)-*graft*-[poly(*n*BA)-*block*-poly(styrene)] with high molecular weight and narrow MWDs (M_n = 1 850 000, $M_w/M_n \approx 1.24$, styrene conv. ≈ 3%). The solid polymer brush with poly(*n*BA) core and poly(styrene) outer layer is successfully, directly observed as one molecule in fully stretched structure on mica surface by atomic force microscopy (AFM).[793] Additionally, the similar TMSHEMA-based macroinitiators (GF-**1** and GF-**2**) were further extended to wide variety of functional side chains consisting of methacrylates carrying amine (DMAEMA, FM-**4**),[794] azobenzene (FM-**79**),[354] poly(ethylene glycol) (FM-**14**, $n = 3$),[795] and glucofuranose (FM-**57**),[796] and acrylamide (DMAA).[794] The amine, amide, and azobenzene-functionalized graft copolymers performed temperature-responsible[794] or phototunable[354] size change in the aqueous solution, and the glucofuranose-based and the deprotected counterparts formed long cyclindrical brush structure on mica in the solid state.[796]

A polymer brush densely grafting polystyrene and poly(L-lactide) chains (GF-**3**)[797] is, in one-pot, prepared by simultaneous combination of CuBr/PMDETA-catalyzed AGET living radical polymerization of styrene and ROCP of L-lactide in the presence of $Sn(Oct)_2$ and a partially bro-

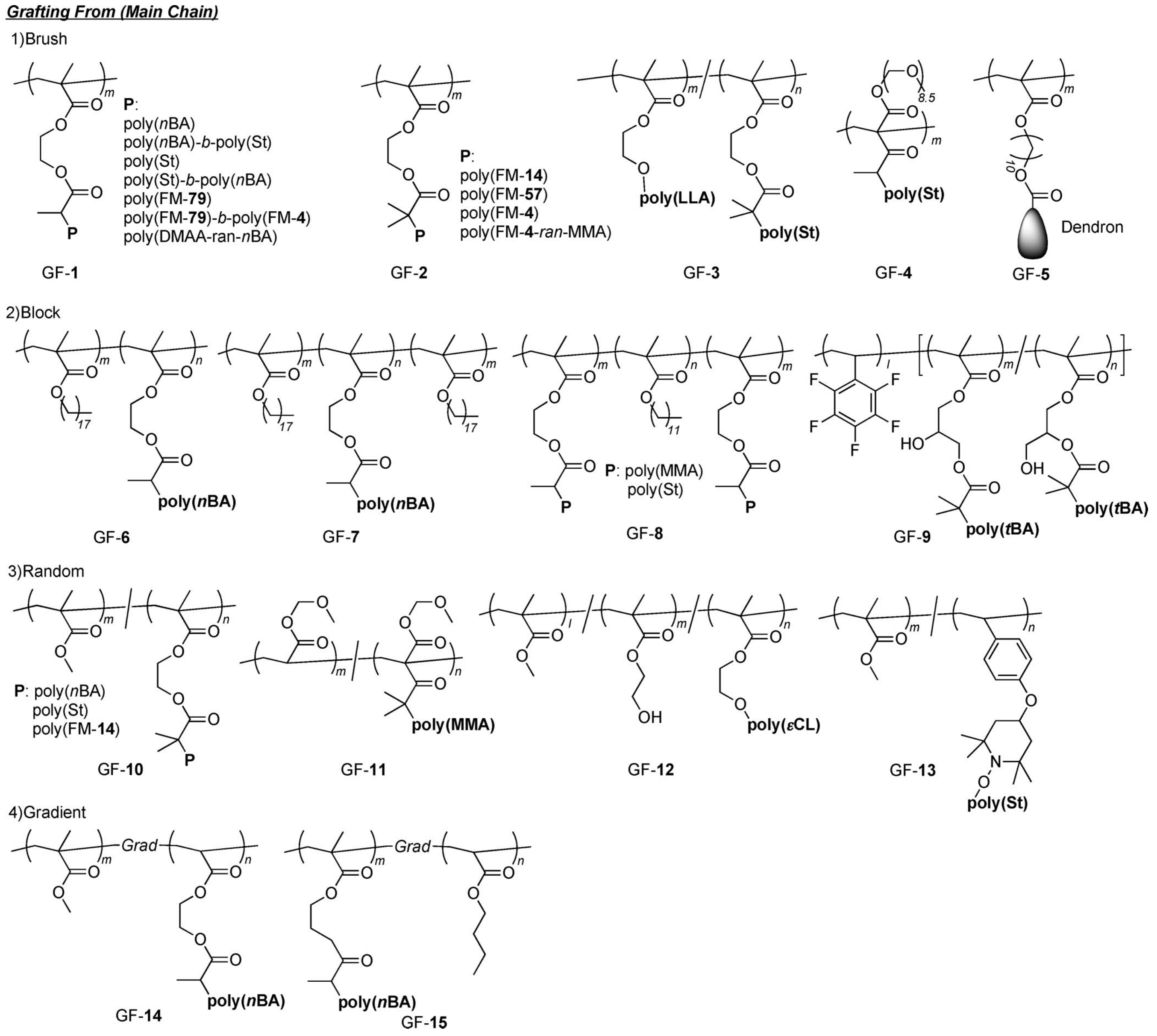


Figure 52. Graft copolymers via grafting from method 1.

moester-bearing poly(HEMA) initiator, in which the $Sn(Oct)_2$ uniquely works not only as a reducing agent for the AGET system but also as a catalyst for the ROCP. An unique α,α-double grafting asymmetric polymer brush (GF-**4**)[798] consists of a polyacrylate backbone and hydrophilic poly(ethylene glycol) methyl ether (PEG) and hydrophobic poly(styrene) side chains. The graft copolymers were prepared according to the three steps: (1) copper-catalyzed living radical polymerization of PEG-bearing acrylate (FM-**16**, $n = 8.4$), (2) introduction of bromoesters into α-carbon of the ester groups in the poly(FM-**16**) backbone via the treatment with lithium diisopropylamine (LDA) and α-bromopropionyl chloride, and (3) copper-catalyzed polymerization of styrene. Bulky polyester-based dendrons (GF-**5**)[799,800] were also efficiently incorporated into the pendants via divergent method from polyacrylates carrying hydroxyl pendants.

Block. Graft block copolymers (GF-**6**,[801] GF-**7**,[801] GF-**8**,[802,803] GF-**9**[804]) are efficiently prepared by grafting from in metal-catalyzed living radical polymerization (Figure 52). Well-controlled GF-**6** and GF-**7** are obtained from copper-mediated block copolymerization of octadecyl methacrylate (OctadecylMA) and TMS-protected HEMA, followed by incorporation of bromoester initiators into the pendant TMS position, subsequent polymerization of *n*BA ($M_w/M_n \approx 1.3$). Analyzed by AFM, solid triblock graft copolymers (GF-**7**) formed wormlike structure on mica substrate due to the strong intermolecular van der Waals interaction of the poly(octadecylMA) segments.

In sharp contrast to GF-**6**, GF-**7**, A_xBA_x-type block-graft copolymers with middle soft segments and outer hard graft chains (GF-**8**) are efficiently synthesized with a ruthenium catalyst.[802,803] Namely, multibromoester functionalized A_x-BA_x-type macroinitiators were directly prepared by $Ru(Ind)Cl(PPh_3)_2$ (Ru-**4**)/n-Bu_3N-mediated living radical block copolymerization of dodecyl methacrylate (DodecylMA) and TMSHEMA with dichloroacetophene, followed by sequential addition of 2-bromoisobutyroyl bromide. The resultant A_xBA_x macroinitiators induced polymerization of MMA[802] and styrene[803] in the presence of a ruthenium catalyst to give well-controlled A_xBA_x-type block-graft copolymers of MMA or styrene ($M_w/M_n = 1.2-1.3$). The solid products showed microphase separation and thermoelastic properties as well as the corresponding ABA triblock copolymers.[803]

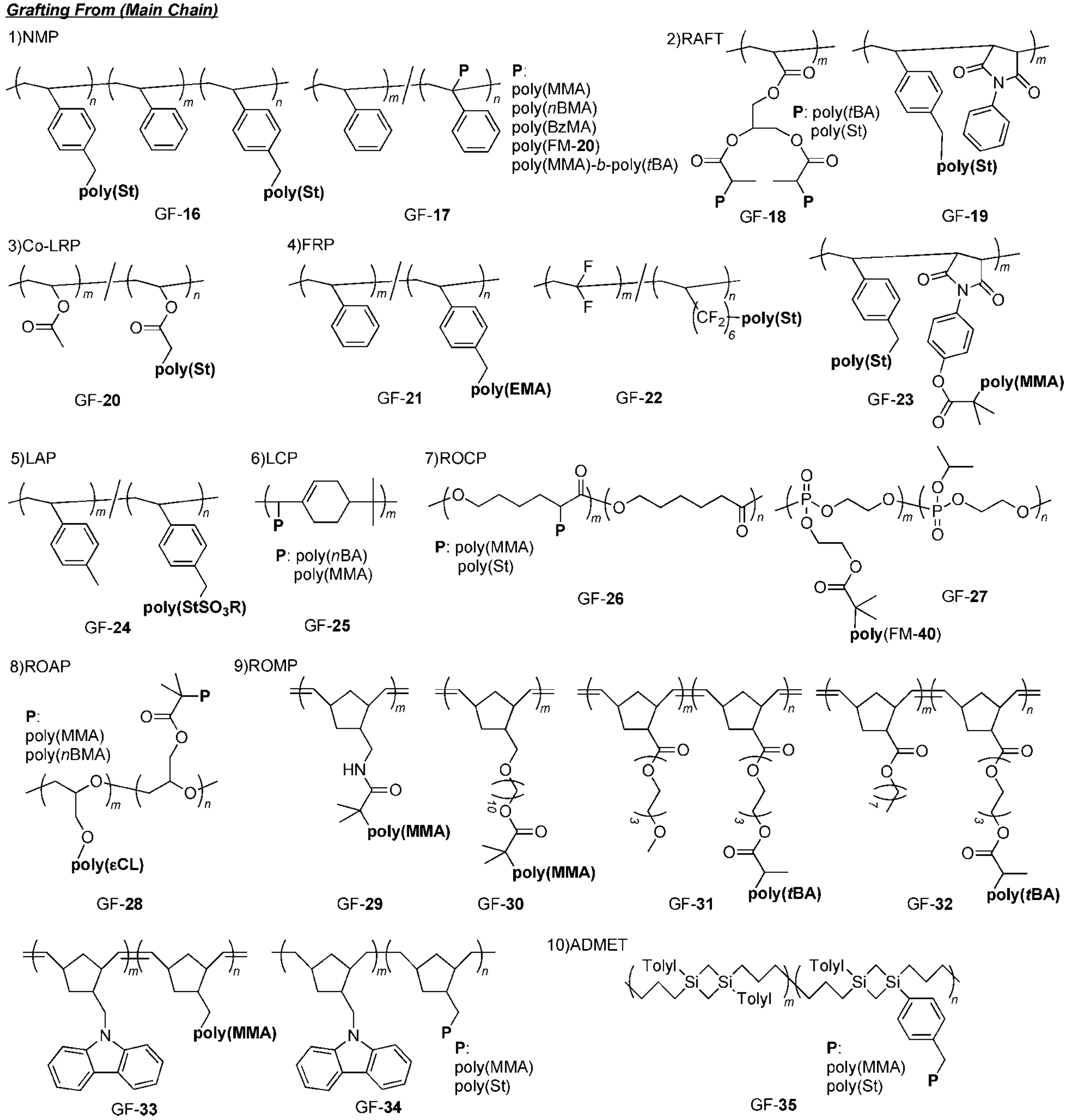


Figure 53. Graft copolymers via grafting from method 2.

Random, Gradient. Naturally, random or gradient main chains (GF-**10**,[795,805] GF-**11**,[806] GF-**12**,[807] GF-**13**[808] GF-**14**,[809] GF-**15**[809]) are also utilized for graft copolymers (Figure 52). As well as graft copolymers described above, GF-**10**[795,805] and GF-**11**[806] are obtained from TMSHEMA with ruthenium or copper catalysts. The grafting pendants in GF-**12**[807] and GF-**13**[808] are synthesized by enzyme-catalyzed ROP of εCL and NMP of St, respectively. Noted that GF-**12**[807] can be, in one-pot, produced by concurrent copper-catalyzed living radical copolymerization of MMA and HEMA (FM-**1**) with a bromide initiator and enzyme (Novozym-453)-catalyzed ROP of εCL from the pendant hydroxyl groups in $scCO_2$ (at 35 °C at 1500 psi), leading to narrow MWDs ($M_w/M_n \approx 1.4$) and 30−40% grafting ratio to the hydroxyl groups. Additionally, gradient multifunctional macroinitiators for GF-**14**[809] and GF-**15**[809] are spontaneously obtained from combination of MMA and 2-(trimethylsilyloxy)ethyl acrylate (TMSHEA) or that of TMSHEMA and *n*BA.

Side Chain via Metal-Catalyzed Living Radical Polymerization. Though the main chains derived from metal-mediated living radical polymerization are just limited for methacrylate or acrylate-based backbones, combination of other polymerization or polymers successfully expands the backbone species of gradient copolymers. Figures 53−55 shows various gradient copolymers with side chains via metal-catalyzed system and main chains via other polymerization and polymers.

Living/Free Radical Polymerization. A series of living radical polymerization, including NMP (GF-**16**,[810] **17**[811]), RAFT (GF-**18**,[812] **19**[813]), and Co-LRP (GF-**20**),[814] and free radical polymerization (FRP) (GF-**21**,[815] **22**,[816] **23**[817]) efficiently provide graft copolymers with various backbone species of styrene (GF-**16**, GF-**17**, GF-**19**, GF-**21**, GF-**23**), vinyl acetate (GF-**20**), *N*-phenyl maleimide (GF-**19**, GF-**23**), and vinylidene fluoride (GF-**22**)-based polymers, in addition to acrylate-based ones (GF-**18**) (Figure 53). Herein, halogen-based initiating moieties for metal-catalyzed system can be directly incorporated into the polymer side pendants via radical polymerization of halogen-bearing monomers such as *p*-chloromethyl styrene (CMS),[810,813,815] vinylchloroacetate (VClAc),[814] 8-bromo-1*H*,1*H*,2*H*,-perfluorooct-1-ene,[816] and a bis(bromoester)-bearing acrylate.[812] Typically, CMS-styrene-CMS triblock copolymers obtained from NMP (GF-**16**)[810] efficiently initiated copper-catalyzed graft copolymerization of styrene to give unique styrene-based dumbbell polymers. Other CMS-based polymers, alternating copolymers of CMS and *N*-phenyl maleimide via RAFT (GF-**19**)[813] and random copolymers of CMS and styrene via FRP (GF-**21**),[815] are also effective for gradient copolymers. α-Bromo multifunctional polystyrene macroinitiators are also developed for GF-**17**[811] by the followings: polystyrenes prepared by NMP are treated with *N*-bromosuccinimide (NBS) and azobisisobutyronitrile (AIBN) to lead to almost quantitatively α-brominated polystyrenes (Br >90%). They efficiently initiate copper-mediated living radical polymerization of various methacrylates.

Ionic Living Polymerization. Ionic living polymerization and subsequent bromination of the products with NBS is also applied to multifunctional macroinitiators for graft copolymers (Figure 53). The main chain for GF-**24**[324] was prepared by living anionic polymerization of *p*-methyl styrene with sec-butyl lithium, followed by the bromination of the pendant methyl groups with NBS, which efficiently initiated copper-catalyzed polymerization of styrene sulfonate ethyl or dodecyl ester ($StSO_3R$). Similar procedures were further employed for β-pinene-based backbone via titanium-mediated living cationic polymerization for GF-**25**.[818]

ROCP, ROAP. Ring-opening cationic polymerization (ROCP) and anionic counterpart (ROAP) are combined with metal-catalyzed living radical polymerization for graft copolymers, which succeed in introduction of polyester (GF-**26**),[819,820] polyphosphate (GF-**27**),[821] and polyester (GF-**28**)[822] into the main chains (Figure 53). For example, ROCP of α-chloro[819] or bromo[820]-ε-caprolactone [αCl(Br)εCL] and ε-caprolactone (εCL) directly gave controlled multifunctional polyester macroinitiators ($M_w/M_n = 1.2-1.5$) without any side reactions, which were effective for copper-catalyzed graft copolymerization of MMA[819] and styrene.[820] Because of a hydrophobic polyphosphate main chain and hydrophilic poly(FM-**40**) side chains, graft copolymers (GF-**27**) were amphiphilic and biodegradable.[821]

ROMP, ADMET. Ring-opening metathesis polymerization (ROMP) (GF-**29**,[398] GF-**30**,[823] GF-**31**,**32**,[824] GF-**33**,[398,825] GF-**34**[825]) and acyclic diene metathesis polymerization (ADMET) (GF-**35**)[826] are utilized for preparation of main chains in graft copolymers (Figure 53). Halogen-carrying initiators for metal-catalyzed living radical polymerization are incorporated into side pendants via ROMP of α-haloamide,[398] α-haloester,[823,824] and haloalkane[825]-bearing norbornene derivatives or ADMET of a tolyl-bearing diene derivative, followed by the bromination with NBS.[826] Though GF-**29**[397] are actually prepared with copper-catalyzed grafting from polymerization of MMA, the controllability is inferior to that with the corresponding grafting through counterpart, because of a certain low solubility originated from the inter- or intramolecular radical coupling reaction

Interestingly, GF-**30**[823] is synthesized by sequential or concurrent tandem catalysis of ROMP of a α-haloester-bearing norbornene derivative and metal-catalyzed polymerization of MMA in the presence of a single ruthenium catalyst [$Cl_2(PCy_3)_2Ru{=}CHPh$]. Namely, a sequential pathway of ruthenium-catalyzed ROMP and living radical polymerization is regarded as an in situ "graft from" method. The sequential pathway demonstrated controllability ($M_w/M_n = 1.5-1.7$) better than the concurrent counterpart ($M_w/M_n > 1.7$) because of the difference of the respectively optimized reaction condition and temperature, in which room temperature is suitable for ROMP and over 60 °C is, in turn, for living radical polymerization. Similar concurrent tandem catalysis was also achieved with a ruthenium catalyst in aqueous miniemulsion.[827]

Coordination Polymerization. Nonpolar olefins such as ethylene and propylene, and styrene are efficiently polymerized by coordination mechanism in the presence of early transition metal catalysts [titanium ($MgCl_2$-suported Zieglar-Natta, metallocene), zirconium, etc] with methylaluminoxane (MAO). Though polyolefins are widespread commodity plastics due to the cost performance and excellent physical properties, it is difficult to further expand the property range in the simple physical blend with other polymers due to the incompatibility. To overcome these problems, polyolefin segments are directly connected onto polar polymers of methacrylates, acrylates, and styrene via "graft from" method in metal-catalyzed living radical polymerization (Figure 54).

Main chain backbones obtained form coordination polymerization contain isotactic polypropylene (GF-**36**,[828] GF-**37**,[829] GF-**38**,[830] GF-**39**,[831]), ethylene copolymer (GF-**40**),[832] syndiotactic polystyrene (GF-**41**,[833] GF-**42**[834]), and polyallene (GF-**43**).[835,836] In all cases, halogen initiating points were introduced on to the side pendants after coordination polymerization, to prevent side reaction between the halogens and the metal catalysts. For GF-**36**,[828] a hydroxyl group-carrying copolymer of propylene and 10-undecen-1-ol is esterified with 2-bromoisobutyl bromide into a bromoester-bearing polypropylene, which efficiently initiated copper-catalyzed polymerization of MMA, *n*BA, and styrene. The products exhibited unique mechanical properties derived from the polar grafting chains.

Other polypropylene or polyethylne-based multifunctional macroinitiators are prepared by the following: (1) treatment of a succinic anhydride-bearing polypropylene with ethanolamine, followed by the esterification of the hydroxyl groups into a bromoester-bearing polypropylene (GF-**37**),[829] (2) chlorination of a propylene/allyldimethylsilane copolymer with $SOCl_2$ into a chlorodimethylsilane-bearing polypropylene (GF-**38**),[830] (3) hydrochlorination of a propylene/divinylbenzene copolymer into a 1-chloroethylbenzene-bearing polypropylene (GF-**39**),[831] and (4) bromination of an ethylene/styrene copolymer with *N*-bromosccinimide (NBS) and AIBN into a α-bromostyrene-embedding polyethylene (GF-**40**).[832] These macroinitiators efficiently induced copper-mediated graft copolymerization of various monomers. Some of the products worked as efficient compatibilizers of their corresponding homopolymer blends.[829,830,832] Additionally, multifunctional macroinitiators for GF-**41**[833] and GF-**42**[834] were also synthesized via Friedel−Crafts acylation of syndiotactic polystyrene.

Conjugated Polymers. Conjugated polymers with unique conductivity and rigid structure are also utilized as multifunctional macroinitiators of graft copolymers in metal-catalyzed living radical polymerization. The conjugated backbones include poly(*p*-phenylene) (GF-**44**),[837] polythiophene (GF-**45**,[838] GF-**46**[839]), poly(phenyleneethynylene) (GF-**47**,**48**),[840] and poly(phenylacetylene) (GF-**49**)[841] (Figure 54). Except for polythiophene-based macroinitiators, other

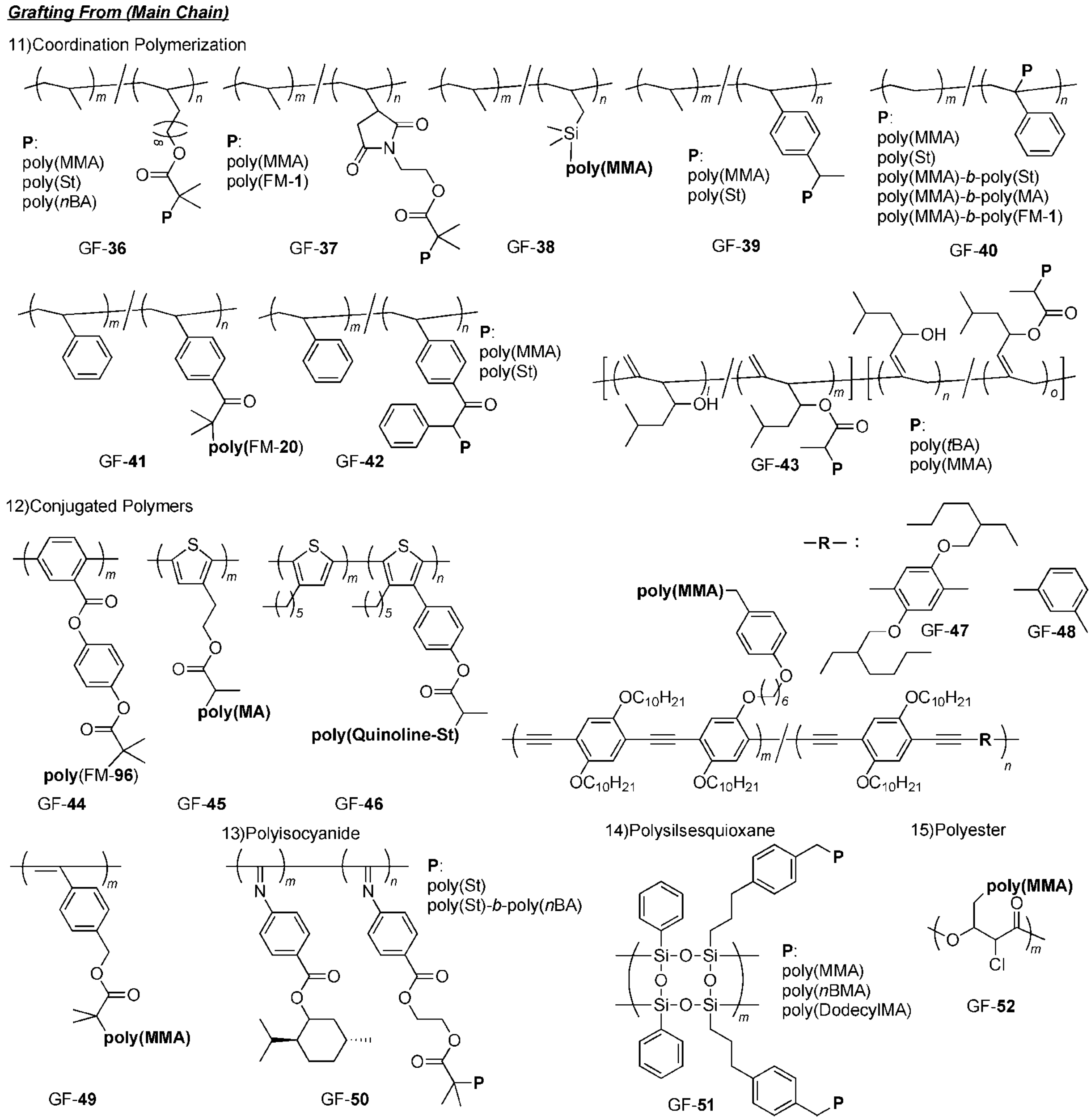


Figure 54. Graft copolymers via grafting from method 3.

conjugated macroinitiators[837,840,841] are directly synthesized with bromoester or bromoalkylbenzene-bearing monomers. All of the macroinitiators are effective for copper-mediated living radical polymerization of not only simple monomers, such as MMA, acrylates, and styrene, but also styrene derivatives carrying a quite bulky, liquid-crystalline group (FM-**96**)[837] or a quinoline group.[839]

Polyisocyanide, Polysilsesquioxane, Polyester. A polyisocyanide with helical structure via Pd−Pt μ-ethynediyl dinuclear complex (GF-**50**),[842] a polysilsesquioxane via polycondensation (GF-**51**),[843] and a poly(3-hydroxybutyrate) via bacterial synthesis (GF-**52**)[844] are used as multifunctional macroinitiators for "grafting from" in copper-catalyzed living radical polymerization of methacrylates. Interestingly, GF-**50**, even after the graft copolymerization, maintained a helical structure similar to the original polyisocyanide multifunctional macroinitiator.[842]

Commercially Available Polymers. Commercially available polymers (Figure 55) are conveniently applied to multifunctional macroinitiators of grafting from in copper-mediated living radical polymerization. Among them, polysaccharides, such as ethyl cellulose (GF-**53**),[845−848] hydroxypropyl cellulose (GF-**54**),[849] chitosan (GF-**55**),[850] and galactomannan (GF-**56**),[318] are effective for backbones of graft copolymers, where their hydroxyl and amino groups are transformed into bromoesters and a bromoamide suitable as initiating points for copper-catalyzed system. Though the chitosan-based initiator induced heterogeneous polymerization, the other ethyl cellulose, hydroxypropyl cellulose, and galactomannan ones are soluble in organic solvents to efficiently perform homogeneous polymerization for the side chains. Especially, thanks to the high solubility in water, a multi-bromoester-bearing galactomannan (GF-**56**)[318] efficiently worked as a macroinitiator for copper-catalyzed aqueous polymerization of various functional monomers including HEMA (FM-**1**), DMAEMA (FM-**4**), PEGMA (FM-**14**), sodium methacrylate (NaMA), sodium 4-vinyl-benzoate ($StCO_3Na$), FM-**42**, FM-**43**, and FM-**44**. Interestingly, cellulose fibers[851] originated

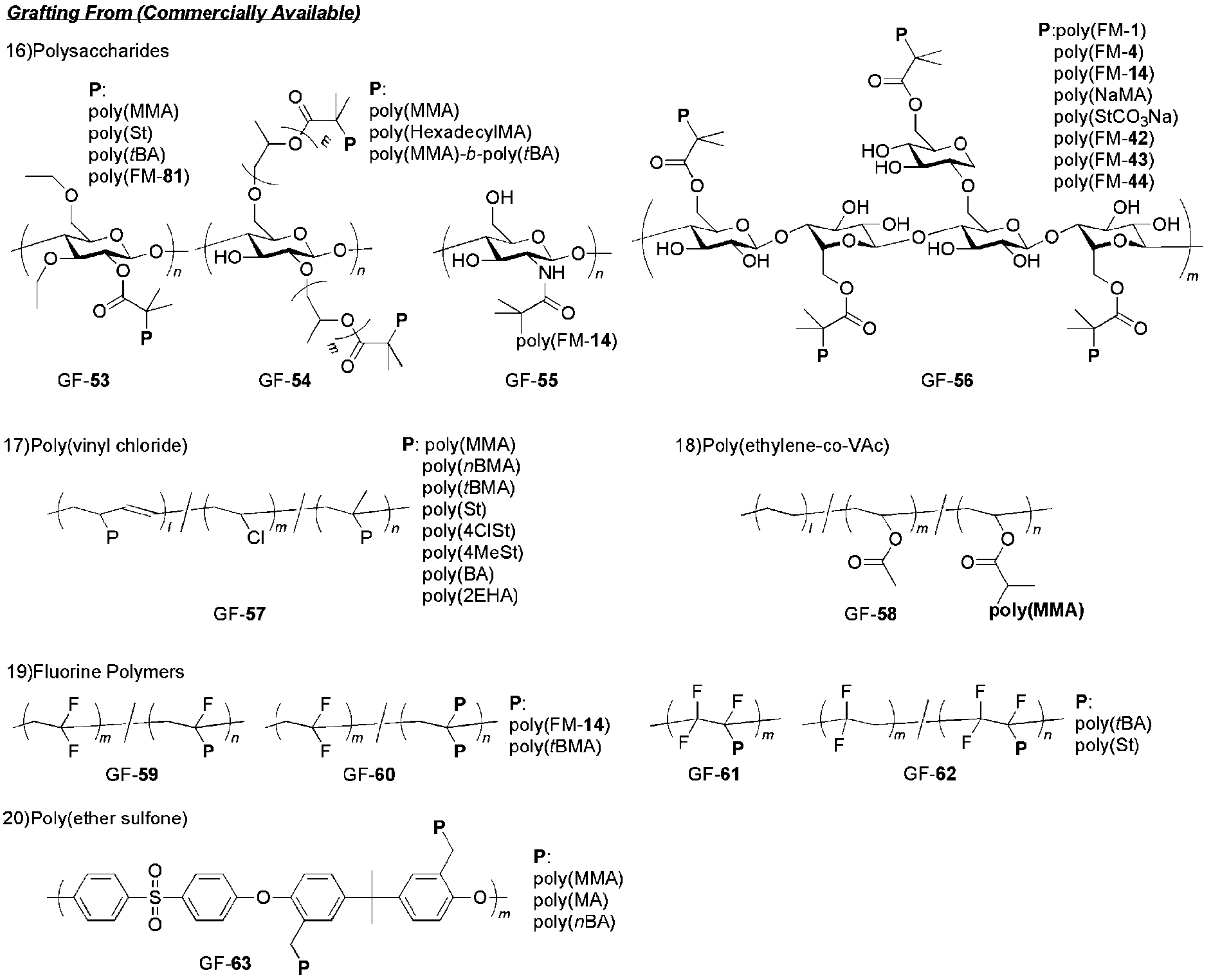


Figure 55. Graft copolymers via grafting from method 4.

from a conventional filter paper, after the bromoesterification of the hydroxyl groups, also induced graft copolymerization of MA.

Other commercially available polymers useful for graft polymer backbones are poly(vinyl chloride, VC) (GF-**57**),[852−855] poly(ethylene-co-vinylacetate, EVA) (GF-**58**),[856] poly(vinylidene fluoride) (GF-**59**,**60**),[857] polychlorotrifluoroethylene (GF-**61**),[858] poly(vinylidene fluoride-co-chlorotrifluoroethylene) (GF-**62**),[858] and aromatic polyether sulfone (GF-**63**).[859] Especially, commercial poly(VC) (GF-**57**)[852−855] contains plenty of allyl chlorides and tertiary chlorides to efficiently, directly initiate copper-catalyzed graft copolymerization of MMA, *n*BMA, *t*BMA, *n*BA, 2-ethylhexyl acrylate (2EHA), styrene, 4-chlorostyrene (4ClSt), and 4-methylstyrene (4MeSt), without any extra incorporation of initiating groups into the poly(VC) backbone. Surprisingly, direct initiation of the carbon−fluorine bonds of poly(vinylidene fluoride), in addition to the carbon-chlorine bonds of (co)poly(chlorotrifluoroethylene), was also achieved by a copper catalyst for graft copolymerization (GF-**59**,**60**,[857] GF-**61**,**62**[858]). Macroinitiators for GF-**58**[856] and GF-**63**[859] are prepared by the following polymer reactions, respectively: hydrolysis of a poly(EVA) into a partially hydroxyl groups-carrying poly(EVA), followed by the esterification with an acylhalide, giving a haloester-bearing poly(EVA);[856] chloromethylation of aromatic poly(ether sulfone) with $SnCl_4$ and chloromethyl methyl ether, giving chloromethylbenzene-bearing poly(ether sulfone).[859]

3.9.2. Grafting Through

Graft copolymers obtained from grafting through in conjunction with metal-catalyzed living radical polymerization of macromonomers are categorized into the following two groups: (1) metal-catalyzed living radical polymerization of macromonomers and (2) metal-catalyzed living radical polymerization for macromonomers.

Metal-Catalyzed Living Radical Polymerization of Macromonomers. As shown in Figure 56, various methacrylate or acrylate-terminal macromonomers (MM-**1** to MM-**16**) are polymerized with metal catalysts to synthesize graft copolymers. In addition to commercially available sources (MM-**3** to MM-**6**), the macromonomers are prepared by combination of polymerization and subsequent organic reaction (MM-**1**, MM-**2**, MM-**7**, and MM-**13** to MM-**15**), that of polymerization alone or sequential in situ treatment (MM-**8** to MM-**12**), and multistep organic reaction (MM-**16**, MM-**17**). Here, the following polymerization systems are employed: metal-catalyzed living radical polymerization, ring-opening cationic or anionic polymerization (ROCP or ROAP), and coordination polymerization.

MM-**1** and MM-**2**[860] are macromonomers typically obtained from metal-catalyzed living radical polymerization. As already described in section 3.3.2, a α-hydroxyl, *ω*-hydrogenated poly(*t*BA) and poly(*n*BA) is directly obtained from a copper catalyst, a large excess of a PMDETA ligand, and a bromide initiator. The esterification of the hydroxyl terminal with methacryloyl chloride finally gives well-

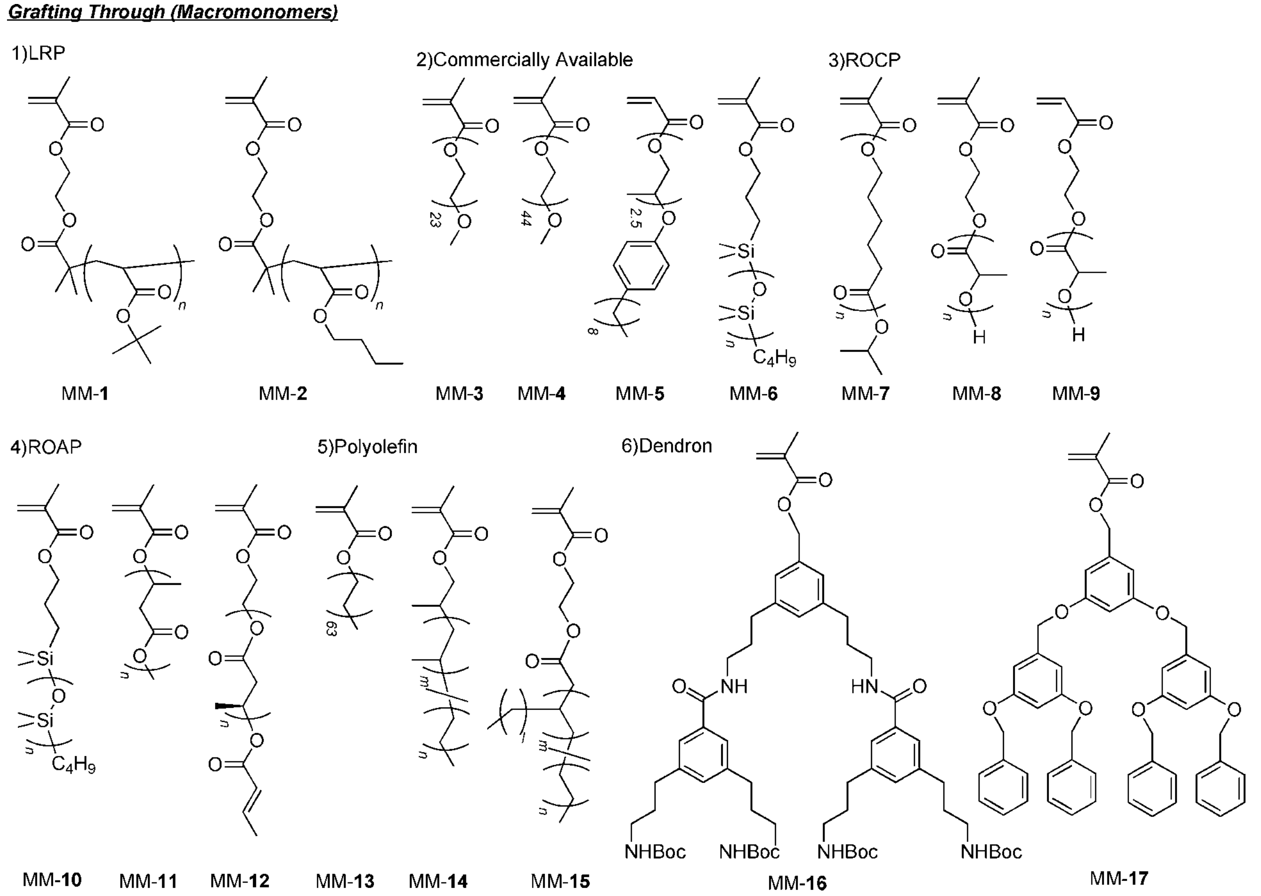


Figure 56. Graft copolymers via grafting through method with macromonomers.

controlled methacrylate-terminal poly(*t*BA) and poly(*n*BA) (MM-**1**, MM-**2**, $M_n = 2000-10\,000$, $M_w/M_n \approx 1.2$).[860] MM-**1** and MM-**2** are efficiently copolymerized with *n*BA and *t*BA in the presence of a copper catalyst, respectively, to yield their corresponding graft copolymers ($M_w/M_n = 1.2-1.7$).

Graft copolymers are conveniently prepared by commercially available macromonomers carrying poly(ethylene glycol) (PEG) [MM-**3** (FM-**14**, $n = 23$; $M_n \approx 1100$)],[861,862] poly(propylene glycol) and a long alkyl chain (MM-**5**, $M_n \approx 420$),[861] and polydimethylsilyloxane (PDMS) (MM-**6**, $M_n \approx 1000$),[862] in addition to macromonomers obtained from commercially available PEG [MM-**4** (FM-**14**, $n = 44$, $M_n \approx 2{,}000$)].[863] MM-**3** succeeds in one-pot production of PEG-pendant graft copolymers ($M_n = 100\,000-300\,000$ (determined by ^{1}H NMR), $M_w/M_n = 1.3-1.7$).[861] By using the difference of monomer reactivity, combination of MM-**3** and MM-**5** with a copper catalyst spontaneously gives gradient graft copolymers from MM-**3** (α-end) to MM-**5** (*ω*-end) ($M_w/M_n < 1.3$).[861] A block graft copolymer of MM-**4** and HEMA (FM-**1**)[863] is also efficiently obtained from a copper catalyst and a bromide initiator. After the hydroxyl groups are transformed into haloester-based initiating points via the esterification, the resultant block multifunctional macroinitiator is further employed for HEMA (FM-**1**) polymerization to lead to PEG and poly(HEMA)-brush graft copolymers [$M_w \approx 220\,000$ (determined by small-angle light scattering), $M_w/M_n \approx 1.7$].[863] Random copolymers of MM-**6** and MM-**3** exhibited physical properties characteristic for soft gels because of the composition of amorphous PDMS fractions and crystallizable PEG segments.[862]

Metal-catalyzed living radical polymerization of poly(*ε*-caprolactone, *ε*-CL) (MM-**7**)[864] or poly(L or D,L-lactide, LLA or DLLA) (MM-**8,9**)[865,866]-bearing (meth)acrylates successfully affords direct incorporation of the corresponding polyesters into polymer side chains. MM-**7** is obtained from ROCP of *ε*-CL, followed by the esterification of the hydroxyl terminal with a methacryloyl chloride [$M_n = 1000-2000$ (determined by ^{1}H NMR), $M_w/M_n = 1.2-1.4$],[864] and MM-**8** and MM-**9**[865,866] are directly prepared by tin-catalyzed ROCP of LLA or DLLA with a HEMA (FM-**1**) or 2-hydroxyethyl acrylate (HEA) initiator [$M_n = 2700-3400$ (determined by ^{1}H NMR), $M_w/M_n \approx 1.2$]. MM-**8** and MM-**9** are efficiently copolymerized with MMA in the presence of a copper catalyst to give gradient or random graft copolymers, where discussion is especially focused on the monomer reactivity of the macromonomers.[865] For MM-**8**, the chirality of the polylactide between LLA and DLLA is independent of the monomer reactivity. Though MM-**8** and MMA are the same methacrylate series, MM-**8** (LLA) is faster consumed than MMA in their copolymerization to spontaneously lead to gradient graft copolymers from MM-**8** (LLA) (α-end) to MMA (*ω*-end). In contrast, copolymerization of MM-**9** (an acrylate-version of MM-**8**) and MMA spontaneously yield gradient graft copolymers from MMA (α-end) to MM-**9** (*ω*-end).

Polydimethylsiloxane (PDMS) (MM-**10**)[866,867] and poly3-hydroxybutylate (MM-**11**,**12**)[868]-bearing methacrylates can be prepared by ring-opening anionic polymerization (ROAP). The former is obtained from ROAP of hexamethylcyclotrisiloxane with *n*-butyllithium, quenched with 3-methyacryloxypropyldimethylchlorosilane ($M_n = 2200-3000$, $M_w/M_n \approx 1.2$), and the latter is done from ROAP of *β*-butyrolactone with sodium methacrylate, quenched with methyl iodide ($M_n = 1500-2300$ (determined by ^{1}H NMR), $M_w/M_n = 1.2-1.4$).

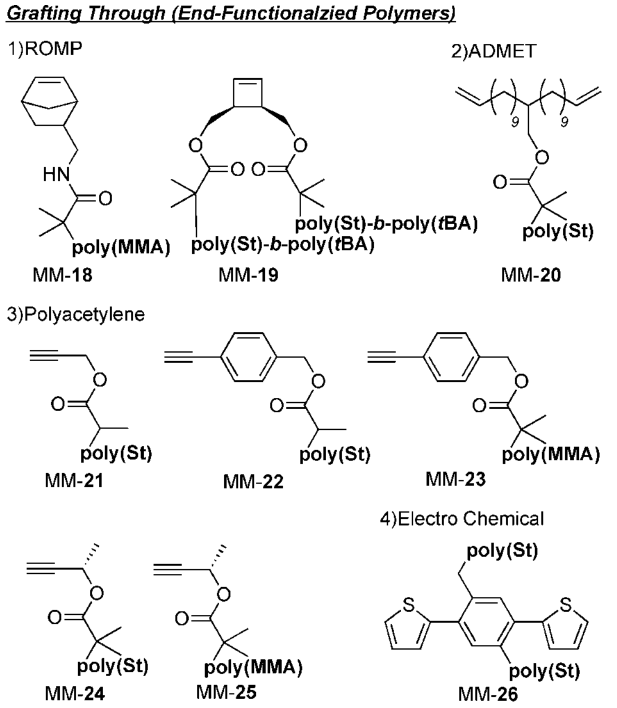


Figure 57. Graft copolymers via grafting through method with end-functionalized polymers.

Copolymerization of a PDMS-bearing methacrylate (MM-**10**) with MMA, MM-**8**, and MM-**9** was deeply examined in conjunction with a copper catalyst and a bromide initiator.[866,867] Atactic and isotactic poly(3-hydroxybutylate)s are successfully introduced into the graft side chains via copolymerization of MM-**11** or MM-**12** with MMA, PEGMA (FM-**14**, $n = 5$), and MM-**3** to give narrow MWDs ($M_w/M_n \approx 1.2$).[868]

Polyolefin-bearing methacrylates (MM-**13**,[869] MM-**14**,[870] MM-**15**[871]) are employed as macromonomers for graft copolymerization. MM-**13**[869] and MM-**14**[870] ($M_n = 940-3000$, $M_w/M_n = 1.6-2.3$) are obtained from a vinyl end-functionalized polyethylene and ethylene/propylene copolymer, respectively, that prepared by coordination polymerization with a zirconium/methylalminoxane-based catalyst. The vinyl terminals were transformed through a hydroxyl one into a methacryloyl one. Typically, MM-**14** was copolymerized with MMA in the presence of a copper catalyst and a mono or tetrafunctional bromide initiator to give linear or four arm graft copolymers of MMA and MM-**14** ($M_w/M_n = 1.3-1.6$). The linear graft copolymer efficiently worked as a compatibilizer in a poly(MMA) and poly(ethylene/propylene) blend. MM-**15** with narrow MWD ($M_n = 10\,600-14\,300$, $M_w/M_n = 1.04$)[871] was also obtained from palladium-catalyzed living coordination polymerization of ethylene, which was also applied to copper-catalyzed graft copolymerization with *n*BA.

Additionally, dendron-bearing methacrylates (MM-**16**[872] and MM-**17**[873]) are utilized in copper-mediated living radical polymerization, which successfully gave well-controlled dendronized polymers and block copolymers in spite of the bulkiness of the pendants ($M_w/M_n = 1.1-1.3$).

Metal-Catalyzed Living Radical Polymerization for Macromonomers. Another grafting through method is to employ end or center-functionalized polymers (macromonomers) (MM-**18** to MM-**26**) obtained from metal-catalyzed living radical polymerization (Figure 57). Namely, the side chain is derived from metal-catalyzed system, while the main chain is done from other system. In actual, the macromonomers include functional groups, such as norbornene (MM-**18**)[398] and cyclobutene (MM-**19**),[874] applicable to ring-opening metathesis polymerization (ROMP), diene (MM-**20**)[875] to acyclic diene metathesis polymerization (ADMET), acetylene (MM-**21**,[876] MM-**22**,**23**,[877] MM-**24**,[878] MM-**25**[879]) to rhodium-catalyzed polymerization, and thiophene (MM-**26**)[880] to electrochemical polymerization. Typically, acetylene-end-functionalized polymers (MM-**21** to MM-**25**) are synthesized by copper-catalyzed living radical polymerization of styrene or MMA in conjunction with an alkyne-functionalized initiator such as FI-**30** (for MM-**21**). They efficiently work as macromonomers in rhodium-catalyzed living polymerization to give well-controlled cylindrical polymer brushes consisting of a highly cis−transoidal poly(phenylacetylene) main chain and either polystyrene or poly(MMA) side chain ($M_w/M_n \approx 1.1$).[877] Polymerization of chirality-containing MM-**24**[878] and MM-**25**[879] predominantly provides one-handed helical structures onto the obtained graft copolymers.

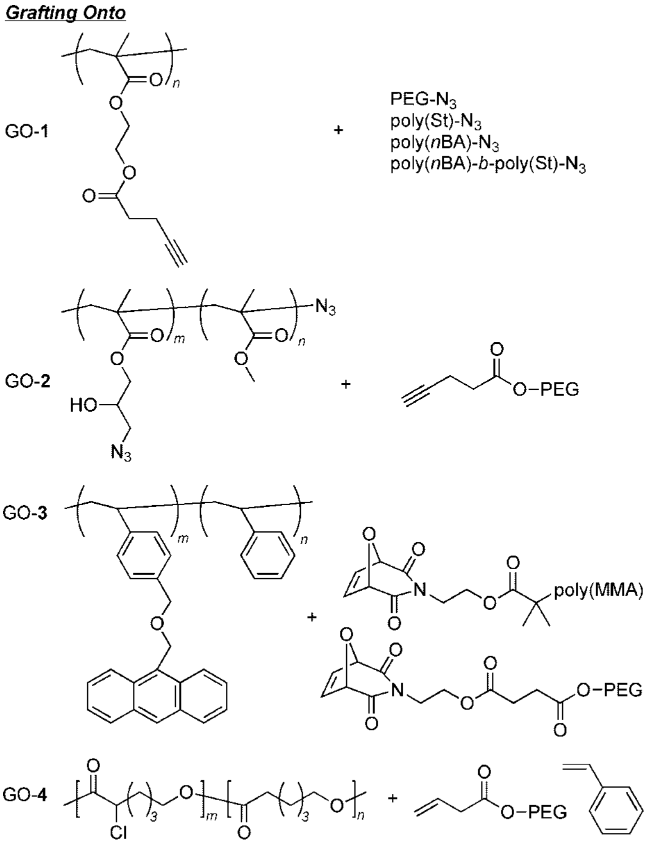


Figure 58. Graft copolymers via grafting onto method.

3.9.3. Grafting Onto

Several grafting onto methods (GO-**1** to GO-**4**) are employed for the synthesis of graft copolymers in metal-catalyzed living radical polymerization (Figure 58). Here, end-functionalized linear polymers are introduced as side chains onto a linear polymer backbone. For this, the following efficient polymer reactions are selected: copper-catalyzed cycloaddition of azide and alkyne[302,303] (GO-**1**,[881] GO-**2**[882]), Diels−Alder reaction (GO-**3**),[883] and copper-catalyzed atom transfer radical addition (ATRA) (GO-**4**).[884] Typically, GO-**1**[881] is obtained from copper-catalyzed cycloaddition of multifunctional alkyne-pendant polymers (main chain) and various azide end-functionalized polymers (side chain) in relatively high coupling yield (62−88%). Here, the alkyne-pendant polymer is obtained from esterification of poly(HEMA: FM-**1**) and pentynoic acid. The side chains include azide-end functionalized polystyrene, poly(*n*-BA), poly(*n*BA)-*b*-polystyrene, and poly(ethylene glycol) (PEG). Combination of a multifunctional azide-pendant polymer and an alkyn end-functionalized polymer (GO-**2**)[882] is also effective for graft copolymers.

Diels−Alder reaction between an anthryl pendant-functionalized polystyrene and a maleimide end-functionalized poly(MMA) or PEG efficiently and almost quantitatively produce graft copolymers (GO-**3**).[883] Here, the protected maleimide-end polymers are in situ deprotected into maleimide counterparts via retro Diels−Alder reaction, subsequently followed by the Diels−Alder reaction with the pendant anthryl groups. Copper-catalyzed atom transfer radical addition of activated chlorine-bearing poly(ε-caprolactone) (main chain) and vinyl-terminal PEG (side chain) is also applied to graft copolymer (GO-**4**).[884] The remaining chlorines on the main chain further efficiently initiate copper-catalyzed living radical polymerization of styrene, to yield hetrograft copolymers carrying a poly(ε-caprolactone) backbone and PEG and polystyrene side chains.

3.10. Hyperbranched and Dendritic Polymers

Hyperbranched polymers[255] are one class among branched macromolecules, such as star polymers, graft polymers, and dendrimers. Hyperbranched polymers have a certain statistical distribution in the molecular weight and structure as well as star, graft polymers, in contrast to dendrimers, while they are easily obtained from metal-catalyzed living radical polymerization. The synthetic pathway now includes the following two ways: (1) (co)polymerization of inimers that carry an initiating group with a vinyl group and (2) (co)polymerization of divinyl compounds. The former is, so-called, self-condensing vinyl polymerization.[885] The latter, a novel strategy recently reported, requires optimizing the reaction condition to prevent macroscopic gelation.

In contrast to conventional hyperbranched polymers with broad MWDs, well-defined dendritic polymers, another kind of hyperbranched polymers with a precision hierarchical branching structure, are also synthesized by the iterative divergent approach combined with metal-catalyzed living radical polymerization and efficient terminal transformation including irreversible terminator multifunctional initiator (TERMINI) and thio-bromo click chemistry.

3.10.1. Inimers

Figure 59 shows inimers (IM-**1** to IM-**7**) consisting of acrylates, methacrylates, styrenes, and a maleimide for hyperbranched polymers. Typically, 2-(2-bromopropionyloxy)ethyl acrylate (IM-**1**) and 4-(2-bromopropionyloxy)butyl acrylate (IM-**2**) are employed for copper-catalyzed self-condensing vinyl polymerization.[886] The polymerization rate of IM-**1** was faster than that of IM-**2** because of the longer spacer segment. The solvent is important to control the polymerization rate and the degree of branching, because it strongly affects the solubility, viz. concentration, of slightly generating high oxidation state Cu(II) species in polymerization solution. Aqueous emulsion copper-catalyzed self-condensing vinyl polymerization is also effective for IM-**1**.[887]

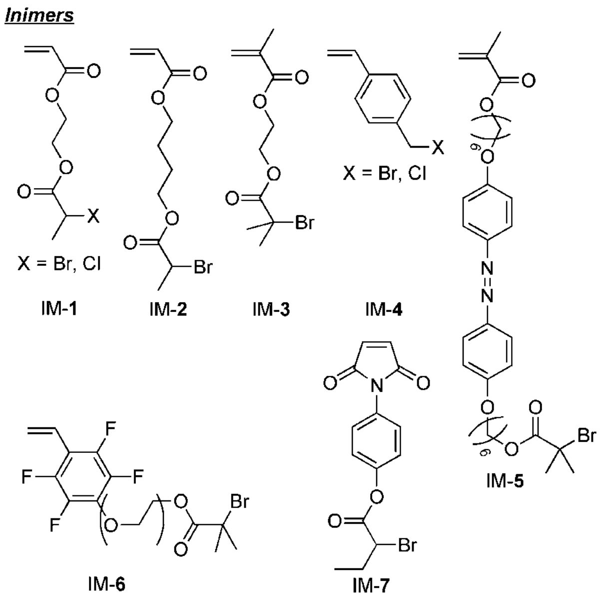


Figure 59. Inimers for hyperbranched polymers.

Hyperbranched acrylate copolymers are prepared by copper-catalyzed self-condensing vinyl copolymerization of an inimer (IM-**1**) and methyl acrylate (MA).[888] Independent of the comonomer ratio ([IM-**1**]/[MA] = 1:95−1:1), the molecular weight gradually increased with increasing their monomer conversion and the MWD was also relatively narrow (M_w/M_n = 1.3−1.7) below a certain monomer conversion (~50%), in sharp contrast to the homopolymerization of IM-**1**. Over the critical conversion, the molecular weight dramatically increased and the MWDs also became quite broader (even bimodal) ($M_w/M_n > 3.0$) because of the intermolecular coupling reactions between the polymer chain radicals and the polymer-bound vinyl groups.

In the presence of tetrafunctional bromoester initiator, an inimer (IM-**1**) is polymerized with a copper catalyst.[889−891] Because of the higher initiation of the tetrafunctional initiator than that of IM-**1**, the tetrafunctional bromoester first predominantly initiate polymerization of IM-**1**, gradually followed by the initiation from the IM-**1** polymers and IM-**1**, resulting in hyperbranched polymers with relatively narrow MWDs (M_w/M_n = 1.5−2.0).[889,890] The same strategy is also quite effective for hyperbranched copolymers of IM-**1** and MA with a copper catalyst.[891] The molecular weight of the polymers increased with increasing the monomer conversions. The MWDs became narrower as the feed ratio of total monomers ([MA] + [IM-**1**]) to the tetrafunctional initiator increased (M_w/M_n = 1.2−1.9). Additionally, the degree of branching increased with increasing the feed ratio of the inimer to MA ([IM-**1**]/[MA]).

Functionalization of hyperbranched copolymers is achieved with copolymerization of inimers and functional or protected monomers. Typically, hyperbranched poly(acrylic acid)s are synthesized by copper-catalyzed copolymerization of IM-**1** and *t*BA, followed by hydrolysis of *tert*-butyl groups,[892] which in turn means efficient synthetic pathway of branched polyelectrolytes. The products are fully characterized in terms of the molecular weight, hydrodynamic radius, solubility, and viscosity. For example, the precursor hyperbranched poly(*t*BA)s exhibited smaller viscosity than the linear counterparts because of the compact, globular structure. The water solubility and the size (hydrodynamic radius) of the hyperbranched poly(acrylic acid)s are dependent on the degree of branching and the solution pH. Amino groups is also introduced into hyperbranched copolymers with methacrylate inimer (IM-**3**) and DMAEMA (FM-**4**),[893] followed by the quaternization with methyl iodide for highly branched cationic polyelectrolytes. Additionally, hyperbranched glycopolymers were obtained with inimers and protected glyco-pendant monomers in the presence of copper- or nickel catalysts (IM-**1**/FM-**58**[335,894] or IM-**3**/FM-**57**[895]), where the deprotection (hydrolysis) was also successful.[335,895] Incorporation of azobenzene groups into hyperbranched polymers was also achieved with IM-**3** and an azobenzene-functionalized monomer (FM-**81**)[896] or an azobenzene-functionalized inimer (IM-**5**) alone.[897]

p-Chloro(bromo)methylstyrene (IM-**4**) is a styrene-based inimer frequently employed for hyperbranched (co)polymers via metal-catalyzed self-condensing vinyl polymerization. Some of hyperbranched fluoro(co)polymers are obtained from IM-**4**[898−900] or IM-**6**.[901] Combination of IM-**4** and chlorotrifluoroethylene (CTFE)[898] uniquely gave a hyperbranched alternating fluorocopolymer (yield = 83%, $M_w/M_n = 2.7$). Herein, since CTFE is an electron-deficient monomer and *p*-chloromethylstyrene (IM-**4**) is an electron-rich monomer, they essentially formed a charge transfer complex to act as one polymerizable monomer during the copolymerization, which spontaneously results in the alternating monomer sequence. 2,3,4,5,6-Pentafluorostyrene (FM-**48**)[899,900] is also efficiently copolymerized with IM-**4** in the presence of a copper catalyst to give a hyperbranched fluorocopolymer with high solubility in wide variety of organic solvent. The fluorocopolymer is a macroinitiator effective for block copolymerization of a polydimethylsiloxane (PDMS)-bearing macromonomer (MM-**6**).[900] Additionally, copper-catalyzed copolymerization of IM-**4**, FM-**48**, and a polydimethylsiloxane (PDMS)-bearing macromonomer (MM-**6**) successfully led to, in one-pot, a hyperbranched fluorocopolymer carrying PDMS graft chains.[900] An oligo(ethylene glycol)-functionalized fluorinated inimer (IM-**6**) with a copper catalyst directly affords amphiphilic hyperbranched fluoropolymers and fluorocopolymers.[901] Copper-catalyzed self-condensing vinyl copolymerization was further extended to maleimide-based inimer (IM-**7**) and styrene.[902]

3.10.2. Divinyl Compounds

(Co)polymerization of divinyl compounds including ethylene glycol dimethacrylate (L-**1**)[903,904] and divinyl benzene (L-**6**)[903] are useful for the synthesis of hyperbranched polymers. However, to prevent macroscopic gelation, optimization of reaction condition is essential. Typically, homopolymerization of L-**1** or L-**6** with a copper catalyst was examined to prepare soluble hyperbranched polymers with lots of vinyl functionalities.[903] The key for the efficient synthesis is to couple a suitable amount of a higher oxidation state copper catalyst [Cu(II), $CuCl_2$] into a normal copper one [Cu(I), CuCl] ($[CuCl]/[CuCl_2] \approx 3/1$). The added $CuCl_2$ enhances the deactivation of the dormant-active equilibrium to prevent gelation until about 60% conversion of the divinyl compounds, leading to well-soluble hyperbranched polymers of L-**1** or L-**6** with lots of pendant vinyl groups. The molecular weight of their polymers increased with increasing the conversion, and the MWDs were also gradually getting broad (products of L-**6**, $M_w = 3800-275\,000$, $M_w/M_n = 1.3-6.0$, SEC-MALLS).

Copper-catalyzed polymerization of MMA in the presence of L-**1** is also effective for hyperbranched copolymers.[904] The feed ratio of a diviny compound (L-**1**) to a initiator and L-**1** to MMA is quite important to obtain soluble branched poly(MMA)s and their optimized ratio is the followings: [initiator]/[L-**1**] = 1/1, [MMA]/[L-**1**] = 20/1−5/1.

3.10.3. Iterative Divergent Approach

Though hyperbranched polymers are easily obtained from inimers or divinyl compounds, they normally have broad MWDs and no precise, homogeneous structure because of the statistical distribution of the branching points and numbers on the each molecule. In contrast, iterative combination of irreversible terminator multifunctional initiator (TERMINI) and metal-catalyzed living radical polymerization efficiently affords precision control of branching points and lengths to induce divergent synthesis of well-defined dendritic polymers with narrow MWDs up to forth generation ($M_w/M_n < 1.2$).[905] The TERMINI consists of one silyl enol ether for quantitative end-capping reaction[375,376] and two thiocarbamate for precursor of initiators. Quite recently, another efficient methodology was also reported in iterative divergent synthesis of dendritic polymers.[906,907] Here, base-mediated thioetherification of thioglycerol with α-bromoesters, nucleophilic thio-bromo "click" reaction,[906] was employed for end-bromine transformation and introduction of precision branching and iterative initiating points in SET-LRP of MA with a tetrafunctional initiator (MI-**8**). The resultant hydroxyl terminals were subsequently esterified with 2-bromopropionyl bromide into bromoester initiators, which successfully afforded SET-LRP of MA for next generation to give dendritic macromolecules.

3.11. Advanced Designer Materials

Metal-catalyzed living radical polymerization has been dramatically advanced after 2001 and now especially employed as a powerful tool for precision polymer synthesis because of the high controllability and tolerance to polar functional groups. Noted that the initiating groups of this polymerization can be efficiently, selectively, and conveniently introduced into desired sites of materials in comparison to those of the other precisely controlled polymerization. These features have promoted the conjugation of metal-catalyzed living radical polymerization and the other research area beyond their boundaries. The typical examples are protein−polymer conjugation[13,14] and surface-graft copolymers.[15,254,256−259]

3.11.1. Protein-Conjugated Polymers

Protein−polymer conjugation is now applied to wide variety of research area such as medicine, nanotechnology, bioengineering and so on. The strategy is simply the following two ways: (1) postpolymer reaction between end-functionalized polymers and proteins and (2) living radical polymerization with protein-bearing initiators.

The former is represented as a kind of grafting onto method, and the latter is, in turn, done as a kind of grafting from method. Thus, the key to efficiently achieve the former method is to precisely prepare end-functionalized polymers via metal-catalyzed living radical polymerization and to select efficient, selective postpolymer reactions on to a protein. Typically conjugating proteins include lysozyme,[412,426] bovine serum albumin (BSA),[285,423,428,429,435] and streptavidine.[332,431,432] A primary-amine-bearing lysozyme is attached with an aldehyde end-functionalized poly(PEGMA: FM-**14**; $n = 23$)[412] or *N*-succinimidyl ester-functionalized poly(FM-**14**).[426] BSA is grafted onto the polymers by using the thiols[285,428,429,435] or primary amines.[423] Especially, ene-thiol reactions between BSA and maleimide end-functionalized polymers are effective for BSA conjugation.[285,428,429,435] Biotin end-functionalized polymers, obtained from FI-**57** or **58**, are in turn efficiently connected onto streptavidine.[332,431,432] Herein, the success of the protein conjugation is efficiently characterized by sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE) in addition to the usual characterization with size exclusion chromatography (SEC), NMR, and so, on. Though the former method with postpolymer reaction is actually effective for protein conjugation, the purification of the products is often complicated because of the removal of excess or unreacted polymers.

To overcome these problems, the latter method with a protein-bearing initiator has been also developed. The purification of the products from residual monomers would be clearly easier than that of the former one from unreacted, excess polymers. However, it naturally requires aqueous, robust polymerization at ambient temperature to maintain the structure and activity of proteins. Among them, copper-catalyzed aqueous polymerization of water-soluble monomers at ambient temperature is excellently suitable. The protein-carrying macroinitiators typically consist of the following proteins: streptavidine,[433] bovine serum albumin (BSA),[908,909,436] lysozyme,[436,908] chymotrypsin,[910] and horse spleen apoferritin.[911] As already described, streptavidine, coupled with four biotin-functionalized initiators (FI-**58**), selectively give four bromine-functionalized streptavidine initiator.[432] In the presence of a sacrificial initiator of a bromoisobutyrate-modified Wang resin with facile removability, the streptavidine-bearing initiator efficiently induces copper-catalyzed aqueous polymerization of NIPAM (FM-**12**) at room temperature to directly produce a streptavidine-poly(NIPAM) conjugate ($M_n = 27\,000$, $M_w/M_n \approx 1.7$). BSA-based macroinitiators are also efficiently obtained from ene-thiol reaction between BSA and maleimide-functionalized initiators[908,909] or intermolecular thiol-disulfide interchange reaction between BSA and FI-**59**.[436] They are effective for aqueous polymerization of PEGMA (FM-**14**),[908] styrene,[909] and NIPAM (FM-**12**).[436] From these results, wide variety of proteins, natural polymers, can be now combined with artificial designer polymers from metal-catalyzed living radical polymerization, contributing to the creation of novel protein-hybrid materials.

3.11.2. Surface-Graft Polymers

In general, surface-graft polymers mean solid materials whose surfaces are modified with polymers. Metal-catalyzed living radical polymerization is quite effective for the solid surface functionalization due to the efficient and convenient introduction of the initiating groups into various solid surfaces and the high versatility of applicable monomers, as well as protein−polymer conjugation. Though nucleus substrates employed for the surface modification were limited in silicon, gold, and polystyrene latex before 2001, they now include various inorganic materials based on silicon, metal, and carbon allotrope, and organic counterparts of polymeric particles, films, and fibers. Actually, articles reported in terms of surface-graft polymers between 2001 and 2008 dramatically increased in comparison to those before 2001. Since the detail results and applications of surface-graft polymers and polymer brushes have been already reviewed in several articles,[15,254,256−259] this section deals with the overviews of their surface-modified polymers, especially focused on the controlling techniques of the surface-initiated polymerization for high density brushes and the variation of surface-initiated substrates.

Silicon. Polymer brushes, surface-graft polymers carrying high-density polymer chains, can be prepared by metal-catalyzed living radical polymerization from the initiator-implanted solid surfaces, that is, a kind of grafting from method. The surface-initiated living radical polymerization can efficiently control the thickness and the density of brush polymers. Among them, silicon-based substrates are one of the most typical surface-functionalized solid initiators for high-density polymer brushes, including silicon wafers,[912−922] silica particles,[923−931] and silica column,[932] which are also quite attractive as organic/inorganic hybrid materials.[15] Importantly, the controlled polymerization with the solid surface initiators requires the following inventions: addition of a free initiator (sacrificial initiator)[912] or a high oxidation state catalyst (deactivator), for example, $CuBr_2$,[914] otherwise the surface-initiated polymerization is never controlled due to the insufficient initiating groups. The both inventions enhance concentrations of high oxidation state catalyst (deactivator) enough to contribute the high controllability.

These techniques were first developed for silicon wafer initiators.[912−922] The former technique with a free initiator gives naturally free polymers in addition to the surface-graft polymers.[912] Though the extra polymers, at a sight, seem to be bothersome side products, they fortunately facilitate the characterization of the surface-graft polymers. Since the molecular weights and molecular weight distributions of the surface-generating polymers are almost close to those of the free polymers,[258] the characterization of the surface-grafting polymers is thereby achieved by that of the free counterparts. The latter coupled with an appropriate amount of a high oxidation catalyst, in turn, directly produce surface-graft polymers alone, apart from an additional process to remove free polymers.[914] As quite recently reported, ARGET system with $CuCl_2$, tin(II) 2-ethylhexanoate, and a free initiator was also effective for the surface-initiated polymerization of *n*BA even in the presence of a small amount of air.[915] This would be correspondent to a kind of synergetic system combined with the former and the latter, and the efficiency and convenience further enhance the availability.

The thickness of the surface modification is direct proportion to the degree of polymerization. The surface polymer brushes are implanted on a silicon wafer in quite high graft density ranging from about 0.5 to about 0.8 chains nm^{-2} and uniquely result in stretching structure, in sharp contrast to those obtained from conventional free radical polymerization, forming mushroom or semidiluted brush structure.[255] Various functional polymers,[916−918] block copolymers,[919,920] and even hyperbranched polymers[921,922] can be introduced on to the silicon wafers. The high density of grafting chains additionally contributes to the unique, applicable physical properties.[258]

As well as silicon wafers, polymer-coated silica particles can be efficiently obtained from surface-initiated living radical polymerization with silica particles (SiO_2).[923−931] For example, the surface-grafting polymerization of MMA from a SiO_2 initiator is well controlled in the presence of a copper catalyst and a free initiator ($M_w/M_n \approx 1.2$).[926] The molecular weight and the MWDs are quite close to those of the generating free poly(MMA)s and the grafting density is also high (0.6−0.7 chains nm^{-2}), close to that on silicon wafers. Aqueous surface-initiated polymerization of functional monomers (FM-**1**, FM-**2**, FM-**7**, FM-**14**) succeeds in the facile surface functionalization of silica particles.[929] Thermoresponsible properties were further adopted onto the surface-grafting silica particles in conjunction with thermosensitive monomers (NIPAM, FM-**12**; PEGMA, FM-**14**).[930,931]

Metal. Metal surfaces can be utilized as initiating points in metal-catalyzed surface-graft polymerization for the surface modification. The metallic substrates are categorized into the followings: metal-coated or metal wafers,[933−940] metal nano particles,[941−950] and metal nanowires.[951] Nowadays, there are wide variety of metal species that initiating points are successfully introduced. Typically, the flat wafers contain gold[933−935] or titanium[936,937]-coated silicon wafers, titanium foil,[938] iron[939] or germanium[940] wafers. Additionally, metal nanoparticles are based on gold,[941−944] CdS quantum dots,[945] TiO_2,[946] ZnO,[947] $Mg(OH)_2$,[948] zeolite,[949] including titanium, zirconium, and vanadium oxo clusters.[950]

Among them, polymer-brush coated gold nanoparticles are one of the most researched materials.[941−944] The gold (Au) nanoparticle-based initiators can be synthesized by aqueous reduction of $HAuCl_4/4H_2O$ with $NaBH_4$ in the presence of a disulfide-bearing bifunctional initiator.[941] The size of the Au-nanoparticle initiator ranged from 0.8 to 7 nm, averaging about 2.7 nm. The surface-initiated polymerization of MMA efficiently proceeds in the conjunction with a copper catalyst and a free initiator, leading to the high controllability and relatively high grafting density [grafting poly(MMA), $M_w/M_n \approx 1.2$; 0.25 chains nm^{-2}],[941] as well as those with the silicon wafer or silica nanoparticle-based initiators.[926,258] The PMMA-grafted gold nanoparticles, cast on a carbon-coated copper microgrid, can be directly observed by TEM, where the particles are uniformly dispersed without any aggregation because of the high-density PMMA hairs.

Carbon. Carbon allotrope materials are efficiently functionalized by surface-initiated living radical polymerization, as well as living cationic polymerization and free radical polymerization.[952] The substrates include carbon black (nano particle),[953,954] nano diamond particle,[955] carbon fiber,[956] and single- or multiwalled carbon nanotubes (SWNTs or MWNTs).[957−961] Among them, carbon nanotubes are often employed as a modification substrate. For example, their nanotube (NT)-based initiators are prepared by the following steps:[957−961] (1) treatment of a NT with HNO_3 for a carboxylic acid-functionalized NT, (2) treatment with $SOCl_2$, followed by the esterification with ethylene glycol, giving hydroxyl group-bearing NT, and (3) esterification with an acyl bromide for bromoester initiator-bearing NT. Bromoester-functionalized NTs, in the presence of a free initiator, successfully initiate copper-catalyzed living radical polymerization of *n*BA,[957] styrene,[958,959] a hydroxyl group-functionalized monomer (FM-**2**),[960] and a sugar-pendant monomer (FM-**57**).[961]

Organic Polymer Particles, Films, and Fibers. In addition to inorganic materials such as silicon, metal, and carbon allotrope, organic polymer particles, films, and fibers can be now modified by surface-initiated living radical polymerization with a copper catalyst toward creation of novel surface-functionalized materials. The substrates are extended to wide variety of polymeric compounds, as shown in the following examples: (1) organic polymer particles polydivinylbenzene,[962] divinylbenzene cross-linked polystyrene latex,[963] polystyrene latex,[964] Wang resin,[965] Merrifield resin,[966] and chitosan;[967] (2) films nylon,[968] poly(ethylene terephthalate),[969] polyimide,[970] polytetrafluoroethylene,[971] poly(vinylidene fluoride),[972] poly(vinyl chloride),[973] and isotactic polypropylene;[974] (3) fibers cellulose of filter paper.[851,975] Conveniently, the poly(vinylidene fluoride) and poly(vinyl chloride) films can directly initiate copper-catalyzed living radical polymerization without any extra introduction of initiating moieties. Thanks to the versatility of applicable monomers and solid surface substrates, metal-catalyzed system tremendously contributes new vistas to synthesis of surface-modified materials with unique functions.

4. Abbreviations

ADMET	acyclic diene metathesis polymerization
AGET	activator generated by electron transfer
AIBN	azobisisobutyronitrile
AN	acrylonitrile
ARGET	activator regenerated by electron transfer
ATRC	atom transfer radical coupling
ATRP	atom transfer radical polymerization
Boc	*tert*-butoxy carbonyl
BPMPrA	bis(2-pyridiylmethyl)propylamine
bpy	2,2′-bipyridine
BSA	bovine serum albumin
BzMA	benzyl methacrylate
Cp*	pentamethylcyclopentadiene
CV	cyclic voltammetry
DEPT	distortionless enhancement by polarization transfer
DETA	diethylenetriamine
DMA	*N*,*N*-dimethylacrylamide
DMAEMA	2-(*N*,*N*-dimethylamino)ethyl methacrylate
DMCBCy	4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]-hexadecane
dNbpy	4,4′-di-(5-nonyl)-2,2′-bipyridine
DSC	differential scanning calorimetry
εCL	ε-caprolactone
Fmoc	9-fluorenylmethylchloroformate
HEMA	2-hydroxyethyl methacrylate
HMTETA	*N*,*N*,*N*′,*N*″,*N*‴,*N*‴-hexamethyltriethylenetetramine
HPLC	high-performance liquid chromatography
ICAR	initiators for continuous activator regeneration
LA	lactide
LCST	lower critical solution temperature
MA	methyl acrylate
MADIX	macromolecular design via the interchange of xanthates
MALDI-TOF-MS	matrix-assisted laser desorption/ionization time-of-flight mass spectrometry
Me_4CYCLAM	tetramethylated 1,4,8,11-tetraazacyclotetradecane
Me_6TREN	tris(2-(dimethylamino)ethyl)amine
MMA	methyl methacrylate
M_n	number-average molecular weight
M_w	weight-average molecular weight
MWD	molecular weight distribution
*n*BA	*n*-butyl acrylate
*n*BMA	*n*-buthyl methacrylate
NCA	*N*-carboxyanhydride
NHC	*n*-heterocyclic carbene
NIPAM	*N*-isopropylacrylamide
NMP	nitroxide-mediated polymerization
NMR	nuclear magnetic resonance
NOPMI	*N*-(*n*-octyl)pyridylmethanimine
NPPMI	*N*-(*n*-propyl)pyridylmethanimine
ODMA	octadecyl methacrylate
PDMS	polydimethylsiloxane

PEG	poly(ethylene glycol)
PEGMA	poly(ethylene glycol) methyl ether methacrylate
phen	1,10-phenanthroline
PMDETA	*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine
PPO	poly(propylene oxide)
θ	cone angle
QTRP	quinone transfer radical polymerization
RAFT	reversible addition−fragmentation chain transfer
ROAP	ring-opening anionic polymerization
ROCP	ring-opening cationic polymerization
ROP	ring-opening polymerization
SEC	size exclusion chromatography
SEC-MALLS	SEC-multiangle laser light scattering
SET-DTLRP	single-electron transfer degenerative chain transfer living radical polymerization
SET-LRP	single-electron transfer living radical polymerization
SR&NI ATRP	simultaneous reverse and normally initiated ATRP
St	styrene
*t*BA	*tert*-butyl acrylate
*t*BMA	*tert*-buthyl methacrylate
TEMPO	2,2,6,6-tetramethylpiperidinyl-1-oxy
TERMINI	terminator multifunctional initiator
TERP	organotellurium-mediated radical polymerization
TMS	trimehtylsilyl
tNtpy	4,4′,4″-tris(5-nonyl)-2,2′:6′,2″-terpyridine
TPEN	tris(2-aminoethyl)amine
TPMA	tris(2-pyridiylmethyl)amine
tpy	2,2′:6′,2″-terpyridine
TREN	tris(2-aminoethyl)amine
UCST	upper critical solution temperature
VAc	vinyl acetate
VC	vinyl chloride
4VP	4-vinyl pyridine

5. References

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