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Metal-Catalyzed Living Radical Polymerization

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A. Background: Precision and Living Polymerization

Rivaling polyolefin production, radical polymerization is most widely employed in industrial- and

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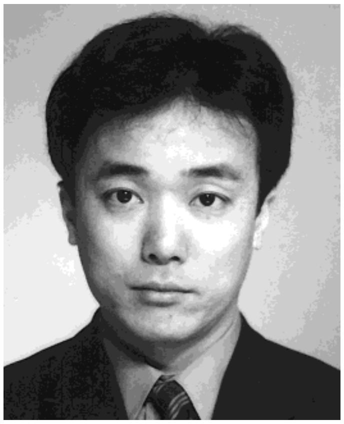
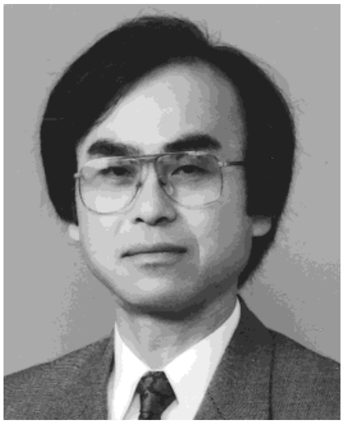


Masami Kamigaito was born in 1965 in Nagoya, Japan. He received his B.S. and M.S. degrees and Ph.D. degree in polymer chemistry from Kyoto University in 1993 under the direction of Professor Toshinobu Higashimura. After postdoctoral research with Professor Mitsuo Sawamoto, he joined the faculty at Kyoto University in 1995, where he is now Associate Professor of Polymer Chemistry. In 1997–1998, he was a visiting scientist under Professor Robert M. Waymouth at Stanford University. He is the recipient of the 1999 Award for the Encouragement of Research in Polymer Science of the Society of Polymer Science, Japan, and the 2001 Arthur K. Doolittle Award of the ACS PMSE Division. His research interests include metal catalysis for precision polymer synthesis, particularly living cationic and radical polymerization.

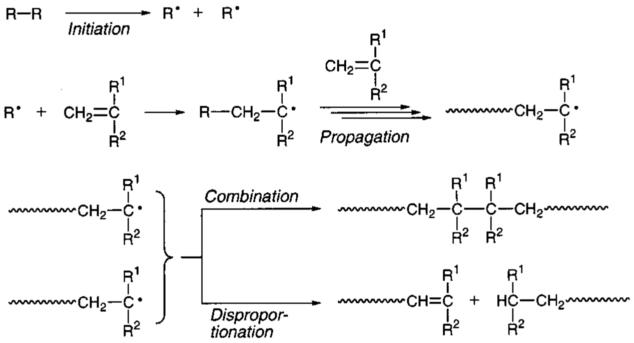
Tsuyoshi Ando received his bachelor degree in 1995, master degree in 1997, and Ph.D. degree in 2000 from Kyoto University. His doctoral study was on the development of transition-metal-catalyzed living radical polymerization systems under the direction of Professor Mitsuo Sawamoto, where he received a Research Fellowship for Young Scientists of the Japan Society for the Promotion of Scientists (1998–2000). He joined the Kyoto University faculty, Department of Polymer Chemistry, Faculty of Engineering, as a research instructor in 2000. His research activity is focused on controlled reactions, including precision polymerization, catalyzed by metal compounds.



Mitsuo Sawamoto, born in Kyoto, Japan (1951), received his B.S. (1974), M.S. (1976), and Ph.D. (1979) degrees in polymer chemistry from Kyoto University under the direction of Toshinobu Higashimura. After postdoctoral research with Joseph P. Kennedy at the Institute of Polymer Science, The University of Akron, Akron, OH (1980–81), he joined the faculty of the Department of Polymer Chemistry, Kyoto University, in 1981 as a research instructor. He was promoted to Lecturer (1991), to Associate Professor (1993), and to Professor (1994), his current position, of the same department. Sawamoto also serves as one of the three Editors of the *Journal of Polymer Science, Part A: Polymer Chemistry* (1995–present) and as an Editorial Advisory Board member of *Macromolecular Chemistry and Physics*, the *Journal of Macromolecular Science, Chemistry*, and *e-Polymers*, and is the recipient of the 1991 Award of the Society of Polymer Science, Japan, the 1998 Divisional Award of the Chemical Society of Japan, the 2001 Aggarval Lectureship in Polymer Science, Cornell University, and the 2001 Arthur K. Doolittle Award of the ACS PMSE Division. With more than 250 articles and reviews, his research interest covers living radical and cationic polymerizations, precision polymer synthesis, and the chemistry of radical and carbocationic reaction intermediates.

laboratory-scale processes for polymer synthesis, because of its tolerance to protic compounds such as water, a high reaction rate, a polymerization temperature usually higher than ambient, and other advantages.[1] Unlike ionic reaction intermediates, however, the growing radical species therein usually suffers from bimolecular termination reactions such as radical recombination and disproportionation (Scheme 1). Radical polymerization had thus been considered unsuitable for precision polymer synthesis, in contrast to the ionic counterparts where the growing species are inherently repulsive to each other.

Scheme 1. Elementary Reactions for Conventional Radical Polymerization



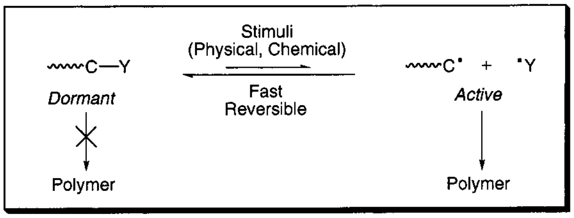
One of the most effective methods for precision polymer synthesis is “living” polymerization, the first example of which was discovered in the anionic polymerization of styrene with sodium naphthalenide in 1956.[2] Living polymerization is free from side reactions such as termination and chain transfer and can thus generate polymers of well-defined architectures and molecular weights, i.e., one polymer chain per molecule of initiator. When the initiation is faster than, or at least comparable in rate to, propagation, the obtained polymers have narrow molecular weight distributions (MWDs) where the ratio of weight-average to number-average molecular weight (M_w/M_n) is around 1.1. In general, however, living anionic polymerization was limited to nonpolar hydrocarbon monomers such as styrenes and 1,3-dienes at first, but has now been developed to polar monomers such as (meth)acrylates and other functional derivatives.[3–6] Similar proliferation has recently occurred in other polymerizations, including cationic,[7–9] coordination,[10] ring-opening,[11] and ring-opening metathesis,[12] for which precise reaction control had been considered difficult for some time. In this regard, living radical polymerization has been among the most challenging frontiers in precision polymer synthesis and polymer chemistry.

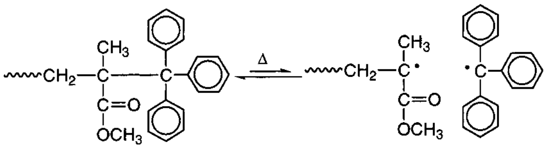
B. Living Radical Polymerization

Given this rapid progress in precision polymerization, living radical polymerization had been one of the most difficult subjects. The difficulty primarily stems from the inherent and "built-in" bimolecular termination of the growing radicals, and the prevailing consensus was (or still is) that it might not be suppressed, though not impossible. Starting with the pioneering works by Otsu et al. in the 1980s,[13,14] however, the number of studies on living radical polymerizations started to mushroom, especially in the 1990s. There are now numerous systems and proposed methodologies for controlling radical polymerizations, even in comparison to some of the "classical" anionic living polymerizations. Typical examples of these systems are summarized in eqs 1−9.

At first glance, the examples vary clearly in mechanism or in chemicals to be employed, but importantly, the concept or the strategy for controlling radical polymerization appears to be common, namely, to lower the (instantaneous) concentration of a growing radical species by introducing a covalent dormant species that exists predominantly over, and in fast equilibrium with, the growth-active radical species. Such a dynamic and rapid equilibrium not only minimizes the extent or probability of the radical bimolecular termination but also gives an equal opportunity of propagation to all polymer (or dormant) terminals via the frequent interconversion between the active and the dormant species. These features thus lead to nearly uniform chain length (molecular weight) determined by the molar ratio of monomers to the dormant species (or the initiator). Another factor for consideration is the so-called "persistent radical",[15] a relatively stable radical that does not react with its own kind but does combine with the growing end. Its importance has been pointed out to be necessary for the control, as reviewed by Fischer in this issue.

The covalent bonds for dormant species include C−C (eq 1),[16,17] C−S (eqs 2 and 9),[13,14,18] C−Se (eq 3),[19] C−O (eqs 4 and 5),[20–25] C−halogen (eqs 6 and 8),[26–28] and C−metal (eq 7),[29] all of which can reversibly and homolytically be activated into the growing radical species by physical stimuli such as heat or light or by chemical stimuli such as a metal catalyst or another radical species. Although the controllability, applicability, and reaction conditions depend on which systems are employed, a wide variety of vinyl monomers such as styrenes, methacrylates, acrylates, dienes, and vinyl acetate can be polymerized in a controlled fashion with the use of these or similar systems. Among these, nitroxide-mediated (eq 4)[20–24] and metal-catalyzed[27,28] systems (eq 6) have most extensively been studied, probably due to the high controllability, the wide applicability, and the relatively easy access to the catalysts and other components to be employed.





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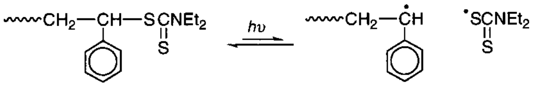

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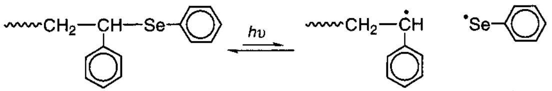

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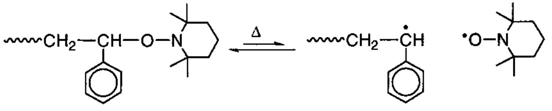

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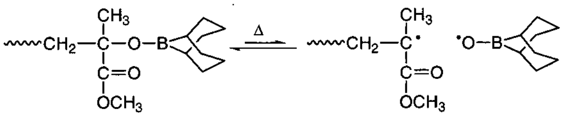

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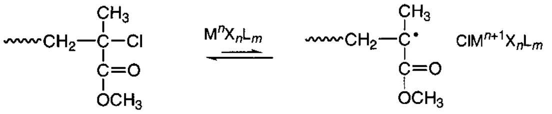

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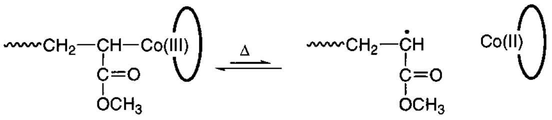

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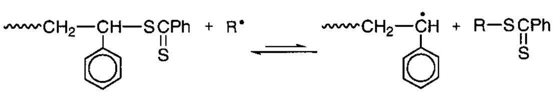


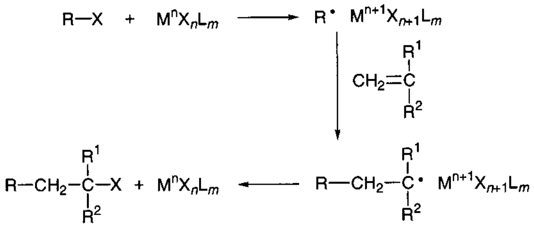
(9)

This review primarily covers the metal-catalyzed living radical polymerizations. As will be discussed, their advantages include dual control of the growing end by the terminal halogen and the metal complex, relatively low temperatures needed (60−100 °C), and commercially available compounds used; among others, the nitroxide-mediated living radical polymerization is reviewed in this issue by Hawker. Another metal-mediated living radical polymerization is based on carbon−metal bonds such as carbon−cobalt (eq 7)[29] and others, which fall outside the scope of this review, because the metals therein do not serve as the catalysts. Some reviews on this topic are available,[30,31] and it is closely related to catalytic chain transfer[32] reviewed by Gridnev and Ittel in a separate paper herein.

C. Overview of Metal-Catalyzed Living Radical Polymerization

Metal-catalyzed living radical polymerization can be traced back to metal-catalyzed radical addition reactions to alkenes, sometimes collectively called Kharasch or atom-transfer radical addition (ATRA) reactions in organic chemistry (Scheme 2).[33] Thus, a radical species generated from an organic halide (R−X, X = halogen) or a related compound in the presence of a metal catalyst attacks an unsaturated compound (e.g., $CH_2{=}CHR'$) to form an adduct ($R{-}CH_2{-}CHR'{-}X$) with a carbon−halogen bond. The metal catalyst thus undergoes a reversible one-electron redox reaction via abstraction of the halogen from the reactant R−X, followed by a one-electron reduction, i.e., release of the halogen now attached to the oxidized metal back to the resulting radical species (R•). The reaction therefore proceeds catalytically and in a chain reaction mechanism, with a high chemo- and regioselectivity, to give the adduct in a high and often quantitative yield, in sharp contrast to other addition reactions via radical intermediates. This is due to the controlled formation of the radical intermediates via metal catalysis, although it is not clear whether free radicals, metal-complexed radicals, or organometallic intermediates are involved. In any case, these features would lead to the following hypothesis: i.e., if the carbon−halogen bond in the adduct is successively activated by the metal complex, a controlled radical polymerization will similarly proceed via the metal-assisted repetitive activation and formation of the carbon−halogen bond (dormant species) at the polymer chain end.

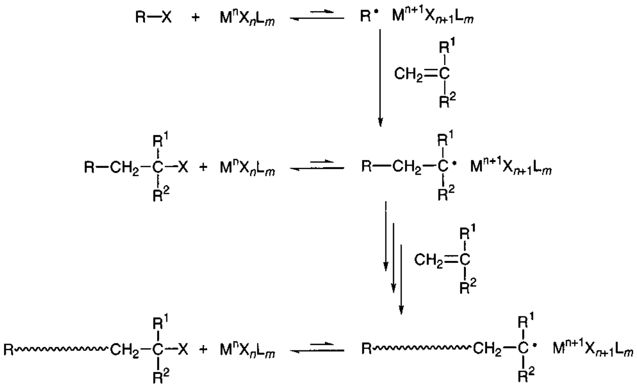
Scheme 2. Metal-Catalyzed Radical Addition Reaction (Kharasch Addition Reaction)



This idea was indeed realized around 1994, which is when we reported the first example, i.e., the living polymerization of methyl methacrylate catalyzed by a ruthenium(II) complex coupled with carbon tetrachloride as the initiator.[27] Shortly after this, an independent report was published for a similar system with styrene and a copper catalyst, which was coined atom-transfer radical polymerization (ATRP) after the predecessor in organic chemistry.[28] In these examples, however reminiscent to classical free radical polymerizations they might be, the number-average molecular weights of the polymers increase in direct proportion to monomer conversion and agree well with the calculated values assuming that one molecule of the halide initiator generates one polymer chain. The molecular weight distributions (MWDs) are as narrow as with the polydispersity (M_w/M_n) below or close to 1.1, comparable to those in living anionic polymerizations.

The metal-catalyzed living radical polymerization thus proceeds (or at least is mostly considered to proceed) via reversible activation of carbon−halogen terminals by the metal complex, where the metal center undergoes redox reactions via interaction with the halogens at the polymer terminal, as shown in Scheme 3. The reaction is usually initiated by the activation (homolytic cleavage) of the carbon−halogen bond in an appropriate organic halide (R−X) via one-electron oxidation of the metal center ($M^nX_nL_m$) to form an initiating radical species (R•) and an oxidized metal compound ($M^{n+1}X_{n+1}L_m$). The R• reacts with the halogen on the oxidized metal to regenerate R−X or adds to the monomer to generate a radial species [$R{-}CH_2{-}C(R^1)(R^2)\bullet$]. It is sooner or later transformed into the adduct [$R{-}CH_2{-}C(R^1)(R^2){-}X$] of R−X and the monomer via abstraction of a halogen atom from $M^{n+1}X_{n+1}L_m$. The carbon−halogen bond of the adduct is subsequently activated by the metal complex, similarly to R−X, to result in a similar carbon−halogen bond at the polymer terminal via a repetitive set of the reactions. The key factors for these reactions are the low concentration of the radical intermediates at a given time and their fast but reversible transformation into the dormant species before undergoing successive addition to monomers.

Scheme 3. Metal-Catalyzed Living Radical Polymerization



In this reaction, one polymer chain forms per molecule of the organic halide (*initiator*), while the metal complex serves as a *catalyst* or as an *activator*, which catalytically activates, or homolytically cleaves, the carbon−halogen terminal. Therefore, the initiating systems for the metal-catalyzed living radical polymerization consist of an initiator and a metal catalyst. The effective metal complexes include various late transition metals such as ruthenium, copper, iron, nickel, etc., while the initiators are haloesters, (haloalkyl)benzenes, sulfonyl halides, etc. (see below). They can control the polymerizations of various monomers including methacrylates, acrylates, styrenes, etc., most of which are radically polymerizable conjugated monomers. More detailed discussion will be found in the following sections of this paper for the scope and criteria of these components (initiators, metal catalysts, monomers, etc.).

The metal-catalyzed living or controlled radical polymerizations can apparently be distinguished from the conventional radical polymerization that involves a metal-assisted formation of the initiating radical species via irreversible redox processes, although the initiating system for the latter also consists of two components, a metal complex and an organic halide.[34,35] In these examples, except for a few,[36,37] the control of molecular weights and MWDs is generally difficult. The use of effective telomers can also make the control of molecular weights better in low molecular weight regions. However, the controllability is much better for the recently developed systems with reversible activation. A few reviews dealing with comparison between the new and the old metal-catalyzed systems are also available.[30,38]

This review covers mainly the scientific literature that has appeared in relevant journals until early 2001 concerning the metal-catalyzed (or atom-transfer) living radical polymerization. The word "living" employed here simply refers to polymerizations that provide control over the molecular weights, the molecular weight distributions, and the chain end reactivity as do other living polymerizations. Its definition and use criteria, along with the word "controlled", are still under discussion and have recently been discussed elsewhere.[39] Thus, the discussion on the difference between these words is not to be treated here.

The review roughly consists of two parts, the scope and design of initiating systems followed by precision polymer synthesis. The former will treat the scope of metal catalysts, initiators, and monomers along with polymerization mechanisms. The latter will focus on the precision synthesis of various polymers with controlled structures and interesting properties or functions, such as block, end-functionalized, star, and other architecturally well-defined polymers. Other reviews are also available, comprehensive,[31,40−44] and relatively short,[45−52] dealing with the recent developments of the field.

II. Design of the Initiating Systems

The initiating systems for the metal-catalyzed living radical polymerizations consist of a metal complex (or catalyst) and an initiator; the former allows the generation of radical species from the latter or the dormant polymer terminal. The choice of the metals and the initiators according to the monomer structures is crucial for controlling radical polymerizations. The rate and control of the polymerization can also be increased by the addition of other compounds or by changing solvents. This first part will deal with the design of the initiating systems from the viewpoint of various components, i.e., metal complex catalysts, initiators, monomers, additives, and solvents, as well as the relevant reaction mechanisms.

A. Transition-Metal Catalysts

One of the most important components in the metal-catalyzed living radical polymerization is the transition-metal complex. As a catalyst, the complex induces reversible activation (homolytic cleavage) of a dormant carbon−halogen bond at a polymer terminal via a one-electron redox reaction of the metal center. In this process, the metal center attacks the halogen at the chain end and is oxidized via a single electron transfer followed by halogen abstraction, thus generating a growing radical species. Sooner or later, the oxidized metal center donates the halogen therein back to the radical growing species, along with reduction of the metal center, before or after the propagation reaction between the radical and monomer. The lower oxidation state of the metal center [e.g., Ru(II)] should be more stable than its higher counterpart [e.g., Ru(III)] so as to establish an extremely low concentration of the radical species as well as a fast reversible reaction with the halogen.

This set of reactions, i.e., the activation/cleavage of a carbon−halogen bond, the formation of a radical species, the repetitive addition (propagation) of the radical species to the monomer, and the regeneration of the carbon−halogen bond, are called the Kharasch or ATRA reactions. There are various metal complexes active for these reactions, as have been utilized in organic synthesis. Indeed, some of the metal complexes active for living radical polymerization were originally developed for the small-molecule reactions, but along with the recent advances in polymerization, new and more active complexes have emerged, too. Although there are still no consistent rules for designing catalysts, there have been several papers dealing with the relationships between the metal center, catalyst structure, or ligand and their catalytic activities.[53,54] In general, it is suggested that the catalytic activity increases with increasing electron density of the metal center or with decreasing redox potential of the complex, because, upon the onset of radical generation, the catalyst should give one electron to the halide terminal. The following sections will focus on the transition-metal catalysts employed for living radical polymerization.

1. Ruthenium

This group 8 transition metal was one of the first whose complexes [$RuCl_2(PPh_3)_3$ etc., Ph = C_6H_5] were demonstrated to induce living radical polymerization.[27] Among the various oxidation states of ruthenium complexes (−2 to +6), the divalent form with phosphine ligands has effectively been employed for the metal-catalyzed living radical polymerization as well as Kharasch addition reactions (Figure 1). The dichloride $RuCl_2(PPh_3)_3$ (Ru-**1**) was the first complex employed for the metal-catalyzed living radical polymerization of methyl methacrylate (MMA) in conjunction with CCl_4 as an initiator in the presence of a metal alkoxide such as $MeAl(ODBP)_2$ (ODBP = 2,6-di-*tert*-butylphenoxy) as an additive.[27] In toluene at 60 °C, the polymerization proceeded homogeneously to give polymers with molecular weights that were controlled by the feed ratio of monomer to initiator and relatively narrow MWDs ($M_w/M_n \approx 1.3$). The radical nature of the polymerization was suggested by inhibition of the polymerization on addition of a radical scavenger or inhibitor such as galvinoxyl and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO).[27,55] The tacticity of the polymers was similar to that prepared in conventional radical systems.[27]

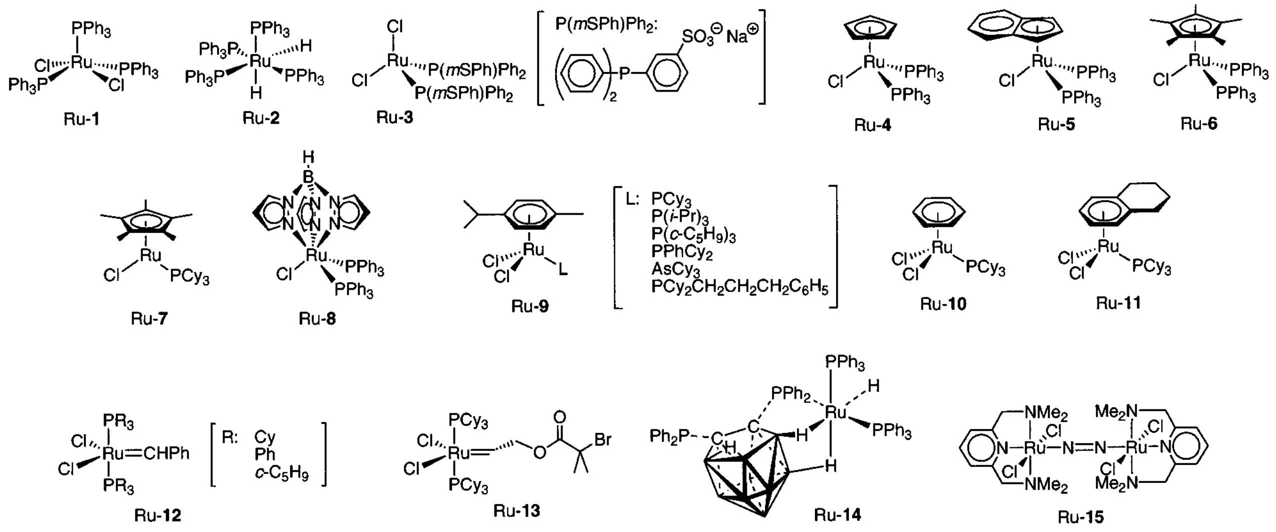


Figure 1. Ruthenium catalysts.

The ruthenium-catalyzed polymerization was further improved by using $CHCl_2COPh$ and Al(O-*i*-Pr)$_3$ in place of CCl_4 and MeAl(ODBP)$_2$, respectively, resulting in very narrow MWDs ($M_w/M_n = 1.1$) of poly(MMA).[56] This complex can also be applicable for styrene polymerization in conjunction with an iodo initiator to give relatively narrow MWDs ($M_w/M_n \approx 1.2$).[57] A similar PPh_3-based ruthenium(II) hydride (Ru-**2**) is more active than the chloride Ru-**1**, thus inducing faster polymerizations.[58] The hydride complex is still active at 30 °C to give polymers with narrow MWDs ($M_w/M_n \approx 1.2$). A ruthenium complex with an ionic phosphine ligand (Ru-**3**), which is soluble in water or methanol, catalyzes homogeneous living radical polymerization of 2-hydroxyethyl methacrylate (HEMA) in methanol;[59] no protection of the hydroxyl group is required for HEMA.

Among a series of the 18-electron half-metallocene-type ruthenium complexes (Ru-**4**, Ru-**5**, and Ru-**6**), the indenyl derivative Ru-**5** led to the fastest living radical polymerization of MMA.[60] In this case, additives such as aluminum alkoxides are not necessary for controlled polymerization. However, addition of an amine such as *n*-Bu$_2$NH dramatically increased the rate to complete the polymerization in 5 h at 100 °C without broadening the MWDs.[61]

Though less active, the Cp* complex Ru-**6** is a versatile catalyst, which enables living radical polymerizations of three different types of monomers, i.e., MMA, styrene, and methyl acrylate (MA), in conjunction with a chloride initiator and Al(O-*i*-Pr)$_3$. The initiating system with Ru-**6** gives controlled molecular weights and narrow MWDs ($M_w/M_n = 1.1-1.2$) for all the monomers in toluene at 80 °C without changing the initiator and reaction conditions according to the monomers.[62] The catalytic activity of these half-metallocene-type complexes increased in the order Ru-**4** < Ru-**5** < Ru-**6**; namely, the lower the redox potential of the complex, the faster the polymerization.[53] Another half-metallocene-type ruthenium complex with 16-electrons (Ru-**7**) is more active than Ru-**6**, because the former has a vacant site that can interact with a halogen at the polymer terminal without release of phosphine ligand.[62] A trispyrazolyl borate-based complex (Ru-**8**), isoelectronic to 18-electron half-metallocene-type complexes, also induced living radical polymerization of MMA either with or without additives, where the rates and molecular weights were not changed on addition of Al(O-*i*-Pr)$_3$.[53]

A series of *p*-cymene-based ruthenium dichloride complexes (Ru-**9**) with various phosphines and related two-electron-donor ligands was synthesized and used for the radical polymerizations of several monomers as well as Kharasch addition reactions.[63,64] Controlled polymerizations were achieved with basic and bulky phosphine or arsenic ligands (L = PCy_3, P(*i*-Pr)$_3$, P(*c*-C_5H_9)$_3$, $PPhCy_2$, $AsCy_3$, $PCy_2CH_2CH_2CH_2C_6H_5$). Among them, the tricyclohexylphosphine complex (L = PCy_3) is most active and efficient in giving well-controlled molecular weights and narrow MWDs ($M_w/M_n \approx 1.1$) for methacrylates.[63] In contrast, less basic or less bulky phosphine-, pyridine-, isocyanide-, and antimony-based ligands led to less efficient and/or less controlled polymerizations. Similar complexes carrying benzene (Ru-**10**) or tetralin (Ru-**11**) can also be employed; the activity decreased in the order *p*-cymene > benzene > tetralin.[65]

A complex with a bridged ligand with arene and phosphine can be obtained via release of the *p*-cymene ligand from Ru-**9** (L = $PCy_2CH_2CH_2CH_2C_6H_5$) on heating to 120 °C, but it was significantly less active than the precursor Ru-**9** (L = $PCy_2CH_2CH_2CH_2C_6H_5$), which induces efficient living radical polymerization.[65] The activation process of these arene-based 18-electron complexes is thus release of arene ligands, which results in active and coordinatedly unsaturated 12-electron complexes.

A series of so-called Grubbs ruthenium−carbene complexes (Ru-**12**) can mediate living radical polymerization of MMA and styrene to afford controlled polymers with narrow MWDs ($M_w/M_n \approx 1.2$).[63,66] The polymerization apparently proceeds via a radical mechanism, as suggested by the inhibition with galvinoxyl. For example, a novel ruthenium−carbene complex (Ru-**13**) carries a bromoisobutyrate group and can thus not only initiate but also catalyze living radical polymerization of MMA without an initiator.[67]

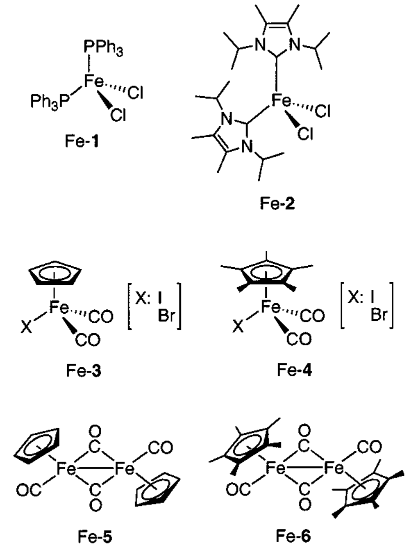


Figure 2. Iron catalysts.

The complex is also active in ring-opening metathesis polymerization of 1,5-cyclooctadiene (COD), where the ruthenium−carbene bond is now the initiating point. Therefore, a mixture of MMA and COD undergoes a dual or tandem living polymerization of both monomers to generate block copolymers of COD and MMA, which can be converted into ethylene-*block*-MMA copolymers on subsequent hydrogenation, also catalyzed by the complex.

Ruthenium−carborane 14-electron complexes were investigated as catalysts for the radical reactions, and among them, a hydride complex (Ru-**14**) proved effective in giving narrow MWDs ($M_w/M_n \approx 1.2$) and controlled molecular weights without additives in the MMA polymerizations.[68] A binuclear azo-bridged complex with nitrogen ligands (Ru-**15**) can be employed for MMA polymerization with CCl_4 as an initiator to give polymers with relatively narrow MWDs ($M_w/M_n = 1.4-1.6$).[69]

2. Iron

As with ruthenium, iron belongs to the group 8 series of elements and can similarly take various oxidation states (−2 to +4), among which Fe(II), Fe(I), and Fe(0) species have been reported to be active in Kharasch addition reactions.[33] For metal-catalyzed living radical polymerizations, several Fe(II) and Fe(I) complexes have thus far been employed and proved more active than the Ru(II) counterparts in most cases (Figure 2). The iron-based systems are attractive due to the low price and the nontoxic nature of iron.

$FeCl_2(PPh_3)_2$ (Fe-**1**) was first employed for the metal-catalyzed living radical polymerization of MMA in conjunction with a chloride or a bromide initiator, and the rate of the polymerization is faster than with $RuCl_2(PPh_3)_3$.[70] The polymerization with Fe-**1** catalyst was best controlled when coupled with $CH_3C(CO_2C_2H_5)_2Br$ as an initiator without additives in toluene at 80 °C ($M_w/M_n = 1.1-1.3$). A similar fast living polymerization of styrene and MMA can be achieved with an iron complex and a higher electron-donating ligand such as imidazolydene (Fe-**2**) in conjunction with a bromide initiator to result in narrow MWDs ($M_w/M_n = 1.1-1.3$).[71] Addition of $FeCl_3$ slowed the polymerization but narrowed the MWDs further ($M_w/M_n = 1.1$).

The use of Cp or Cp*-based ligands is also beneficial for the iron-based systems in controlling radical polymerization. For instance, $FeCpI(CO)_2$ (Fe-**3**, X = I) induced a living radical polymerization of styrene in conjunction with an iodide initiator $[(CH_3)_2C(CO_2C_2H_5)I]$ in the presence of Ti(O-*i*-Pr)$_4$ to give very narrow MWDs ($M_w/M_n = 1.1$) and controlled molecular weights.[72] The rate was increased with the use of the corresponding bromide, while the MWD was narrowed by replacement of Cp with Cp*.[73] A faster and controlled polymerization was possible with dinuclear Fe(I) complexes (Fe-**5** and Fe-**6**) in the absence of metal alkoxides.

Mixtures of iron(II) halides ($FeBr_2$ and $FeCl_2$) and ligands were also employed for living radical polymerization. Similar controlled radical polymerizations of MMA and styrene were achieved with $FeBr_2$ and nitrogen- and phosphine-based ligands such as n-Bu$_3$N, n-Bu$_3$P, and 4,4′-bis(5-nonyl)-2,2′-bipyridine.[74] Halide anions derived from ammonium or phosphonium salts [n-Bu$_4$NX (X = Cl, Br, I) and n-Bu$_4$PBr] were also available as ligands for $FeBr_2$ to mediate controlled polymerizations of styrene, MMA, and MA, although the systems were heterogeneous.[75] In search of less toxic ligands, dicarboxylic acids $[NH(CO_2H)_2$, C_6H_4-1,3-$(CO_2H)_2$, and $HO_2CCH_2CH_2CO_2H]$[76−79] and acetic acid[78] were used for $FeCl_2$, and the resulting complexes induced controlled polymerizations of MMA and styrene to give relatively broad MWDs ($M_w/M_n = 1.3-1.8$).

Fe(III) species can also be employed in a so-called reverse or alternative atom-transfer radical polymerization (section II.B.9). A mixture of $FeCl_3$ and PPh_3 can mediate a controlled polymerization of MMA in the presence of AIBN to give similarly narrow MWDs ($M_w/M_n = 1.1-1.3$).[80] An ammonium halide such as n-Bu$_4$NBr can be employed in place of PPh_3 as a ligand for $FeBr_3$ in the AIBN-initiated radical polymerization.[74]

3. Copper

Copper catalysts have been extensively employed for the metal-catalyzed living or controlled radical polymerizations. Most of the polymerizations are conducted by a mixture of copper(I) bromide or chloride and a nitrogen-based ligand (Figure 3), and in select examples by isolated complexes (Figure 4). A wide variety of nitrogen ligands have been searched and employed (Figure 3), and they can be classified into bidentate (L-**1** to L-**17**, e.g., bipyridines, pyridinimines, diamines), tridentate (L-**18** to L-**26**), quadridentate (L-**27** to L-**33**), and formaly hexadentate (L-**34**). An overview of some of these ligands has been described in recent papers.[54,81] The following gives specific examples of these ligands, though no systematic relationship has been established between their activity or utility and structures. However, quite recent papers deal with the relationships between the structure and the activity for several ligands.[82,83]

The Cu(I)-based initiating system was first reported for styrene polymerization by Wang and

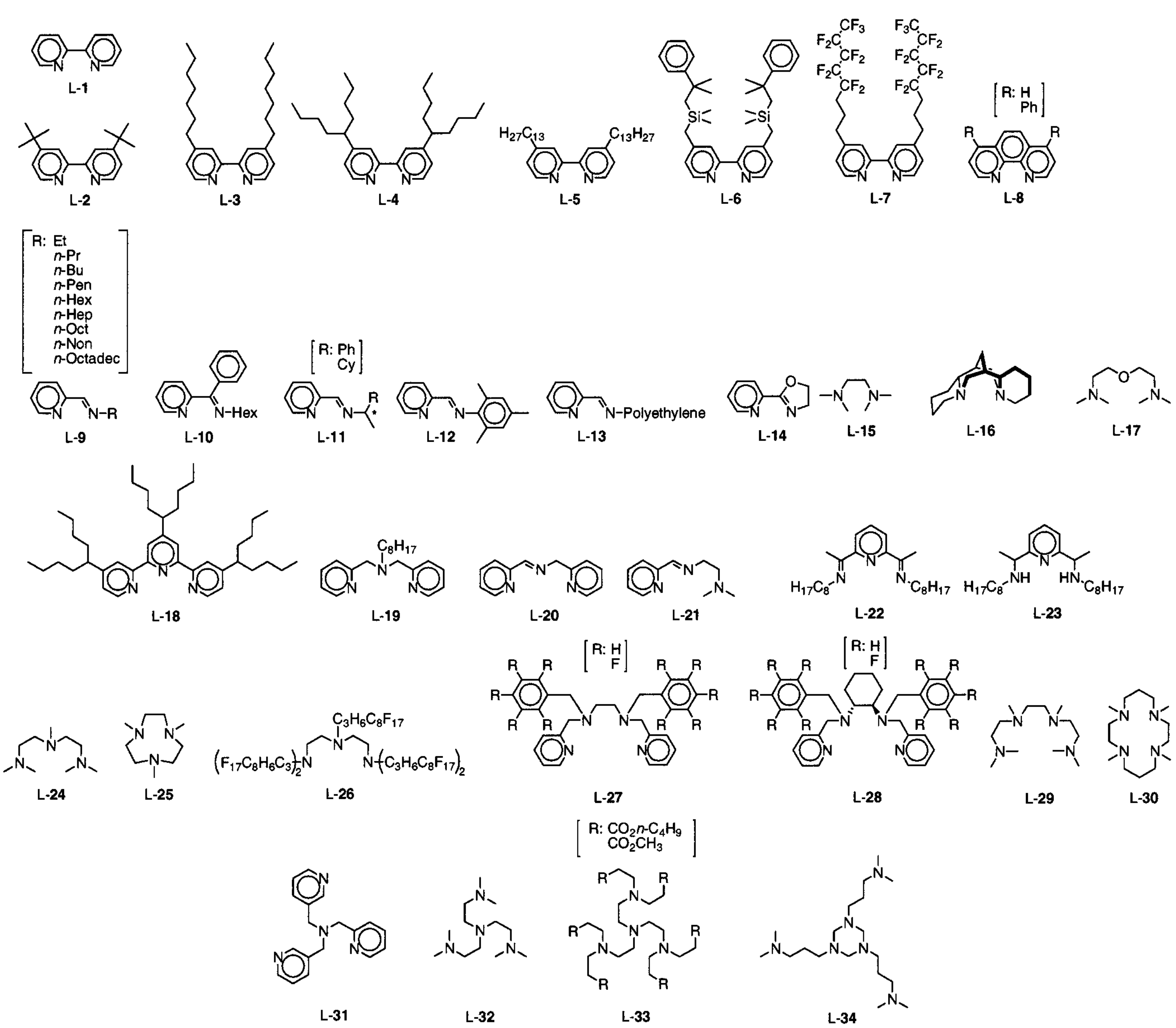


Figure 3. Ligands for copper catalysts.

Matyjaszewski and has subsequently been applied to a wide range of monomers. The first system consists of CuCl and 2,2′-bipyridine (L-**1**) ligand, coupled with 1-phenylethyl chloride as an initiator.[28] Though a heterogeneous system, the polymers had controlled M_n, in direct proportion to monomer conversion up to 100000 amu, and narrow MWDs ($M_w/M_n < 1.5$). The Cu(I)/L-**1** system also proved effective for other monomers such as MA. The use of CuBr and a bromide initiator narrows the MWDs of polystyrene and poly(MA) ($M_w/M_n \approx 1.1$), while broader MWDs ($M_w/M_n \approx 1.4$) were obtained for poly(MMA).[84]

In an effort to solubilize the catalyst, long-chain alkyl groups on the 4,4′-positions of bipyridine were introduced. Typical ligands in this line include L-**2**, L-**3**, and L-**4**. Homogeneous polymerizations have been achieved with L-**3**[85] and L-**4**[86] independently and almost simultaneously by two research groups. The polymerizations proceeded faster than the heterogeneous ones to give polystyrene of very narrow MWDs ($M_w/M_n = 1.05$). A longer alkyl chain substituent (L-**5**) is similarly efficient.[87] Alternatively, homogeneous polymerization of styrene can be achieved even with the CuBr/L-**1** system by adding 10% DMF, while the MWDs were relatively broad ($M_w/M_n = 1.4-1.8$).[88]

A difficulty in isolation and clarification of the active Cu(I)–bipyridine complexes was overcome with the use of a silyl-containing bipyridyl ligand (L-**6**), which generates an ionic complex (Cu-**1**) on mixing with an equimolar amount of CuBr.[89,90] The complex as well as an equimolar mixture of CuBr and L-**6** showed levels of control similar those with L-**3** and CuBr. An active Cu(I) species with bipyridine-type ligands presumably has a tetrahedral 18-electron species, as suggested for the similar complexes isolated after the polymerization of MA with L-**4**.[91,92]

A Cu(II) complex with a bipyridine-type ligand (Cu-**4**) is effective in the controlled polymerization of styrene and acrylates in the presence of Al(O-*i*-Pr)$_3$, which most probably serves as a reducing agent of Cu(II) into Cu(I).[93,94] A fluoroalkyl-substituted bipyridine ligand (L-**7**) was also employed in supercritical carbon dioxide for the polymerization of fluorinated acrylates and methacrylates.[95] Similar pyridine-based bidentate ligands, 1,10-phenanthroline and its

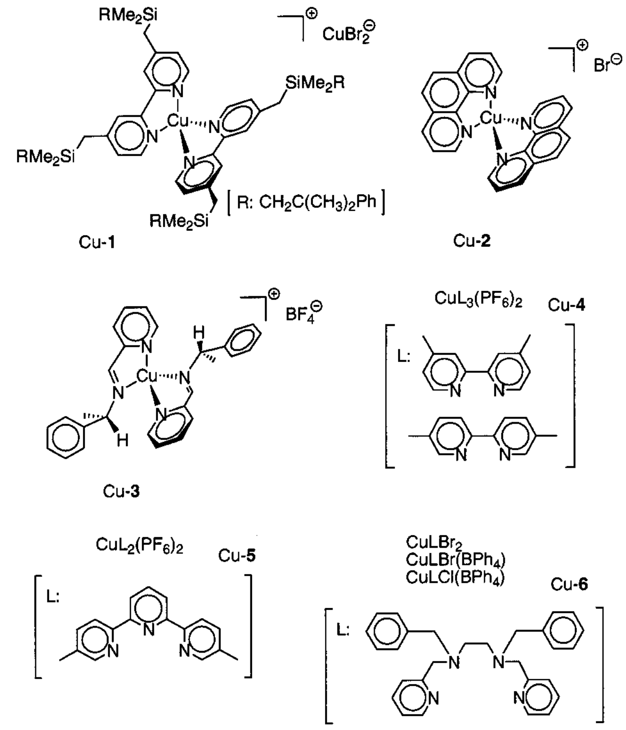


Figure 4. Isolated copper catalysts.

derivatives (L-**8**, R = H, Ph), were also used for CuCl,[96,97] CuBr,[98] and Cu(0)[99] in controlled polymerizations of styrene and MMA. A homogeneous polymerization of styrene proceeds with the diphenyl-substituted ligand (L-**8**, R = Ph) with CuCl in 1,2-dimethoxybenzene to afford better controlled polymers than L-**4** does under the same conditions.[96] A preformed and isolated complex (Cu-**2**) induced a similar controlled polymerization of styrene although the mixture was heterogeneous with the unsubstituted phenanthroline.[98]

A series of Schiff-base or pyridinimine-type bidentate ligands (L-**9**) has been efficiently used for the homogeneous living radical polymerization of methacrylates (M_w/M_n = 1.1−1.2) with CuBr and a bromide initiator in nonpolar solvents such as toluene and *p*-xylene.[100−102] These ligands can therefore clearly differ from bipyridines, which need some special solvent such as ethers for controlling polymerizations of methacrylates (section II.E.1). However, an active Cu(I) species has a similar tetrahedral structure, as suggested by an isolated Cu(I) complex with tetrafluoroborate anion.[101] The solubility depends on the alkyl substituents (R), and homogeneity can be achieved with alkyl chains longer than *n*-Bu at 90 °C. The rate increases on going from R = Et to R = *n*-Pr; however, no increase was observed with longer alkyl chains. Slower and less controlled polymerizations occurred when branching was introduced into the α-position of the side chain (L-**10**).[102] A similar ligand, diazabutadiene or diimine, which has no pyridine moiety, does not induce controlled polymerization most probably due to the high stability of Cu(I) complexes with regard to oxidation.[102] The catalysts prepared in situ by the addition of ligands L-**9** to CuBr prior to the polymerizations are similarly effective.[101]

Possible control of stereochemistry was investigated with the use of chiral Schiff bases L-**11** (R = Ph, Cy) as ligands or their recrystallized catalyst Cu-**3** in the polymerizations of MMA with a bromide initiator in xylene at 90 °C.[103] Unfortunately, the tacticity of the polymers is not different from that in conventional polymerizations, while control of molecular weights was achieved.

Styrene polymerization was investigated with some pyridinimine ligands. Homogeneous living polymerizations can be achieved with L-**9** (R = *n*-Oct) in xylene[104] and with L-**12** in the bulk,[105] both with a bromide initiator and CuBr, where the former gave narrower MWDs than the latter (M_w/M_n = 1.2 and 1.5−1.8, respectively). L-**9** (R = *n*-Oct) is also applicable for MA polymerization to give relatively narrow MWDs.[81]

Catalyst removal is efficient with the use of a polyethylene-segmented pyridinimine ligand (L-**13**) in the polymerization of MMA with CuBr.[106] A similar ligand, 2-(2′-pyridyl)-4,5-dihydroxyloxazole (L-**14**), is employed for CuCl-mediated polymerizations of methacrylates.[107]

Diamine compounds such as L-**15** coordinate to copper species, but their use for MA, MMA, and styrene results in slower polymerizations and broader MWDs (M_w/M_n = 1.3−2.5) than those with bipyridine-based bidentate ligands.[81,108] An increase of the number of amine linkages and bulkier substituents further broadened the MWDs.[81] Sparteine (L-**16**), a bicyclic diamine, was found to be an efficient ligand for homogeneous living radical polymerization of styrene and MMA with CuBr and CuCl, respectively, to give better-controlled polymers (M_w/M_n = 1.1−1.3).[109] A diamine with an ether moiety (L-**17**) was also employed in a CuCl-based system.[110]

Tridentate nitrogen ligands form 1:1 uncharged complexes with copper, in contrast to bidentate ligands that form tetrahedral ionic complexes.[81] Well-controlled polymers of styrene and MA are obtained with a substituted terpyridine (L-**18**), whereas the unsubstituted derivative induced a heterogeneous and uncontrolled polymerization.[111] A similar controlled polymerization of styrene was reported for a substituted terpyridine-based complex of Cu(II) (Cu-**5**) coupled with Al(O-*i*-Pr)$_3$.[112] A tridentate ligand with two pyridines and one amine (L-**19**) gave narrow MWDs for styrene, MA, and MMA (M_w/M_n = 1.1−1.4), although the M_n values for PMMA were slightly higher than the calculated values.[113] Another tridentate ligand (L-**20**) with two pyridines and one imine was effective for styrene and MA.[81] A ligand (L-**21**) with one pyridine moiety gave narrow MWDs of styrene.[81] Diiminopyridine L-**22** can be employed for controlled radical polymerizations of MMA (M_w/M_n < 1.3), while diaminopyridine L-**23** is effective for MA and styrene (M_w/M_n < 1.3).[114]

A substituted linear triamine (L-**24**) is effective for three types of monomers, styrene, MA, and MMA, to give relatively narrow MWDs (M_w/M_n = 1.1−1.4), where the polymerizations of styrene and MA are faster than those with L-**1**.[108] A cyclic triamine (L-**25**) with ethylene linkers is similarly effective.[81] A perfluoroalkyl-substituted triamine (L-**26**) is useful

Cu(I)

CuCl
CuBr
Cu(OTf) [$Cu(OTf)_2$ + Cu]
$CuPF_6$
Cu(OAc)
Cu(2-thiophenecarboxylate)
CuSCN
Cu_2O
Cu_2S
Cu_2Se
Cu_2Te
CuSPh
CuSBu
CuC≡CPh

Cu(0)

Cu

Cu(II)

CuS
CuSe
$CuCl_2$
$CuBr_2$

Figure 5. Copper catalysts.

in living radical polymerization of MMA under fluorous biphasic conditions, where the reaction mixtures were homogeneous under the reaction conditions but were heterogeneous under the workup conditions.[115] The obtained polymers had narrow MWDs, and the catalysts can be reused at least twice without a significant loss of activity.

Ligands with four nitrogen-based coordinating sites were also studied by several researchers. A series of ligands with two pyridine and two amine parts (L-**27** and L-**28**) were employed for MMA in conjunction with CuBr and a bromide initiator to lead to controlled polymerization (M_w/M_n = 1.1−1.4) in the presence of Cu(0).[116] Slower polymerizations occurred with fluorinated derivatives. Some isolated Cu(II) complexes (Cu-**6**) were effective in the presence of Cu(0), similar to the Cu(I) catalysts preformed in situ. No changes in tacticity were observed even with the use of chiral ligands (L-**28**). A linear quadridentate amine (L-**29**) was effective similarly to a tridentate amine (L-**24**) to induce fast controlled polymerizations of styrene, MA, and MMA.[108] A cyclic quadridentate amine (L-**30**) afforded broad MWDs but induced fast and quantitative polymerizations of *N*,*N*-dimethylacrylamide.[117] Controlled polymerizations of styrene and acrylates are achieved with tripodal ligands such as L-**31**[113] and L-**32**,[118,119] where very fast living polymerizations of acrylates proceeded to reach 80% conversion within 3 h even at 22 °C with L-**32**. A tripodal ligand with ester substituents (L-**33**) was effectively employed for 2-(dimethylamino)ethyl methacrylate.[120] A multidentate ligand with six possible coordination sites (L-**34**) was reported for MMA in THF or in γ-butyrolactone.[121]

Copper(I) salts other than bromides and chlorides were also employed as catalysts coupled with nitrogen-based ligands (Figure 5). These salts seem to accelerate polymerization due to the formation of unbridged monomeric and highly active Cu(I) species, whereas copper(I) halides generally form bridged dimeric complexes in organic solution. However, in most cases, broadening of the MWDs originates from the rate of polymerization being faster than generation of dormant species (deactivation of the radical species), as well as irreversible termination via transfer of halogens from a polymer terminal to the complex, i.e., the formation of copper halides. Copper(I) triflate [Cu(OTf), Tf = CF_3SO_2], generated from $Cu(OTf)_2$ and Cu(0) in situ, induced faster polymerizations of MA and styrene in the presence of L-**24**.[122] A much faster polymerization of MA was attained with $CuPF_6$/L-**4**, where the apparent polymerization rate constant is 40 times greater than that with CuBr, to give controlled molecular weights but broader MWDs (M_w/M_n = 1.4−1.6).[123] Copper(I) carboxylates such as Cu(OAc) and Cu(2-thiophenecarboxylate) with L-**4** also led to faster polymerizations of styrene but broader MWDs.[124] Addition of copper(I) or copper(II) halide was effective in improving the controllability for M_n and MWDs without deceleration. With a sulfonyl chloride as initiator, CuSCN leads to a polymerization of MMA faster than copper halides do; however, the less active C−SCN terminal accumulates via a ligand exchange reaction.[125]

Dicopper chalcogens induced controlled polymerizations of MMA and *n*-butyl methacrylate (nBMA), where the rate increased in the order $Cu_2O < Cu_2S < Cu_2Se <$ (CuCl <) Cu_2Te, in the presence of L-**1** or L-**4** with a sulfonyl chloride initiator. The polymers had controlled molecular weights and MWDs (M_w/M_n = 1.1−1.2) at high conversions (>80%).[126,127] There was an induction period, which decreased in the order $Cu_2O > Cu_2S > Cu_2Se > Cu_2Te$. These copper salts are converted presumably into reactive and soluble CuCl complexes via the reaction with the chlorine in the initiator during the induction period, although the mechanism has not been established yet. Organocopper species such as CuSPh are also effective in the controlled polymerizations of MMA in the presence of L-**1** and a sulfonyl chloride, where the rate increased in the order CuC≡CPh < CuSPh < (CuCl <) CuSBu.[128] Similar ligand exchange reactions occur with these systems to form CuCl and result in low initiation efficiency especially at the high concentrations of organocoppers employed.

Metallic copper, Cu(0), can also be employed for controlled radical polymerization in the absence or presence of copper(II) or copper(I) halides.[126,129] Cu(0) is most probably converted in situ into an active Cu(I) species via abstraction of halogen from the initiator and the polymer terminal or from added copper(II) or copper(I) halides. The use of Cu(0) as an accelerator or reducing agent of Cu(II) species will be discussed later (section II.D).

Cu(II) species such as CuS and CuSe can induce controlled polymerizations, the rate of which is decreased when compared with their Cu(I) counterparts (Cu_2S and Cu_2Se).[127] These Cu(II) species are presumably converted into copper(I) halides via a ligand exchange reaction with the initiator or polymer chain end similarly to Cu_2S and Cu_2Se. Copper(II) halides such as $CuCl_2$ and $CuBr_2$ per se are not active but can be converted into active copper(I) halides by combination with a conventional radical initiator such as AIBN.[130,131] This system is sometimes called a reverse or alternative atom-transfer radical polymerization, which will also be discussed later (section II.B.9).

4. Nickel

Among the various oxidation states of nickel (0−IV), Ni(II) and Ni(0) are the most stable. There have been only a limited number of examples of nickel-catalyzed Kharasch addition reactions, in contrast to those of ruthenium, iron, and copper, probably be-

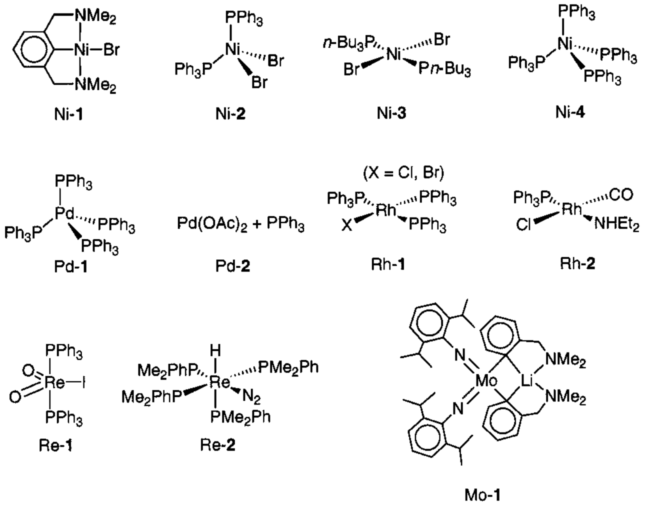


Figure 6. Other metal catalysts.

cause nickel easily undergoes oxidative addition and reductive elimination, which accompanies a two-valence change in its oxidation state rather than the one-electron redox cycle as required in the radical addition processes. However, several Ni(II) and Ni(0) complexes with selected ligands can act as efficient catalysts for living radical polymerizations via a one-electron redox cycle, especially when coupled with bromide initiators (Figure 6). The activity of nickel complexes thus far developed is relatively mild in contrast to that of more active Ru(II) and Cu(I) complexes.

A Ni(II) complex with a bis-ortho-chelating nitrogen ligand (Ni-**1**) was successfully employed for the living radical polymerization of methacrylates with CCl_4 or $(CH_3)_2C(CO_2C_2H_5)Br$ as an initiator.[132] The polymerization proceeded homogeneously and reached 80% conversion in about 1 day at 80 °C to give polymers with narrow MWDs (M_w/M_n = 1.1−1.2), although the initiation efficiency was lower (I_{eff} = 0.8). The radical nature of the polymerizations was suggested by the effects of radical inhibitors such as galvinoxyl and also by the tacticity of the polymers.

A phosphine-based nickel(II) bromide complex (Ni-**2**) also induces living radical polymerization of MMA specifically when coupled with a bromide initiator in the presence of Al(O-*i*-Pr)$_3$ as an additive in toluene at 60 and 80 °C.[133] The reaction rates and the effects of radical inhibitors are similar to those with Ni-**1**, whereas chloride initiators are not effective in reaction control. Additives are not necessary when the polymerization is carried out in the bulk or at high concentrations of monomer, either methacrylate or *n*-butyl acrylate (nBA).[134] An alkylphosphine complex (Ni-**3**) is thermally more stable and can be employed for MMA, MA, and nBA in a wide range of temperatures (60−120 °C) without additives.[135] A fast polymerization proceeds at 120 °C to reach 90% conversion in 2.5 h. A zerovalent nickel complex (Ni-**4**) is another class of catalyst for living radical polymerization of MMA in conjunction with a bromide initiator and Al(O-*i*-Pr)$_3$ to afford polymers with narrow MWDs (M_w/M_n = 1.2−1.4) and controlled molecular weights.[136] The Ni(0) activity is similar to that of Ni(II) complexes whereas the controllability is inferior. Mechanistically, the role of the zerovalent complex apparently needs further clarification.

5. Palladium

Palladium belongs to the group 10 elements, and as with nickel, it forms stable Pd(0) and Pd(II) complexes. The use of such complexes (Pd-**1** and Pd-**2**) has been reported for the polymerization of MMA with CCl_4 initiator in toluene at 70 °C.[137] The activity is moderate (conversion 70−80% in 24 h), similar to that of the nickel complexes. The M_n increased in direct proportion to monomer conversion, while the MWD was broader ($M_w/M_n \approx 1.8$). In contrast, polymerizations of styrene and acrylates were not controlled with Pd catalysts.

6. Rhodium

Among possible oxidation states of rhodium ranging from +4 to −3, the most common are +1 and +3. One of the most famous Rh(I) complexes(Rh-**1**), the so-called Wilkinson catalyst, widely used for hydrogenation, was investigated for living radical polymerization by several researchers. The chloride complex Rh-**1** (X = Cl) was first examined for styrene in the bulk at 130 °C coupled with sulfonyl chloride as an initiator.[86] The obtained polymers had broader MWDs (M_w/M_n = 1.7) than those with the ruthenium or copper catalysts. In contrast, it induced faster polymerizations of MMA in the presence of CCl_4 or $CHCl_2COPh$ in THF or in a mixture of THF and water at 60 °C, where conversion reached 90% in 4 h in the latter medium to give PMMA with a slight reduction in the MWDs (M_w/M_n = 1.3−1.7).[138] The effects of galvinoxyl and the tacticity of PMMA are again in agreement with the radical nature of the polymerization. A bromide complex (Rh-**1**, X = Br) in conjunction with a bromide initiator afforded PMMA with narrower MWDs (M_w/M_n = 1.3).[139]

In another example, the novel Rh(I) complex Rh-**2** was employed with CCl_4 for MMA and styrene bulk polymerizations at 60 °C, which reached 90% conversion in 14 h.[140] The MWD of PMMA was narrower than that of polystyrene (M_w/M_n = 1.43 vs 2.08), while the initiation efficiency was very low in both cases.

7. Rhenium

Rhenium belongs to the group 7 elements, which, in general, display the characteristics of early and late transition metals. It can take a wide range of oxidation states and give stable high-valent complexes as do group 8−10 metals. A rhenium(V) iodide complex (Re-**1**) induced efficient living radical polymerizations of styrene coupled with an iodide initiator and Al(O-*i*-Pr)$_3$ over a wide range of temperatures between 30 and 100 °C.[141] Conversion reached 90% within 6 h at 100 °C, and its catalytic activity for styrene is higher than that of Ru-**1**. The MWDs became narrower with decreasing temperature (M_w/M_n = 1.2−1.5). The radical nature of the polymerization was suggested by inhibition of the polymerization by TEMPO. However, the terminal iodide group was not converted into the nitroxyl group, most probably due to a low concentration of radical species as well as deactivation of the Re(V) complex via interaction with TEMPO. The system can equally be employed for acrylate polymerizations, although the MWDs are broader ($M_w/M_n = 1.6-1.8$).[142]

There is also a report on the use of a Re(I) complex (Re-**2**) in 1,2-dichloroethane at 50 °C, where the increase of molecular weights with conversion was observed in the MMA polymerization.[143] Due to the absence of initiator, the solvent presumably serves as a supplier of the initiating radical species. The radical nature of the polymerization was suggested from the copolymerization behavior of MMA and styrene.

8. Molybdenum

A group 6 metal complex can be a candidate as a catalyst for radical polymerization because of its variable oxidation states, despite its sensitivity to air and protic compounds. A lithium molybdate(V) complex (Mo-**1**) can polymerize styrene in conjunction with benzyl chloride in toluene at 80 °C to yield polystyrene with relatively broad MWDs ($M_w/M_n = 1.5-1.7$).[144] The initiation efficiency was low (~10%), and decomposition of the complex was observed.

9. Immobilized Catalysts

Immobilized catalysts have been studied in metal-catalyzed living radical polymerization for, in part, easy removal of the catalysts from the products. In most examples, the catalytic metal centers are attached to solid supports, such as silica gel and polystyrene beads, via spacers and/or coordinating ligands (Figure 7). The central metals thus far employed include copper and ruthenium.

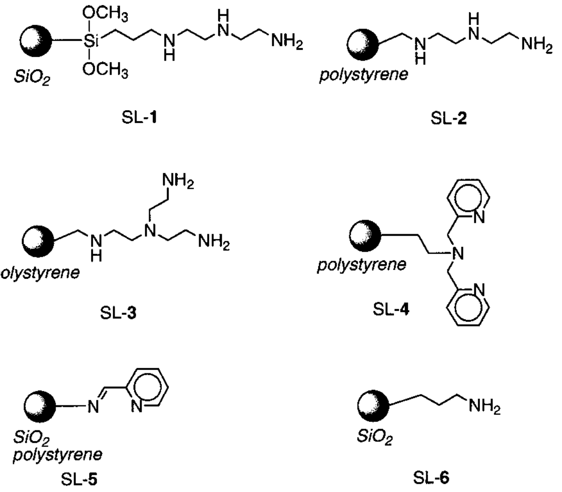


Figure 7. Ligands for immobilized catalysts.

Several silica-based materials such as silica gels, silica powder, and fumed silica (Aerosil) were employed as supports for CuBr by modification of their surface as in SL-**1**.[145] Thus, for instance, bulk polymerization of styrene was investigated but resulted in polymers of uncontrolled molecular weights and broad MWDs ($M_w/M_n = 2-10$) due to the slow deactivation or initiation of the growing radical species relative to propagation. Organic polymer-supported ligands on a cross-linked polystyrene (Merrifield resin) such as SL-**2** and SL-**3** also resulted in uncontrolled polymerizations of acrylates, methacrylates, and styrene. A better control can be achieved with the use of SL-**4** for a mixture of $CuBr_2$ and CuBr in the polymerization of MA, where the molecular weights became closer to the calculated values, and the MWDs became narrower ($M_w/M_n = 1.6-2.0$).[145] The residual copper in the reaction mixture was estimated about 3% of the initial amount, which indicates that the metal was effectively bound to the resin.

The use of another supported ligand such as SL-**5** on silica gels and polystyrene resins induced controlled radical polymerization of MMA, resulting in narrower MWDs ($M_w/M_n = 1.5-1.6$), although the molecular weights were higher than the calculated values.[146,147] Block copolymerization and the reuse of the catalysts have also been achieved. Physically adsorbed catalysts obtained by mixing silica gels or amino-functionalized silica gels with CuBr in the presence of free ligands gave narrower MWDs ($M_w/M_n = 1.3-1.4$) but resulted in coloring of the solution due to free copper complexes.

A ruthenium complex (Ru-**1**) can also be supported on a silica gel such as SL-**6**.[148] The ruthenium-catalyzed MMA polymerization gave controlled molecular weights, closer to the calculated values, and narrow MWDs ($M_w/M_n = 1.5-1.7$). Block copolymerization as well as the reuse of the catalysts is possible. The polymerization was faster in the presence of SL-**6** than in the absence, most probably due to the effects of amines as additives as will be discussed below (section II.D). The residual ruthenium in the reaction mixture was estimated to be about 10% of the initial feed.

A similar, physically bound CuBr catalyst on a silica gel support (L-**29**) was also employed for MMA polymerization.[149] The polymers had narrow MWDs ($M_w/M_n \approx 1.3$), but the molecular weights were higher than the calculated values. The recycled catalysts have a lower activity but lead to better control of molecular weights; i.e., the M_n agreed well with the calculated values, and the MWDs were narrower ($M_w/M_n \approx 1.2$). The physically supported catalysts were further employed for the synthesis of end-functionalized polymers.[150] When physically supported silica gel catalysts are packed into a continuous column reactor, a controlled polymerization is possible.[151]

In contrast, unsupported catalysts can be removed by precipitation of polymers,[152] passing through an alumina column,[152] or using an absorbant,[27] but complete removal is difficult. The use of ion-exchange resins was investigated and seems more practical.[153] Another efficient method for catalyst removal is to use special ligands or catalysts such as L-**26**[115] and Ru-**3**,[59] which can be removed with the use of fluoro solvents and water, respectively. Ionic liquid can also be employed for catalyst removal (section II.E.5).

B. Initiators

The role of the initiator in metal-catalyzed living radical polymerization is to form an initiating radical species via homolytic cleavage of its labile bond such as C−halogen by the metal catalysts. In most cases,

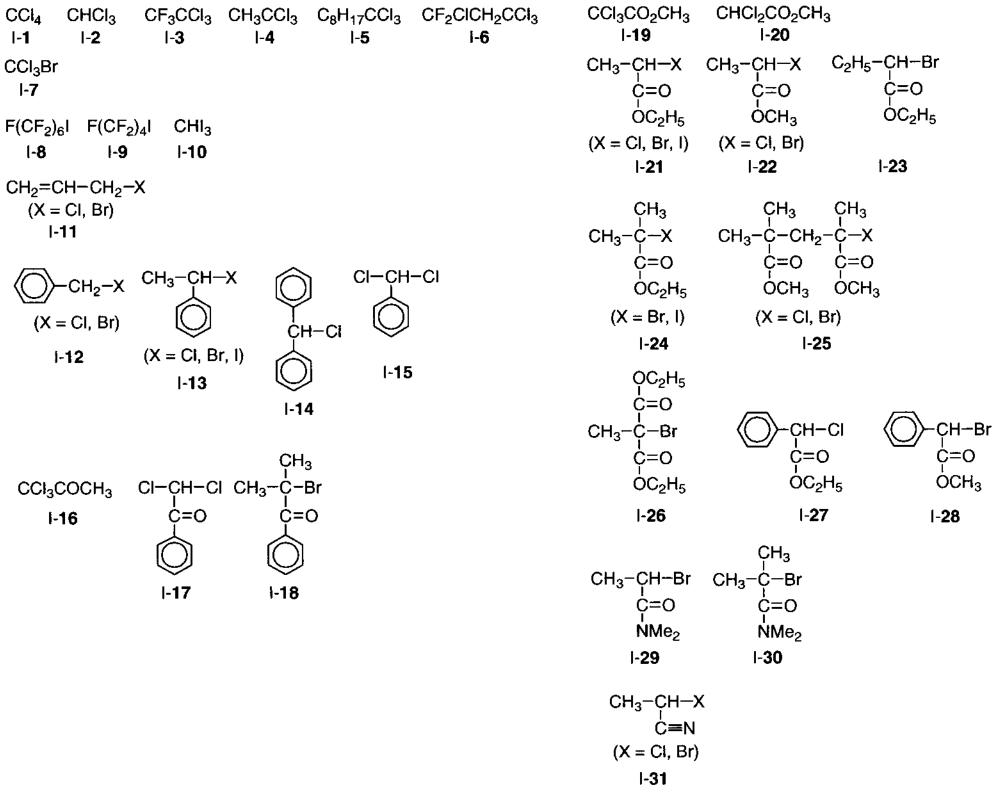


Figure 8. Organic halide initiators.

the dissociated halogen or its equivalent is subsequently reattached to the propagating radical chain end to give a dormant species. The initiator is thus chosen so that the initiation occurs fast and is quantitative, with the dormant polymer chain end being stable during the polymerization. This means that the initiator should be carefully selected in accordance with the structure and reactivity of the monomers and metal complexes.

Most of the initiators thus far successfully employed are organic halides with a potentially active carbon−halogen bond, which can easily generate a radical species through electronic and steric effects of their substituents (Figure 8). These organic halides therefore possess surplus halogens or conjugated substituents such as allyl, aryl, carbonyl, and cyano groups for stabilization of the generated radical species by the inductive and/or resonance effects. However, in some cases, an extensive stabilization of the initiating radical may disturb its addition to the monomer and thus result in slow initiation, which causes uncontrolled molecular weights and/or broad MWDs. An organic halide, the structure of which is similar to that of the dormant chain end of the polymer, is preferentially used so that the activity of the carbon−halogen bond in the initiator is similar to that of the dormant polymer terminal.

Halogens (X) in the initiators (R−X) include chlorine, bromine, and iodine, where the reactivity of the C−X bond increases in the order Cl < Br < I, but the stability of the C−X bond decreases vice versa. Chlorides and bromides have thus been widely employed.

The following summarizes various initiators in terms of their structures, focusing on available monomers and metal complexes. There have been some papers discussing various halide initiators in the metal-catalyzed living polymerization.[154,155]

1. Haloalkanes

Carbon tetrachloride (I-**1**) was the first initiator employed for the metal-catalyzed living radical polymerization of MMA in conjunction with Ru-**1**.[27] The M_n values increase with conversion and are controlled by the molar ratio of monomer to initiator. They agree with the calculated values assuming that one molecule of CCl_4 generates one living polymer chain, but become smaller at the later stages of the polymerizations. Despite CCl_4 being a chain-transfer agent or a telomer in free radical polymerization, no evidence is found to suggest such reactivity in the metal-mediated processes; the initiator is quantitatively consumed during the early stages. A similar result was also obtained in the Cu(I)-catalyzed MMA polymerizations.[156,157]

Another possible problem is that such polyhalogen compounds may act as multifunctional initiators to give telechelic or star polymers. The initiating moiety thus involved midchain (---CCl_2---) may also induce side reactions, and in fact the lower M_n at the latter stages of the polymerizations of MMA is due to the generation of new polymer chains via chain transfer.[156] CCl_4 can be also employed for other metal complexes such as Fe,[70] Ni,[132] Pd,[137] and Rh[138,140] as well as other monomers such as styrene[84] to give well-controlled molecular weights and relatively narrow MWDs ($M_w/M_n = 1.3$).

A series of 1,1,1-trichloroalkanes (I-**2** to I-**6**) were examined as initiators for the Cu(I)-catalyzed polymerizations of styrene,[158] MMA,[156] and MA.[156] These polychloroalkanes are efficient initiators to give controlled molecular weights and narrow MWDs (M_w/M_n = 1.1−1.7; narrowness depending on the initiators and monomers), with most of them serving as bifunctional initiators. In contrast, $CHCl_3$ (I-**2**) is not a good initiator in the Ru-**1**-based system probably due to the low activity or the high redox potential of the ruthenium complex relative to the copper catalyst.[154] 1,1-Dichloroalkanes such as CH_2Cl_2 and $CH_3CCl_2CH_3$ and monochloroalkanes such as C_4H_9Cl are totally inactive with Cu(I) and Ru(II) complexes.[84,154,156]

A haloalkane with mixed halogens (I-**7**) led to living polymerization of methacrylates, acrylates, and acrylamides when coupled with ruthenium and nickel complexes.[133,135,159,160] The weak C−Br bond is preferentially activated, while multifunctional initiation is possible. However, CCl_3Br is the initiator of choice if obtaining narrow MWDs is desired without paying attention to monomer structures.

The use of perfluoroalkyl iodides I-**8** and I-**9** and iodoform (I-**10**) was also studied in the Ru(II)- and Cu(I)-based systems for styrene and MA.[57,142] Fine control of molecular weights and MWDs was attained for the former monomer, although an iodine-transfer mechanism could not be totally ruled out.

2. Allyl Halides

Allyl radical is relatively stable due to the conjugation of a vinyl group with the carbon-centered radical. Allyl chloride and bromide (I-**11**, X = Cl, Br) were thus employed as initiators for controlled radical polymerization of styrene in conjunction with CuCl/L-**1** and CuBr/L-**1**, respectively.[161] The molecular weights agreed well with the calculated values assuming the formation of one living polymer chain per initiator and increased in direct proportion to monomer conversion. The MWDs were narrower with bromide than with chloride ($M_w/M_n \approx$ 1.2 vs 1.3).

3. (Haloalkyl)benzenes

A series of (haloalkyl)benzenes (I-**12** to I-**15**) were extensively examined and proved effective specifically for polymerizations of styrene and its derivatives, due to the benzyl radical being similar to the growing radical chain ends therein. Among them, benzyl chloride (I-**12**, X = Cl), which forms a primary radical, has the strongest carbon−halogen bond, but induces the controlled radical polymerization of styrene with CuCl/L-**1** in the bulk at 130 °C.[84] The MWD is slightly broader than that obtained with CCl_4 under similar conditions, due to the slow initiation (M_w/M_n = 1.45 vs 1.30). A similar slow initiation was observed for benzyl bromide (I-**12**, X = Br) in the polymerization of styrene with CuBr/L-**4**, while the MWDs were quite narrow (M_w/M_n = 1.2).[162] This initiator can also be employed with the CuCl/L-**4** pair for MMA to give relatively narrow MWDs ($M_w/M_n \approx$ 1.3); note that this system involves halogen exchange between the initiator/dormant end and the metal catalyst (section II.F.5).

1-Phenylethyl halides (I-**13**, X = Cl, Br, I), adducts of styrene and the corresponding hydrogen halide, can be considered as a unimer of the dormant C−X terminal of polystyrene, and thus they are particularly suited for controlling polymerizations of styrenes. The first example of the controlled radical polymerization of styrene indeed involves I-**13** (X = Cl) and CuCl/L-**1**, where the M_n increased in direct proportion to monomer conversion and agreed well with the calculated values in a molecular weight range from 4000 to 100000.[28] The relatively broad MWDs with the chloride I-**13** (X = Cl) are improved by using the bromide counterpart I-**13** (X = Br) for CuBr/L-**4** ($M_w/M_n \approx$ 1.5 vs 1.1).[84,85]

The activity of the carbon−halogen bonds of I-**13** (X = Cl, Br) as well as I-**12** (X = Br) in the Cu(I)/L-**3** system was examined by monitoring the capping of the generated radical species by TEMPO in toluene-d_8.[163] The activation energy of the C−X bonds decreased in the order I-**13** (X = Cl) > I-**12** (X = Br) > I-**13** (X = Br), which would reflect the rate of initiation and thereby the MWDs of the produced polymers. The bromo initiator I-**13** (X = Br) can be also employed with iron complexes such as Fe-**2**[71] and a mixture of $FeBr_2$ and a nitrogen- or phosphine-based ligand[74] to give polystyrene with narrow MWDs (M_w/M_n = 1.1−1.2). The chloride I-**13** (X = Cl) and the bromide I-**13** (X = Br) are not suited for the styrene polymerization with ruthenium (Ru-**1**), giving broader MWDs [M_w/M_n > 2 (X = Cl), ≈ 1.9 (X = Br)] while the molecular weights were controlled with the latter.[57] However, the iodide I-**13** (X = I) gives controlled molecular weights and narrower MWDs ($M_w/M_n \approx$ 1.5) in conjunction with Ru-**1**. The use of an iodide complex such as Re-**1** is preferred with such an iodide initiator to avoid halogen-exchange reactions, and polystyrenes with narrower MWDs ($M_w/M_n \approx$ 1.2) are produced.[141]

Radical species can be generated more easily from benzhydryl chloride (I-**14**), carrying two phenyl groups. This compound induced the radical polymerization of MMA catalyzed by CuCl/L-**4** to give narrow MWDs (M_w/M_n = 1.1−1.2),[164] although it should be added slowly into the mixture to suppress bimolecular termination of the initiating radical spceis.[155] Introduction of an additional chlorine at the α-position, as in I-**15**, is effective in narrowing MWDs in the Cu(I)-catalyzed polymerization of styrene and MMA.[165] It serves as a bifunctional initiator for the former and a monofunctional initiator for the latter.

4. Haloketones

As described above, radical formation is favored by introducing an electron-withdrawing and conjugating substituent in the α-position relative to the C−halogen bonds. A series of haloketones (I-**16** to I-**18**) proved effective especially in Ru(II)- and Ni(II)-mediated living radical polymerizations of MMA. The PMMA obtained with trichloro- (I-**16**) and dichloroketones (I-**17**) in the presence of Ru-**1** had controlled M_n in direct proportion to monomer conversion, in good agreement with the calculated values, and narrow MWDs (M_w/M_n = 1.1−1.2).[56] A similar living polymerization is possible with more active Ru(II) complexes such as Ru-**2**[58] and Ru-**5**.[60] The controllability of polymerizations with I-**17** is superior to that with CCl_4 when coupled with Ru-**1**, while it serves as a bifunctional initiator.[154] A monofunctional bromoketone (I-**18**) is specifically effective in nickel-catalyzed living radical polymerizations of MMA.[132,135,136] However, haloketones are generally too reactive for the copper-catalyzed homogeneous systems and result in uncontrolled polymerizations probably due to the reduction of the electrophilic radical species into anions by the highly active Cu(I) catalysts.[155]

5. Haloesters

Relative to haloketones, haloesters have been successfully employed with a wider range of metal complexes, including Ru, Fe, Cu, Ni, etc. A less electron-withdrawing ester group can moderately activate the carbon−halogen bond and does not make the resulting radical too electrophilic. This type of initiator can be more versatile for various monomers including styrenes, methacrylates, acrylates, etc. by careful design of their structures. Some specific examples follow.

Trichloroacetate I-**19** and dichloroacetate I-**20** can be employed for the Ru-**1**-mediated living radical polymerization of MMA to give narrow MWDs ($M_w/M_n \approx 1.2$), where the latter seems to be monofunctional.[56,154]

A series of α-halopropionates (I-**21** and I-**22**, X = Cl, Br), model compounds of the dormant polymer terminal of acrylates, are suitable for not only acrylates but also styrenes and acrylamides. Ethyl 2-chloropropionate (I-**21**, X = Cl) was employed for the controlled radical polymerizations of MA and styrene catalyzed by CuCl/L-**1** to afford relatively narrow MWDs ($M_w/M_n \approx 1.5$).[84] A better controlled polymerization of MA is achieved with the bromides I-**21** and I-**22** (X = Br) in conjunction with CuBr/L-**1** to give narrower MWDs ($M_w/M_n \approx 1.2$).[84] A similar result was obtained with the combination of I-**23** and CuBr/L-**1** for the polymerization of styrene.[166] A nickel-based system with Ni-**2** and I-**21** (X = Br) gave another controlled polymerization of nBA.[134] The iodide compound I-**21** (X = I) is specifically effective in conjunction with an iodide complex such as Re-**1** to induce controlled polymerization of styrene.[141]

α-Halopropionates are generally less suitable for MMA polymerization due to the low reactivity of their C−X bonds compared with that of the dormant methacrylate terminal, due to the difference in the reactivity of secondary and tertiary halides.[154] However, the use of a halogen-exchange method for I-**21** (X = Br) and CuCl/L-**1** improves MMA polymerization to give controlled molecular weights and narrow MWDs ($M_w/M_n = 1.2-1.4$), where a less reactive chlorine-capped dormant species is generated after the initiation.[167] Controlled polymerization of *N*,*N*-dimethylacrylamide has been achieved with I-**22** (X = Cl) in conjunction with CuCl in toluene at 20 °C.[168]

2-Bromoisobutyrate I-**24** (X = Br), a unimer model of poly(methacrylate) with a dormant C−Br terminal, is more versatile for various monomers such as methacrylates, acrylates, and styrenes; various metal complexes including Ru, Fe, Cu, and Ni can be employed in this case. Living or controlled radical polymerization of MMA was successfully done with I-**24** (X = Br) coupled with ruthenium,[56] iron,[70,71] copper,[84,100] and nickel[132−136] complexes to give well-controlled molecular weights and narrow MWDs ($M_w/M_n = 1.1-1.5$). Similarly, I-**24** (X = Br) is suitable for styrene and acrylates with ruthenium,[60] iron,[73] copper,[84] and nickel catalysts.[135] An iodoester (I-**24**, X = I) was specifically employed with iodo complexes of Re and Fe to initiate living radical polymerization of styrenes and acrylates, where it performs as a better initiator than other iodides such as I-**13** (X = I) and I-**21** (X = I).[72,73,141,142,169] In contrast, the chloride versions such as $(CH_3)_2C(CO_2CH_3)Cl$ are poor initiators for MMA, although they can be regarded as a unimer of PMMA with a C−Cl dormant terminal.[170] The problem with the chloride initiators can be overcome with a dimer type of initiator, i.e., MMA dimers capped with chlorine (I-**25**, X = Cl), which achieves fast initiation catalyzed by Ru-**1** to give well-controlled molecular weights and narrower MWDs ($M_w/M_n \approx 1.3$). This is most probably due to electronic and/or steric effects. The former is related to the electron-deficient α-carbon atom, which is suggested by the lower-field ^{13}C NMR chemical shifts relative to that in the unimer I-**24**, while the latter factor is related to the so-called back strain effect, which makes the dissociation of the C−Cl bond easier during the rehybrdization of the α-carbon from sp^3 to sp^2, thus relieving steric hindrance. When coupled with Ru-**6**, the dimer initiator is highly versatile and can be employed for not only MMA but also styrene and MA to give narrow MWDs under the same conditions ($M_w/M_n = 1.1-1.2$) as describe above.[62] A similarly higher reactivity of the dimer-type compound was observed for the bromide version I-**25** (X = Br), which can be employed for MMA with Ru-**1**[170] and Ni-**3**.[60,135]

The malonate-type initiator I-**26** can generate a stabilized initiating radical rapidly and can be employed for the living radical polymerization of MMA with Ru-**1**[154] and Fe-**1**[70] to afford narrow MWDs ($M_w/M_n \approx 1.2$) but slightly higher M_n values than the calculated values. Control of molecular weights for PMMA is achieved with the I-**26**/CuBr/L-**4** system, while no polymerizations occurred with $CH(CO_2Et)_2Br$.[155]

A compound such as I-**27**, which possesses one ester and one phenyl group adjacent to the chlorine atom, induces controlled polymerization of both MMA and styrene in the presence of CuBr/L-**1**.[171] The initiation occurs faster than with I-**21** (X = Cl) and $CH_2ClCO_2C_2H_5$, both of which have no phenyl substituent. A bromide (I-**28**) with a similar structure proved effective in the CuBr/L-**24**-mediated polymerization of MMA.[149]

6. Haloamides

Bromides with *N*,*N*-alkylamide groups (I-**29** and I-**30**) can be good initiators for acrylamides. They were employed for the Ru-catalyzed polymerization of *N*,*N*-dimethylacrylamide (DMAA) to give controlled molecular weights and broad MWDs ($M_w/M_n \approx 1.6$).[160] In contrast, the chloride version $CH_3CH(CONMe_2)Cl$ failed to give controlled molecular weights,[160] and similar halides without alkyl substituents on the amide nitrogens, such as CH_3CH-

(CONH$_2$)X (X = Cl, Br), do not lead to controlled polymerization of DMAA.[172]

7. Halonitriles

Halonitriles I-**31** (X = Cl, Br), unimer models of halogen-capped dormant poly(acrylonitrile), are specifically employed for the polymerization of acrylonitrile with copper halides. Controlled molecular weights and narrow MWDs ($M_w/M_n = 1.1-1.4$) are achieved.[173,174] The strong electron-withdrawing cyano group facilitates the formation of the initiating radical, and may thus be employed for other monomers such as MMA with Fe catalysts[74] and styrene with CuCl/L-**1**.[84]

8. Sulfonyl Halides

Sulfonyl halides, particularly arenesulfonyl halides, can afford radical species much faster than carbon halides by the assistance of a metal complex and efficiently add to olefins with little dimerization of sulfonyl radicals in comparison to carbon-centered radicals. Another feature of the compounds is that there is little effect of the substituents on the rate of addition to an olefin. These properties make sulfonyl halides an efficient and “universal” series of initiators for the metal-catalyzed living radical polymerizations of various monomers including methacrylates, acrylates, and styrenes (Figure 9).[152,175−177]

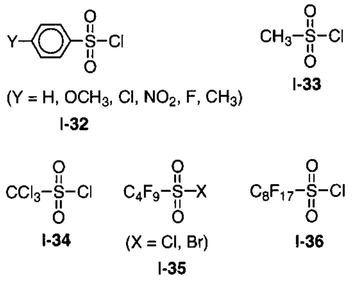


Figure 9. Sulfonyl halide initiators.

Arenesulfonyl halides I-**32** were first employed for the CuCl/L-**1**-catalyzed polymerization of styrene in the bulk at 130 °C to give polymers with controlled molecular weights and relatively narrow MWDs ($M_w/M_n = 1.4-1.8$).[152] No significant effects were observed with different ring substituents.

The polymers possess one sulfonyl group per chain, which can be utilized as end-functional polymers as discussed later (section III.B.1). Narrower MWDs ($M_w/M_n = 1.2-1.4$) were obtained in MMA polymerization with I-**32** as well as I-**33** and I-**34** in conjunction with CuCl/L-**1** in *p*-xylene at 90 °C.[175] In a homogeneous system with CuCl/L-**4**, I-**32** can afford narrow MWDs ($M_w/M_n = 1.1-1.3$) for styrene, MMA, and nBA.[176] The fast addition of the sulfonyl radical to these monomers was evidenced by ^{1}H NMR analysis of the reactions, where the apparent rate constants of initiation are 4 (for styrene and MMA), 3 (nBA), and 2 (MA) orders of magnitude higher than those of propagation. A similar controlled and homogeneous polymerization of MMA with I-**32** (X = CH$_3$)/CuBr/L-**4** was reported in diphenyl ether at 90 °C.[178] A better control of molecular weights and MWDs with I-**32** (X = CH$_3$)/CuBr/L-**9** in diphenyl ether was also observed when compared with that of bromoisobutyrate [I-**24** (X = Br)]/CuBr/L-**9** in *p*-xylene.[179]

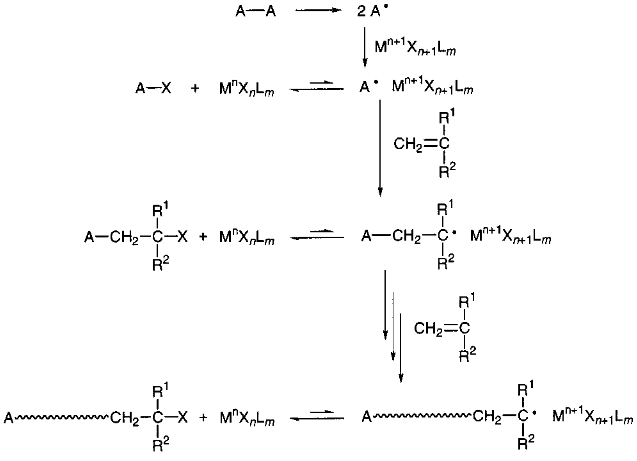
Perfluoroalkanesulfonyl halides I-**35** and I-**36** induced controlled polymerization of styrene and MMA in the presence of copper catalysts, although the initiation efficiency is lower.[177] With the alkanesulfonyl halides I-**35** and I-**36**, decomposition by loss of SO$_2$ from the initial sulfonyl radical occurs to give a perfluoroalkyl radical, which then adds to the monomer to initiate the polymerization.

The use of arenesulfonyl halides was also investigated for the ruthenium-catalyzed polymerization of MMA.[180] Living polymers are indeed attained, where the α-end group ($F_n \approx 1.0$) and the MWDs are controlled ($M_w/M_n = 1.2-1.5$), whereas the M_n values were higher than the calculated values due to low initiation efficiency ($I_{eff} \approx 0.4$).

9. Conventional Radical Initiators

Another route to the metal-catalyzed living or controlled radical polymerization is through initiation by a conventional radical initiator (A−A) such as AIBN in conjunction with a metal complex [$M^{n+1}X_{n+1}L_m$] at a higher oxidation state, for example, CuCl$_2$/L-**1** (Scheme 4). This system is sometimes called a “reverse (or alternative)” atom-transfer radical polymerization.[80,130] The difference between the normal route with R−X/$M^nX_nL_m$ and the reverse route lies in the initiation mechanism. The latter is initiated by the formation of radical species A• via homolytic cleavage, while the former by the formation of radical species from R−X assisted by $M^nX_nL_m$. The radical species thus generated (A•) gives an adduct (A−X) by abstraction of halogen from $M^{n+1}X_{n+1}L_m$, leaving a metal complex at a lower oxidation state [$M^nX_nL_m$]. Alternatively, A• adds to the monomer to form an initiating radical species [A−CH$_2$−C(R^1)(R^2)•] or a propagating species, which is also converted into a similar covalent species with a C−X bond accompanying reduction of $M^{n+1}X_{n+1}L_m$. After formation of the dormant C−X species and the metal catalyst at a lower oxidation state, the polymerization proceeds similarly to the normal-type metal-catalyzed processes already discussed. Figure 10 summarizes

Scheme 4. Reverse-Type Metal-Catalyzed Living Radical Polymerization



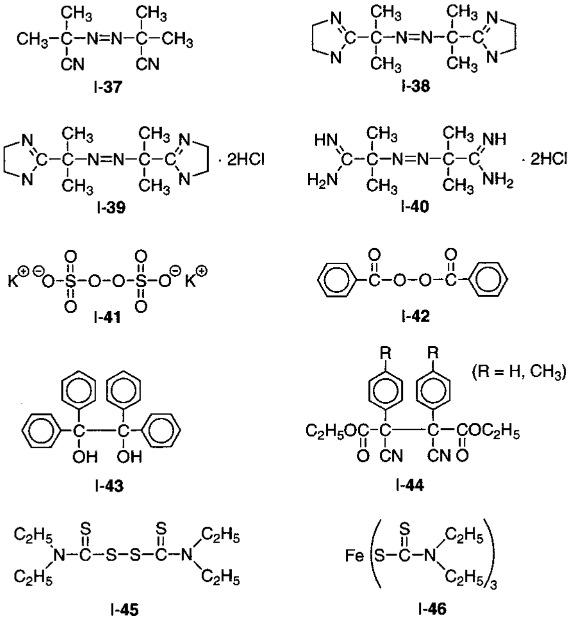


Figure 10. Conventional radical initiators employed for metal-catalyzed polymerizations.

the initiators thus far employed in such reverse-type polymerizations.

This type of polymerizations was first reported for the bulk polymerization of styrene with AIBN (I-**37**)/$CuCl_2$/L-**1** at 130 °C.[130] The M_n increased in direct proportion to monomer conversion and agreed well with the calculated values assuming that one AIBN molecule forms two polymer chains. The MWDs were narrow ($M_w/M_n = 1.3-1.6$). However, the heterogeneous system with L-**1** is not applicable for other monomers such as methacrylates and acrylates. This can be overcome with the use of the homogeneous $CuBr_2$/L-**4** system for MA and MMA polymerization[131] or by lowering the initiation temperature to 65−70 °C followed by polymerization at 100 °C for MA even in the heterogeneous system.[181]

Iron(III) chloride ($FeCl_3$) with PPh_3 ligands can be similarly employed with AIBN for MMA[80] and styrene,[182] while the AIBN/$FeBr_3$/n-Bu_4PBr system is effective in MMA and MA polymerization.[75]

An azo compound with an imidazoline group (I-**38**) is applicable to MMA coupled with $FeCl_3$ and PPh_3.[183] Water-soluble azo compounds such as I-**39** and I-**40** with $CuBr_2$ and L-**4** induced emulsion living radical polymerization of nBMA ($M_w/M_n = 1.2-1.6$), though the initiation efficiency is rather low.[184] A similar emulsion polymerization was conducted with I-**41**.[184]

A conventional peroxide initiator such as BPO (I-**42**) does not work in a manner similar to that of azo initiators in the homogeneous system for styrene with $CuBr_2$ and L-**4**.[185] In this polymerization, the Cu(I) species is generated via reduction of Cu(II) species by a styryl radical and further acts as an accelerator in the decomposition of BPO. It then reacts with the remaining BPO to form the benzoyloxy radical and inactive copper(II) benzoate salts again. Thus, no polymerization occurs. However, the use of a heterogeneous system and low-temperature initiation at 70 °C followed by the polymerization at 110 °C in fact induces styrene polymerization. The polymers had narrow MWDs ($M_w/M_n = 1.2-1.4$) and controlled M_n values, which agreed well with the calculated values assuming the formation of one polymer chain per BPO molecule.[186] The polymerizations of styrene and MMA with BPO can be controlled with copper(I) halide.[185,187]

There were also several reports on the use of other radical generators such as I-**43**[188,189] and I-**44**[190−192] in conjunction with $FeCl_3/PPh_3$ or with $CuCl_2$/L-**1** for MMA and styrene. Polymers obtained with I-**43** have a methyl group at the α-end because a hydrogen radical is the initiator. Low temperatures are enough for I-**44** (75 °C for R = H, 85 °C for R = CH_3) to afford PMMA with narrow MWDs ($M_w/M_n = 1.2-1.3$), although the M_n values were lower than the calculated values.

In situ heating of a mixture of I-**45** and $FeCl_3$ with PPh_3 results in the formation of dithiocarbamate−iron complexes that decompose into $Et_2NC(S)S-Cl$ and $FeCl_2/PPh_3$, and finally initiates the polymerization via activation of the S−Cl bond by $FeCl_2$.[193] The bulk MMA polymerization at 100 °C reaches 80% in 8 min to give controlled molecular weights and narrow MWDs ($M_w/M_n \approx 1.1$). A similar polymerization of MMA can also be done with an iron(III) complex system (I-**46**/$FeCl_3/PPh_3$).[194] Air could be a radical source for methacrylate polymerization with $CuCl_2$/L-**29** and results in polymers with high molecular weights up to 700000 and narrow MWDs ($M_w/M_n \approx 1.1$).[195]

In addition to the wide variety and number of initiators shown in Figures 8−10, various "functionalized" initiators have been designed and examined, as will be separately treated later (cf. Figure 13).

C. Monomers

The rapid progress and proliferation of metal-catalyzed living radical polymerization has allowed a variety of vinyl monomers to be polymerized into well-defined polymers of controlled molecular weights and narrow MWDs. Most of them are conjugated monomers such as methacrylates, acrylates, styrenes, acrylonitrile, acrylamides, etc., except dienes, which possess not only alkyl substituents but also aprotic and protic functional groups. This fact attests to the versatility and flexibility of metal catalysis for precision polymerization.

However, less conjugated monomers such as vinyl acetate, vinyl chloride, and ethylene are still difficult to polymerize in a controlled way by metal-catalyzed polymerizations. This is most probably due to the difficulty in activation of their less reactive carbon−halogen bonds. The following sections will discuss these aspects from the viewpoint of the monomers listed in Figure 11. Functional monomers will be discussed later in another section, Precision Polymer Synthesis.

1. Methacrylates

Living radical polymerization of methacrylates has been achieved by the use of various complexes including ruthenium, iron, copper, nickel, palladium, and rhodium. Among them, the most precisely con-

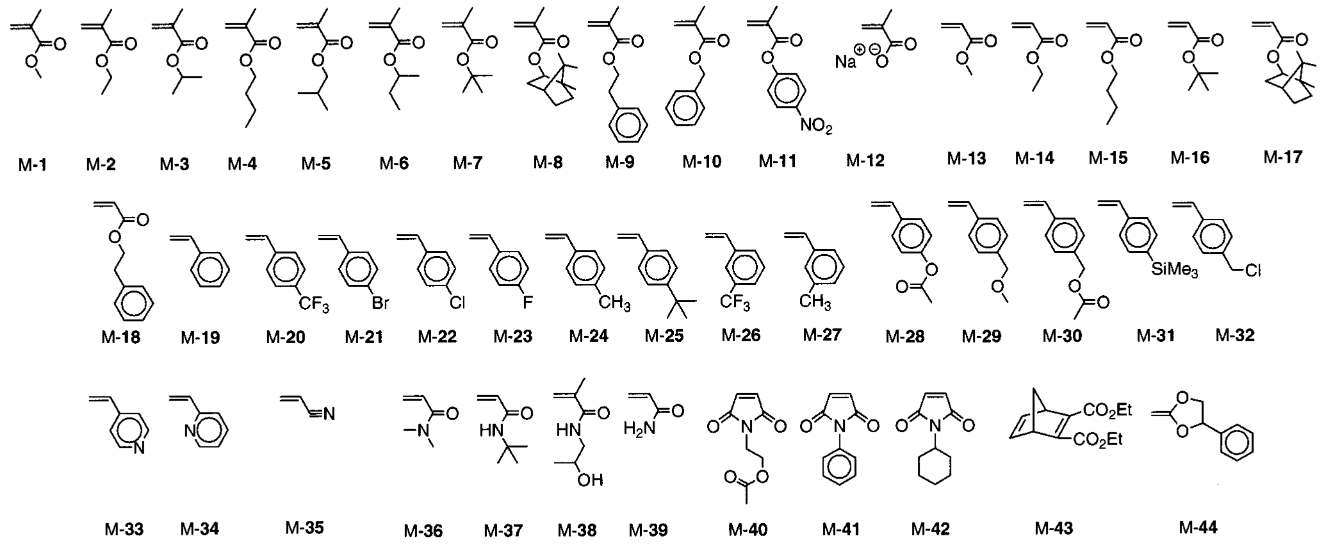


Figure 11. Monomers.

trolled polymerizations (M_w/M_n = 1.1−1.2) were reported with the R−Cl/Ru,[56] R−Br/Ni,[133] R−Br/Cu,[100] and RSO_2Cl/Cu[176] systems, where R−X means an initiator with a particular halogen (X). The carbon−halogen bonds derived from methacrylates are highly reactive, in contrast to those from other monomers due to the two substituents, methyl and ester groups, which stabilize the relevant radical species. This may in turn require relatively mild metal complexes such as ruthenium and nickel, whereas some special issues, such as use of polar solvents[84] or a halogen-exchange reaction,[196] should be considered for the copper/bipyridine-based systems.

Recommended initiators for methacrylate polymerizations are I-**24** (X = Br) and I-**25** (X = Cl), both of which are unimer and dimer models of poly(methacrylate) dormant terminals, respectively. For example, PMMA with precisely controlled molecular weights, very narrow MWDs (M_w/M_n = 1.1), and nearly perfect end-capping with halogen was obtained with the I-**25** (X = Cl)/Ru-**5**/Al(O-*i*-Pr)$_3$ initiating system.[60,197] Alternatively, arenesulfonyl chlorides can lead to well-controlled poly(methacrylate)s with narrow MWDs (M_w/M_n = 1.1−1.2) in combination with copper catalysts.[126,176]

The alkyl substituents of methacrylates are varied as methyl (M-**1**),[27,84,100,132,133,176] ethyl (M-**2**),[102,198] isopropyl (M-**3**),[199] *n*-butyl (M-**4**),[102,132,176,198] isobutyl (M-**5**),[102] *sec*-butyl (M-**6**),[102] *tert*-butyl (M-**7**),[63,102] isobornyl (M-**8**),[63] 2-phenylethyl (M-**9**),[195] benzyl (M-**10**),[199] and 4-nitrophenyl (M-**11**)[166] methacrylates were also polymerized in a controlled way, and the polymer from M-**11** can be converted easily into poly(methacrylic acid) via deprotection of the nitrophenyl group. Sodium methacrylate (M-**12**), an ionic monomer, can be polymerized directly into poly(methacrylic acid) sodium salt with controlled molecular weights and narrow MWDs (M_w/M_n = 1.2−1.3) with a water-soluble bromide initiator and CuBr/L-**1** in water under alkaline conditions (pH 8−9) at 90 °C, although the polymerization stopped around 70−80%.[200]

2. Acrylates

Acrylates generate highly reactive radical species but give less reactive carbon−halogen bonds than those of methacrylates. These differences from the methacrylate counterparts thus call for active catalysts with lower redox potentials. Copper-based systems have most extensively been studied and are best suited in controlling the MWDs (M_w/M_n = 1.1−1.2)[84,85,176] of poly(acrylate)s, but ruthenium,[62] iron,[201] nickel,[134,135] and rhenium[142] catalysts are often effective too. In the Cu(I) catalysis, chloride and bromide initiators may be coupled with CuBr and CuCl in conjunction with various nitrogen-based ligands. For example, CuBr with I-**31** (X = Br) and L-**3** afforded poly(MA) with very narrow MWDs (M_w/M_n = 1.1) in the bulk at 110 °C.[85] In contrast, bromide and iodide initiators are preferably used with other metals such as Ru(II)[62] to increase the reactivity of the dormant C−X bonds. Among the most suitable initiators are unimer models of poly(acrylate)s such as I-**21**.

Similarly to methacrylates, various alkyl groups are available as substituents including methyl (M-**13**),[62,84,85,135,142,176,201] ethyl (M-**14**),[94] *n*-butyl (M-**15**),[84,134,142,176,201] *tert*-butyl (M-**16**),[201−203] isobornyl (M-**17**),[204] and 2-phenylethyl (M-**18**).[195]

3. Styrenes

A large number of styrenic monomers have been investigated in metal-catalyzed radical polymerizations. Polymerization of styrene (M-**19**) can be controlled with copper,[28,84,85,152,176] ruthenium,[57,60,62,66,86,205] iron,[71−75] rhodium,[86,140] rhenium,[141] and molybdenum catalysts.[144] The polymerizations have actively been studied with the copper-based systems, among which precisely controlled molecular weights and very narrow MWDs (M_w/M_n = 1.1) were obtained in a homogeneous system consisting of I-**13** (X = Br), CuBr, and L-**3** in the bulk at 130 °C.[85] Similar well-controlled polymerizations are feasible with several ruthenium (Ru-**5**)[60] and iron (Fe-**2**,[72] Fe-**3**,[73] and Fe-**4**[71]) complexes in conjunction with a bromide or iodide initiator. Even a chloride initiator (I-**25**, X = Cl) can afford narrow MWDs (M_w/M_n = 1.1) when coupled with the Ru(II)−Cp* complex (Ru-**6**) in the presence of Al(O-*i*-Pr)$_3$ in toluene at 80 °C.[62]

A series of substituted styrenes (M-**19** to M-**27**) were polymerized with the I-**13** (X = Br)/CuBr/L-**1** system in diphenyl ether at 110 °C to give controlled M_n that increased in direct proportion to monomer conversion.[206] The polymerization rate was faster with more electron-withdrawing substituents due to the increase of monomer reactivity and the carbon−halogen bond in the dormant species. The MWDs of the polymers with electron-donating substituents (M-**24** and M-**25**) were relatively broad (M_w/M_n = 1.4−1.7). Introduction of a strongly electron-donating substituent such as a methoxy group gave only oligomers, probably because of the formation of cationic propagating species via the heterolysis of the dormant C−Br.

Though not in the late-transition-metal family, a rhenium complex is applicable for both electron-donating (M-**24**) and -withdrawing (M-**22**) groups to give well-controlled molecular weights and narrow MWDs (M_w/M_n = 1.2−1.3).[169] Living radical polymerization of 4-acetoxystyrene (M-**28**) was reported with the use of a copper-[207] or iron-based[169] system. The acetoxy groups in the polymers can be removed after the polymerization to form poly(*p*-vinylphenol) with controlled molecular weights.[208] Copolymerizations of M-**29** or M-**30** with styrene were studied with the copper-based systems to give well-controlled copolymers.[209] Rhenium (Re-**1**) and iron (Fe-**5**) complexes induced polymerization of M-**30** in conjunction with I-**24** (X = I) to give controlled molecular weights but relatively broader MWDs ($M_w/M_n \approx 1.8$) due to side reaction of its benzyl group.[169] Controlled polymerization of a silyl-substituted styrene (M-**31**) was also achievable.[210] 4-(Chloromethyl)styrene (M-**32**), which has a reactive C−Cl bond in the unit, is polymerized with the copper-based systems to produce a hyperbranched or linear polymer depending on the conditions.[211−213] This will be discussed later in Precision Polymer Synthesis (section III.I).

4. Vinylpyridines

Metal-catalyzed living radical polymerizations of vinylpyridines were investigated with the copper-based systems. One of the difficulties in the polymerization is a decrease of catalytic activity imposed by the coordination of the monomers by the metal complex. Controlled radical polymerization of 4-vinylpyridine (M-**33**) was achieved by an initiating system consisting of a strong binding ligand such as L-**32** and a chloride-based system [I-**13** (X = Cl)/CuCl] in 2-propanol at 40 °C.[214] The M_n increased in direct proportion to monomer conversion, and the MWDs were narrow (M_w/M_n = 1.1−1.2). In contrast, 2-vinylpyridine (M-**34**) can be polymerized in a controlled way with chlorine-capped polystyrene as an initiator and the CuCl/L-**1** pair in *p*-xylene at 140 °C.[215] Block copolymers with narrow MWDs (M_w/M_n = 1.1−1.2) were obtained therein.

5. Acrylonitrile

A good control of molecular weights and MWDs was accomplished for this monomer (M-**35**) with a copper-based system, consisting of I-**31** (X = Cl, Br), CuX (X = Cl, Br), and L-**1** in ethylene carbonate at 45−65 °C.[173,174] The M_n is controlled up to 30000, keeping relatively narrow MWDs ($M_w/M_n < 1.5$). The end-group analysis showed some loss of the terminal halogen most probably due to the reduction of the growing radical by CuX to form the corresponding polymer anion that subsequently deactivates quickly.

6. Acrylamides

Polymerizations of acrylamides were investigated with several systems based on copper and ruthenium. The system with Ru-**1** and a bromide initiator such as I-**29** in the presence of Al(O-*i*-Pr)$_3$ induced quantitative polymerizations of M-**36** in toluene at 60−80 °C to give polymers of controlled molecular weights and relatively broad MWDs ($M_w/M_n \approx 1.6$).[160] In contrast, molecular weight control is difficult with a chloride initiator. The copper-based systems are applicable, but the polymerization strongly depends on the initiators, copper halides, ligands, temperatures, and solvents. Namely, in some cases the polymerizations were not quantitative due to side reactions such as cyclization and loss of terminal halogens.[117,168,172] Among them, I-**22** (X = Cl)/CuCl/L-**32** induced the best controlled polymerization in toluene at 20 °C to give narrow MWDs (M_w/M_n = 1.1−1.2), though limited to 80% conversion.[168] Similar controlled polymerizations were also feasible for M-**37** and M-**38** with the same initiating system.[168] Unsubstituted acrylamide (M-**39**) was polymerized with CuCl/L-**1** in conjunction with benzyl chloride I-**12** (X = Cl) or with a surface-confined initiator in DMF at 130 °C.[216−218] The polymers obtained with I-**12** were analyzed by matrix-assisted laser desorption−ionization time-of-flight mass spectrometry (MALDI-TOF-MS), which showed monomodal MWDs, but there was no detailed analysis of the polymer. The polymer obtained by the surface initiation had narrow MWDs (M_w/M_n = 1.1−1.3).

7. Other Monomers

Via metal catalysis, cyclic monomers such as *N*-substituted maleimides M-**40**, M-**41**, and M-**42** do not homopolymerize but can copolymerize with vinyl monomers, among which alternating copolymers can be obtained with styrene via a radical mechanism. The I-**13** (X = Br)/CuBr/L-**1** system induced alternating copolymerizations with styrene to give controlled molecular weights and narrow MWDs (M_w/M_n = 1.1−1.4) in the bulk or anisole at 80−110 °C.[219−222]

A bicyclic monomer containing a maleate ester unit (M-**43**) undergoes a very slow 2,6-addition polymerization with I-**12** (X = Cl)/CuCl/L-**1** in the bulk at 130 °C to afford narrow MWDs ($M_w/M_n \approx 1.2$) (11% conversion in 2 weeks).[223] Enchainment of this monomer to the chlorine-terminated polystyrene increases the decomposition temperature of the polymer.

Ring-opening living radical polymerization was also reported for M-**44**, where the I-**23**/CuBr/L-**1** system gave polymers with controlled molecular weights and narrow MWDs in the bulk at 120 °C.[224] However, unlike in conventional radical polymerization, the content of the ring-opened units is not 100% but varies from 38% to 67% depending on the conditions. Cationic polymerizations concurrently occur, which can be suppressed by the addition of pyridine.

As pointed out, living radical polymerization of less conjugated monomers such as vinyl acetate has not been achieved yet. However, irreversible activation of the carbon−halogen bond in CCl_4 with $Fe(OAc)_2$/L-**24** generates trichloromethyl radical to induce radical polymerization of vinyl acetate via the radical telomerization mechanism.[225] The molecular weights can be controlled by the molar ratio of monomer to CCl_4 although the MWDs were broad in the usual radical telomerization ($M_w/M_n \approx 1.8$).

Polymerization of ethylene is one of the most important unsolved problems in metal-catalyzed living radical polymerization. This is due to the difficulty of the activation of the primary carbon−halogen bond. The unpolymerizable nature of ethylene can be utilized for the end-functionalization of PMMA with a terminal CH_2CH_2Br group (section III.B.2).[226]

D. Additives

Metal-catalyzed living or controlled radical polymerizations can generally be achieved with initiating systems consisting of an organic halide as an initiator and a metal complex as a catalyst or an activator as described above. However, these polymerizations are slow in most cases due to low concentration of the radical species, as required by the general principle, the dormant-active species equilibria, for living radical polymerization (see the Introduction).

A promising solution for this inherent problem is the use of additives. Some additives are needed for acceleration and/or better control of the polymerizations. These additives most probably can effectively reduce the metal species in higher oxidation states or form more efficient catalysts via coordination.

Metal alkoxides such as Al(O-*i*-Pr)$_3$ are employed for the ruthenium-, iron-, nickel-, rhenium-, and copper-catalyzed polymerizations and are effective in increasing the polymerization rate as well as narrowing the MWDs of the produced polymers. In fact, the use of such additives can be found in the first examples of metal-catalyzed living radical polymerization. Thus, for the mild catalyst Ru-**1**, MeAl(ODBP)$_2$ was added to achieve a faster and quantitative polymerization of MMA with CCl_4 in toluene at 60 °C.[27] A trialkoxide [Al(O-*i*-Pr)$_3$] is less active as an additive but more effective in controlling the molecular weights and MWDs than MeAl(ODBP)$_2$.[56,198] Other metal alkoxides such as Ti(O-*i*-Pr)$_4$ and Sn(O-*i*-Pr)$_4$ induce faster polymerizations of MMA with Ru-**1** than Al(O-*i*-Pr)$_3$, while the controllability is lower.[227] Aluminum acetylacetonate [Al(acac)$_3$] is an alternative mild additive that does not induce an ester-exchange reaction between the ester group and the monomer or monomer units in the polymer chain, which might occur with aluminum alkoxides.[228] These metal alkoxides are also effective for other complexes such as Fe-**3**,[72] Ni-**2**,[133] Re-**1**,[141] and CuBr/L-**1**.[229] Al(O-*i*-Pr)$_3$ can even make the Cu(II) species active, where the controlled polymerizations of styrene, MMA, and EA were possible with an organic bromide and $CuBr_2$ in the presence of Al(O-*i*-Pr)$_3$.[93,94]

The addition of aluminum compounds was initially intended to increase the monomer reactivity via coordination to its carbonyl group or to increase the reactivity of the terminal group via the coordination of the terminal carbonyl group.[27] However, this possibility proved less probable, because strong Lewis acids such as $SnCl_4$ were not effective in a similar acceleration.[227] There was no increase in the halogen-exchange rate in the model reaction between I-**24** (X = Br) and Ru-**1** on addition of Al(O-*i*-Pr)$_3$, while under similar conditions the polymerization rate was clearly increased relative to that of the additive-free system.[170] Possible interactions between the added Al(O-*i*-Pr)$_3$ and monomer, terminal group, and ruthenium complex were investigated with the use of kinetics, NMR, and cyclic voltamometry.[227] These studies suggest that the added metal compounds most probably interact with the metal catalysts in their higher oxidation states, or increase the concentrations of radical species out of the coordination spheres, resulting in smooth redox reactions. Further studies are required to clarify these interesting features of metal-mediated radical processes.

Zerovalent metals such as Cu(0) and Fe(0) can effectively reduce $CuBr_2$ and $FeBr_3$ into active CuBr and $FeBr_2$, respectively, to dramatically increase the polymerization rate.[129] For example, addition of Cu(0) to the polymerization mixture of MA with I-**22** (X = Br)/CuBr/L-**4** in the bulk at 90 °C increased the rate by about 10 times; i.e., the reaction reached 97% conversion in 570 min without additives, whereas 96% in 55 min in the presence of Cu(0). This is attributed to the removal of a small amount of Cu(II) species generated via irreversible termination of the growing or the initiating radical species. A similar fast polymerization is possible with $CuBr_2$ in the presence of Cu(0). This allows the controlled radical polymerization even in the presence of oxygen or without purification of the monomer, where Cu(0) and Fe(0) can reduce the generated Cu(II) and Fe(III) species into active Cu(I) and Fe(II), respectively.[230] The I-**13** (X = Br)/$CuBr_2$/Cu(0)/L-**4** system induced a fast polymerization of unpurified styrene at 110 °C to reach 90% conversion within 2 h. Controlled molecular weights and narrow MWDs are available even when the polymerization is performed in ampules sealed in air. However, no polymerization occurred open to air.

Phenols usually serve as radical inhibitors in conventional radical polymerization but can enhance the polymerizations of MMA with I-**21** (X = Br)/CuBr/L-**9** (R = *n*-Pen).[231] For example, on addition of 10 equiv of 2,6-di-*tert*-butyl-4-methylphenol with respect to initiator ([I-**21**]:[CuBr]:[L-**9**]:[phenol] = 1:3:1:10), the conversion increased from 55% to 75% in 4 h in xylene at 90 °C without any changes in the MWDs. Similar effects were observed for 4-methoxyphenol, phenol, and 2,6-di-*tert*-butylphenol.[231−233] No inhibition but enhancement of the polymerization by the addition of phenols may suggest that the growing species is different from that in conventional radical polymerization. However, phenols do not act as inhibitors even for some conventional free radical (meth)acrylate polymerizations as suggested elsewhere.[155] An explanation is that the added phenols substitute nitrogen-based ligands on copper catalysts to increase the catalytic activity, which is suggested by the isolation of methanol-coordinated catalysts[234] and NMR analysis of the mixture of catalysts and phenols.[233]

Benzoic acid also increases the polymerization rate with copper catalysts, most probably via displacement of the nitrogen ligand and creation of a coordination site on the metal.[235] Similarly, carboxylate salts such as sodium benzoate and acetate have remarkable effects on rate enhancement.[107] Addition of sodium benzoate, 4 equiv with respect to CuCl, to I-**32** ($Y = OCH_3$)/CuCl/L-**1** enhances the polymerization rate of nBMA 2.4 times in diphenyl ether at 120 °C, where the reaction reaches 90% conversion in 1 h. The MWDs were still narrow. A similar rate enhancement was observed with a mixture of para-substituted benzoic acids and metal carbonates M_2CO_3 (M = Cs, K, Na, Li). These are due to in situ formation of cuprous carboxylate that has higher activity as described above (section II.A.3).

The ruthenium-catalyzed living radical polymerizations provide good cases for considerable acceleration by the addition of alkylamines.[61,236] For example, on addition of *n*-butylamines to the polymerization of MMA with I-**25** (X = Cl)/Ru-**1** in toluene at 80 °C, the rate was increased dramatically. Time for 75% conversion: 269 h (no additive) > 29 h [$Al(Oi\text{-}Pr)_3$] > 17 h ($n\text{-}Bu_3N$) > 9 h ($n\text{-}Bu_2NH$) > 4 h ($n\text{-}BuNH_2$). $n\text{-}Bu_3N$ and $n\text{-}Bu_2NH$ gave narrow MWDs ($M_w/M_n = 1.2$) and controlled molecular weights, similarly to $Al(O\text{-}i\text{-}Pr)_3$, but broad MWDs were obtained with $n\text{-}BuNH_2$ ($M_w/M_n \approx 1.8$). These added amines most probably coordinate to the ruthenium complex to produce more active complexes, as suggested by NMR analysis of amine/Ru(II) catalyst mixtures. An increased catalytic activity was also observed on addition of silica gel supported amine ligands.[148]

In the heterogeneous systems based on Cu_2O/L-**1** and Cu(0)/L-**1**, phase-transfer catalysts such as $C(CH_2OCOPh)_4$ and poly(ethylene glycol) can increase the rate and control the polymerization more precisely.[107]

Rate enhancement can also be achieved by irradiation of visible light.[237] The polymerization of MMA with I-**17**/CuCl/L-**1** in toluene at 80 °C in the dark ceased around 40% conversion, but under irradiation of visible light, the polymerization became quantitative. This is due to a photochemical effect on the inner-sphere complex between the catalyst and the dormant alkyl chloride.

E. Solvents

Metal-catalyzed living radical polymerizations may be carried out either in solution or in the bulk. Importantly, unlike conventional free radical polymerization, the Trommsdrof or gel effect is absent in these living processes in the bulk.[238] For the solution processes, nonpolar or less polar solvents are employed, such as toluene, xylene, and benzene. Polar solvents are sometimes employed for not only solubilizing the monomers, the produced polymers, and the catalysts but also acceleration and better control of the polymerization. Due to the radical nature of the polymerizations, even protic solvents such as alcohol and water can be employed. Some of these solvents, e.g., toluene, are known as chain-transfer agents, but the effects of potential chain-transfer agents have not yet been examined well in metal-catalyzed living radical polymerizations.

1. Aprotic Polar Solvents

Aprotic polar solvents thus far employed in metal-catalyzed polymerizations include dimethoxybenzene (DMB), diphenyl ether (DPE), ethylene carbonate, acetonitrile, *N*,*N*-dimethylformamide (DMF), and acetone, among others. Most of them are employed for copper catalysts because of their low solubility. For well-solubilized Ru(II), Ni(II), and Fe(II) complexes with phosphine or other ligands, such an additional precaution is not necessary, and toluene or other relatively nonpolar solvents have mostly been used.

Unsubstituted 2,2′-bipyridine (L-**1**) cannot completely solubilize copper halide in the bulk or nonpolar solvents, and thus the polymerization systems are heterogeneous as described above. Various solvents were thus investigated in the polymerization of nBA with I-**22** (X = Br)/CuBr/L-**1**, and ethylene carbonate proved effective in fast and homogeneous living polymerizations.[239] Relative to the heterogeneous systems, these reactions give polymers of narrower MWDs. This is due to the increased solubility of the copper complex and/or to the change in the structure of the copper species (known to form a dimeric species in organic media) into a monomeric form. Similar effects were observed for DMF and acetone in *tert*-butyl acrylate (tBA) polymerizations with I-**22** (X = Br)/CuBr/L-**24**.[202] Styrene polymerization with I-**13** (X = Cl)/CuCl/L-**1** at 130 °C became homogeneous in the presence of a limited amount of DMF (~10% v/v) to give polymers with well-controlled molecular weight up to 40000.[88] Copper-based systems with bipyridines, such as R−Cl/CuCl/L-**4**, are not suited for controlling methacrylate polymerization in the bulk or in nonpolar solvents, but are effective in DPE solvent, where monomeric copper species may form.[107,126,164,178,240] Acetonitrile is another choice of solvent in some Cu-catalyzed polymerizations.[93,112,167,241]

In the homogeneous MMA polymerization with I-**32** ($Y = CH_3$)/CuBr/L-**9** (R = *n*-Pen), the rate increased in the order xylene < DMB < DPE,[179] probably due to the differences in the dielectric constant and coordination ability of the solvents. With the homogeneous Ru-**1** catalyst, the polymerization of MMA was faster in a polar solvent such as CH_2Cl_2 than in toluene.[159] A more detailed analysis on solvent effects was carried out by end-capping a polymer radical with hydroxyl-TEMPO, where the radical intermediate was generated from bromide macroinitiators via CuBr/L-**4** catalyst.[242] A polar solvent such as butyl acetate increases the radical-generation rate from poly(acrylate)s but not from polystyrene. On the other hand, no rate increase was found for both macroinitiators in DMF, which is considered not only a polar solvent but also a coordinating ligand.

2. Protic Polar Solvents

Protic polar solvents such as alcohols are necessary to solubilize polar functional monomers and their polymers. Due to the robust nature of several catalysts to hydroxyl groups, alcohols can be employed in the metal-catalyzed living or controlled radical polymerization.

Ruthenium complexes such as Ru-**1** are stable in alcohol and can induce living radical polymerization of MMA in toluene/methanol mixtures or in methanol, isobutanol, and *tert*-amyl alcohol to give polymers with controlled molecular weights and narrow MWDs ($M_w/M_n \approx 1.2$).[55,159] The polymerization proceeds faster in methanol than in toluene.

Methanol is a good solvent for HEMA and its polymer, and thus can be employed for its homogeneous living radical polymerization with Ru-**3**, which is also highly soluble in methanol.[59] Copper-based systems also give homogeneous living radical polymerizations of HEMA in a mixture of methyl ethyl ketone and 1-propanol,[243] of acrylamides in methanol,[117,172] and of 4-vinylpyridine (M-**33**) in 2-propanol.[214]

3. Water

In homogeneous free radical polymerization, water is often employed as solvent for water-soluble monomers and polymers with more polar functional substituents such as hydroxyl, amino, oxyethylene, ammonium, and carboxylate groups, along with emulsion, suspension, and dispersion processes. This is also the case for metal-catalyzed living radical polymerization.

2-Hydroxyethyl acrylate (HEA) can be polymerized homogeneously in water at 90 °C with the I-**22** (X = Br)/CuBr/L-**1** initiating system to give polymers with relatively narrow MWDs ($M_w/M_n = 1.34$), although the polymerization was slower, and the MWDs were broader than in the bulk ($M_w/M_n < 1.2$).[244] A similar controlled polymerization of an amino-functionalized methacrylate 2-(dimethylamino)ethyl methacrylate was achieved with the same initiating system in water.[245] Monomethoxy-capped oligo(ethylene oxide) methacrylate, a highly hydrophilic monomer, can be polymerized very fast with I-**21** (X = Br)/CuCl/L-**1** in water at 20 °C.[246] The polymerization reached 90% within 30 min to give narrow MWDs ($M_w/M_n < 1.2$). The fast reaction is attributed to the formation of mononuclear copper(I) species.

Water is the solvent of choice for ionic monomers such as sodium methacrylate, where a direct radical polymerization (i.e., with the nonprotected form of the monomer) is carried out with the copper-based systems in aqueous media (pH 8−9) at 90 °C to afford controlled molecular weights and narrow MWDs.[200] Another ionic monomer, sodium 4-vinylbenzoate, is polymerized very fast in aqueous media (pH 11) at 20 °C.[247] An ammonium salt monomer, [2-(methacryloxy)ethyl]trimethylammonium chloride (FM-**6**; Figure 12), was polymerized in water with CuBr/L-**1** in conjunction with a surface-confined initiator, while the polymerization was heterogeneous due to the hydrophobicity of the initiator.[248]

4. Suspension, Dispersion, and Emulsion Polymerizations in Water (Heterogeneous System)

In industrial processes, radical polymerization is usually performed under heterogeneous conditions such as suspension, dispersion, or emulsion. The metal-catalyzed radical polymerization also proceeds under such aqueous/organic biphasic conditions but often suffers from difficulties in controlling the molecular weights and MWDs of the products and in keeping particles or latexes from coagulation. The former problem stems from the partioning of the metal species into the aqueous phase while the growing polymer terminal exists in the organic phase. The latter is caused by some undesirable interactions among metal catalysts, ligands, and additives such as dispersants or surfactants. However, these problems can be overcome by careful choices of initiators, catalysts, dispersants or surfactants, temperatures, and concentrations according to the monomers as summarized in a review for the copper-catalyzed systems.[249]

Another problem involves the classification of these metal-based heterogeneous systems into suspension, dispersion, and emulsion polymerizations similarly to conventional systems. This is due to not only a lack of detailed analysis of reaction mechanisms and particle sizes but also fundamental differences in several aspects such as the locus of initiation and the molecular weight of polymers in comparison with the conventional counterparts. The terms suspension and emulsion will be used in the following sections for simple classification but are not based on the strict definition for conventional free radical systems.

Various metal complexes of Ru, Fe, Cu, Ni, and Pd are active in the radical polymerizations of hydrophobic methacrylates, acrylates, and styrenes under aqueous heterogeneous conditions to yield polymers with controlled molecular weights and relatively narrow MWDs. Importantly, a variety of these organometallic catalysts are tolerant to water, despite the fact that many similar complexes often lose their catalytic activity in the presence of water or even moisture.

A ruthenium-based system with Ru-**1** and organic halides (initiators) induces living radical polymerization of MMA in mixtures of toluene and water, where the M_n increased in direct proportion to monomer conversion up to 10^5, and the MWDs were as narrow as those obtained in toluene ($M_w/M_n \approx 1.2$).[55,159] The polymerization proceeded in a suspension system under vigorous stirring irrespective of the absence of suspension stabilizers (dispersants). The controlled polymerization can also be achieved even in the absence of toluene (i.e., bulk monomer containing a catalyst system is dispersed in water), though the MWDs became broader ($M_w/M_n \approx 1.4$) due to the low solubility of the complex in the monomer and/or the high viscosity of the organic particles. A rate increase was observed by the addition of water to the ruthenium-based system in organic media, and similarly, faster living polymerizations proceed in these dispersed systems with Ru catalysts.

A similar effect of water was observed in the iron-catalyzed polymerization of styrene.[76,250] An iron complex is less stable in water than ruthenium and thus considered difficult to use as an active catalyst in such an aqueous suspension system. For example, $FeBr_2(PPh_3)_2$ (Fe-**1**, X = Br; Figure 2) rapidly decomposes upon exposure to water. However, a Cp-based iron complex (Fe-**3**; Figure 2) proved effective in living radical suspension polymerizations of acrylates and styrene to give narrow MWDs ($M_w/M_n = 1.1-1.2$).[250] These polymerizations are also clearly faster than those in organic media under otherwise similar conditions.

Nickel (Ni-**1**) and palladium (Pd-**2**) complexes were employed for suspension polymerization of MMA in the presence of a small amount (1−5 wt %) of sorbitane monooleate poly(ethylene glycol) (20) (Tween 80) as a surfactant.[132,137] The obtained polymer had controlled molecular weights and moderate MWDs ($M_w/M_n = 1.4-1.7$) similarly to those obtained in toluene, although there was no detailed analysis on the size of the particles.

Detailed studies were performed on the copper-catalyzed suspension or emulsion polymerizations.[249] Living or controlled emulsion radical polymerization of nBMA can be achieved in the presence of nonionic poly(oxyethylene)-based surfactants such as Brij 97, Brij 98, and Tween 20 with the I-**21** (X = Br)/CuBr/L-**3** or L-**4** system.[249,251,252] The M_n increased in direct proportion to monomer conversion up to 5×10^4 ($M_w/M_n = 1.1-1.2$). The particle sizes are around 1000−4000 nm, suggesting a suspension, but can be reduced to about 300 nm with the use of hexadecane as a cosurfactant along with ultrasonication.[249,252]

Surfactants largely affect the polymerizations. Anionic surfactants such as sodium dodecyl sulfate adversely affect the control of molecular weights and MWDs, whereas poly(ethylene glycol) facilitates molecular weight control but leads to coagulation.[251] Water-soluble or more hydrophilic ligands such as L-**1**, L-**24**, L-**32**, and L-**9** (R = $CH_2CH_2CHPh_2$) are detrimental to the control of molecular weights due to unfavorable partioning of the Cu(II) species into water.[249,251,253] Other monomers such as MMA, nBA, and styrene can also be polymerized with the copper-based systems in emulsion to give polymers with controlled molecular weights and MWDs.[249,251,253]

Random and block copolymerizations of these monomers were also investigated with ruthenium, iron, and copper catalysts and gave successful results depending on the conditions.[110,250,254]

The so-called reverse atom-transfer radical polymerization is feasible in aqueous emulsion too. This system enables the formation of initiating radical species in the water phase with the use of water-soluble initiators such as I-**39**, I-**40**, and I-**41** as in conventional emulsion radical polymerization.[184,249,252,255] The copper-catalyzed emulsion radical polymerization of nBMA afforded polymers with narrow MWDs ($M_w/M_n = 1.1-1.4$), but the M_n values were much higher than the calculated values due to the termination between the initiating radicals in the aqueous phase.[184,255] The emulsions are relatively stable and their particle sizes are around 100−300 nm even without sonication.[184,255] There were no effects of the size and number of particles on the polymerization rate.[252] It is suggested that the nucleation mechanism in the reverse atom-transfer emulsion radical polymerization is different from that in the conventional processes, because of the lack of formation of high molecular weight polymers during the early stages.[255]

Another aqueous heterogeneous polymerization was recently reported for the precipitation polymerization of MMA and styrene complexed with methylated β-cyclodextrin.[256] The polymerization was carried out in water with I-**21** (X = Br)/CuBr/L-**4** to give polymers with controlled molecular weights and relatively narrow MWDs ($M_w/M_n = 1.3-1.8$). Initially, the reaction mixture was homogeneous with the hydrophilic cyclodextrin-complexed MMA, but sooner or later it became heterogeneous due to the formation of water-insoluble polymers.

5. Other Special Solvents

Apart from water, supercritical carbon dioxide ($scCO_2$) is an environmentally friendly solvent and currently attracts much attention as a medium for organic reactions and polymerizations. The solvent was also employed for the copper-catalyzed radical polymerizations of fluorinated (meth)acrylates with the I-**22** (X = Br)/CuCl initiating system in the presence of Cu(0) and bipyridine-based ligands such as L-**1**, L-**4**, and L-**7**.[95] A fluorinated ligand (L-**7**) induced a homogeneous polymerization without any visible precipitation to give polymers with controlled molecular weights. This system is equally applicable for random and block copolymerizations between the fluorinated monomers and MMA. Dispersion polymerization of MMA was also conducted in $scCO_2$ with poly(perfluorinated acrylate)s as dispersants to form PMMA with controlled molecular weights and relatively narrow MWDs ($M_w/M_n = 1.4$).

The use of fluorous solvents or ligands leads to so-called fluorous biphasic conditions, where at an ambient temperature two phases separate, the phases becoming miscible at a higher temperature. This permits the homogeneous polymerization at high temperatures, and the facile separation of products from the catalysts under ambient conditions. A fluorous biphasic system consisting of I-**24** (X = Br), CuBr, and L-**26** was employed for polymerizations of MMA in an equivolume mixture of (perfluoromethyl)cyclohexane and toluene.[115] The polymerization proceeded most likely in a homogeneous phase to give polymers with controlled molecular weights and narrow MWDs ($M_w/M_n = 1.2-1.3$). They are easily isolated from the organic phase as a colorless glassy solid with a minimum contamination of copper. It is also reported that the catalysts, largely remaining in the fluorous phase, can be recycled for second and third polymerizations without loss of catalytic activity.

Another special class of solvent, ionic liquids such as 1-butyl-3-methylimidazolium hexafluorophosphate, was used for the polymerization of MMA with I-**24** (X = Br)/CuBr/L-**9** (R = *n*-Pr), which proceeded even at 30 °C, reached 90% conversion within 5 h, and gave polymers with narrow MWDs ($M_w/M_n = 1.3-1.4$).[257] The products are easily removed by washing with toluene, while the catalyst is highly soluble in the ionic liquid and can be reused.

F. Mechanisms

The metal-catalyzed living polymerizations most probably proceed via a carbon-centered radical species reversibly generated from a carbon−halogen terminal (dormant species) and a metal catalyst. The radical nature of the polymerizations has been suggested by several facts and observations, some of which were already discussed above. This part deals with the analysis of the polymerizations based on various methods and apparatuses for mechanistic investigation. Short overviews on the mechanistic studies are also available.[258−262]

1. Radical Scavengers

One of the most useful methods to determine a polymerization mechanism is to examine the effects of additives or potential terminating agents (scavengers or quenchers). Since the beginning of development of metal-catalyzed living radical polymerization, therefore, terminating experiments have been carried out extensively, and they were particularly important at that time, because combinations of haloalkanes and transition-metal catalysts do not automatically warrant radical-growth mechanisms. As potential terminators, two classes of compounds have primarily been employed: protic compounds such as water and alcohols, and radical scavengers such as galvinoxyl, 1,1-diphenyl-2-picrylhydrazyl (DPPH), and TEMPO. Namely, there are well-known terminators for anionic and radical growing species, respectively, and their use was based on the fact that the monomers employed in the early-phase development were primarily MMA and styrene, which polymerize by both mechanisms.

It was soon realized that almost all of the metal-catalyzed living processes are not quenched by the protic compounds but clearly by the radical scavengers, and this phenomenon was the case for such metal catalysts as ruthenium,[29,55,56,58,63,66] copper,[28] nickel,[132,133,135] rhodium,[138] and rhenium.[141] The carbon-centered radical most probably reacts with these scavengers (Y) to produce a dead polymer chain end with inactive covalent C−Y or C−H bond or unsaturated carbon−carbon double bond.

The first set of quenching experiments has been reported for the Ru-mediated polymerization of MMA,[27,55] and the Kyoto group observed the reaction is immune to methanol and alcohol but is quantitatively terminated with galvinoxyl, DPPH, and TEMPO added in 5−10-fold molar excess over the initiator. End-group analysis on the quenched products revealed that the terminating moieties are not attached to the growing end; rather *exo*-olefins result via hydrogen abstraction from the MMA's α-methyl group.

On the other hand, the formation of C−Y bonds was observed in the copper-catalyzed model reactions between the isolated polymers or model compounds such as I-**13** and TEMPO or hydroxy-TEMPO.[163,242] However, TEMPO may also deactivate the metal complexes to form inactive metal species in higher oxidation states instead of giving the C−TEMPO terminal.[141] A similar inhibition by these compounds was also observed for living anionic polymerizations and group-transfer polymerizations of MMA, both of which proceed via an anionic mechanism.[263] Alternatively, some of the phenols, which are scavengers in conventional radical polymerizations of styrene, can increase the polymerization rate as mentioned above (section II.D).[231] Though these inhibition effects cannot completely prove radical-growth mechanisms for the metal-catalyzed living polymerizations, they are at least consistent with the proposed pathways.

2. Stereochemical Structures

The stereochemistry of polymers, in general, provides useful information about the polymerization mechanism by which they are formed. More specifically in the metal-catalyzed living radical polymerization, it has been anticipated that the proposed mechanism via metal-assisted reversible radical generation (cf. Scheme 3) might induce different and/or better stereochemical control than in the classical radical counterpart, in which the growing end is a really "free" radical. The anticipation originates from the fact that the oxidized metal catalyst, with the halogen from the dormant species, might reside in close vicinity to the resulting radical end, inducing a situation reminiscent of ion pair growing species in ionic polymerizations where the counterions exert a strong influence on the stereochemistry of propagation.

Surprisingly or not, the tacticity of PMMA obtained with various metals including Ru,[27,56,58,63] Cu,[28,84,97,100,102,103,116,232,263] Fe,[70,80] Ni,[132,133] Pd,[137] and Rh[138] was almost the same (almost atactic, slightly syndiotactic) as the tacticity of those obtained with conventional radical initiators such as AIBN under similar conditions. The triad ratio of *rr*:*mr*:*mm* as determined by ^{13}C NMR is usually 58:38:4 and does not change even with the use of chiral and/or bulky ligands.[103,116] These results may exclude a coordination mechanism and suggest a radical nature. However, the stereochemical structure alone is not strong evidence for the radical polymerization because, for example, group-transfer polymerization, basically via an anionic mechanism, results in a stereo structure of PMMA similar to those for free radical processes.[263]

3. Copolymerizations

Monomer reactivity ratios in copolymerization and copolymer structures can also give insight into the mechanism of the polymerizations. As observed with ruthenium[205] and copper,[264,265] MMA−styrene and related copolymerizations turned out to be "living" if initiated with the metal catalysts effective for the corresponding homopolymerizations. Besides these synthetic aspects to be covered later in this review (section III.D), the results also give some insight into the reaction mechanisms. With a ruthenium catalyst (Ru-**1**), MMA and styrene were copolymerized at varying monomer feed ratios.[205] The products were true copolymers, as evidenced by single MWD profiles by size-exclusion chromatography (SEC) and a set of heteroenchainment NMR signals, among others. The MWDs were fairly narrow, clearly narrower than those from the corresponding AIBN-initiated samples, and the M_n was directly proportional to the total weight (overall conversion) of the consumed monomers. All these findings demonstrate that the copolymers are living.

Equally important, the two comonomers were polymerized in parallel, with MMA consumption slightly faster, and the copolymer composition curve shows a shallow S-shaped profile, similar but not identical to those for the textbook examples of free radical MMA/styrene copolymerization. Thus, once again, the observation is consistent with some radical growth in the metal catalysis, and their difference from a conventional radical copolymerization is not deniable but not conclusive.

Kinetic analyses were done for several copper-catalyzed copolymerizations of MMA/nBMA,[263] nBA/styrene,[264,266] and nBA/MMA.[267] All these studies show that there were no significant differences in reactivity ratio as well as in monomer sequence between the copper-catalyzed and conventional radical polymerizations. Only a difference was observed in the copolymerizations between MMA and ω-methacryloyl-PMMA macromonomers where the reactivity of the latter is higher in the metal-catalyzed polymerizations.[267] However, this can be ascribed not to the different nature of the propagating species but to the difference in the time scale of monomer addition or other factors. Simulation has also been applied for the copolymerization study.[268]

4. EPR

One of the most effective and direct ways to prove a radical mechanism is to detect the radical intermediate by electron paramagnetic resonance (EPR), but this approach has not been fruitful yet for the detection due to the low concentrations of the radical species or other factors.

EPR was indeed applied to the copper-catalyzed radical polymerization of styrene, MA, and MMA.[162,269−271] Invariably, it was difficult to detect any radical growing species because of the low concentrations of the radical species, but just specifically for copper, the accumulated paramagnetic Cu(II) species was generated via radical termination. This indicates that 3−6% of the initially added Cu(I) catalyst is converted into the Cu(II) counterpart during the polymerization (especially its initial stage).

5. NMR

In the mechanistic study of metal-catalyzed living polymerization, this method has thus far been utilized primarily for analysis of model reactions to uncover the interaction between a metal catalyst and a carbon−halogen dormant end.[170,176] Typical models for the dormant end include α-haloesters, such as alkyl haloisobutyrate and MMA dimer halides I-**25** (Figure 8) (for methacrylate), alkyl 2-halopropionate (for acrylate), and α-phenylethyl halide (for styrene).

NMR analysis of model reactions for the polymerizations and polymer terminal groups revealed that the halogens at a dormant polymer terminal exchange with those in a metal catalyst.[154,155,170,196,272,273] According to the proposed homolytic cleavage mechanism (Scheme 3), the halogen-exchange reaction proceeds via abstraction of (one of) the terminal halogens by the metal catalyst followed by return of one of the halogens on the metal species onto the growing radical center; thus, the process presumably occurs via a radical intermediate.

In a typical example, the MMA dimers I-**25** were employed as authentic terminal models for PMMA.[170] NMR readily distinguishes chlorine replacement at the bromine ends in I-**25**. Taking this advantage, the Kyoto group examined the halogen-exchange reactions by treating I-**25** (X = Br) and Ru-**1** in NMR sample tubes, mimicking the radical-generation process of their Ru(II)-mediated living polymerizations. Almost immediately after mixing the two components followed by heating to the polymerization temperature, the chloride version of I-**25** (X = Cl) was clearly detected by NMR, and it increasingly predominated, demonstrating that the bromine end is rapidly replaced (exchanged) by the chlorine in the metal catalyst.

Another interesting aspect of the model reactions has been reported for copper-mediated processes.[273] Thus, optically active methyl 2-bromopropionate was mixed with a CuCl catalyst, and the reaction was followed by NMR and polarimetry. The latter analysis showed, as in solvolysis, that the model quickly undergoes racemization; i.e., the halogen on the chiral carbon dissociates and recouples.

The degrees of the exchange reactions depend on several factors, the central metals, the ligands, the structures of the terminal groups, and the reaction conditions. The absence of carbon−metal species, which would form via oxidative addition of the metal complexes into the carbon−halogen bonds, also excludes the coordination mechanism.

6. MS

The polymers and their terminal groups (α and ω) in metal-mediated living radical polymerizations have been analyzed by modern mass spectrometry, particularly MALDI-TOF-MS,[100,125,173,174,197,239,244,274−277] time-of-flight static secondary ion mass spectrometry (TOF-SSIMS),[278,279] and electrospray ionization mass spectrometry (ESIMS).[172,277,280] All these analyses support the existence of fairly stable carbon−halogen terminals.

The MALDI-TOF-MS spectra of the obtained polymers basically show only one series of peaks separated exactly by the mass of each monomer. The observed mass of each peak agrees well with the theoretical one, which possesses one initiator fragment at the α-end and one halogen terminal group at the ω-end in each polymer chain (with a single degree of polymerization) (Scheme 3). The observed isotopic distribution was in excellent agreement with the simulated profile based on the neutral abundance of ^{2}H, ^{13}C, etc.[197] In some cases, laser irradiation of the samples leads to partial or complete loss of the terminal halogens during the analysis depending on the polymer structures and analytical conditions.[197,239,244,276] In other cases, MS analysis in turn reveals that some polymers suffer from halogen loss during polymerizations.[172,174,275]

7. CV

The correlation between the physical parameters of the catalysts and their catalytic activity will clarify polymerization mechanisms. The redox potential of the metal complexes is certainly among these parameters, because metal-assisted living radical polymerization is triggered by oxidation of the metal complex; i.e., a single electron is transferred from the metal to a dormant carbon−halogen terminal. The redox potential was thus measured for ruthenium,[53,227] iron,[73] and copper[54] complexes by cyclic voltammetry (CV). These studies basically indicate that a complex with a lower redox potential induces a faster reversible cleavage (activation) of a carbon−halogen terminal and, in turn, generates more radical species. For example, among half-metallocene−ruthenium complexes (Ru-**4**, -**5**, and -**6** in Figure 1) the redox potential decreases in the order Ru-**4** > Ru-**5** > Ru-**6**, and the halogen exchange rate follows the same order (Ru-**6** gives the fastest).[53]

However, there is no definite correlation between the polymerization rate and the redox potential, partly because a higher concentration of the radical species may lead to a higher probability of bimolecular termination and a higher concentration of persistent radical species.[54,261] Another possibility of side reaction is due to the reduction of the radical into an anion with metal complexes with extremely low redox potential. An appropriate range for the redox potential of the metal catalysts was suggested between −0.3 and +0.6 V (versus NHE) for living radical polymerization.[54]

8. Kinetics

Kinetic analysis of metal-catalyzed radical polymerization was extensively performed for homogeneous copper-based systems.[123,164,176,281] Almost invariably, the polymerization follows a first-order kinetics with respect to the monomer, initiator, and copper(I) halide as expected from the proposed mechanism; i.e., the reaction between the monomer and the radical species, which is generated via the Cu(I)-catalyzed activation of the carbon−halogen terminal, originated from the initiator. Addition of Cu(II) species retards the polymerization by shifting the equilibrium between the covalent and radical species. However, the polymerization kinetics were not simple inverse first order with respect to the initial copper(II) halide concentration due to the persistent radical effect, which resulted in an increase in Cu(II) concentration during the initial stages of the polymerization.[123,164,281] This also indicates the presence of irreversible bimolecular termination reactions, prone to the radical polymerizations. The equilibrium constants for the activation/radical dissociation process are calculated on the assumption that the absolute propagation rate constant in the metal-catalyzed polymerization is the same as that in the conventional free radical processes, and the values vary with the monomers from 10^{-9} to 10^{-7} and increase in the order acrylates < styrene < methacrylates.[123,176] The concentration of the radical species is thus estimated to be very low, between 10^{-8} and 10^{-7} mol/L, which may minimize bimolecular termination.

The kinetic parameter for the radical dissociation of a carbon−halogen terminal was obtained with the use of an isolated polystyrene with a terminal C−Br bond in the presence of a copper catalyst and a conventional radical initiator with a long half-life.[282,283] The result was compared with that of low molecular weight compounds of similar carbon−halogen bonds.[163] The second-order rate constant of the model compound I-**13** (X = Br), an effective initiator for styrene, is comparable to that of the polymer terminal. Alternatively, rate constants can be obtained by using a combination of nitroxide-exchange reactions and HPLC analysis.[242]

Computer simulations were also done for these polymerizations although the details are omitted in this review.[284−287]

9. Other Mechanistic Analyses

While the radical nature of the metal-catalyzed polymerizations seems to be generally accepted, there still remains a question whether the propagating radical species therein is the same in nature as the "free radicals" in the conventional systems. The metal-assisted radical formation most probably proceeds through an inner-sphere electron transfer from the metal to the carbon−halogen terminal as reported in Kharasch addition reactions.[288,289] The resulting radical species may temporarily be confined in the coordination sphere of the complex in a higher oxidation state. The confined situation or environment might exert some effects on the polymerization such as suppression of bimolecular termination. Although this possibility was suggested for some systems around the time when the metal-catalyzed systems were discovered,[27,100,132] there is still no strong supporting evidence.[290] In this aspect, the lack of stereoregulation (see above) is particularly frustrating.

If similar radical species are involved in both living and conventional polymerizations, it follows that the metal-assisted growing species may suffer from side reactions prone to free radical systems, however well suppressed in the living systems. This then determines the lifetime of the growing end as well as the maximum molecular weights to be achieved therein. The highest molecular weights are still below 10^6 with all the reported living systems.

Side reactions such as termination and transfer were investigated in the polymerizations of styrene,[291] acrylates,[292] and methacrylates.[293] The occurrence of thermally initiated radical polymerizations was observed in the copper-catalyzed styrene polymerization, while the resulting polymer chain can be converted into the dormant polymer terminal via abstraction of halogens from the persistent metal radical in higher oxidation states.[294]

The effects of chain-transfer agents such as octanethiol on copper-catalyzed polymerizations are similar to those on conventional radical polymerizations.[295] These may also mean little difference among the growing species generated from the carbon−halo-

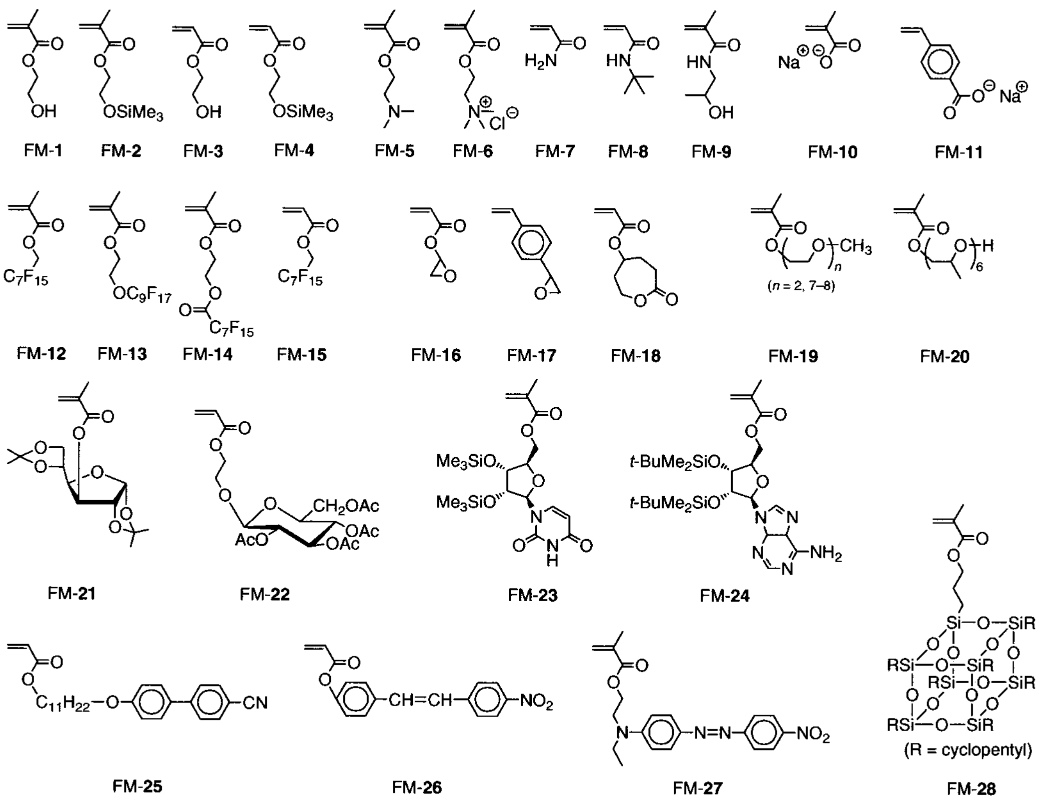


Figure 12. Functional monomers.

gen terminals and in conventional radical systems. Another interesting observation is that a simultaneous metal-catalyzed and nitroxide-mediated living radical polymerization of styrene is possible via fast scrambling of terminal halogen and TEMPO groups to form a single type of polymer chains.[296]

These suggest, in part, that a key to metal-catalyzed radical polymerizations might be the persistent radical effect,[15,297,298] as pointed out for nitroxide-mediated systems. More detailed mechanistic studies are required.

III. Precision Polymer Synthesis

One of the most distinguishable characteristics of the metal-catalyzed living radical polymerization is that it affords polymers with controlled molecular weights and narrow MWDs from a wide variety of monomers under mild conditions even in the presence of a protic compound such as water. This permits the synthesis of a vast number of polymers with controlled structures such as end-functionalized polymers, block copolymers, star polymers, etc., where they are widely varied in comparison with those obtained by other living polymerizations. This is primarily due to the tolerance to various functional groups and the polymerizability/controllability of various vinyl monomers as mentioned above.

This section is thus directed to precision polymer synthesis with the use of metal-catalyzed living radical polymerizations. In this synthetic aspect, numerous reviews are available already. [219,265,299−310]

A. Pendant-Functionalized Polymers

Radical polymerization, in general, is more tolerant of polar functionality than its ionic counterpart, and as we have already seen in this review, this advantage is apparently passed on to the metal-catalyzed living polymerizations. This in turn leads to direct polymerization of functionalized monomers and the synthesis of pendant functionalized polymers of well-defined structure and molecular weights without tedious protection and deprotection processes. These functional groups include not only hydroxyl, amino, and amido groups but also ionic and other special groups, which are, in most cases, introduced directly into methacrylates, acrylates, and styrenes as substituents. Figure 12 is a nearly complete inventory of functionalized monomers for which metal-mediated living radical polymerizations have been reported.

A hydroxyl-functional monomer, HEMA (FM-**1**), can be polymerized in a controlled way with several transition-metal complexes including ruthenium,[59] copper,[241,243] and nickel[311] in the bulk and in alcohols. In view of the relatively broad MWDs of the products (M_w/M_n = 1.3−1.8), further optimization of the reaction conditions is needed, although the catalyst and the growing terminal keep the activity during the polymerizations. Better-controlled polymerizations of a protected form of HEMA with a trimethylsilyl group (FM-**2**) were also conducted with ruthenium, copper, and nickel.[243,312] 2-Hydroxylethyl acrylate (FM-**3**), an acrylate with a hydroxyl group, can be polymerized with the I-**22** (X = Br)/CuBr/L-**1** system in the bulk and in water to give narrow MWDs (M_w/M_n = 1.2−1.3) where the polymerization is faster and better controlled in the bulk.[244] Its protected version (FM-**4**) was polymerized with I-**22** (X = Br)/CuBr/L-**24** in the bulk to give similarly narrow MWDs ($M_w/M_n \approx 1.2$).[313] Soluble in organic media, these silyloxy-protected monomers (FM-**2** and FM-**4**) can be effectively employed for block or random copolymerizations with aliphatic methacrylates.[243,312,313]

Amino- and amido-functionalized monomers can also be polymerized directly with metal catalysts. Living radical polymerization of 2-(dimethylamino)-ethyl methacrylate (FM-**5**) was achieved with I-**31** (X = Br)/CuBr/L-**29** in dichlorobenzene at 50 °C.[314] Its ammonium salt (FM-**6**) was polymerized from the surface of a cross-linked polystyrene latex with CuBr/L-**1** in water at 80 °C to generate hydrophilic shells, although there were no data for polymer molecular weight.[248] As described above (section II.C.6), (meth)-acrylamides with at least their amido protons unprotected (FM-**7**, FM-**8**, and FM-**9**) can be polymerized with copper-based systems,[117,168,217,218] but a further optimization seems to be necessary.

Ionic monomers carrying a carboxylate salt, such as FM-**10**[200] and FM-**11**,[247] can be polymerized with a water-soluble bromide initiator in conjunction with CuBr and L-**1** in aqueous media to give moderately controlled molecular weights and MWDs (M_w/M_n = 1.2−1.3). The reaction media should be kept under alkaline conditions (pH 8−11) to avoid loss of the catalytic activity; seemingly free acid functions in the monomers and/or polymers are detrimental.

Perfluoroalkyl (meth)acrylates FM-**12** and FM-**15** have been polymerized homogeneously in $scCO_2$ with copper catalysts/fluorinated ligand systems, but the MWDs of the products are not reported due to the lack of appropriate analytical methods.[95] Other fluorinated monomers (FM-**13** and FM-**14**) were used for block copolymerization with styrene and acrylates with CuBr/L-**1** in the bulk under heterogeneous conditions.[315]

Epoxy and lactone groups seem to remain intact under the conditions for metal-catalyzed living radical polymerization. Therefore, glycidyl acrylate (FM-**16**) can be exclusively polymerized via the vinyl moiety with I-**22** (X = Br)/CuBr/L-**4** in the bulk at 90 °C to high conversion ($M_w/M_n \approx 1.2$).[316] Statistical copolymers of styrene and FM-**17**, an epoxy-functionalized styrene, with controlled molecular weights were obtained with a CuBr-based system at 100 °C, whereas a similar reaction with TEMPO gave products of bimodal MWDs that might come from the high reaction temperature (124 °C).[317] An acrylate with ϵ-caprolactone can be polymerized with I-**21** (X = Br)/Ni-**2** in the bulk at 90 °C to result in polymers with controlled molecular weights (M_w/M_n = 1.1−1.3).[318]

Methacrylates with pendant oxyethylene units (FM-**19**) were polymerized in a controlled way with metal catalysts in the bulk or in water. The catalytic systems include a bromide initiator coupled with Ni-**2** for $n = 2$ (bulk, 80 °C)[319] and CuCl for $n = 7-8$.[246,320] The latter polymerization proceeded very fast in aqueous media at 20 °C to reach 95% conversion in 30 min and gave very narrow MWDs (M_w/M_n = 1.1−1.3). The fast reaction is attributed to the formation of a highly active, monomeric copper species complexed by the oxyethylene units. A statistical copolymerization of FM-**19** ($n = 7-8$) and FM-**20**, a methacrylate with a oligo(propylene oxide) pendant group, led to hydrophilic/hydrophobic copolymers with narrow MWDs (M_w/M_n = 1.2).[320]

Polymers containing sugar moieties, so-called glycopolymers, have been attracting attention as biocompatible materials. Some of them have been obtained by the polymerization of FM-**21**[321] and FM-**22**[322] with CuBr-based initiating systems. Their block copolymerizations with styrene are also feasible as described below (section III.C.1).

Metal-catalyzed living radical polymerization can be further extended to multifunctional nucleoside-containing monomers. Examples are silyl-protected monomers with uridine (FM-**23**) or adenosine (FM-**24**) groups, both of which can be polymerized with a combination of a bromide initiator, CuBr, and L-**9** (R = *n*-Pen) or L-**32** homogeneously in toluene (M_w/M_n = 1.1−1.4).[323]

Side-chain liquid-crystalline polymers with controlled molecular weights have been obtained by the polymerization of FM-**25** with I-**22** (X = Br)/CuBr/L-**3** in the bulk at 100 °C, to examine the thermotropic transition as a function of the MWD.[324] Second-order nonlinear optical materials with branched structure were prepared by the copper-catalyzed radical polymerization of FM-**26** and FM-**27** using hyperbranched poly[4-(chloromethyl)styrene] as a multifunctional initiator.[325]

A methacrylic monomer with polyhedral oligomeric silsesquioxanes (FM-**28**) as a pendant group can be polymerized with I-**24** (X = Br)/CuBr/L-**32** in toluene (M_w/M_n = 1.14).[326] Block and star copolymers of this partially inorganic monomer with MA and nBA are expected to function as new hybrid materials.

B. End-Functionalized Polymers

As in other living polymerizations, metal-catalyzed living radical processes can be employed for the synthesis of end-functionalized polymers. To this end, there are two general methods, i.e., a functional initiator method and an end-capping method, and both are indeed applicable therein. In the former, living radical polymerization is initiated with a functionalized organic halide initiator coupled with a metal catalyst to form polymers with an α-end (head) functionality. In the latter, a metal-catalyzed living radical polymerization is terminated with a functionalized quencher that in turn introduces an ω-end (tail) functionality. An alternative method for ω-end functionalization is to transform a stable carbon−halogen ω-terminal via polymer reactions. Examples of these approaches will be discussed below.

1. α-End-Functionalized Polymers

Taking advantage of the tolerance of living radical polymerization for functional groups, a variety of functionalized initiators have been designed. A general way is to attach a functional group to a halogen compound such as a haloester, (haloalkyl)benzene, haloalkane, or sulfonyl halide. Most of the functional groups therein are insulated from the initiation moiety via a spacer to avoid possible side reactions, as shown in Figure 13, where entries are grouped in terms of the intended α-functionalities.

For instance, hydroxyl-functionalized initiators (FI-**1** to FI-**6**) were employed for living radical polymerization of MMA,[134,139,156,157,274,327] MA,[280] nBA,[134]

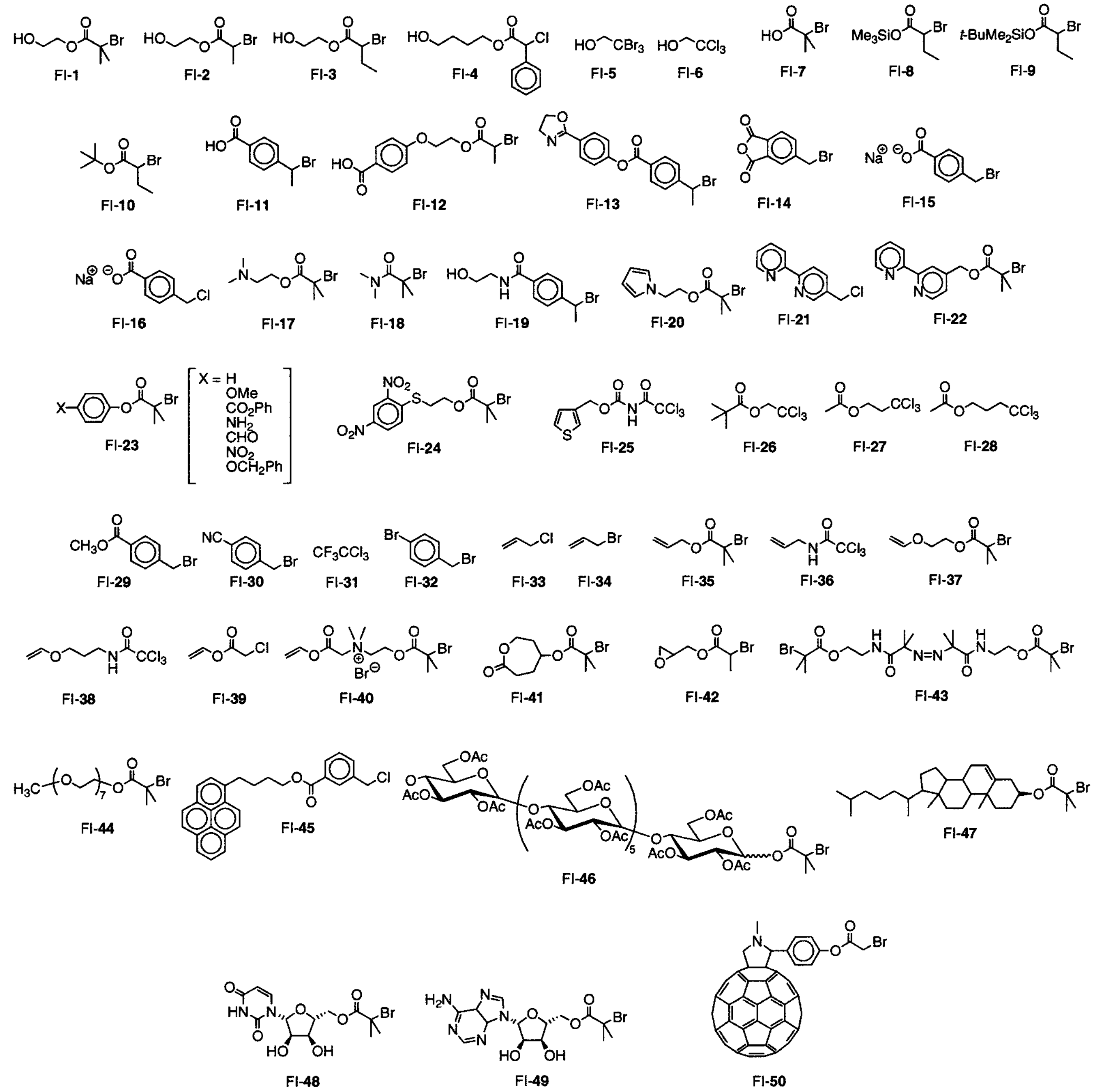


Figure 13. Organic halide functional initiators.

tBA,[328] styrene,[280,329] and sodium methacrylate.[200] Note that for these no protection of the protic function is required, in sharp contrast to similar initiators for ionic living polymerizations. Initiator FI-**1** generates an HEMA radical and thus is applied to MMA with CuBr/L-**9** (R = *n*-Pr) in xylene at 90 °C; near complete attachment of the α-end function has been shown by MALDI-TOF-MS.[274] This initiator can also be employed for sodium methacrylate[200] and tBA.[328] An acrylate version FI-**2** is for MA with CuBr/L-**4**, but the initiation efficiency for styrene is reported to be lower ($I_{eff} \approx 0.7$) due to side reactions upon initiation.[280] In contrast, a nearly quantitative initiation was achieved with FI-**3** in the styrene polymerization with CuBr/L-**1**.[329] A chloride FI-**4** is another interesting initiator that can generate a radical doubly stabilized by a carbonyl and a phenyl substituent and has been employed for MMA/CuBr/L-**1**.[327] Simpler initiators such as FI-**5**[134,139] and FI-**6**[156,157] are commercially available and applied to MMA, nBA, and styrene with CuBr/L-**1** or L-**4** as well as Ni-**2**, although the plural carbon−halogen bonds therein might cause multiple initiations.

Carboxyl groups were also introduced at the α-end of poly(methacrylate)s[134,235,320] and polystyrene[330,331] by using unprotected and protected initiators. 2-Bromoisobutyric acid (FI-**7**) was employed for MMA coupled with CuBr/L-**9** (R = *n*-Pen)[235] and with Ni-**2**[134] to give narrow MWDs ($M_w/M_n = 1.1-1.3$) but M_n values higher than the calculated values. This unprotected initiator, on the other hand, has poor efficiency ($I_{eff} = 0.10$) for styrene, probably because of the intramolecular cyclization into a γ-butyrolactone after addition of one styrene unit.[330] Protection of the acid function by trimethylsilyl (FI-**8**), *tert*-butyldimethylsilyl (FI-**9**), or *tert*-butyl (FI-**10**) groups leads to improved initiation efficiencies (ca. 0.6, 0.8, and 1.0, respectively). Benzoic acid initiators with a well-separated halogen (FI-**11** and FI-**12**) afforded well-defined polystyrenes with narrow MWDs at relatively high initiation efficiencies ($I_{\mathrm{eff}} \approx 0.7$); thus, rigid aromatic spacers may help.[330] Similar results were obtained with protected initiators such as FI-**13** and FI-**14**.[331] Salt-type initiators FI-**15** and FI-**16** are specifically employed for the aqueous-phase polymerization of hydrophilic monomers such as FM-**19** (Figure 12).[320]

Nitrogen-containing groups such as amine, aniline, amide, pyrrole, and pyridine are also available for the functional initiator method. A bromoester with a dimethylamino group (FI-**17**) was used in aqueous media for oligo(ethylene glycol) methacrylate (FM-**19**) ($M_{\mathrm{w}}/M_{\mathrm{n}} \approx 1.4$).[246,320] Poly(tBA)[328] and polystyrene[331] with terminal amide functions were prepared with FI-**18** and FI-**19**, respectively. The pyrrole-containing initiator FI-**20** induced living radical polymerization of methacrylates, acrylates, and styrene with Ni-**2** or CuBr/L-**1**, giving macromonomers for electrochemical polymerization.[319] The 2,2′-bipyridine unit in FI-**21** and FI-**22** is to attach binding sites onto polystyrene[332] and poly(MMA),[333] respectively, for macroligand chelation with Ru and other metal cations. A series of 4-substituted-phenyl 2-bromoisobutylates (FI-**23**) with amino, nitro, and aldehyde groups, etc. were successfully employed for MMA with CuBr/L-**9** (R = *n*-Oct) ($M_{\mathrm{w}}/M_{\mathrm{n}} = 1.1-1.2$; $I_{\mathrm{eff}} = 0.8-1.0$).[199]

Thiols also provide good binding points toward a metal surface such as gold for the synthesis of polymer brushes, etc. A protected initiator (FI-**24**) gave thiol-functionalized PMMA with Ni-**2** as a catalyst.[334] The thiophene-capped PMMA from FI-**25** can be employed as a macromonomer for electrochemical copolymerization with pyrrole,[335] as with those from FI-**20** (see above).

A series of poly(chloroalkyl ester)s (FI-**26** to FI-**28**) can be employed for styrene polymerization with CuCl/L-**1** to give polymers with ester groups at the α-end.[158] Benzyl bromides FI-**29**[317] and FI-**30**[328] are another possibility for α-end functionalization.

Multiple halogen compounds FI-**31**[158] and FI-**32**[328] seem interesting to attest the chemoselectivity of transition-metal catalysis, and the CF_3– and the aromatic bromide therein, respectively, remain intact during the living polymerizations to afford α-end functions, though their utility might be limited.

End-functionalized polymers with polymerizable groups such as double bonds and heterocycles of course provide macromonomers; allyl, vinyl ester, vinyl ether, lactone, and epoxy are examples of such a category whose α-ends are not susceptible or have little susceptibility to metal-catalyzed radical polymerization. As discussed above, for example, allyl chloride and bromide (FI-**33** and FI-**34**) are effective initiators to be used for styrene with CuCl and CuBr catalysts,[161] while allyl compounds with remote halogens such as FI-**35** and FI-**36** allow the polymerization of methacrylates with high initiation efficiency.[120,150] Vinyl ether derivatives FI-**37** and FI-**38** can initiate living polymerizations of styrene, methacrylates, and acrylates with copper catalysts from their halogen moiety, though carefully selected reaction conditions are required.[150,336] Thus, the vinyl ether double bonds are susceptible to radical addition at higher conversions to result in bimodal MWDs and termination. Interestingly, vinyl acetate groups can be introduced at the α-end of polystyrenes and poly(methacrylate)s by using FI-**39**[337] and FI-**40**,[246,247,320] because they only poorly copolymerize with styrene and methacrylates even under radical conditions. Macromonomers for ring-opening polymerizations can be obtained from FI-**41**[328] and FI-**42**[312] for tBA and MMA.

An azo bromoester bifunctional compound FI-**43** induces a living polymerization of nBA with a highly active catalytic system (CuBr/L-**32**) at 30 °C from the latter function alone.[338] The low temperature allows the azo group to elude concurrent thermal dissociation (<0.5%). The obtained polymers of narrow MWDs were employed for block copolymerization with vinyl acetate at 90 °C.

End-functionalized polymers with relatively long hydrophilic segments can be prepared from an initiator (FI-**44**) with oligo(oxyethylene glycol) units.[200,246,247,320] Initiators FI-**45** to FI-**50** are for other functionalities of special interest. For example, the pyrenyl group in FI-**45** can become a tag for distinguishing the end-functionalized polymers from nonfunctionalized byproducts and was used in simultaneous metal-catalyzed and nitroxide-mediated living radical polymerizations of styrene.[296] Biologically related functions such as oligosaccharide,[339] cholesterol,[340,341] and nucleosides[323] are incorporated in FI-**46** to FI-**49** for CuBr/L-**9** (R = *n*-Pen or *n*-Oct), whereas FI-**50** (with CuBr/L-**1**) is to introduce a C_{60} or fullerene terminal.[342]

In addition to the carbon-centered radical initiators, arenesulfonyl halides are simple and efficient functionalized initiators by introducing a variety of functional termini; conjugation between the aryl and the sulfonyl groups is absent (FI-**51** to FI-**58**; Figure 14).[175] Typically, a series of monosubstituted derivatives (FI-**51**) are commercially available and afford hydroxyl, carboxyl, nitro, and halo groups in living

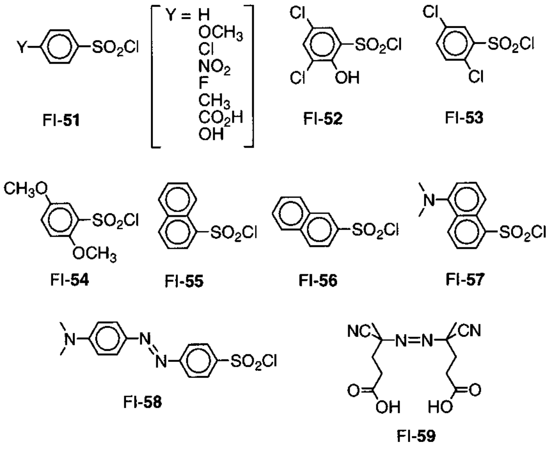


Figure 14. Sulfonyl halide and conventional radical functional initiators.

radical polymerization of styrene, MMA, and nBMA with the copper[152,175] or ruthenium[180] catalysts (end functionality $F_n \approx 1.0$). Other sulfonyl chlorides (FI-**52** to FI-**58**) are similarly applicable.[126,175,343]

An alternative and perhaps simpler way to synthesize α-end-functionalized polymers is to use a functional azo initiator (FI-**59**) in the presence of transition metals in a higher oxidation state such as $FeCl_3$ with PPh_3 as a ligand.[80] This method is a variant of the reverse atom-transfer polymerization and gives polystyrenecarboxylic acid with narrow MWDs ($M_w/M_n = 1.14$).

2. ω-End-Functionalized Polymers

In contrast to the frequent use of the initiator method and the wide variety of available functional initiators, the end-capping method is not as frequently employed, primarily because of the difficulty in selective and quantitative quenching radical polymerization, particularly in the metal-catalyzed living systems involving dormant halogen species. This stems from several factors: the extremely low concentration of the radical species relative to the dormant species, the highly stable dormant carbon−halogen bond, and the limited availability, thus far, of suitable quenchers that can add to the growing carbon radical without deteriorating the metal complex catalyst. However, with the use of selected compounds, the halogen terminal can be converted into functional groups via metal-catalyzed radical reactions or other reactions.

Metal-catalyzed end-capping via a radical mechanism can be carried out either by in situ quenching of the polymerization or by the reaction of isolated halogen-capped polymers. Mostly the same quencher may be used for both methods. Despite the less frequent applications, however, a wide variety of quenching end-capping agents have been reported (EC-**1** to EC-**15**) (Figure 15). Most of these compounds have a vinyl group that can add to a polymer terminal under metal-catalyzed conditions to form much less reactive carbon−halogen bonds or unsaturated groups via release of low molecular weight halogen compounds.

The first of these are silyl enol ethers EC-**1** with a phenyl group or α-(silyloxy)styrenes. They can effectively quench the ruthenium-catalyzed living radical polymerization of MMA to give the ω-end-functionalized PMMA with a ketone group with high end functionality ($F_n \approx 1.0$).[293,344] The method is also useful to attach an aromatic ω-end group not only for end-functionalization (via the substituent on the ring) but also for end-group analysis (via the aromatic protons). The quenching reaction is considered to proceed via addition of the growing radical to the vinyl group of EC-**1** to generate another radical terminal that is stabilized by the α-phenyl group, followed by elimination of the trimethylsilyl group with the chlorine at the polymer terminal (or on the metal center) due to their high affinity toward halogens (Scheme 5). The quenching is quantitative and selective, and proceeds faster with an electron-donating substituent (X; $OCH_3 > H > F > Cl$) on the phenyl group of EC-**1** and at its higher concentration.

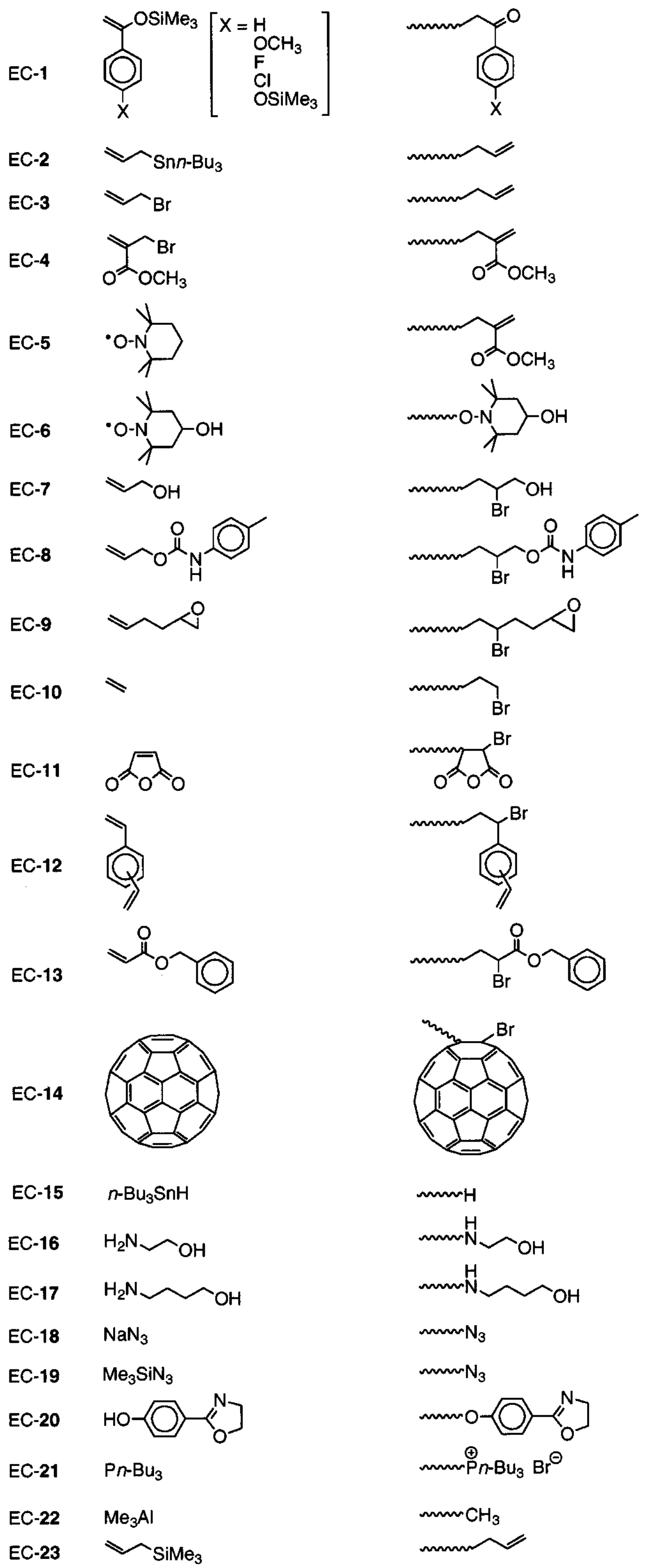
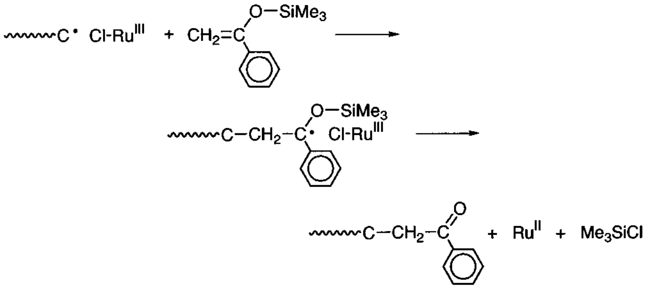


Figure 15. End functionalization of carbon−halogen terminals.

In contrast, silyl enol ethers with an α-alkyl group (α-silyloxy vinyl ethers) proved less efficient, indicating the stability of the resultant silyloxyl radicals is among the critical factors in designing good quenchers of this class. These are due to the degree of the affinity of the PMMA radical toward the vinyl groups in the quenchers. This silyl enol ether capping is applicable for copper-catalyzed polymerizations [with

Scheme 5. Quenching of Metal-Catalyzed Living Radical Polymerization with Silyl Enol Ethers



EC-**1** (X = $OSiMe_3$)], in the reported examples, carried out on isolated PMMA. The quenching has been carried out, not in situ, but on isolated PMMA samples.[226] The trimethylsilyloxy group at the 4-position can be also converted into the phenol function.

An interesting application of the silyl enolate capping reaction has been developed by Percec, who coined the capping agents "TERMINI" (irreversible terminatior multifunctional initiator).[345] This refers to a "protected functional compound able to quantitatively terminate a living polymerization and, after deprotection, to quantitatively reinitiate the same or a different living polymerization in more than one direction". Typical TERMINI agents are designed to possess one silyl enolate function for quenching (as in Scheme 5) and two or more protected sulfonyl chlorides for subsequent multiple initiation of metal-catalyzed living radical polymerization. Obviously from this design the TERMINI method is applicable for the efficient and well-defined synthesis of dendrimers and their libraries, along with other polymers of complex and multibranched architectures.

The silyl enolate quenching process (Scheme 5) is, in principle, similar to addition fragmentation reactions as well as the more recent reversible addition fragmentation chain transfer (RAFT; see also eq 9),[18] in that all three involve an initial addition of the growing radical across a reactive vinyl group that carries both a radical-stabilizing group (a phenyl and an ester) and a good (radical) leaving group. The difference among them is whether the released radical via fragmentation is capable of reinitiating radical polymerization (e.g., capable in RAFT, incapable in the silyl enolate capping).

Allyltri-*n*-butylstannane (EC-**2**) similarly terminates the copper-catalyzed polymerization of MA to give allyl-functionalized polymers via elimination of the stannyl group accompanying the bromine originated from the dormant polymer terminal.[346] Allyl ω-end PMMA was obtained also by the copper-catalyzed reaction between allyl bromide (EC-**3**) and the isolated bromine-capped PMMA, although the functionalization was 57%.[226] Another allyl derivative (EC-**4**) similarly leads to methacrylate-based macromonomers quantitatively in the presence of Cu(0).[347]

The same poly(methacrylate)-based macromonomer can be obtained via the TEMPO (EC-**5**)-promoted elimination of hydrogen and bromine from the isolated bromine-ended PMMA in the presence of CuBr/L-**9** (R = *n*-Pr), though the functionality was 78%.[226] In contrast, the carbon−bromine bond in the polystyrene and poly(nBA), which have no α-methyl substituent, can be displaced into the carbon−TEMPO terminal via the copper-catalyzed reaction with EC-**6**.[242]

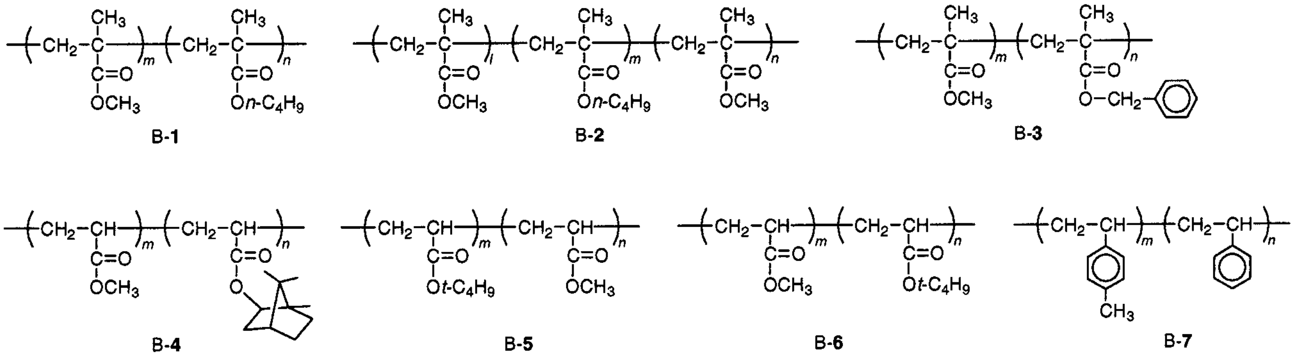
Allyl compounds ($CH_2{=}CH{-}CH_2R$) without good radical leaving groups react with the growing radical in the metal-catalyzed polymerizations to result in an inactive carbon−halogen terminal (---$CH_2{-}CHX{-}CH_2R$). Thus, the reaction is, formally, an addition of alkyl halide (the halogen-capped growing end) across an olefin. For example, copper-catalyzed radical polymerizations of MA[280] and MMA[327] were quenched with allyl alcohol (EC-**7**) to generate a β-bromo alcohol terminal. A similar reaction was reported with EC-**8**[327] and EC-**9**.[346] Ethylene (EC-**10**) cannot polymerize with the metal-based radical systems but can react with the terminal carbon of isolated halogen-capped PMMA in the presence of CuBr and L-**9** (R = *n*-Oct) to yield a primary bromide end quantitatively.[226] Similarly, a single unit of maleic anhydride (EC-**11**) can be introduced to polystyrene and PMMA.[226,348] Even one unit of divinylbenzene (EC-**12**) can be attached quantitatively at a low temperature (25 °C), where the homopolymerizations are suppressed.[226] However, the end-capping yield with benzyl acrylate (EC-**13**), a more reactive monomer, cannot exceed 62%.[226] An interesting application of these one-step olefin additions is found with EC-**14** to attach a C_{60} end (35% yield).[349]

Almost all metal-catalyzed living polymerizations give polymers capped with halogens that are stable after the usual workup. These terminal halogens would be undesirable, because they may lower the polymer's thermal stability. Dehalogenation by tributyltin hydride (EC-**15**) is of importance in this respect and effectively works for the bromide terminals in polystyrene, PMMA, and poly(MA) in the presence of copper catalysts.[277]

An alternative method for ω-end functionalization is to transform the terminal halide by ionic reactions. Thus, nucleophilic substitution was examined with compounds EC-**16** to EC-**23**. For example, an amino alcohol (EC-**16**) in DMSO at room temperature gives polystyrene with hydroxyl groups.[280,350] However, an amino alcohol with a longer spacer (EC-**17**) should be employed for poly(MA) to avoid multiple alcohol functionalities.[280]

Transformation into azide groups was achieved for polystyrene, poly(MA), and poly(nBA) with the use of sodium azide (EC-**18**)[351−353] or trimethylsilyl azide (EC-**19**)[161,351,354] in the presence of tetrabutylammonium fluoride. The azide groups can be further converted into amino ($-NH_2$) groups by treatment with PPh_3/H_2O[351] or $LiAlH_4$.[354] The reaction between the azide end group in polystyrene and C_{60} was also examined.[353]

Nucleophilic substitution with the phenolate anion derived from EC-**20** and K_2CO_3 induced 30% substitution, along with elimination of hydrogen bromide.[331] Phosphonium groups can be introduced at the polystyrene and poly(MA) terminal via reaction with EC-**21**,[355] and methyl groups with Me_3Al (EC-**22**).[356] An allyl terminal is obtained also via an ionic pathway, where the polystyryl carbocation generated



B-1 B-2 B-3

B-4 B-5 B-6 B-7

Figure 16. Block copolymers between the same family of monomers.

from the chlorine terminal polystyrene in the presence of $TiCl_4$ reacts with allyltrimethylsilane (EC-**23**).[356] The allyl terminal was further transformed into epoxy and alcohol.

C. Block Copolymers

One of the most important applications of living polymerization is obviously block copolymerization. Block copolymers are usually obtained via sequential living polymerization of a monomer followed by another. This is also true for the metal-catalyzed living radical polymerization, which permits synthesis of a wide variety of block copolymers and apparently is more versatile than other living polymerizations. Another way is the use of isolated halogen-capped polymers as macroinitiators, taking advantage of the stability of the dormant carbon−halogen terminal even toward air and moisture. The procedure for the former method is apparently simpler than the latter because the reaction can be done in one pot. However, the problem therein is contamination of the first monomer's unit(s) in the second segments, because the second monomer is often added before the complete consumption of the first monomer to avoid side reactions at high conversion.

The synthetic strategy for a wider variety of block copolymers is to combine the metal-catalyzed living radical and other living polymerizations. This can be accomplished by the introduction of a potentially active carbon−halogen bond into the polymers obtained commercially or by some living processes.

This section discusses the block copolymer syntheses by these two approaches, and Figures 16−25 give comprehensive lists of reported block copolymers.

1. Block Copolymers via Sequential Metal-Catalyzed Living Radical Polymerization

A wide variety of block copolymers can be obtained by the metal-catalyzed living radical polymerizations, which are now applicable to numerous monomers. Most of them are block copolymers prepared from methacrylates, acrylates, and styrenes; combinations are therefore within the same family or between different families.

Block Copolymers between the Same Family of Monomers. Block copolymers derived from the same family of monomers (Figure 16) are obtained relatively easily, because the two monomers can normally be polymerized with common initiating systems and under similar reaction conditions.

Block copolymers between alkyl or related methacrylates (B-**1**,[132,198,357] B-**2**,[198] and B-**3**[115,146,148]) were prepared via the ruthenium-, copper-, and nickel-catalyzed living radical polymerizations. These block copolymers can be synthesized both via sequential living radical polymerizations and via the living radical polymerization initiated from isolated polymers. For example, the ruthenium-catalyzed sequential living radical polymerization of MMA followed by nBMA affords AB block copolymers B-**1** with narrow MWDs ($M_w/M_n = 1.2$), which can be extended further into ABA block copolymers B-**2** with similarly narrow MWDs ($M_w/M_n = 1.2$).[198] Star block copolymers with B-**1** as arm chains were similarly synthesized but with multifunctional initiators.[357]

Block copolymers between alkyl acrylates such as B-**4**,[358] B-**5**,[202,203] and B-**6**,[203] on the other hand, have been synthesized by the macroinitiator methods mostly with copper catalysts. Star block copolymers with a soft poly(MA) core and a hard poly(isobornyl acrylate) shell were synthesized by using multifunctional initiators.[358] Poly(tBA) segments in B-**5** and B-**6** can be converted into hydrophilic poly(acrylic acid).[203] Block copolymers between *p*-methylstyrene and styrene (B-**7**) were also prepared by the rhenium-catalyzed living radical polymerization in conjunction with an alkyl iodide initiator.[169]

Block Copolymers between Different Families of Monomers. Block copolymers among different families of monomers (e.g., methacrylate/acrylate) can be efficiently prepared by metal-catalyzed radical polymerizations (Figure 17). Though widely feasible, the synthesis often calls for specific care, and in particular the initiating systems including terminal halogens, metals, and ligands should be carefully selected so that they are effective for both monomers in different families. For the macroinitiator method, in contrast, the catalysts for the first and the second polymerizations should not be necessarily the same.

Most of the block copolymers consisting of methacrylates and acrylates (B-**8** to B-**12**) have been prepared via macroinitiator methods. AB- and BA-type block copolymers of MMA and MA (B-**8**[76,135,359] and B-**9**[359]) were prepared with nickel, copper, and iron catalysts. Due to the higher activity of the carbon−halogen terminals in poly(methacrylate)s than in poly(acrylate)s, block copolymerization from PMMA is successfully performed via both sequential and macroinitiator methods, where the controllability seems better in the copper-based system. Similar

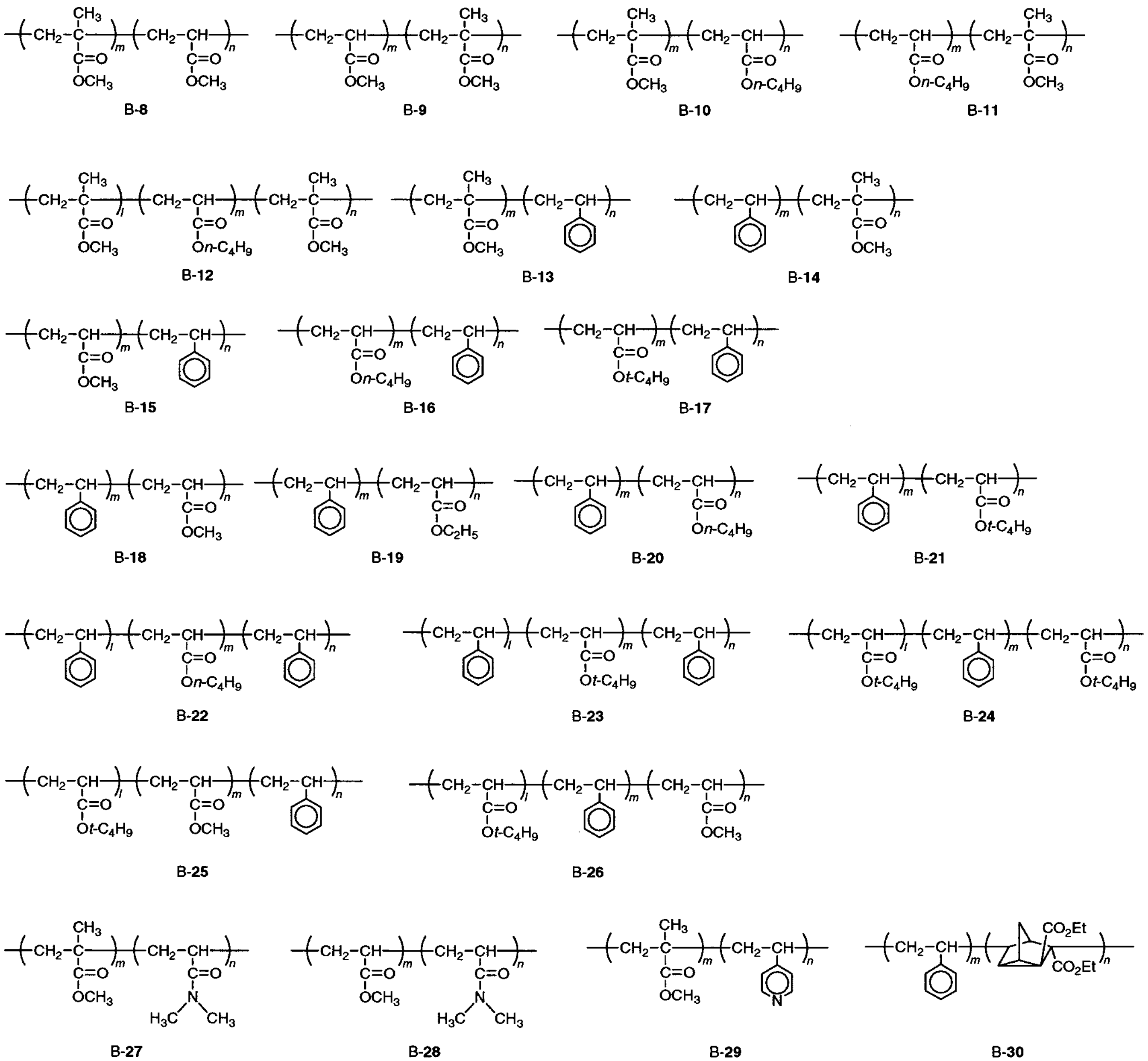


Figure 17. Block copolymers between different families of monomers.

results were also obtained for B-**10**.[135,138,359] In contrast, for BA-type block copolymers from MA, halogen-exchange reactions from C−Br into C−Cl terminals (see above) should be employed so that the initiation from the less active dormant terminal of acrylates can be quantitative and faster.[359] This method gave B-**9** with fairly narrow MWDs ($M_w/M_n = 1.15$) without contamination of homopoly(MA). A similar block copolymer with nBA and MMA (B-**11**) can be prepared by the same method.[360]

ABA-type block copolymers B-**12** with a hard PMMA as the outer segment (A) and a soft poly(nBA) as the inner segment (B) are expected as all-acrylic thermoplastic elastomers. Examples of B-**12** have been prepared with copper and nickel catalysts via bifunctional initiation.[359−364] Unfortunately, the copolymers by R−Br/Ni-**2** via the macroinitiator method were reported to be inferior as thermoplastic elastomers to those by living anionic polymerizations. A possible reason is the presence of short PMMA segments caused by the lower activity of the C−Br terminal of poly(nBA).[363] The use of halogen-exchange methods with the copper-based systems can narrow the MWDs of the ABA block copolymers.[359,360,364]

The MMA/styrene block copolymers of both AB and BA types (B-**13** and B-**14**) were synthesized with copper and iron catalysts, although the MWDs were slightly broader ($M_w/M_n = 1.4{-}1.5$) than those of the other block copolymers.[76,94,241,365]

A wider range of acrylate/styrene block copolymers have been prepared by copper catalysts, partially because the homopolymerizations of both monomers can be controlled with common initiating systems. Both AB- (B-**15** to B-**17**)[202,230,254,366,367] and BA-type (B-**18** to B-**21**)[28,112,169,230,366,368,369] block copolymers were obtained from macroinitiators prepared by the copper-based systems. The block copolymerizations can also be conducted under air[230] and under emulsion conditions with water.[254] Combination of the Re- and Ru-mediated living radical polymerizations in

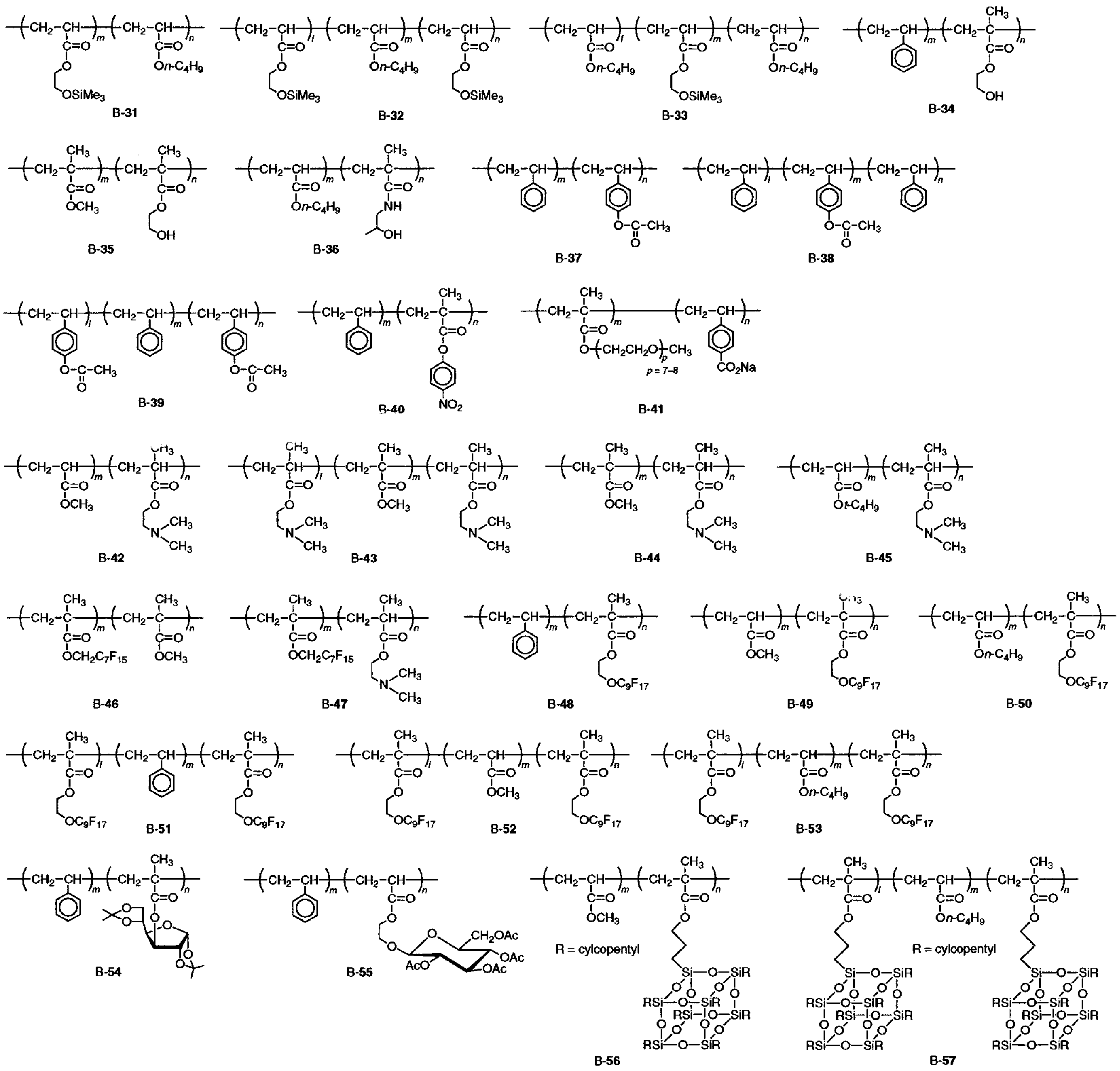


Figure 18. Block copolymers with functional segments.

the macroinitiator method is effective for the synthesis of B-**18**.[169]

A series of ABA- and BAB-type triblock copolymers (B-**22** to B-**24**) were obtained by two-step block copolymerization with bifunctional initiators[202] or by three-step block copolymerization with monofunctional initiators.[202,366,368] ABC-type block copolymers B-**25**[203] and B-**26**[202] consisting of styrene, MA, and tBA can be obtained by the latter method; the tBA segment may be hydrolyzed to give amphiphilic triblock copolymers.

Acrylamide-based block copolymers B-**27**[370] and B-**28**[117] were prepared by the ruthenium- and copper-based systems, respectively. The vinylpyridine (B-**29**)[214,371] segment can be introduced into the block copolymers with MMA. The polystyrene-based block copolymers B-**30** with short segments of a bicyclic monomer had a higher decomposition temperature than the homopolystyrene with C–Br terminals.[223]

Block Copolymers with Functional Segments. Various block copolymers with functional groups can be prepared by direct block copolymerization of functional monomers or by sequential polymerizations of their protected forms, followed by deprotection (Figure 18).

Block copolymers with hydroxyl segments were prepared by various ways: An example utilizes the copper-catalyzed sequential copolymerizations of nBA and 2-[(trimethylsilyl)oxy]ethyl acrylate by the macroinitiator method into B-**31** to B-**33**. The copolymers were then hydrolyzed into amphiphilic forms by deprotection of the silyl groups.[313] A direct chain-extension reaction of polystyrene and PMMA with HEMA also afforded similar block copolymers with hydroxyl segments (B-**34** and B-**35**).[241,243] In block polymer B-**36**, a hydroxy-functionalized acrylamide provides a hydrophilic segment.[117] Block copolymers of styrene and *p*-acetoxystyrene (B-**37** to B-**39**), prepared by iron and copper catalysts, were precursors of amphiphilic block copolymers with hydroxy groups.[169,208,372]

Carboxyl groups may be introduced into block copolymers via direct polymerizations of free-acid monomers or protection−deprotection procedures. Block copolymers of styrene and nitrophenyl methacrylate (B-**40**) are used for the latter method, where the activated ester pendant is effectively converted into methacrylic acid or acrylamide under mild conditions.[166] A homogeneous aqueous system with copper catalysts gives block copolymers with benzoate groups (B-**41**) via sequential block copolymerization of the two water-soluble monomers.[247]

Block copolymers with pendant amino groups can be obtained by the block copolymerization of (meth)-acrylates and 2-(dimethylamino)ethyl methacrylate catalyzed by copper to afford B-**42** to B-**45**.[243,373]

Perfluoroalkyl groups are also introduced into block copolymers with methacrylates, acrylates, and styrene (B-**46** to B-**53**), which can be synthesized in scCO$_2$ or in the bulk.[95,315] Amphiphilic block copolymers based on glycopolymer segments (B-**54** and B-**55**) are synthesized by copper-catalyzed polymerizations.[321,322] Comonomers with a polyhedral oligomeric silsesquioxane unit afforded hybrid polymers between organic and inorganic components (B-**56** and B-**57**).[326]

2. Block Copolymers via Combination of Other (Living) Polymerizations

Block copolymers can be prepared by combination of metal-catalyzed living radical polymerization and other polymerizations. Namely, polymers with carbon−halogen terminals may be synthesized by some living polymerization, and the product is further used to initiate living radical polymerization in the presence of transition-metal catalysts. Therefore, this method is essentially a variant of the macroinitiator method discussed above. Such carbon−halogen terminals can be obtained by transformation of the polymer terminal with some reagents or by use of halogenated initiators for the first-step living polymerization. In some cases, there is no need for the transformation since the first-step polymerization also proceeds via similar carbon−halogen chain ends as in living cationic polymerization (see below). Reviews on block copolymer synthesis based on mechanism transformation are available elsewhere.[301,302]

Another method is based on initiation of other polymerizations from the polymers prepared by living radical polymerization as macroinitiators. The following sections give specific examples.

Anionic Vinyl Polymerization. The carbanionic terminals in living anionic polymerization can be transformed into carbon−halogen bonds suited for radical generation. The backbones utilized thus far for this approach include polystyrene (B-**58** to B-**62**)[215,374] and polyisoprene (B-**63** and B-**64**),[374,375] although the former segment can also be prepared by the living radical polymerization (Figure 19).

For B-**58** to B-**60** and B-**62**, the polystyryllithium terminal was converted into a bromide by the reaction with styrene oxide followed by treatment with 2-bromoisobutyryl bromide.[374] The same method is utilized for isoprene as in B-**64**.[374] Such macroinitiators induced living radical polymerization of methacrylates, acrylates, and styrene in the presence of the copper catalysts to give block copolymers with narrow MWDs ($M_w/M_n = 1.1-1.2$). The use of ethylene oxide for quenching the living anionic polymerization of styrene followed by treatment with SOCl$_2$ resulted in a carbon−chlorine terminal for a subsequent polymerization of 2-vinylpyridine (B-**61**).[215]

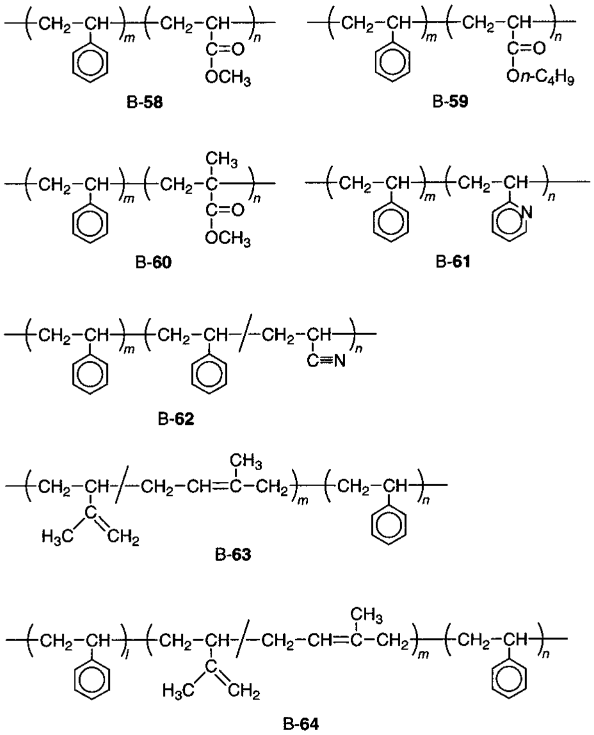


Figure 19. Block copolymers prepared via living anionic polymerization.

A transformation method can introduce some functional groups at the junction as in B-**63**, which bear a fluorescent dye between the polyisoprene and polystyrene segments.[375] The preparation is based on quenching the living anionic polymerization of isoprene with 1-(9-phenanthryl)-1-phenylethylene followed by addition of excess α,α′-dibromo-*p*-xylene, which affords a C−Br terminal effective for the copper-catalyzed radical polymerization of styrene.

Cationic Vinyl Polymerization. Living cationic polymerizations, in general, are based on the reversible activation and heterolytic dissociation of carbon−halogen terminals by a Lewis acid.[7−9] Despite the difference in the activation processes, some of the carbon−halogen bonds obtained in living cationic polymerization can be used as an initiating site for metal-catalyzed living radical polymerization without any modification. Figure 20 shows block copolymers obtained in this way.

The polystyrene obtained by living cationic polymerization with R−Cl/Lewis acid possesses a carbon−chlorine terminal that is subsequently used for the living radical polymerizations of acrylates and methacrylates to give block copolymers such as B-**65** to B-**67**.[376−378]

Chlorine-capped polyisobutylene, prepared via cationic polymerization, was also used as a macroinitiator for the copper-catalyzed radical polymeriza-

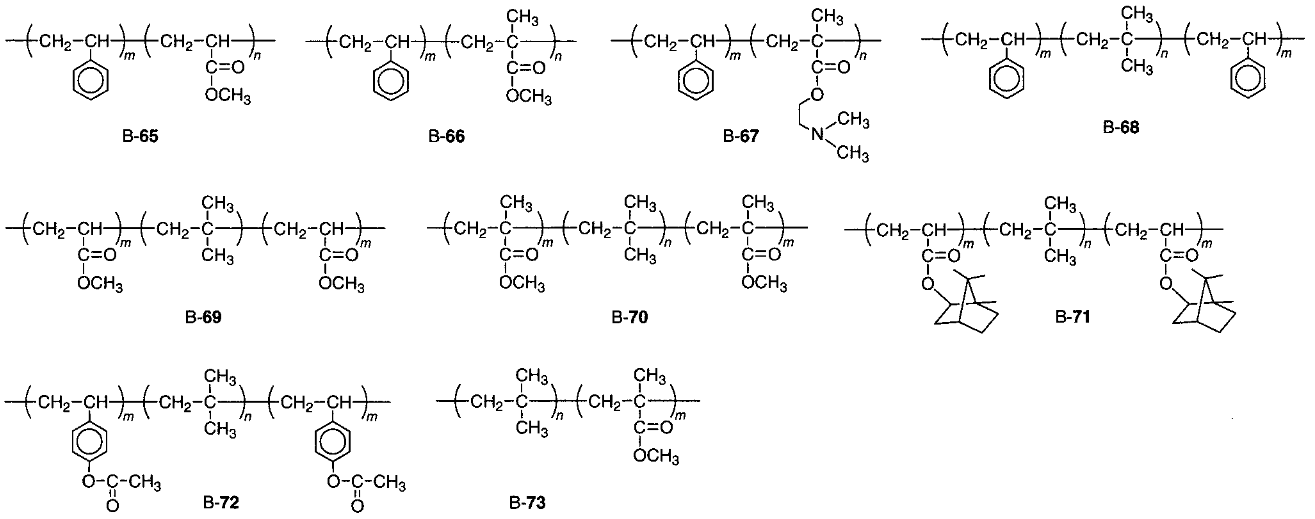


Figure 20. Block copolymers prepared via living cationic polymerization.

tions of acrylates, methacrylates, and styrenes as in B-**68** to B-**73**.[204,379−381] The C−Cl terminal of the polyisobutylene cannot initiate the living radical polymerization due to its lower activity for redox reactions, but it can be modified into an active form by inserting several units of styrene. Polymers B-**68** to B-**72** were prepared in this way from bifunctional initiators.[204,380] Another method is based on transformation of the chloride terminal into hydroxyl functions followed by esterification with 2-bromopropionyl[379] and 2-bromoisobutyryl halides[381] as employed in the preparation of B-**68** and B-**73**, respectively.

Radical Vinyl Polymerization. Conventional radical polymerization and telomerization can also be beneficial for block copolymer synthesis, because in some cases they polymerize monomers inactive for metal catalysts, although side reactions often render the block copolymers in low yield and with ill control of molecular weights. However, a combination with conventional radical polymerizations affords novel block copolymers in higher yields than before (Figure 21).

Halogen compounds such as chloroform and carbon tetrachloride are well-known telomers in conventional radical polymerizations. They give oligomers or polymers with a CCl_3 terminal, which can act as an initiating group for metal-catalyzed radical polymerization. This method was employed for vinyl acetate to prepare AB block copolymers with styrene (B-**74**)[338,382] or with nBA (B-**75**).[330,338] The block copolymers based on vinylidene fluoride (B-**76** to B-**80**) were similarly prepared with $CHCl_3$,[157,383] perfluoroalkyl iodides,[384] and bromides[385] as telomers followed by the copper-catalyzed radical polymerizations.

Another route to block copolymers in conjunction with conventional radical systems is to use azo initiators bearing reactive carbon−halogen bonds such as (chloromethyl)benzyl, 2-bromoisobutyroyl, and trichloromethyl groups.[338,386] This method can afford diblock (B-**74** and B-**75**) and triblock (B-**81**) copolymers, depending on the mode of termination reactions in the conventional radical polymerizations with the azo compounds. In these cases, the order of the two polymerizations can be reversed, where conventional radical polymerization is initiated by the azo macroinitiators prepared by a metal-catalyzed radical polymerization.[338]

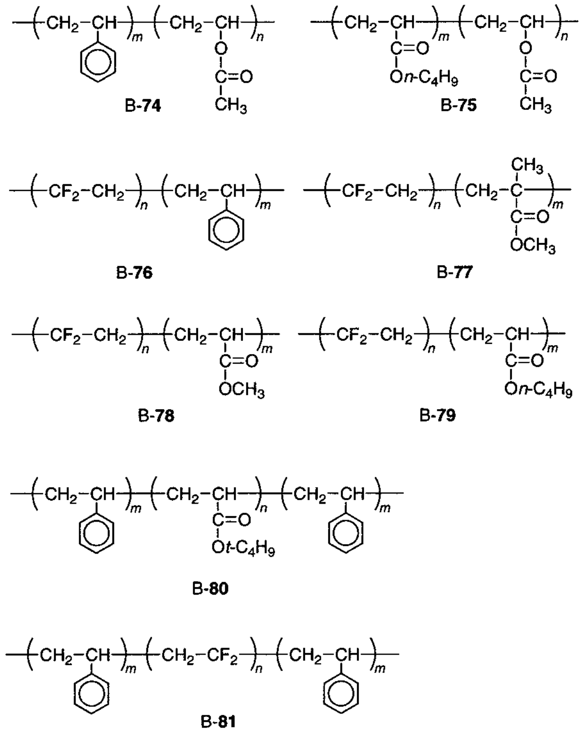


Figure 21. Block copolymers prepared via conventional radical polymerization.

Ionic Ring-Opening Polymerization. Living ionic ring-opening polymerization of cyclic ethers, esters, and siloxanes gives polymers with controlled molecular weights and defined terminal structures and is thus applied to the synthesis of block copolymers coupled with the metal-catalyzed living radical polymerizations (Figure 22).

Transformation of cationic ring-opening polymerization of THF into the copper-catalyzed radical polymerizations of styrene, acrylates, and methacrylates leads to various block copolymers (B-**82** to B-**88**).[387,388] Diblock (B-**82** to B-**84**) and ABC-type triblock (B-**85**) copolymers were prepared via the

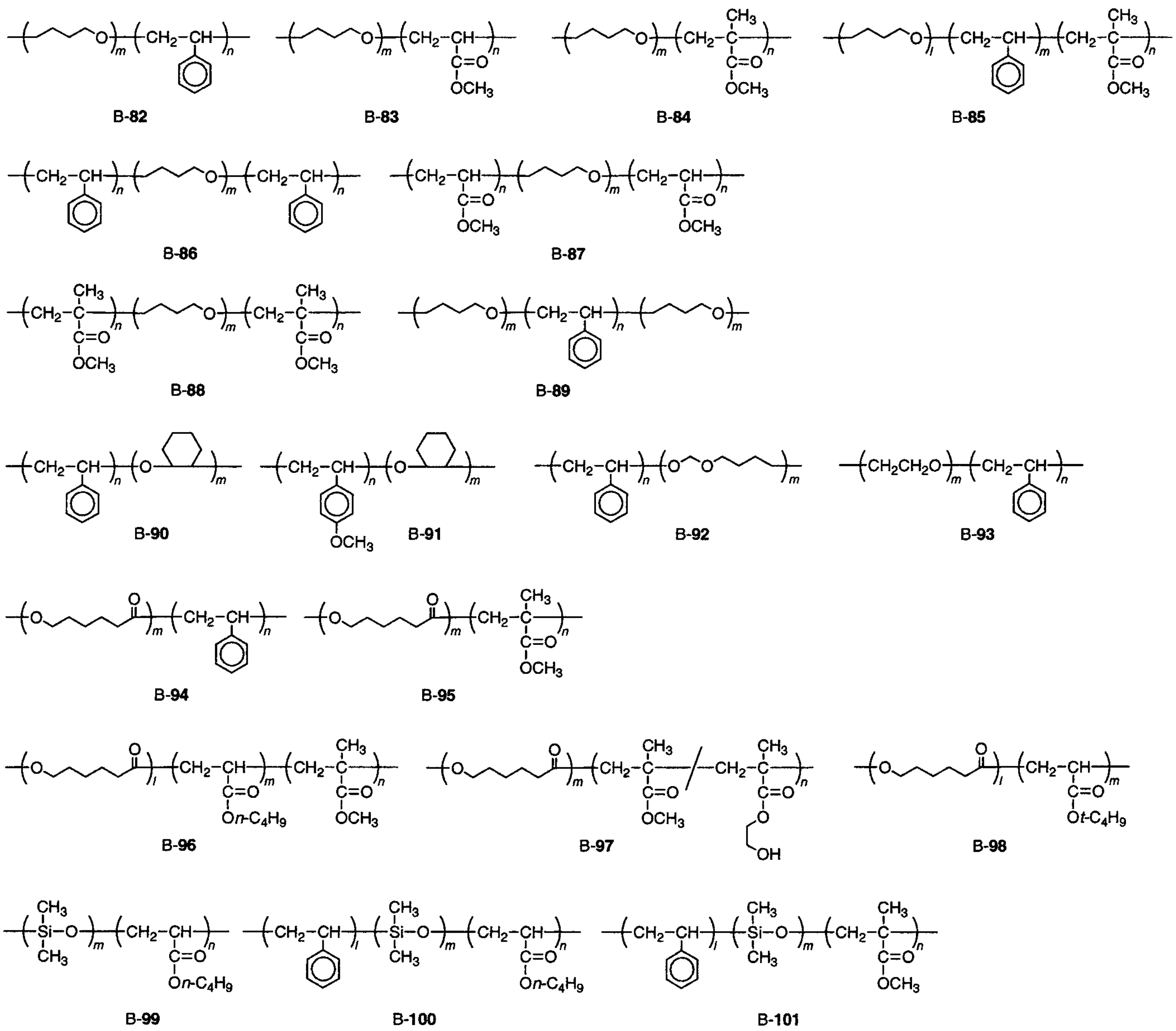


Figure 22. Block copolymers prepared via ionic ring-opening polymerization.

copper-catalyzed radical polymerizations from poly(THF) macroinitiators obtained with 2-bromopropionyl bromide and silver triflate.[387]

The ABA-type block copolymers B-**86** to B-**88** were synthesized via termination of telechelic living poly(THF) with sodium 2-bromoisopropionate followed by the copper-catalyzed radical polymerizations.[387] A similar method has also been utilized for the synthesis of 4-arm star block polymers (arm B-**82**), where the transformation is done with β-bromoacyl chloride and the hydroxyl terminal of poly(THF).[388] The BAB-type block copolymers where polystyrene is the midsegment were prepared by copper-catalyzed radical polymerization of styrene from bifunctional initiators, followed by the transformation of the halogen terminal into a cationic species with silver perchlorate; the resulting cation was for living cationic polymerization of THF.[389] A similar transformation with $Ph_2I^+PF_6^-$ was carried out for halogen-capped polystyrene and poly(*p*-methoxystyrene), and the resultant cationic species subsequently initiated cationic polymerization of cyclohexene oxide to produce B-**90** and B-**91**, respectively.[390] Another route coupled with cationic ring-opening polymerizations is accomplished for polymer B-**92** with the use of a hydroxyl-functionalized initiator with a C−Br terminal, where the OH group initiates the cationic polymerizations of 1,3-dioxepane in the presence of triflic acid.[329] Poly(ethylene oxide)-based block copolymers B-**93** are obtained by living anionic polymerization of ethylene oxide and the subsequent transformation of the hydroxyl terminal into a reactive C−Br terminal with 2-bromopropionyl bromide, followed by the copper-catalyzed radical polymerization of styrene.[391]

Living ring-opening polymerization of ϵ-caprolactone with aluminum alkoxide or alkylaluminum can be combined with nickel-catalyzed living radical polymerization for the synthesis of linear and dendrimer-like star block copolymers B-**94** to B-**98**.[139,392−394] Such block copolymers were first synthesized via living radical polymerization with CBr_3CH_2OH, where the C−Br bond is a radical initiating site and the hydroxyl group is for the subsequent ring-opening

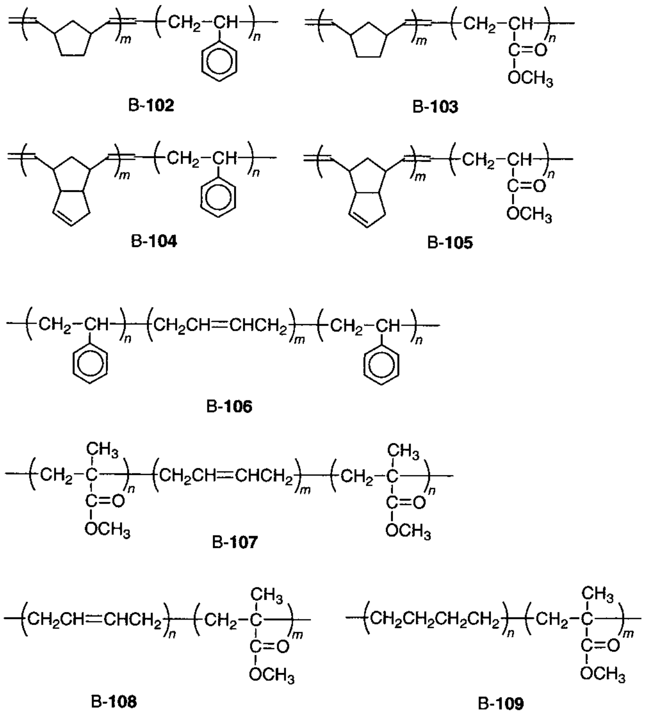


Figure 23. Block copolymers prepared via ring-opening metathesis polymerization.

polymerization. The reverse order of the two processes is also possible.[139] More interestingly, the two living polymerizations can be performed simultaneously; namely, MMA and ϵ-caprolactone undergo parallel growth initiated by the CBr_3CH_2OH/Ni-**2**/Al(O-*i*-Pr)$_3$ system.[392] The aluminum compound might have a dual function, one as a catalyst for anionic ring-opening polymerization and the other as an additive for Ni-**2** to facilitate the living radical process.[133]

Poly(dimethylsiloxane) segments can also be introduced into the block copolymers as in B-**99** to B-**101**, where the silane terminal of poly(dimethylsiloxane) or block copolymers of styrene and dimethylsiloxane are converted into the C−Br terminal by hydrosilylation of 3-butenyl 2-bromoisobutyrate.[395]

Ring-Opening Metathesis Polymerization. When coupled with living radical systems, living ring-opening metathesis polymerization (ROMP) also permits the synthesis of other types of block copolymers (Figure 23) such as B-**102** to B-**108**.[67,396,397] A molybdenum carbene or ROMP intermediate is converted into a benzyl bromide-type terminal by quenching the ROMP with *p*-(bromomethyl)benzaldehyde by a retro-Wittig reaction.[396] The macroinitiator thus obtained induced living radical polymerizations of styrene and MA with copper catalysts to afford B-**102** to B-**105**.

Poly(1,4-butadiene) segments prepared by the ruthenium-mediated ROMP of 1,5-cyclooctadiene can be incorporated into the ABA-type block copolymers with styrene (B-**106**) and MMA (B-**107**).[397] The synthetic method is based on the copper-catalyzed radical polymerizations of styrene and MMA from the telechelic poly(butadiene) obtained by a bifunctional chain-transfer agent such as bis(allyl chloride) or bis(2-bromopropionate) during the ROMP process. A more direct route to similar block copolymers is based on the use of a ruthenium carbene complex with a C−Br bond such as Ru-**13** as described above.[67] The complex induced simultaneous or tandem block copolymerizations of MMA and 1,5-cyclooctadiene to give B-**108**, which can be hydrogenated into B-**109**, in one pot, catalyzed by the ruthenium residue from Ru-**13**.

Condensation Polymerization. Condensation polymerization generally affords telechelic polymers with functional terminals, which thus can be transformed into reactive carbon−halogen bonds for the metal-catalyzed radical polymerizations (Figure 24).

Polysulfones obtained from bisphenol A and bis(4-fluorophenyl) sulfone were converted into telechelic macroinitiators by the reaction with 2-bromopropio-

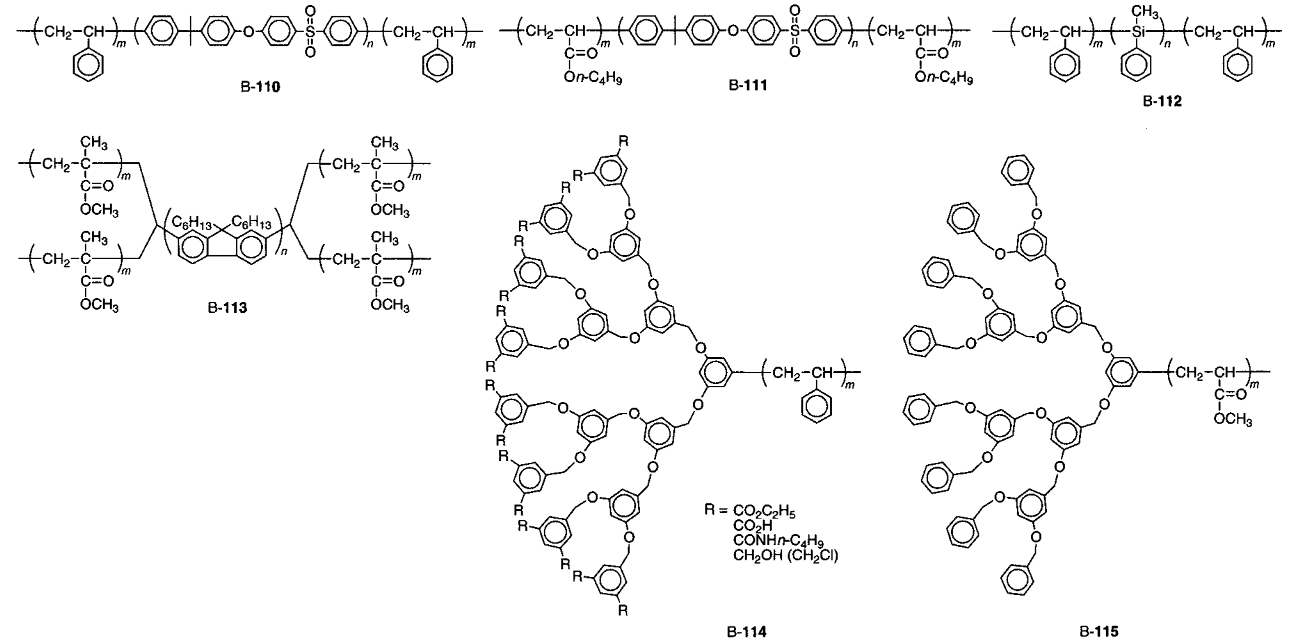


Figure 24. Block copolymers prepared via condensation polymerization.

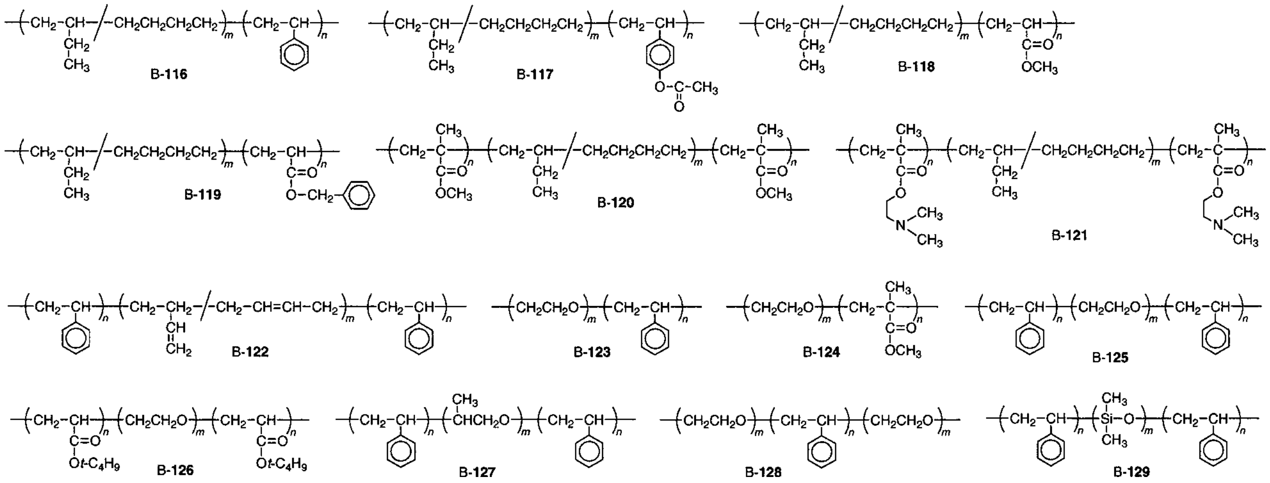


Figure 25. Block copolymers prepared from commercially available polymers.

nyl bromide. The telechelic bisbromide was subsequently employed for the copper-catalyzed block polymerization of styrene or nBA to give B-**110** and B-**111**, respectively.[398] A polysilylene-based block copolymer (B-**112**) was synthesized similarly from a telechelic polysilane macroinitiator with benzyl chloride terminals.[399] Another block copolymer (B-**113**) consisting of a fluorene unit in the midsegment was obtained by two-step polymerizations, the Ni(0)-mediated condensation polymerization of 2,7-dibromo-9,9-dihexylfluorene and the Ni(II)-mediated living radical polymerization of MMA after the transformation of the telechelic terminals.[400]

Polystyrene B-**114**[401] and poly(acrylate) B-**115**[402] are connected to a dendrimer at its focal core. These are prepared with dendrimer-type macroinitiators with a benzyl bromide at the focal point, from which are initiated the copper-catalyzed living radical polymerizations of styrene and acrylates, respectively. For B-**114**, various functional groups (R) were introduced into the periphery.

Commercially Available Polymers. Modification of terminal groups for block copolymer synthesis can be applied to commercially available end-functionalized polymers although most of them are produced by living anionic polymerization. Thus, some of the block copolymers shown in Figure 25 were already described above.

Hydroxyl-capped poly(ethylene-*co*-butylene), a so-called Kraton, was converted into a macroinitiator via esterification with 2-bromopropionyl chloride, and then employed for the block copolymerizations of styrene and *p*-acetoxystyrene (B-**116** and B-**117**).[403] A similar method is utilized for B-**118** to B-**121** where the esterification is with 2-bromoisobutyroyl bromide.[341] A commercially available polybutadiene is also employed for B-**122** via a similar transformation into the chloroacetyl group.[404]

Poly(oxyethylene) units can be introduced by using commercially available poly(ethylene oxide)s and poly(ethylene glycol)s via esterification of the terminal hydroxyl groups with appropriate acyl halides. Various AB- (B-**123** and B-**124**) and ABA-type (B-**125** and B-**126**) block copolymers were thus prepared,[171,327,405−408] along with a poly(propylene oxide)-based version (B-**127**).[404] The polymer coupling between a telechelic polystyrene with terminal maleic anhydride units and a commercially available poly(ethylene glycol methyl ether) gave B-**128**.[348]

Polysiloxane-based ABA-type block copolymers B-**129** can be prepared from commercially available poly(dimethylsiloxane) as a stating material followed by functionalization and the subsequent copper-catalyzed radical polymerization of styrene.[409]

D. Random Copolymers

A distinctive advantage of radical polymerization is that a variety of monomer pairs can readily be copolymerized into true random/statistical copolymers.

A mixture of two monomers that can be homopolymerized by a metal catalyst can be copolymerized as in conventional radical systems. In fact, various pairs of methacrylates, acrylates, and styrenes have been copolymerized by the metal catalysts in random or statistical fashion, and the copolymerizations appear to also have the characteristics of a living process. The monomer reactivity ratio and sequence distributions of the comonomer units, as discussed already, seem very similar to those in the conventional free radical systems, although the detailed analysis should be awaited as described above. Apart from the mechanistic study (section II.F.3), the metal-catalyzed systems afford random or statistical copolymers of controlled molecular weights and sharp MWDs, where, because of the living nature, there are almost no differences in composition distribution in each copolymer chain in a single sample, in sharp contrast to conventional random copolymers, in which there is a considerable compositional distribution from chain to chain. Figure 26 shows the random copolymers thus prepared by the metal-catalyzed living radical polymerizations.

There are several examples of random copolymers of methacrylates (R-**1** to R-**3**). MMA/nBMA copolymerization was carried out with a copper catalyst, but the products were of low molecular weight because this study was directed to mechanistic studies.[263] Random copolymers of MMA and nBMA (R-**1**) were also obtained in emulsion ($M_w/M_n = 1.2-1.3$).[254] Two monomers were consumed almost simultaneously to give a random or statistical distribution of repeat units along the chains. Copolymerization of MMA

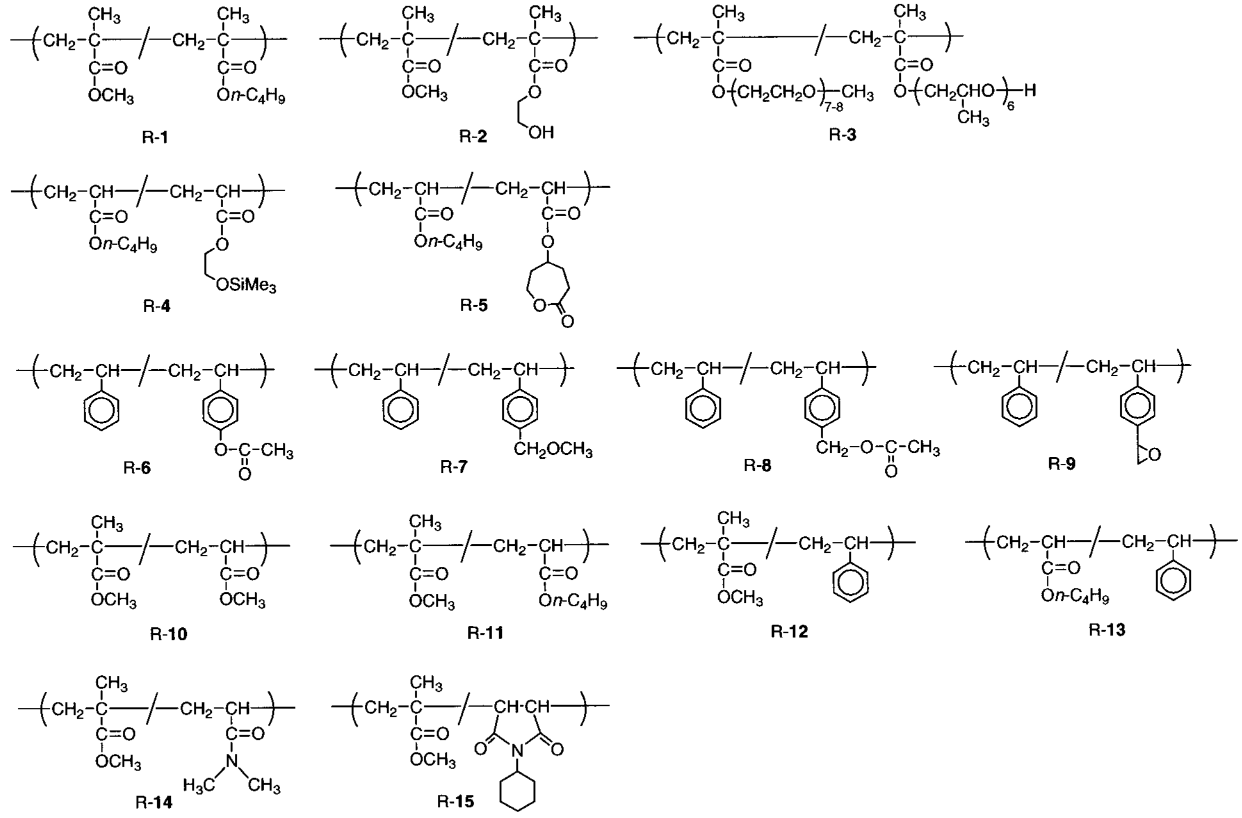


Figure 26. Random copolymers.

and HEMA was investigated by ruthenium and rhodium catalysts to give random copolymers R-**2** which possess hydroxyl functions randomly distributed along the chains.[59,138] Random copolymers between hydrophilic and hydrophobic segments (R-**3**) were also synthesized by the copper catalysts in water.[320]

Random copolymers between acrylates (R-**4** and R-**5**) were prepared by the copper and nickel catalysts. The former one has random distribution of the hydroxyl groups along with the chains similarly to R-**2** and shows different behavior in water in comparison to the block copolymers.[313] In copolymer R-**5**, the ε-caprolactone units are distributed randomly and can function as linking agents in the subsequent copolymerizations with ε-caprolactone.[318]

For styrene-based random copolymers, functional groups can be introduced into the polymer chains via copolymerization with functional styrene derivatives, because the electronic effects of the substituents are small in the metal-catalyzed polymerizations in comparison to the ionic counterparts. Random copolymer R-**6** is of this category, synthesized from styrene and *p*-acetoxystyrene.[372] It can be transformed into styrene/*p*-vinylphenol copolymers by hydrolysis.[380] The benzyl acetate and the benzyl ether groups randomly distributed in R-**7** and R-**8** were transformed into benzyl bromide, which can initiate the controlled radical polymerizations of styrene in the presence of copper catalysts to give graft copolymers.[209] Epoxy groups can be introduced, as in R-**9**, by the copper-catalyzed copolymerizations without loss of epoxy functions, while the nitroxide-mediated systems suffer from side reactions due to the high-temperature reaction.[317]

Metal-catalyzed radical polymerization enables the controlled random copolymerization of the monomers that belong to different families such as methacrylates, acrylates, and styrenes, in contrast to the fact that the living anionic counterparts give their block copolymers in most cases. However, some of the metal-catalyzed systems may suffer from slight broadening of the MWDs due to the difference in the cross-propagation processes and in reactivity of the dormant carbon–halogen terminals depending on which monomer pair is employed. Another problem is that, at least thus far, the available metal catalysts are more or less “monomer-specific” and few of them are universally applicable to different families of monomers such as methacrylates and styrenes.

Copolymerizations of an equimolar mixture of MMA and MA (R-**10**) or nBA (R-**11**) with the nickel catalysts led to simultaneous consumption of the two monomers and gave their random copolymers with controlled molecular weights and relatively narrow MWDs ($M_w/M_n \approx 1.5$).[135] The copper-catalyzed systems also induced controlled random copolymerizations of MMA and nBA in organic solvents and in emulsion ($M_w/M_n \approx 1.2$).[254,267] However, methacrylate/acrylate copolymerization may result in gradient structures rather than random structures (section III.F).

The styrene-based random copolymers R-**12** and R-**13** were prepared by ruthenium and copper catalysts, respectively. For the former copolymer (R-**12**), the copolymerizations were investigated with various compositions of the two monomers, which revealed that the composition curve is similar to that of conventional radical copolymerizations.[205] The latter copolymers (R-**13**) obtained with R–Br/CuBr have narrow MWDs ($M_w/M_n = 1.1-1.2$) because the systems are effective in controlling homopolymerizations of both styrene and nBA.[264] The R−Cl/CuCl system also gave R-**13** although the MWDs became slightly broader ($M_w/M_n = 1.3-1.4$).[366]

Other methacrylate-based copolymers are also possible with acrylamide (R-**14**)[370] and maleimide (R-**15**),[410] which can be prepared by ruthenium and copper catalysts, respectively. Both copolymers have amide groups randomly distributed in the PMMA chains.

E. Alternating Copolymers

Alternating copolymers can be obtained from the monomers that cannot homopolymerize alone but can copolymerize in conjunction with the appropriate monomers. As described above, *N*-substituted maleimides copolymerize with styrene in this fashion in the presence of copper catalysts to give alternating copolymers with controlled molecular weights ($M_w/M_n = 1.1-1.2$). The substituents in the maleimides include 2-acetoxylethyl, phenyl, and cyclohexyl groups.[219−222]

F. Gradient Copolymers

Another type of copolymer with controlled composition or sequence distribution is a gradient copolymer, in which the repeat-unit composition (sequence) changes along a backbone; i.e., “A” units are predominant, for example, near the α-end, and their abundance continuously decreases, while “B” units increasingly predominate near the ω-end. Such polymers can be prepared by metal-catalyzed radical polymerization; two methods are known so far: One method is based on the automatic formation of a gradient composition due to an inherent monomer reactivity difference, and the other is based on continuous addition of a second monomer at a controlled rate into a polymerizing solution of the first monomer. The former is exemplified in the copolymers obtained of MMA and nBA.[411] Although they are considered random copolymers, detailed analysis indicates that there is a gradient structure therein. The latter method was applied for pairs of styrene/nBA and styrene/acrylonitrile. The physical properties of the copolymers were studied in comparison to those of other copolymers.

Another copolymer with compositional change along the chains is an ABC-type block/random copolymer that consists of three segments, each of which is a copolymer of the two monomers with a different composition. A mixture of styrene/MMA (3:1 molar ratio) was polymerized with the ruthenium-based systems, and two portions of MMA were sequentially added at varying styrene conversions.[205] The styrene/MMA sequential compositions from the α- to the ω-end in the final products with relatively narrow MWDs ($M_w/M_n \approx 1.5$) are about (3:1)−(1:1)−(1:4). These interesting experiments show not only that the Ru-catalyzed MMA/styrene copolymerization is in fact living irrespective of the initial monomer composition, but also that the reaction might lead to new copolymers differing from statistical or gradient derivatives.

G. Telechelic and Star Polymers

Telechelic and star polymers can be obtained by a so-called multifunctional initiator method where metal-catalyzed living radical polymerizations are initiated from halogen compounds with plural reactive carbon−halogen bonds. This method can give multiarmed or star polymers with a predetermined number of arms that corresponds to the number of the carbon−halogen bonds in the initiator. Numerous polyhalogen compounds are accessible and synthesized from various polyfunctional compounds as summarized in Figures 27 and 28, where the arm numbers may be varied between 2 and 12.

Another route to synthesizing star polymers by living polymerization involves the use of multifunctional end-capping agents, but this method is not suited for metal-catalyzed radical polymerizations, at least so far, due to the lack of universal and convenient terminating agents, as described above (section III.B.2).

The third method is based on a polymer-linking reaction where the liner polymers are obtained by the living radical polymerization with divinyl compounds. This can afford star polymers with a relatively large number of arms, up to several hundred per molecule, while the number of arms by definition involves a statistical distribution in a single sample.

1. Telechelic Polymers with Bifunctional Initiators

Halogen compounds with two reactive carbon−halogen bonds can be bifunctional initiators for metal-catalyzed living radical polymerizations to give telechelic polymers. The effective bifunctional initiators include MI-**1** to MI-**26** with various spacers between the initiating sites.

α,α′-Dichloro-*p*-xylene (MI-**1**, X = Cl) is a bifunctional initiator for the copper-catalyzed living radical polymerization of styrene to give telechelic polymers with controlled molecular weights and narrow MWDs ($M_w/M_n = 1.45$).[84] The bromide version of MI-**1** (X = Br) is more versatile and gives telechelic polymers of stryene,[84,315,348] MA,[84,315] nBA,[315] and *p*-acetoxystyrene[207] with narrow MWDs ($M_w/M_n = 1.1-1.3$). The telechelics are further employed as macroinitiators for ABA-type block copolymers. The copper-catalyzed radical polymerization of MMA with MI-**2** gave polymers with narrow MWDs ($M_w/M_n = 1.2$) but in low initiation efficiency ($I_{eff} = 0.13$).[412] The obtained PMMA possesses one anthracene unit in the middle of the polymer backbone. α,α-Dichlorotoluene (MI-**3**) serves as a bifunctional initiator for the copper-catalyzed radical polymerization of styrene, while it works as a monofunctional version for MMA polymerization due to the low reactivity of the second C−Cl bond after the initiation.[165]A haloketone, dichloroacetophenone (MI-**4**), induces living radical polymerization of MMA in the presence of ruthenium catalysts to give polymers with extremely narrow MWDs ($M_w/M_n \approx 1.1$).[56] As it turned out, both of the carbon−chlorine bonds in the initiator initiate living polymerization.[154]

Ester-type bifunctional initiators can readily be prepared by a reaction of dialcohols or diphenols with β-haloacyl halides. For example, bis(dichloroacetate)s

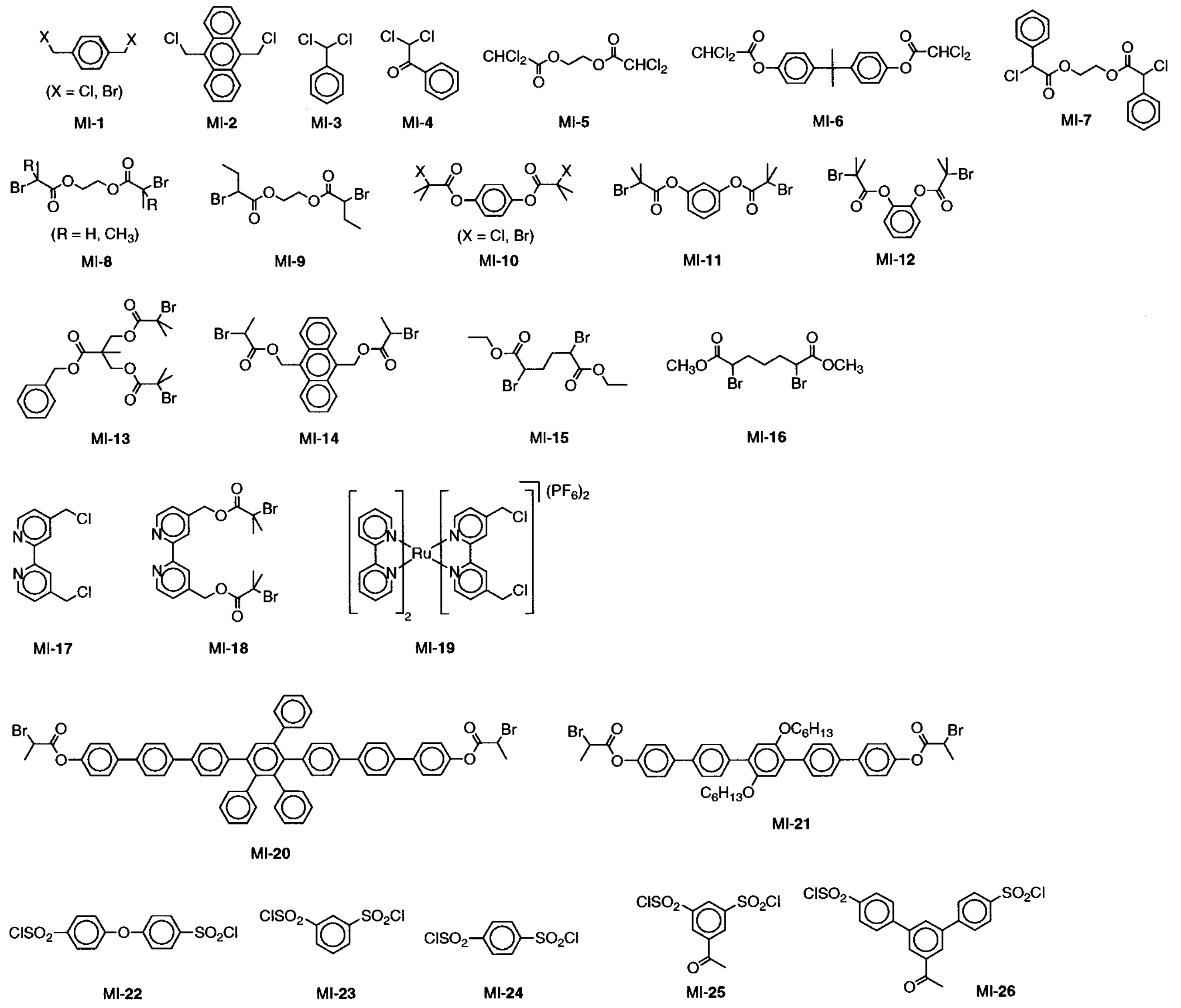


Figure 27. Bifunctional initiators.

such as MI-**5** and MI-**6** serve as a bifunctional initiator for MMA in the presence of Ru-**1** and Al(acac)$_3$ to give telechelic PMMA with controlled molecular weights and narrow MWDs ($M_w/M_n = 1.3-1.4$). In contrast to dichloroacetophenone (see above), one dichloroacetate unit serves as a monofunctional initiator in the ruthenium catalysis (Ru-**1**).[228] Another chloride-type bifunctional initiator (MI-**7**) affords telechelic polystyrene in the presence of copper catalysts.[171] Bromoesters MI-**8** and MI-**9** derived from ethylene glycol were employed for acrylate and styrene with copper catalysts.[313,326,358,359,368,389,413] These telechelic polymers can further be employed as bifunctional macroinitiators for ABA block copolymers.[313,326,359,368,389] The obtained telechelic polystyrenes can produce polymer network gels by a copper-mediated linking reaction with divinylbenzene.[413] A series of bromoesters (MI-**10** to MI-**12**), derived from diphenols and 2-bromoisobutyroyl bromide, are effective in the copper-mediated living radical polymerizations of various acrylates and styrene ($M_w/M_n \approx 1.1$).[263] A chloroester (MI-**10**, X = Cl) gave similar polymers with slightly broader MWDs ($M_w/M_n \approx 1.2$). Telechelic PMMA can be obtained from MI-**13** with Ni-**2** as a catalyst.[414] Anthrathene-labeled polystyrene can be synthesized with the copper-catalyzed polymerizations initiated with MI-**14**; the aromatic tag or probe is located near the midpoint of a polymer chain.[415] Dibromoacetates MI-**15** and MI-**16** are commercially available and effective for methacrylates, acrylates, and styrene with nickel and copper catalysts.[134,256,360-362] The resultant telechelic polymers have been subsequently employed for the synthesis of various ABA triblock copolymers.

Functional groups can also be introduced in the spacer units. Bifunctional initiators with bipyridine units such as MI-**17** and MI-**18** induced the living radical polymerizations of styrene and MMA, respectively, with copper catalysts to give polymers that carry a coordination site at the middle of the chain.[87,333] These polymers can be connected together into star polymers with a ruthenium cation at the core, where the arm numbers are varied among three, four, five, and six in combination with the polymers obtained from the monofunctional initiator with a bipyridine unit (FI-**21** and FI-**22**; Figure 13).[416] A modified method for the coupling reaction with the metal center can also afford heteroarm star polymers consisting of polystyrene and PMMA chains.[417] The bifunctional initiator complexed with ruthenium prior to the polymerization (MI-**19**) is also effective in the copper-catalyzed polymerization.[87,333]

Bifunctional initiators with oligophenylenes as a rigid spacer unit (MI-**20** and MI-**21**) generate rigid/flexible triblock copolymers of styrene.[418]

Disulfonyl halides such as MI-**22** to MI-**26** are effective bifunctional initiators for various monomers including methacrylates, acrylates, and styrenes, because the sulfonyl halide part, as pointed out for their monofunctional versions, can induce fast initiation without a bimolecular termination reaction between the sulfonyl radicals.[240,343]

2. Star Polymers with Multifunctional Initiators

Halogen compounds with more than two reactive carbon−halogen bonds afford star polymers, the arm number of which is defined by the number of the initiating sites, whereas the arm length therein is determined simply from the initial molar ratio of monomer to initiator. The multifunctional initiator method gave various star polymers with 3 (MI-**27** to MI-**33**), 4 (MI-**34** to MI-**42**), 5 (MI-**43**), 6 (MI-**44** to MI-**50**), 8 (MI-**51** and MI-**52**), and 12 arms (MI-**53** and MI-**54**).

A benzyl bromide-type initiator (MI-**27**) was utilized for the copper-catalyzed synthesis of 3-armed poly(acrylate)s with mesogen units as side-chain groups.[324] The effect of molecular architecture on the thermotropic behavior was compared with the corresponding linear polymers in both living and conventional polymerizations.

Haloester-type trifunctional initiators are obtained from triols by a method similar to those for bifunctional haloesters. 3-arm star polymers of MMA are obtained with dichloroacetates MI-**28** and MI-**29**, for which Ru-**1** and Al(acac)$_3$ are employed.[228] The polymers have controlled molecular weights and narrow MWDs. Similarly, MI-**30** and MI-**31** with copper catalysts gave 3-arm star polymers of styrene, acrylates, and methacrylates; suitable copper catalysts vary with each monomer.[199,326,358,368] The obtained star polymers can be further transformed into star block copolymers comprised of hydrophilic/hydrophobic[368] or organic/inorganic[326] segments by block copolymerizations of other monomers.

Trisulfonyl chlorides MI-**32** and MI-**33** are also efficient in the copper-catalyzed radical polymerization of methacrylates and styrene ($M_w/M_n = 1.1-1.4$).[343] The polystyrene arms can be cleaved from the core with a base, giving polymers (arms) whose molecular weights are about 1/3 of the original.

Tetra(bromomethyl)benzene (MI-**34**) was employed for alternating radical copolymerization of styrene and *N*-cyclohexylmaleimide to give controlled molecular weights and narrow MWDs ($M_w/M_n = 1.2-1.4$).[221] Another benzyl halide initiator (MI-**37**) with a cyclosiloxane core induced styrene polymerization ($M_w/M_n = 1.16$).[358] An ester-type initiator (MI-**35**) is effective in the copper-catalyzed radical polymerization of nBA.[358] A tetrafunctional sulfonyl chloride (MI-**38**) from the same tetraol can be employed for methacrylates and styrene polymerization.[343]

Another tetrafunctional ester (MI-**36**) is the smallest number of a series of dendrimer-type initiators such as MI-**46** and MI-**53** for 6- and 12-arm star polymers, respectively.[414,419,420] These initiators induce the living radical polymerizations of MMA with Ni-**2** to give the corresponding multiarmed polymers with controlled molecular weights although the arm number with MI-**53** is slightly lower than 12 due to incomplete initiation from all the carbon−bromine bonds.

A series of calixarene-core-type initiators (MI-**40**, MI-**47**, and MI-**51**) were prepared and employed for the radical polymerizations of MMA, styrene, and tBA. Ruthenium catalysts[357] were first employed, and copper catalysts are equally effective.[421,422] PMMA obtained with the dichloroacetate version of MI-**40** had narrow MWDs ($M_w/M_n = 1.1-1.2$) and controlled numbers of arms, which were ascertained by the scission of arms from the cores after the polymerizations.[357]

The star polymers obtained with the bromoester-type calixarene-based initiators were analyzed by SEC equipped with a multiangle laser light scattering (MALLS) detector. The arm numbers were well controlled (close to the initiator's functionality), although the octafunctional initiator MI-**51** induced star−star coupling in the styrene-polymerization at conversions higher than 20%.[421] A similar series of tetra-, hexa-, and octafunctionalized initiators with calixarene cores were synthesized for sulfonyl chloride versions (MI-**41**, MI-**48**, and MI-**52**) and employed for copper-catalyzed MMA polymerizations.[343]

Carbosilane-based dendritic bromoesters MI-**39** and MI-**54** are also effective as multifunctional initiators for 4- and 12-arm star PMMA with narrow MWDs ($M_w/M_n = 1.1-1.2$).[423] However, star−star coupling was observed with the use of MI-**54**.

A pentafunctionalized initiator can be obtained from esterification of β-D-glucose, and star PMMA with 5 arms are obtained.[340] Inorganic cores, other than silicon, can also be employed such as the cyclotriphosphazene (MI-**44** and MI-**45**), which gives 6-arm polymers from styrene, acrylates, and methacrylates.[303,358] Tetra- (MI-**42**)[87,332] and hexafunctionalized initiators (MI-**49**[87,332] and MI-**50**[424]) with a ruthenium center can be also employed for the radical polymerizations of styrene and MMA in the presence of appropriate catalysts such as copper, ruthenium, and nickel.

Other multifunctional initiators include star polymers prepared from initiators via living radical or other living polymerizations. In particular, all of the star polymers via metal-catalyzed living polymerization, by definition, carry a halogen initiating site at the end of each arm, and thus they are potentially all initiators. Thus, star-block copolymers with three polyisobutylene-*block*-PMMA arms and four poly(THF)-*block*-polystyrene or poly(THF)-*block*-polystyrene-*block*-PMMA were synthesized via combination of living cationic and copper-catalyzed living radical polymerizations.[381,388] Anionically synthesized star polymers of ϵ-caprolactone and ethylene oxide have

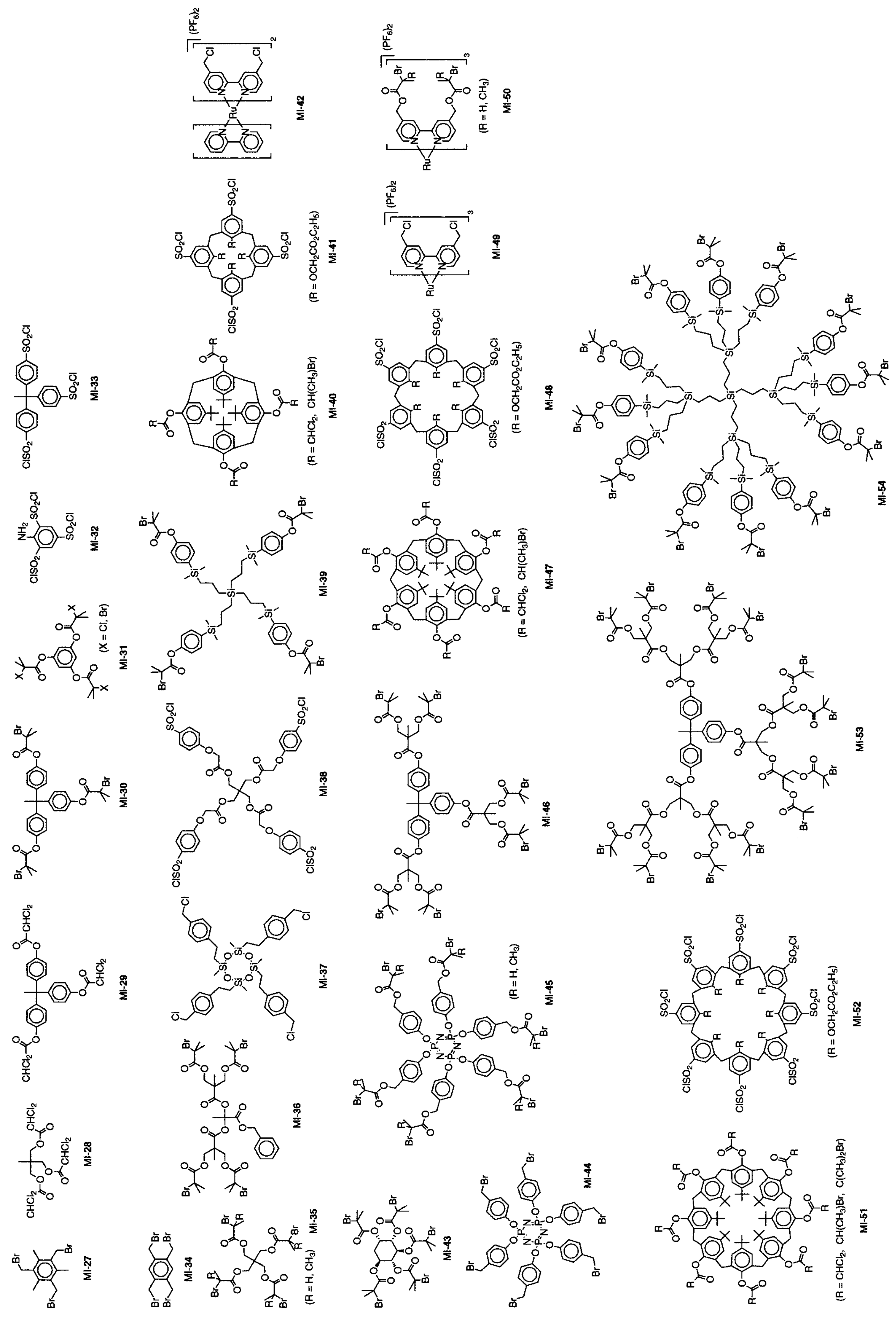


Figure 28. Multifunctional initiators.

hydroxy groups at their terminal, which can be transformed into C−Br bonds. The functionality of C−Br bonds to be introduced thereby can be either mono-, bi-, or tetrafunctional, and thus one can increase the initiating sites on the transformation. With the use of this method, the arm numbers of PMMA chains can be increased up to 24 arms.[393] This method can also afford miktoarmed PEO-*block*-(polystyrene)$_2$ and (polystyrene)$_2$-*block*-PEO-*block*-(polystyrene)$_2$ H-type copolymers.[391]

3. Star Polymers by Linking Reaction

As in known in anionic and other living polymerizations, star polymers with a large number of arms (>10) can be prepared conveniently by a linking reaction of linear polymers with divinyl compounds. Similar to the synthesis of block copolymers (section III.C.1), there are two ways for the synthesis by metal-catalyzed radical polymerizations, where the linking reaction is done via sequential addition of the divinyl compounds into the polymerization mixture after the almost completion of the vinyl monomers, or via isolation of halogen-capped monofunctional linear polymers followed by linking reaction in the presence of the metal catalysts and the divinyl compounds. The former method may involve incorporation of the first vinyl monomer units (remaining at the first stage) in the cores while the latter is free from such contamination though more cumbersome than the first. Also, the former one can be carried out in a one-pot reactor.

The sequential-addition method was systematically employed for the ruthenium-catalyzed living radical polymerization of MMA followed by in situ linking reaction with various dimethacrylates and related bifunctional monomers.[425] The yields of star polymers depend on several factors such as halogens at the polymer terminal and the spacer-unit structure (length and rigidity) in the linking agents, where chloride terminals and a soft aliphatic or a rigid long aromatic spacer are favorable. The best yield reached 93%. The arm number of the star-polymers was also determined form the molecular weights measured by static light scattering or by SEC coupled with MALLS. In an example, about 20 arms of PMMA chains were linked together into one star polymer. Divinyl compounds with amide and alcohol groups form core-functionalized star polymers with 20−640 PMMA arms in the ruthenium-catalyzed living radical polymerization of MMA.[426] In particular, bisacrylamides are good linking agents, and they give interesting star polymers in the core of which a large number of amide functions are embedded.

The copper-based system gave star polymers consisting of polystyrene and poly(tBA) arms by the linking reaction of isolated linear polymers.[328,427] The linking reaction of Br-terminated polystyrenes was examined with three divinyl compounds, divinylbenzene, 1,4-butanediol diacrylate, and ethylene glycol dimethacrylate with CuBr/L-**1** catalyst.[427] The first agent gave soluble star polymers, while the acrylate and methacrylate versions resulted in insoluble gels, attributed to star-star coupling. The formation of star polymers with divinylbenzene can be accelerated with L-**24** as a ligand, up to 85−90% yield. The linking reaction of a poly(tBA) with a bromide terminal was also possible with divinylbenzene, whereas the other two divinyl compounds led to side reactions.[328] The yield of star polymers can be increased up to 95% with the use of additives. The α-end-functionalized linear polymers afford surface-functionalized star polymers with various functional groups such as alcohols, amines, epoxides, and nitriles.

H. Comb and Graft Copolymers

Comb and graft copolymers were also prepared by metal-catalyzed living radical polymerizations. There are two methods available for the synthesis, one of which is via the metal-catalyzed radical polymerization of macromonomers in the absence or the presence of comonomers ("grafting through" method), and the other is via graft polymerization from the reactive carbon−halogen bonds attached to the main chains ("grafting from" method). In contrast to ionic living polymerizations, there have been no reports on the use of "grafting onto" method, partly due to the lack of efficient ω-end capping agents as described above (section III.B.2).

1. Comb Polymers

Comb or densely grafted polymers are defined as polymers that have at least one polymeric chains per monomer unit of the main chain, and Figure 29 shows examples obtained by metal-catalyzed living radical polymerization. Comb polymers possess physical properties similar to those of star polymers in solution.

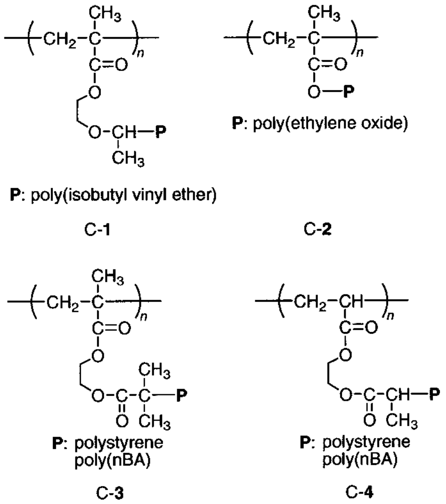


Figure 29. Comb polymers.

Combination of a living ionic polymerization and a metal-catalyzed radical polymerization also leads to comb polymers, where both the molecular weights of the arm and main-chain polymers are well controlled. PMMA with poly(vinyl ether) arm polymers of controlled molecular weights (C-**1**) were prepared by the copper-catalyzed radical polymerization of methacrylate-capped macromonomers carrying a poly(isobutyl vinyl ether), which were obtained by living cationic polymerization with a methacryloxy-capped end-functionalized initiator.[428] Comb polymers with poly(oxyethylene glycol) with varying molecular weights between 400 and 2000 were also obtained by the copper-catalyzed radical polymerizations of the corresponding macromonomers.[319,320,429] However, this method is not always suitable for high molecular weight macromonomers because the polymerization suffers from incomplete conversion and limits the degree of polymerization of the main-chain units.

Another method is based on the metal-catalyzed polymerization from carbon−halogen bonds in the main-chain units, which was applied for the synthesis of C-**3** and C-**4**.[430] For C-**3**, the main chain polymers with controlled molecular weights were prepared via the copper-catalyzed radical polymerization of trimethylsilyl-protected HEMA followed by the transformation of the silyloxyl group into 2-bromoisobutyrate. The pendant C−Br bonds were subsequently activated by the copper catalysts to polymerize styrene and nBA. A more direct way is employed for C-**4**; i.e., via conventional radical polymerization of 2-[(2-bromopropinonyl)oxy]ethyl acrylate followed by the copper-catalyzed graft polymerization of styrene and nBA from the C−Br substituent.

2. Graft Polymers

Various graft copolymers were synthesized by metal-catalyzed radical polymerizations, as detailed in Figure 30. Most of them were from random copolymerization of a macromonomer with a low molecular weight comonomer.

In a study, copper-catalyzed radical copolymerization of nBA and methacryloxy-capped poly(MMA) was compared with conventional radical copolymerization.[267,431] The graft copolymers G-**1** obtained with copper catalysts are more homogeneous in terms of MWD ($M_w/M_n \approx 1.6$ vs 3) and the number of side chains. This is attributed to diffusion control being less important in the metal-catalyzed radical polymerization, where the growing radical species is rapidly converted into the dormant covalent species.

There are several examples of graft copolymers obtained from macromonomer prepared by the metal-catalyzed polymerizations. Conventional radical copolymerization of *N*-vinylpyrrolidione and vinyl acetate-capped polystyrene synthesized with copper catalysts gave graft copolymers G-**2**, which formed hydrogels in water.[337] Electrochemical copolymerization of pyrrole and thiophene-capped poly(MMA) affords G-**3**.[335]

A graft copolymer consisting of poly(ϵ-caprolactone) as main chain and PMMA as branches was also synthesized by ring-opening copolymerization of ϵ-caprolactone and ϵ-caprolactone-capped PMMA macromonomer; the macromonomer was prepared by a nickel catalyst.[312] The obtained graft copolymers have relatively narrow MWDs ($M_w/M_n = 1.3-1.4$) because both the polymerizations are living. There are two other ways for the preparation; one is graft polymerization of MMA from the C−Br moiety in the pendant groups of poly(ϵ-caprolactone), and the other is simultaneous or dual living polymerization of MMA and ϵ-caprolactone in the presence of a functionalized ϵ-caprolactone with C−Br bond (FI-**41**). Both the methods afford similar products with narrow MWDs.

Another dual living polymerization of MMA and ϵ-caprolactone in the presence of HEMA gave graft copolymers with poly(ϵ-caprolactone) as branches (G-**5**) because the hydroxyl group in HEMA serves as an initiating site for ϵ-caprolactone.[392] A similar graft structure is obtained in graft polymerization of ethylene oxide from the hydroxyl group.[393]

The metal-catalyzed copolymerization from carbon−halogen bonds in the main chain can be employed widely for graft polymer synthesis. A combination of nitroxide-mediated and copper-catalyzed living radical polymerizations, for example, gives graft copolymers G-**6**, where the main chain is prepared by the former.[432] The chlorobenzyl unit in the copolymer is not active during the polymerization but, upon copper catalysis, it can initiate living radical polymerizations of styrene and methacrylates.

A similar well-defined graft copolymer consisting of polystyrene main chain and branches (G-**7**) can be prepared simply via repetition of copper-catalyzed living radical polymerizations.[209] Thus, the synthesis starts with the copolymerization of styrene and *p*-(acetoxymethyl)styrene or *p*-(methoxymethyl)styrene, followed by bromination of the substituent into the benzyl bromide moiety, which then initiates the copper-catalyzed radical polymerization of styrene to give graft polymers with 8−14 branches.

A combination of metallocene-catalyzed syndiospecific styrene polymerization and the metal-catalyzed radical polymerization affords various graft copolymers consisting of syndiotactic polystyrene main chains (G-**8**).[433] The reactive C−Br bonds (7−22% content) were generated by bromination of the polystyrene main chain with *N*-bromosuccimide in the presence of AIBN.

Another graft copolymer with polystyrene segments in main chain is derived from the triblock copolymers of polyisobutylene and poly(*p*-methylstyrene) prepared by living cationic copolymerizations (G-**9**).[434] The grafting point was generated by the bromination of the *p*-methyl groups into benzyl bromide, which are then employed for the copper-catalyzed polymerization of styrene and *p*-acetoxystyrene. A similar graft copolymer (G-**10**) can be obtained from a commercially available polymer (EXXPRO) consisting of isobutylene, *p*-methylstyrene, and *p*-(bromomethyl)styrene units.[265,435] The mechanical properties of the graft copolymers were also investigated. Another commercial product, poly(styrene-*block*-ethylene-*co*-propylene) (Kraton 147) with 29.0 wt % styrene units, is also used as a backbone.[436] About 6.4 mol % chloromethylated styrene units are first introduced by chloromethylation, which then initiates graft polymerization of ethyl methacrylate to give the products G-**11**.

A polyolefin-based graft copolymer such as G-**12** is prepared from a commercially available EPDM rubber (Vistollon 2727).[437] The allyl group is partially converted into allyl bromide moiety, and living radical polymerization of MMA initiated therefrom with copper catalysts. Graft copolymers of polyethylene (G-**13**) were synthesized from commercially available poly(ethylene-*co*-glycidyl methacrylate) as a starting material, the epoxy groups of which were esterified

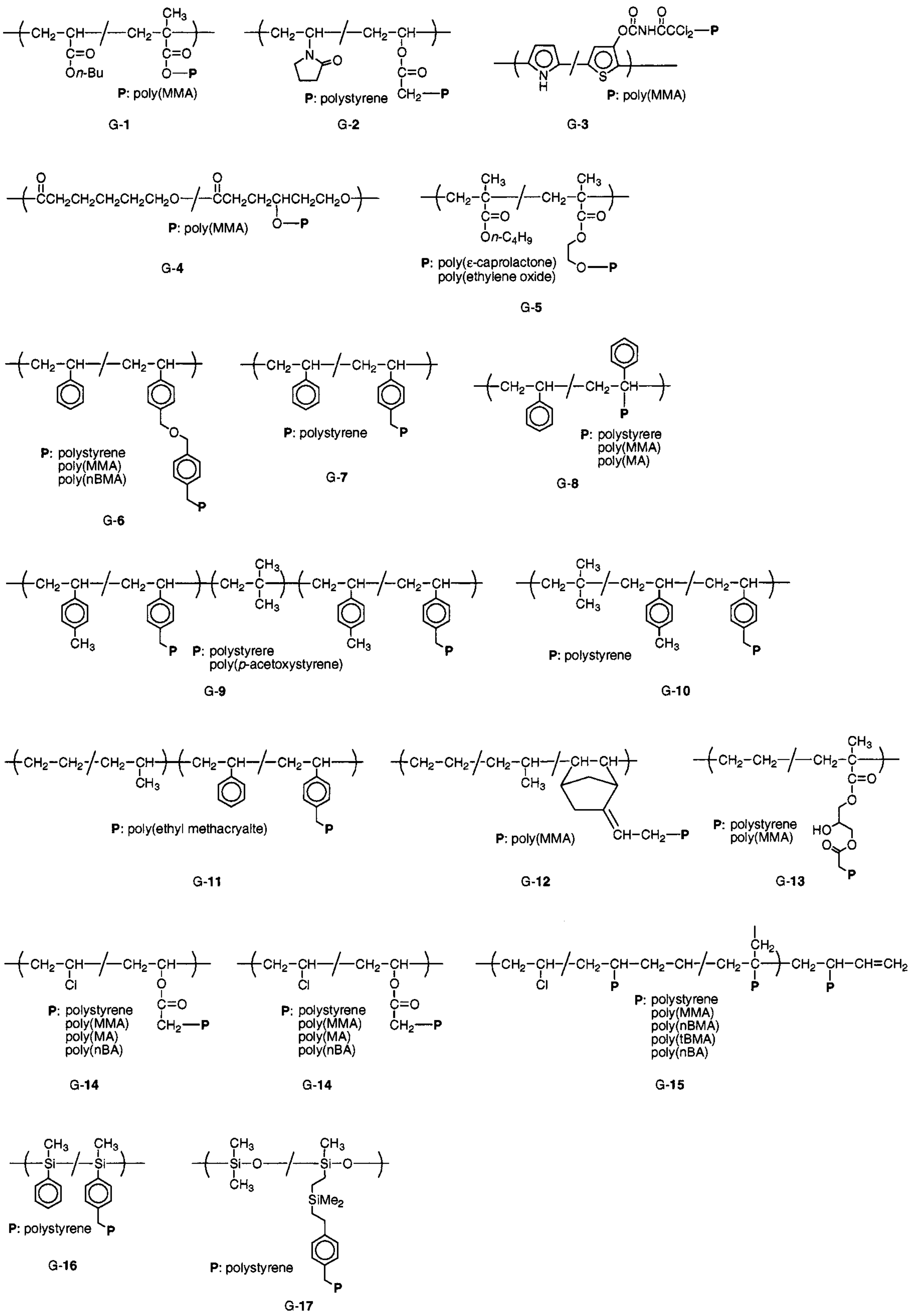


Figure 30. Graft polymers.

with chloroacetic acid and 2-bromopropionic acid into the reactive carbon−halogen bonds.[438] The functionalized polymers then initiate the copper-catalyzed radical polymerizations of styrene and MMA to afford arm polymers with controlled lengths.

Graft polymers with a poly(vinyl chloride) backbone and various branches (G-**14**) were obtained from the copolymer of vinyl chloride and 1 mol % vinyl chloroacetate.[439] Glass transition temperature (T_g) of the copolymer with nBA decreases with increasing content of nBA. A more direct and simple way for poly(vinyl chloride)-based graft copolymers is to use the allyl chloride and tertiary chloride units as structural defects in the base polymers for the initiating moiety in the metal-catalyzed living radical polymerization.[440] This method can afford various graft copolymers G-**15**, which was characterized by SEC, NMR, DSC, and film preparation.

Hybrid graft copolymers having silicon-based polymer backbones were also prepared by the metal-mediated radical polymerizations of styrene. The phenyl groups of poly[(methylphenyl)silylene] were bromomethylated and then employed as the grafting points of polystyrene (G-**16**).[294,441] Polysiloxane can be employed also as a backbone (G-**17**) by introduction of benzyl chloride units into the pendant vinyl-functionalized poly(dimethylsiloxane).[409]

I. Hyperbranched Polymers

In vinyl polymerization, hyperbranched polymers can be obtained from the monomers that have an initiating group along with a vinyl group (Figure 31).

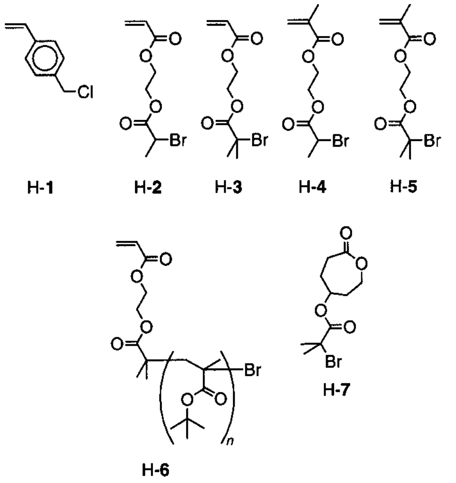


Figure 31. Monomers for hyperbranched polymers.

The self-condensing vinyl polymerization, which was initially developed for living cationic polymerization,[442] is also applicable for metal-catalyzed living radical polymerizations.

For example, *p*-(chloromethyl)styrene (H-**1**) was employed for copper-catalyzed self-condensing vinyl polymerizations.[211] The hyperbranched structure was supported by the fact that the molecular weight measured by SEC was lower than those by viscosity and light scattering. The average number of branches per polymer chain was estimated to be 25. In contrast, another paper reported that the reaction conditions should be changed for the synthesis of hyperbranched structure.[213] A high catalyst-to-monomer ratio around 0.1−0.3 should be employed to minimize the formation of linear polymers due to the difference in reactivity between the primary and the secondary benzylic halide sites. The residual carbon−halogen bonds were transformed into functional groups such as cyano, ester, thioether, and imide to generate multifunctionalized hyperbranched polymers.

Acrylic hyperbranched polymers are obtained by the copper-catalyzed radical polymerizations of H-**2**, where addition of $CuBr_2$ is needed to decrease the concentrations of the radical species generated from the monomers.[443] Under appropriate conditions, nearly ideal self-condensing vinyl polymerizations proceed. The obtained polymer was a viscous solid with a subambient T_g (−11 °C). Detailed kinetic and mechanistic studies were carried out to determine the difference in reactivity among the C−Br bonds in terminals and side chains.[212,444,445] Similar meth(acrylic) hyperbranched polymers were prepared from H-**3** and H-**5** while the products with H-**4** were most likely linear polymers. [446]

The self-condensing copper-catalyzed polymerization of macromonomer of poly(tBA) with a reactive C−Br bond (H-**6**) affords hyperbranched or highly branched poly(tBA).[447] Copolymerization of H-**1** and *N*-cyclohexylmaleimide induced alternating and self-condensing vinyl polymerization.[448] The residual C−Cl bond was further employed for the copper-catalyzed radical homopolymerization of styrene to give star polymers with hyperbranched structures. Hyperbranched polymers of H-**1** further serve as a complex multifunctionalized macroinitiator for the copper-catalyzed polymerization of a functional monomer with polar chromophores to yield possible second-order nonlinear optical materials.[325]

The graft copolymers with poly(H-**1**) arms have multiple carbon−halogen bonds that can initiate copper-catalyzed radical polymerization to give highly branched dendrigraft polymers.[432] The products with styrene or nBMA had relatively narrow MWDs because each chain was prepared by living polymerization.

A combination of other polymerization pathways also results in some hyperbranched structures. Multifunctional hydroxyl groups in polyglycerol with hyperbranched structure, prepared by anionic polymerization of glycidol, were esterified with 2-bromoisobutyroyl bromide and then employed as a hyperbranched multifunctional macroinitiator for the copper-catalyzed radical polymerization of MA to give products with 45−55 poly(MA) arms.[449]

Another method for hyperbranched polymers is based on a simultaneous or dual living polymerization such as metal-catalyzed radical and ring-opening ionic polymerizations.[311] In this method, copolymerizations of HEMA and H-**7** are carried out in the presence of Ni-**2** and $Sn(Oct)_2$, where the C−Br bond in H-**7** serves as an initiating point for the nickel-catalyzed radical polymerization of HEMA and the OH group in HEMA for the tin-catalyzed ring-opening polymerization of H-**7**. The products had hyperbranched structures, similarly to those obtained in self-condensing vinyl polymerizations. Addition of MMA and/or ϵ-caprolactone into the system gave looser hyperbranched structures.

J. Polymer Brushes

Polymer brushes can be obtained by metal-mediated living radical polymerization from the initiator moiety confined to the surface of a substrate via spacers. The surface-initiated living polymerization can control the thickness and the density of brushes; the former is regulated by brush’s chain length and

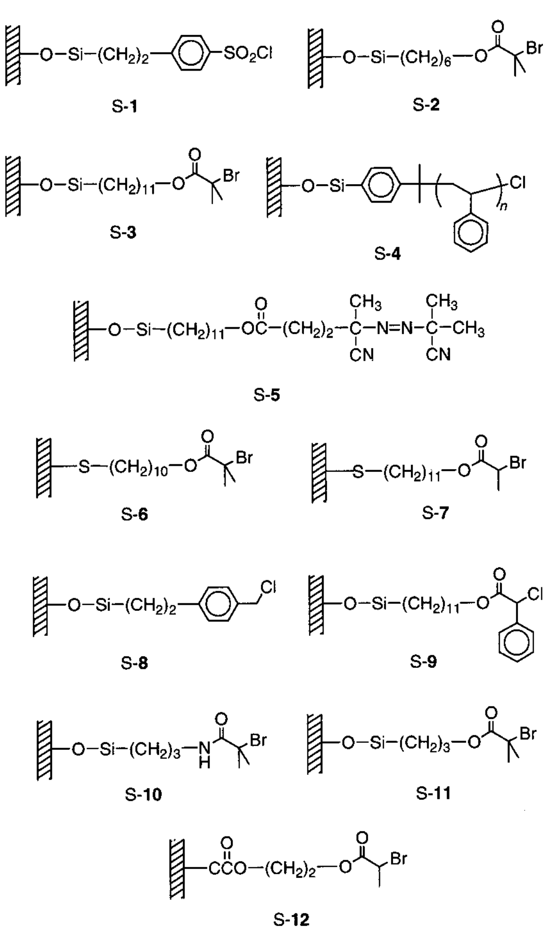


Figure 32. Initiating moiety for polymer brushes.

the latter by the density of the attached initiator. The substrate for these polymer brushes include silicon wafer, silica bead, silica nanoparticle, porous silica gel, silica capillary, polymer latex, and gold, and the attachment of polymer brushes alter the chemical properties of their surface for various applications. Figure 32 summarizes the initiating moiety employed for such surface modification.

1. Silicon Wafer

The control of the molecular weights, MWDs, and surface density of graft chains was achieved by the copper-catalyzed radical polymerization of MMA from sulfonyl chloride initiators attached to silicon wafer (S-**1**) by the Langmuir–Blodgett technique.[450] The surface-initiated polymerization is better controlled on addition of free or unconfined initiators such as *p*-toluenesulfonyl chloride, because uncontrolled molecular weights and broad MWDs were obtained in the absence. This may be attributed to a low concentration of Cu(II) species, which convert the radical species into the dormant, originating from the low concentration of the initiator moiety confined on the surface. The thickness of the polymer layer increased up to 70 nm in direct proportion to the molecular weights of free polymers produced in solution, although the molecular weights of the graft polymers were unknown. The graft density can be varied in a wide range between 0.07 and 0.7 chains/nm^2 by photodecomposing the surface-fixed initiator, where the highest value is at least 10 times larger than those of the polymer brushes prepared by the adsorption of block copolymers on surface.[451,452] Glycopolymer and block copolymers of MMA and 4-vinylpyridine were grown from the surface by the same technique.[371,453] A similar PMMA layer was also obtained in the nickel-catalyzed surface-initiated polymerization from S-**2** in the presence of ethyl 2-bromoisobutyrate as a free initiator, where the thickness increased up to 50 nm.[454]

Such a controlled radical polymerization can be performed even in the absence of free initiators, where larger amounts of Cu(II) species are added in the system.[369] The polystyrene layer obtained from S-**3** in the presence of 5 mol % Cu(II) relative to Cu(I) increased up to 20 nm in thickness, in direct proportion to the M_n of the polymers prepared in the other experiments with ethyl 2-bromopropionate but without surface-confined initiator under similar conditions. For MA, the layer thickness increases up to 60 nm. Block copolymer layers were also prepared by block copolymerization of MA or tBA from the polystyrene. Modification of the hydrophilicity of a surface layer was achieved by the hydrolysis of the poly(styrene-*block*-tBA) to poly(styrene-*block*-acrylic acid) and confirmed by a decrease in water contact angle from 86° to 18°.

Block copolymer surface was also prepared by the copper-catalyzed radical polymerization of MMA from a surface-confined macroinitiator of polystyrene (S-**4**) obtained by living cationic polymerization although the blocking efficiency was unknown.[378] The block copolymerization increased the film thickness by 9 nm and changed the water contact angles. Other monomers such as MA and 2-(*N*,*N*-dimethylamino)ethyl methacrylate were also polymerized from S-**4**.[377] The changes in contact angles were observed by treatment of the surface with several solvents and air.

An azo-type initiator (S-**5**) can also be attached to the silicon wafer and induces the controlled radical polymerization of styrene in the presence of $CuBr_2$.[365] The block copolymerization of MMA from the surface-confined polystyrene macroinitiator was also conducted.

2. Gold

Polymer brushes can be grown from gold surface in a similarly controlled manner by the metal-catalyzed surface-initiated radical polymerization. The attachment of the initiator moiety can be attained via the thiol group as in S-**6**[455] and S-**7**.[456]

Several monomers such as tBA, MMA, isobornyl methacrylate, 2-(*N*,*N*-dimethylamino)ethyl methacrylate, and HEMA were polymerized from S-**6** with copper catalysts to form layers ranging from 5 to 48 nm with varying contact angles depending on the polymers. The brushes of PMMA grow from the surface with a high graft density as indicated by the low value of the area per PMMA chain (200 Å^2/chain). However, a grafting efficiency is estimated around 10% from the surface confined initiators. The initiator can be attached also on the patterned area by microprinting method. The hydrophobic polymers as brushes are resistant to etchants, which permits the selective etching of gold surface.

Another example is the copper-catalyzed surface-initiated radical polymerization of MMA from S-**7** at room temperature without addition of free initiator. The molecular weights and MWDs of the polymers were directly measured after removing the brushes from the surface. For example, the surface with 40 nm thickness had M_n of 68900 and MWDs of 1.45. A high graft density (180 Å^2/chain) and decreased surface roughens (0.54 nm) were observed. This method is free from solution and thermal polymerizations due to the absence of free initiators and a low polymerization temperature, which permits a simple washing step without Soxhlet extraction.

3. Silica Particle and Bead

Surface-initiated living radical polymerization is also applied for spherical surfaces such as silica nanoparticles and beads.

Spherical silica nanoparticles, with an average diameter of 70 nm, modified with the initiator moiety (S-**8**) were employed for the copper-mediated radical polymerization of styrene.[457] The diameter of the particles and the molecular weights of the obtained polymers increased with conversion. For example, the average diameter of the particles obtained at 58.8% monomer conversion was increased to 188 nm, where the M_n and MWDs of the arm polymers were 26500 and 1.33, respectively. Given a narrow size distribution (<10%), the nanoparticles within the film domains were observed to pack into hexagonal arrays. A smaller silica nanoparticle with 14 nm was employed also for the copper-catalyzed radical polymerization of styrene initiated with S-**9**.[458]

Silica microspheres (~3 μm) with initiating moiety (S-**8**) induced the copper-catalyzed radical polymerization of benzyl methacrylate to form polymer layers on the surface.[459] The thickness of polymer shell can be increased to 550−600 nm, where the M_n and MWDs of the arm polymers were 26500 and 1.26, respectively. Removal of the core silica by chemical etching gave uniform hollow polymer microspheres.

4. Silica Gel and Silica Capillary

Organic polymer layer on the surface of silica gels or porous silica can modify the surface to increase the resistance of the silica surface to basic compounds.

The first example of the surface-initiated metal-catalyzed radical polymerization was reported for acrylamide from the initiator moiety S-**8** attached to porous silica gels.[216] A silica gel with an average pore size of 860 Å gave polyacrylamide with film thickness of 100 Å after the polymerization, where polymer molecular weights were around 13000−15000.[218] The silica gels coated with polyacrylamide can even separate a basic protein without significant damages of silica gels by size-exclusion mode. The same technique was also employed for the silica capillaries and results in polymer coating without clogging of narrow capillaries.[217]

Functionalized methacrylates with pendent nucleosides such as uridine and adenosine (FM-**23** and FM-**24**) were also polymerized from the surface of silica gels in the presence of the copper catalysts.[460] For the polymerizations, bromide-type initiator fragments S-**10** and S-**11** were attached to the surface and initiated the homopolymerization or copolymerizations. A higher loading of the polymers was observed with S-**11** than S-**10**.

5. Polymer Latex

Organic compounds such as polystyrene latexes were also used as substrates for the surface-initiated radical polymerizaiton.[248] Reactive C−Br bonds (S-**12**) were introduced at the surface via radical emulsion copolymerization of styrene and 2-(2-bromopropionyloxy) ethyl methacrylate in the presence of divinylbenzene under selected conditions. The surface-initiated polymerization of hydrophilic monomers such as FM-**3** and FM-**6** resulted in hydrophilic shell and hydrophobic core latexes.

IV. Conclusions

This paper has provided, we believe, a comprehensive, up-to-date, critical, and objective review on the discovery and the subsequent fast development of living radical polymerizations catalyzed by transition-metal complexes in the period from 1994 to early 2001. These metal-catalyzed living radical polymerizations have rapidly been developing since their discovery in 1994, and the scope of applicable monomers, metal catalysts, and initiators has been expanding. Their advantages include versatility toward a variety of monomers, feasibility in a wide range of reaction conditions, and relatively easy access to the materials. This permits many researchers to use the systems for the precision synthesis of various polymers with controlled architectures.

As in many other fields of science, however, these extensive developments have also elicited a number of interesting and challenging problems that are still waiting for solutions and answers. These may include the kinetics and mechanism of the polymerizations, the nature of the true growing intermediates that are considered to associate with the metal catalyst (e.g., are they really radicals identical or similar to those in classical “free” radical polymerizations?), the guiding principles for designing metal catalysts, and the “novel” polymers that can be synthesized by the metal-based systems but cannot be by other (living) radical polymerizations. In addition to these problems, future research efforts will therefore be directed toward the development of more efficient and versatile catalyst systems for various monomers including nonconjugated vinyl monomers, as well as the synthesis of specific polymers with special architectures and the application to industry processes.

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