Stereospecific Living Radical Polymerization: Dual Control of Chain Length and Tacticity for Precision Polymer Synthesis

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Contents

1. Introduction 5120
2. Living Radical Polymerization 5121
3. Stereospecific Radical Polymerization 5123
  3.1. Polymerization in Confined Media 5124
    3.1.1. Crystalline Solid-State Polymerization 5124
    3.1.2. Inclusion Polymerization 5125
    3.1.3. Polymerization in Porous Materials 5127
    3.1.4. Template Polymerization 5128
  3.2. Inherent Stereospecificity in Monomer Structure 5128
    3.2.1. Polymerization of Bulky Monomers 5128
    3.2.2. Monomers with Chiral Auxiliary 5133
    3.2.3. Monomers with Self-Assembling Group 5135
  3.3. Stereocontrol by Solvents or Additives 5136
    3.3.1. Solvent-Mediated Stereospecific Polymerization 5136
    3.3.2. Lewis Acid-Mediated Stereospecific Polymerization 5139
    3.3.3. Ionic Bonding or Interaction 5141
    3.3.4. Multiple Hydrogen Bonding Interactions 5142
4. Stereospecific Living Radical Polymerization 5143
  4.1. Acrylamides and Methacrylamides 5143
  4.2. Methacrylates and Acrylates 5146
  4.3. Vinyl Esters, Vinyl Amides, and Vinyl Chloride 5148
  4.4. Stereoblock and Stereogradient Polymers 5149
    4.4.1. Stereoblock Polymers 5149
    4.4.2. Stereogradient Polymers 5151
5. Conclusions 5151
6. Acknowledgments 5152
7. References 5152

1. Introduction

Because the word "radical" evokes something active, taming a radical polymerization into a controlled reaction has been difficult compared with ionic counterparts, in which the reactivity and selectivity of the growing species can be regulated by the electronic interaction with the counterion.[1−9] Despite such notorious images, radical polymerization is one of the most favorable chemical reactions employed in both industry- and laboratory-scale chemical productions, because it can convert a wide variety of vinyl monomers into high molecular weight polymeric materials without extensive purification of commercially available monomers and solvents or even in the presence of large amounts of water and polar compounds.[10,11] Such high versatility, productivity, and tolerance of the radical polymerization can be attained by the neutral growing species, which is highly reactive toward the carbon−carbon double bonds of various vinyl compounds, at the expense of the chemo-, regio-, and stereoselectivities during reaction.

In radical polymerizations, the growing radical species ($\sim\sim\sim C^{\bullet}$) rapidly reacts with the C═C double bonds of the monomers, which significantly exist in the reaction media, to yield the polymers efficiently. However, it also reacts extremely rapidly with another growing radical chain end ($\sim\sim\sim C^{\bullet}$), which is present at a very low concentration, to result in termination or abstracts hydrogen relatively slowly from C−H bonds in the polymers or solvents to induce chain-transfer reaction. Although the contents of these undemanding reactions for the chain propagation depend on both the absolute reaction rate constant and the concentration of the counterparts, such defects in the chemoselectivity reduce the control of the molecular weights and chain-end groups in the polymerizations. In addition, especially for unconjugated monomers like vinyl acetate, which forms a highly reactive unstabilized growing radical species, some degree of head-to-head propagation occurs due to the imperfect regioselectivity of the carbon radical species toward the two carbon atoms of the vinyl group in the monomer. Furthermore, a radical reaction generally induces nonstereoselective propagation to give almost only atactic polymers from monosubstituted vinyl monomers due to the lack of an asymmetric environment around a planar-like sp^2-carbon radical species. Although these difficulties might have discouraged synthetic polymer chemists from developing controlled radical polymerizations, much higher demands for obtaining well-controlled polymers from various vinyl monomers with polar functional groups and possible strong impacts of the developments on the related research areas including their applications have been pushing them to challenge the topics.

Due to the significant efforts of predecessors, some radical polymerization controls have now become possible. Especially, tremendous developments in the controlled/living radical polymerizations from the 1990s have enabled not only the control of molecular weights for various vinyl polymers[10−36] even in aqueous solvents[37−42] but also the synthesis of the finely controlled structures of polymers, such as block, end-functionalized, graft, star, and more complicated architecture polymers.[43−49] These developments have been further continuing and being applied to related research areas involving novel materials via conjugation with natural or biopolymers, inorganics or ceramics, metals, etc., due to the compatibility of the radical polymerization with other components.[50−59]

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In contrast, although stereochemical control is still considered the “Holy Grail”[10] in the field of radical polymerization and has not reached satisfactory levels for applications to other areas, various strategies have been adopted and enabled tacticity control even for various common polar vinyl monomers at a certain level.[11,60] The stereochemical control is also an important issue in developing excellent novel materials because the thermal and mechanical polymer properties highly depend on the tacticity. A further remaining target in radical polymerization is dual control of the molecular weight and the tacticity,[61−63] which would contribute to more precise design of polymeric materials with excellent properties. Although it is more difficult than single control, recent developments in each control have paved the way for the dual control and an increased number of scientific papers about this topic.

This review primarily covers stereospecific living radical polymerizations for dual control of molecular weights and tacticity of the resulting polymers, which has now been achieved by combining controlled/living radical polymerization and stereospecific radical polymerization. Thus, it also treats fundamental aspects and recent developments in each topic before covering the simultaneous control in detail. However, the part for the controlled/living radical polymerization in this review is limited and only covers the papers related to stereochemical control due to the existence of many recent excellent reviews[12−34] on controlled/living radical polymerization including the review by Sawamoto et al. in this issue,[64] while more space is allowed to tacticity control by stereospecific radical polymerization especially for the recent papers dealing with control in homogeneous solution systems.

2. Living Radical Polymerization

Almost all of the recently developed controlled/living radical polymerizations are based on the controlled formation of the growing radical species from the polymer terminus via reversible activation of the dormant species.[10,11] During these polymerizations, most of the polymer chain ends are in the dormant state, while a very small fraction of the dormant terminals are activated into the highly active growing radical species to allow an intermittent propagation. Although this reversible capping reaction of the growing chain end does not seem to contribute to stabilizing the growing radical species itself and changing the reactivity, the interchange reaction can control the chain growth by giving almost the same chance for propagation to all the polymer chains and reducing the probability of termination between the growing neutral radical species by the equilibrium being shifted to the dormant side. The origin of such controlled/living radical polymerizations can be traced back to the living ionic polymerizations via reversible activation of the dormant species into anionic or cationic growing polymer chain ends, which were discovered and established in the 1980s,[2−9] as well as the “iniferter” system developed by Otsu et al. in the 1980s for radical polymerizations.[65,66]

Another way to reduce the termination reactions is to use some confined space, such as particles, in emulsion polymerization, where compartmentalization of the radical species prevents the encounter with another growing radical chain end in the other particle. This more or less physical approach to living radical polymerization was advocated in the 1970s and successfully employed for the synthesis of polymers with narrow molecular weight distributions (MWDs) and diblock and triblock copolymers by using a heterogeneous polymer initiator,[67−70] which might induce a very fast propagation and was removed by filtration once the polymerization started. However, this system has several drawbacks, such as difficulties in the procedures and obtaining the polymers with predictable molecular weights as well as the limitations to emulsion systems for styrene-based polymerizations.

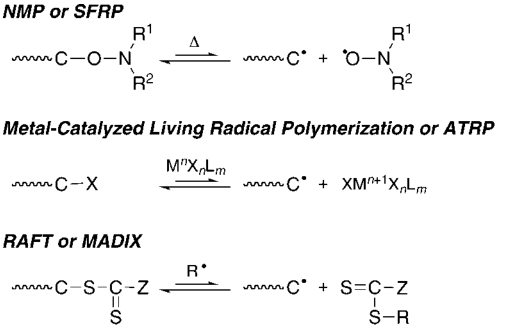


Figure 1. Representative controlled/living radical polymerizations based on reversible activation of dormant species into growing radical species.

Figure 1 shows three representative modern controlled/living radical polymerizations, nitroxide-mediated or stable free radical polymerizations (NMP or SFRP), metal-catalyzed living radical polymerization or atom transfer radical polymerization (ATRP), and reversible addition−fragmentation chain-transfer (RAFT) or macromolecular design via the interchange of xanthate (MADIX), all of which are based on the transient fast and reversible activation of the dormant species into the growing radical species.[10,11] The key to molecular weight control mainly lies in the predominant formation of the dormant species from the growing radical species, as well as the establishment of an extremely fast activation−deactivation process relative to the fast propagation. For attaining fine molecular control, the initiating systems should be carefully chosen or designed depending on the monomers, because the propagating rate and the strength of the covalent dormant species varies with the types of the monomers. In addition to the three systems, there are now other efficient systems for giving polymers with precisely controlled molecular weights based on similar reversible activations,[30−36,71−74] though the detailed descriptions about these living/controlled radical polymerizations are omitted except for the reports relating to the stereochemistry issue and left to other reviews or books.[12−36]

In NMP or SFRP, the covalent C−ON bond is cleaved upon heating to generate the growing carbon radical species along with the stable aminoxyl or nitroxyl radical. During the polymerization, the growing radical polymer chain end is reversibly capped with the stable counterpart to induce controlled propagation at almost the same rate for each polymer chain. While 2,2,6,6-tetramethylpiperidin-*N*-oxyl (TEMPO) was employed as the radical capping agent or as a mediator for the synthesis of block copolymers,[75] this first relevant use for controlling the molecular weight was reported for styrene polymerization with TEMPO at a relatively high temperature (125 °C).[76] The TEMPO-based system requires a high temperature due to the relatively high dissociation energy of the C−ON bond derived from styrene and TEMPO and is exclusively limited to the control of styrenic monomers. However, several designed nitroxides now permit the controlled polymerization at a lower temperature (∼90 °C) and are effective for other monomers, such as acrylates, acrylamides, and dienes.[12−16,75−79]

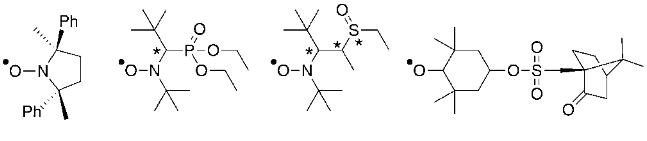


Figure 2. Chiral nitroxides for living radical polymerization.

Several nitroxides with asymmetric carbon atoms were prepared and then examined for possible stereochemical control during the NMP. The first attempt was done for styrene bulk polymerization at 130 °C in the presence of chiral **NO-1** with the (*R*,*R*)-configuration (Figure 2).[80] Although the semiempirical calculation suggested a more favorable formation of its styrene adduct with the *R*-configuration terminus, the obtained polystyrene showed essentially the same tacticity as those obtained in the presence of the racemic mixture of **NO-1** or TEMPO or without nitroxides. These data indicated that propagation appeared to exclusively occur from the state where the nitroxide completely dissociates from the growing polymer chain. Another attempt was conducted using a diastereomer-rich alkoxyamine (diastereomers ratio 9/1), which was prepared from *tert*-butyl acrylate (*t*BA) and racemic mixtures of **NO-2** with a chiral center for *t*BA polymerization in bulk 120 °C.[81] For the adducts of this nitroxide with methyl acrylate or styrene, the diastereomers possessing the (*R*,*R*)+(*S*,*S*) configuration proved predominant over the (*R*,*S*)+(*S*,*R*).[82] However, the obtained polymers were almost atactic (*mm*/*mr*/*rr* = 18/47/35), similar to those obtained by the copper-ATRP or free radical polymerizations, while the polymer terminal structure showed the predominant formation (7/1) of one of the diastereomeric chain ends. This also indicated that the last unit of the dormant chain may be one strongly preferred configuration, but its contribution to chain growth is negligible. A similar diastereomeric effect on the C−ON dissociation rate was reported for **NO-3**, in which the alkoxyamine with the (*R*,*R*,*R*)+(*S*,*S*,*S*) configuration possessed a higher dissociation rate constant than the (*S*,*R*,*R*)+(*R*,*S*,*S*) to induce a more effective molecular weight control at 90 °C in the radical polymerizations of ethyl and *n*-butyl acrylates.[83] Another nitroxide (**NO-4**) with a chiral *d*-(+)-camphorsulfonyl substituent was employed for the styrene polymerization to produce optically active polystyrene due to the chirality of the chain-end group though the tacticity was unknown.[84]

Metal-catalyzed living radical polymerization or ATRP was originally developed from the metal-catalyzed Kharasch addition or atom-transfer radical addition (ATRA),[85,86] in which the carbon−halogen (C−X) bond is homolytically cleaved via oxidation of the metal center to generate the carbon radical species and to induce addition to the C=C double bond followed by regeneration of a new C−X bond via the reduction of the oxidized metal center. The molecular weight control is thus achieved by the fast reversible activation of the C−X dormant species by the one-electron redox reaction of the metal center, which includes various transition metals, Ru,[87] Cu,[88−90] Fe,[91,92] Ni,[93,94] Pd,[95] Rh,[96] Mo,[97] Re,[98] etc. The polymerization can be tuned by the central metals and their ligands as well as the halogens (Cl, Br, I) in the dormant terminals depending on the monomers and reaction conditions.[17−22] This system can be employed for various vinyl monomers including methacrylates, acrylates, acrylamides, acrylonitrile, and styrenes at temperatures varying from −80 to 150 °C. The controlled polymerizations can be used for functional monomers or in aqueous solutions; however, the metal catalyst should be carefully chosen because these polar groups may deactivate the metal catalyst via complexation.

For the metal-catalyzed living radical polymerization, a possible tacticity change was expected since its discovery, because the oxidized metal center might reside in close

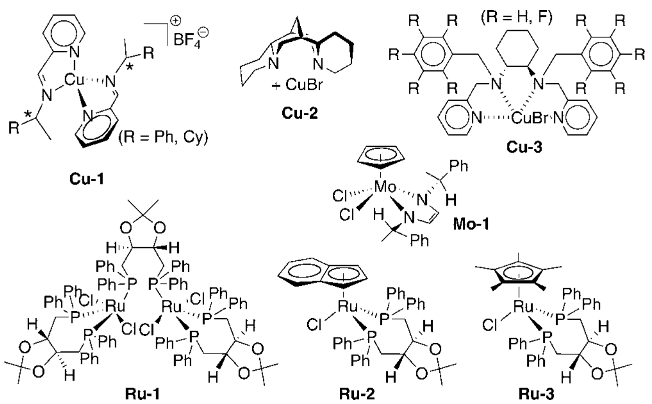


Figure 3. Chiral metal complexes for living radical polymerization.

vicinity to the growing radical chain end to exert an influence on the stereochemistry of the propagation. However, all the poly(methyl methacrylate)s [poly(MMA)] obtained with Ru,[87] Cu,[88,90] Fe,[91] Ni,[93] Pd,[95] and Rh[96] catalysts showed almost the same tacticity as that obtained from the free radical polymerizations.

Several chiral metal complexes were also examined for possible stereochemical control (Figure 3). The copper catalyst (**Cu-1**) with chiral aryl or alkyl pyridylimine ligands was first employed for the living radical polymerization of MMA in conjunction with ethyl 2-bromoisobutyrate in xylene at 90 °C.[99] The system yielded polymers with narrow MWDs, while the chiral catalysts did not significantly affect the tacticity. A commercially available chiral ligand, sparteine, was also used for the MMA and styrene polymerizations with CuBr. No ^{1}H NMR spectral changes were observed for the polystyrene obtained with CuBr/sparteine (**Cu-2**) although the tacticity was not measured.[100] Another paper on copper ATRP of MMA with chiral ligands was reported using quadridentate ligands (**Cu-3**) coupled with CuBr, in which the tacticity (*mm*/*mr*/*rr* = 2.7/33.9/63.5) was almost the same as that obtained with a similar but achiral quadridentate ligand (*mm*/*mr*/*rr* = 2.6/34.0/63.5) and was consistent with the Bernoullian statistics.[101] For possible tacticity control by coordination of the metal catalyst to monomer, a half-sandwich molybdenum catalyst (**Mo-1**) with a chiral ligand was thus synthesized and used for ATRP of MMA.[102] However, no notable difference was detected compared with the polymers obtained by free radical polymerization. In contrast to these insufficient results on induction of stereospecificity in polymerization, an asymmetric radical addition reaction was reported using ruthenium complexes (**Ru-1**) with a bidentate chiral phosphine ligand, where the adducts obtained from arensulfonyl chloride (RSO_2Cl) and styrene derivatives showed an enantiomeric excess up to about 20−40%.[103] This might suggest that the radical was confined in the coordination sphere of the ruthenium complex with a chiral ligand. More recently, a series of the ruthenium catalysts (**Ru-1**−**3**) with the same ligand were employed for the metal-catalyzed radical addition as well as the polymerization of various vinyl compounds, such as styrene, MMA, and MA.[104] Almost all of the radical additions between CCl_3Br and the vinyl compounds resulted in an adduct with an enantiomeric excess up to 32%, while almost no effects on the tacticity of the polymer main chain were observed. These results also showed that the oxidized metal species diffused away from the growing radical species and could not control the stereochemistry during its addition to the monomer. Concerning how fast the stereochemistry of the growing radical species changes, the rate of racemization in ATRA and ATRP was measured for (*S*)-(−)-methyl 2-bromopropionate in the presence of the copper catalyst.[105] The racemization rate was similar to those of the halogen exchange with CuCl and trapping reactions with TEMPO, also indicating that free radical intermediates were formed during the ATRP.

In contrast to no effects of the chiral ligands on the tacticity, interesting results were reported for the enantiomer-selective radical cyclopolymerization of racemic dimethacrylate by the metal catalysts with chiral ligands or additives (Figure 4).[106−109] A racemic mixture of (*R*,*R*)- and (*S*,*S*)-2,4-pentanediyl dimethacrylate (CM-**1**) was polymerized with CuBr in the presence of chiral bi- or tridentate nitrogen-based ligands in anisole to give optically active polymers with controlled molecular weights via cyclopolymerization, in which the enantiomeric excess of the recovered monomer was 6.8−15.3%. A similar enantiomer-selective radical cyclopolymerization was also achieved by $RuCl_2(PPh_3)_3$ in the presence of chiral additives to provide an enantiomeric excess of 16.9−22.6%, in which the growing chain ends of the (*R*,*R*)- and (*S*,*S*)-monomer units preferentially reacted with the (*R*,*R*)-monomer. Although the working mechanism of the chiral catalyst for the enantiomer selectivity was not clarifeid, these results suggested some effects of chiral moieties of the catalysts on the stereoselection.

RAFT polymerization is the newest one[110,111] among the three and can be used for a variety of monomers including not only the conjugated monomers like methacrylates, acrylates, acrylamides, acrylonitrile, styrenes, and dienes, but also unconjugated ones like vinyl esters and vinyl amides by designing the appropriate RAFT agents depending on the monomers.[23−27] The polymerization was conducted relatively easily just by the addition of thiocarbonylthio compounds as reversible chain-transfer agents to the polymerization with azo-initiators. The dormant C−SC(S)Z bond is reversibly activated by another carbon-radical species via addition−fragmentation processes. The RAFT reagents and the analogous polymer chain-end groups are generally stable to polar and ionic groups, which allows molecular weight control under various conditions. Irrespective of the absence of any relevant reports on the use of chiral RAFT agents, no essential tacticity control would be expected based on the mechanism of the RAFT polymerizations.

As described in this section, no tacticity control has been attained only by the initiating systems or the catalyst for the controlled/living radical polymerizations. These results also suggest that the growing radical species in the controlled/living radical polymerization behaves as a "free" radical species inducing nonstereospecific propagation. Therefore, for dual control of the molecular weight and tacticity, some other methods for stereospecific radical propagation should be combined with the living radical polymerization processes, as will be discussed later.

3. Stereospecific Radical Polymerization

Stereoregularity affects many important properties of the polymers, such as solubility, crystallinity, melting point, glass transition temperature, and mechanical strength. The stereoregularity of polymer main chain is referred to as tacticity, which deals with the relationship between two adjacent monomer units consisting of meso (*m*) and racemo (*r*) diads. In the most simplified case, the tacticity of the product

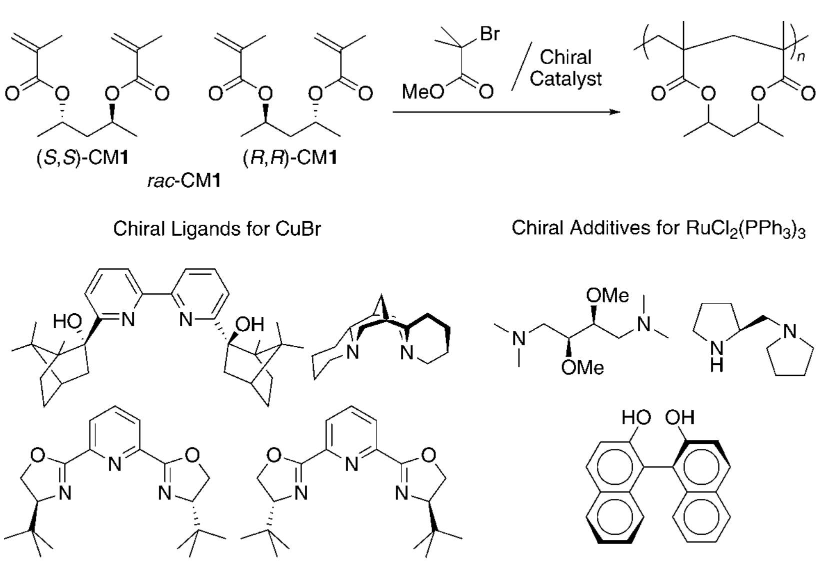


Figure 4. Enantiomer-selective living radical cyclopolymerization by metal catalysts with chiral ligands or additives.

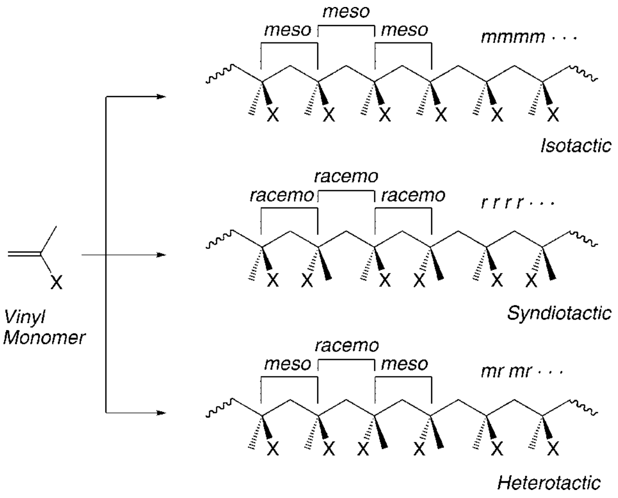


Figure 5. Tacticity of vinyl polymers.

polymers obeys a classical Bernoullian statistics, in which the stereochemistry of the growing terminus is determined only by a single parameter independent of the penultimate unit. In most of the radical polymerizations of usual vinyl monomers, tacticity roughly obeys the Bernoullian model, while a more strict analysis has revealed that it slightly deviates from the Bernoullian and can be fit to a first- or second-order Markov model.[112,113] For obtaining highly stereoregular polymers such as isotactic (*mm*), syndiotactic (*rr*), and heterotactic (*mr*) sequences, highly diastereoselective reactions would be necessary, where an asymmetric environment between the pendent groups and incoming monomer could be created (Figure 5). Most of the vinyl polymers and even these stereoregular polymers possess a mirror plane and do not show optical activity except for the chirality in the vicinity of the chain ends or the postulated chirality with much higher-ordered hexad or more sequences.[114,115]

In sharp contrast to ionic and coordination polymerizations, the control of stereochemistry during radical polymerization has been considered to be much more difficult, most probably because the sp^2-planar or planar-like propagating radical species generally does not support efficient methods for the stereospecific propagation. However, the solutions for this problem are also becoming available at moderate or relatively high levels even for radical polymerization using some methodologies, although there are some limitations of the monomers or reaction conditions.[116−118] This part will deal with the already known methodologies for tacticity control during radical polymerization.

3.1. Polymerization in Confined Media

Many attempts to produce stereospecific or stereoregular polymers have been made in confined media, such as the solid state, inclusion compounds, porous materials, and templates.[119] The radical polymerizations in confined media often induce a stereospecificity because the monomer and growing radical species are confined in a certain space and obstructed from free rotation and diffusion. Although these methods would be applied only for specific monomers, the well-organized media lead to a highly stereospecific propagation. Furthermore, such a confinement of the growing radical species gives not only stereospecificity but also a long-lived nature to the growing radical species by suppressing the bimolecular terminations of disproportionation and combination, which consequently leads to chain length control. Namely, the polymerizations in confined media possibly enable not only tacticity control but also some amount of molecular weight control without using additional reagents for the living radical polymerization, although the molecular weight distributions are rather broad. The following sections will focus on the confined media employed for stereospecific radical polymerization.

3.1.1. Crystalline Solid-State Polymerization

The specific polymerization rate, regio- and chemoselectivity, and tacticity of the resultant polymers for polymerization in a crystalline solid could be due to the well-organized media. Stereospecific radical polymerizations in a solid crystal have been mainly investigated via two processes. One is when the monomer molecules are crystalline themselves (topochemical polymerization), and the other is when the monomers are included in the host crystals (inclusion polymerization).

Topochemical polymerization was first discovered in the 1,4-diacetylene polymerization by Wegner as a polymerization from monomer single crystal to polymer single crystal upon irradiation or heat.[120] This method is promising for stereochemical control of radical polymerizations; however,

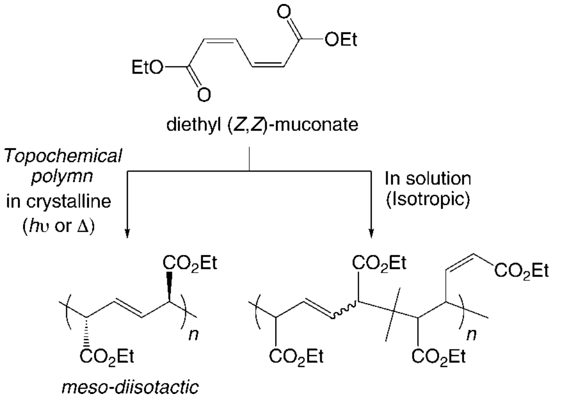


Figure 6. Topochemical polymerization of diethyl (*Z*,*Z*)-muconate.

monomers that can be topochemically polymerized are still limited because of the difficulties in preparing the polymerizable crystal lattice of the monomers.[121−125]

In the topochemical polymerization of 1,3-diene derivatives, the monomer crystal sometimes affords polymers without deforming the crystal structure as well as with high stereoregularity.[118,126−128] In 1994, the first diene topochemical polymerization was reported by Matsumoto et al. for diethyl (*Z*,*Z*)-muconate, which resulted in highly regio- and stereoregular polymer crystals when polymerized.[129] Photopolymerization of diethyl (*Z*,*Z*)-muconate in the crystalline state gave a tritactic *meso*-diisotactic *trans*-2,5 polymer, whereas atactic and regio-irregular polymers were obtained by a conventional solution polymerization (Figure 6).[130] The topochemical polymerizations were found to proceed under photoirradiation of crystals of muconic acid derivatives, such as their esters or ammonium salts.[131,132] In these cases, weak intermolecular interactions, such as hydrogen-bonding networks, aromatic-ring stacking, and CH/π or halogen interactions, account for the columnar organization of the muconic or sorbic acid derivatives in the crystalline state, of which the stacking distance is close to 0.5 nm.[133] Other asymmetric sorbates or dienes were also found to be polymerized into highly stereoregular polymers via topochemical polymerization.[134] The obtained highly stereoregular polymer crystals of muconic acid were water-insoluble and could also be reversibly converted to ammonium layers intercalated by alkylamines similar to an inorganic layered clay.[135] As for the molecular weight control, high molecular weight polymers were generally obtained by the topochemical polymerizations. The molecular weights of the produced polymers could be controlled depending on the original crystal structures and decreased as the size of the original monomer crystals became smaller, while the defects in the crystal should be crucial.[136−138]

Irrespective of the *E*- and *Z*-configurations of the original dienes, all the 1,3-dienes produced similar 1,4-structures. In addition, along with advances in organic crystal engineering particularly on the rational design of complex solid architectures through supramolecular preorganization, all of the stereoregular polymers of the substituted 1,3-dienes have now been synthesized, that is, *meso*-diisotactic, *racemo*-diisotactic, *meso*-disyndiotactic, and *racemo*-disyndiotactic polymers (Figure 7).[139−141] (*E*,*Z*)-Dienes in the translational molecular packing in the crystals like naphthylmethylammonium (*E*,*Z*)-muconate were polymerized into *racemo*-diisotactic polymers, whereas the (*E*,*E*)- or (*Z*,*Z*)-isomers afforded polymers with a *meso*-diisotactic specificity.[142] On the other hand, an alternate molecular stacking was formed in the column of the crystals by weak hydrogen bondings of the CH/π or halogen−halogen interactions of a muconate, such as di(4-substituted benzyl)muconate, to produce disyndiotactic polymers, although most of the dienes give diisotactic polymers via translational stacking.[143] Thus, it is important for stereoregular poly(dienes) via topochemical polymerization to control the stacking of the symmetrical or asymmetrical monomers via supramolecular preorganization. Although topochemical radical polymerization gives highly stereoregular polymers, the scope of the stereospecific polymerization of vinyl compounds is exclusively limited to 1,3-diene monomers and could not be used for common vinyl monomers. For vinyl monomers, it is difficult to prepare well-organized crystals, but it is noteworthy that solid-state polymerization of MMA gave lower syndiotactic polymers than that in solution probably due to the confinement effect.[144]

3.1.2. Inclusion Polymerization

Inclusion polymerization is a solid process where monomer molecules are included as the guest in channel-like cavities of host clathrate crystals (Figure 8). Inclusion polymerization usually proceeds in a small cavity of less than 1 nm in diameter of the host molecules and results in composites of the host crystal and guest polymers.[145,146]

The first example of radical polymerization of an included monomer was reported in the late 1950s.[147] In 1960, White and Brown reported that the inclusion polymerization of various monomers such as 1,3-butadiene took place in urea (**H1**) or thiourea (**H2**) canals, the diameters of which were 0.53 and 0.61 nm, respectively, under γ-ray irradiation.[148,149] From their extensive studies onward, many stereospecific polymerizations were examined via inclusion polymerization. As for the urea-mediated inclusion polymerizations of common vinyl monomers, it was first suggested that the polymerization of vinyl chloride (VC) in urea canals under γ-ray irradiation predominantly affords syndiotactic crystalline polymers.[150] Acrylonitrile (AN) could also be converted into isotactic crystalline polymers by γ-ray irradiation on an AN−urea canal complex at a low temperature, where the long-lived nature of the free radical species in the canals was also suggested.[149,151,152] These are because the polymerization proceeds in a small channel-like cavity where the growing free radical species cannot freely rotate or diffuse to cause stereospecific propagations with no bimolecular terminations. Under further optimized polymerization conditions in terms of the mole ratio of AN to urea, aging time, irradiation dose, and temperature, a highly isotactic poly(AN) was obtained ($mm/mr/rr$ = 87/10/3).[153]

Farina et al. used a *trans,anti,trans,anti,trans*-isomer of perhydrotriphenylene (PHTP, **H3**) as the host crystalline compound for the polymerization of *trans*-1,3-pentadiene as the guest to give highly isotactic polymers in the inclusion solid state.[154] They also reported that the *trans*-1,4-polypentadiene obtained in a chiral PHTP had an optical activity originating from the prevailing configuration of the methyl pendant group (Figure 9). Note that such substituted 1,4-diene polymers have no mirror plane; thus the optical activity would be induced by the chiral environment within the clathrate canal.[155,156]

Another chiral host for stereospecific and asymmetric polymerization could be found in naturally occurring compounds. Steroidal bile acids, such as deoxycholic acid (DCA,

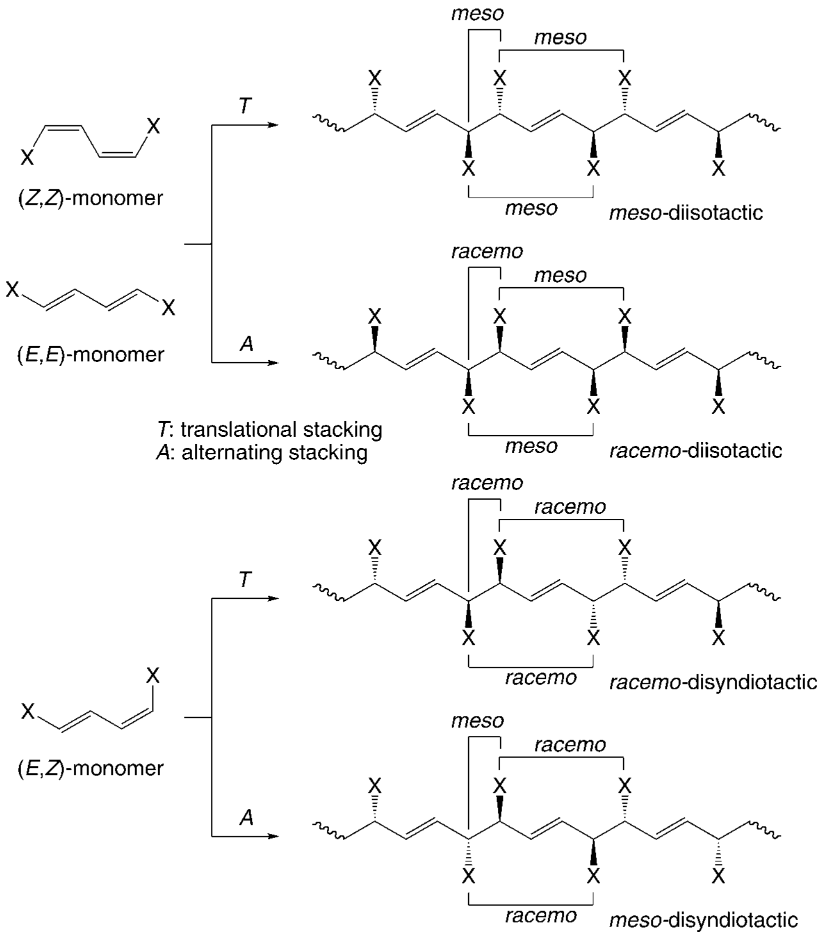


Figure 7. Stereoregular sequences for *trans*-1,4-poly(1,3-diene).

H4), as the host molecules also gave highly regulated polymers and the inclusion polymerization of *trans*- or *cis*-2-methyl-1,3-pentadiene under γ-ray irradiation resulted in asymmetric polymers with different optical activities.[157−159] The tacticity of the optically active polymer obtained with DCA was not highly regulated, but its isotacticity increased with the optical activity of the polymers (*mm*/*mr*/*rr* = 52/34/14 and 34/47/19 with $[\alpha]_D^{25} = -21°$ and $-3°$, respectively).[160] Apocholic acid (ACA, **H5**), which forms a slightly larger channel than DCA, was also employed as the host molecule for the asymmetric polymerization of the dienes.[161] Miyata et al. proposed that the scope of the polymerizable monomers in the inclusion polymerization depends on the space size of both the host clathrate crystals and the monomer structures.[146] Although cholic acid (CA, **H6**) also forms a larger channel space than those of DCA and ACA,[162,163] the crystalline structure was easily deformed during polymerization and gave less regulated polymers.[164] As in the case of the urea clathrate, however, the inclusion polymerization of vinyl chloride (VC) in CA produced a higher syndiotactic polymer (*mm*/*mr*/*rr* = 10/42/48) than the commercial poly(VC) (*mm*/*mr*/*rr* = 24/48/28).[165] Chenodeoxycholic acid (CDCA, **H7**) forms hexagonal crystals with helical assemblies. Inclusion polymerizations in CDCA clathrate for various vinyl monomers were also performed via a guest exchange method. The polymer obtained in CDCA exhibited no significant specificity in tacticity but had relatively narrow molecular weight distributions ($M_w/M_n \approx 1.2$) for some bulky methacrylates.[166] It was suggested that a long-lived reclusive propagating radical would be achieved in such an inclusion polymerization.[167]

Cyclotriphosphazene compounds such as tris(*o*-phenylenedioxy)cyclotriphosphazene (**H8**) and tris(2,3-naphthalenedioxy)cyclotriphosphazene (**H9**) are also known to form a clathrate tunnel of ca. 0.5 nm in diameter, in which dienes and vinyl monomers could undergo radical polymerization.[168,169] In those clathrates, 1,3-dienes also gave polymers with a 1,4-structure, and the polymerization of *trans*-2-methyl-1,3-pentadiene resulted in an isotactic specificity.[170] For the vinyl monomer polymerization, certain stereospecific features were also obtained. For examples, the isotactic specificity increased for the polymerizations of AN, methyl acrylate (MA), methyl vinyl ketone, and *p*-substituted styrenes.[171,172] Furthermore, the polymers derived from divinyl compounds, such as *p*-divinylbenzene and acrylic anhydride, in the clathrate tunnel were not cross-linked in contrast to those obtained by other methods with highly cross-linking propagation.[169,171]

Another series of candidates as organic hosts for inclusion polymerization is cyclodextrin (CD, **H10**), that is, cyclic oligosaccharides consisting of six (α), seven (β), or eight (γ) glucopyranose units, which can form cavities of different size depending on the unit number (0.57, 0.78, and 0.95 nm, respectively). The polymerization in a CD cavity, the crystal of which forms an aligned channel, would lead to not only a stereospecific radical polymerization but also the formation of rotaxane-type polymers.[173] Recently, it was suggested that isotactic polystyrene would fit better in channels with the γ-CD host than the syndiotactic one.[174] The inclusion polymerization of styrene was then examined in narrow γ-CD channels to produce rotaxane-like polymers with a slightly unusual tacticity.[175,176] However, most host γ-CD molecules

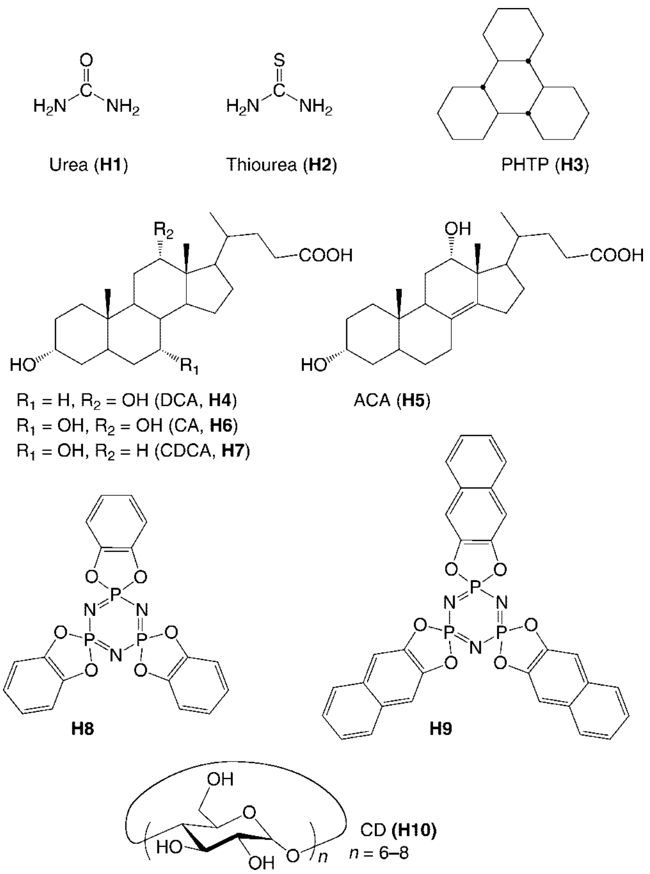


Figure 8. Host clathrate compounds for inclusion polymerization.

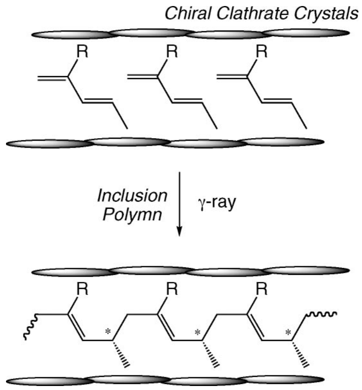


Figure 9. Asymmetric inclusion polymerization of 1,3-diene derivatives.

slipped off during polymerization, which led to deformation of the channel structure.[177]

The polymerizations in the aforementioned channels often exhibited the long-lived free radicals, each of which would be isolated in a single cavity and free from any bimolecular termination. Electron spin resonance (ESR) provided direct evidence for the existence of the long-lived free radical as well as information about its conformation.[178] The ESR observation revealed the long-lived radicals in the inclusion for urea,[179] apocholic acid,[146] and PHTP.[180] Given the long-lived growing radicals, however, precise control of the chain length has still been difficult because of unpredictable initiating numbers and locations in the cavities as well as the concurrent initiation reaction.

3.1.3. Polymerization in Porous Materials

As in the inclusion polymerization in the organic clathrate compounds, radical polymerizations in porous inorganic materials with a larger channel have also been studied. The early studies had focused on the graft polymerization onto the inorganic substance, on which the absorbed monomers underwent polymerization.[181−183] For tacticity of the polymers obtained from the absorbed monomers, γ-ray-induced polymerizations of AN and MMA adsorbed on Linde zeolite 13X were studied as a function of the amount of adsorbed monomer and the irradiation dose.[184] For tacticity of poly(AN) and poly(MMA), which could be recovered by destroying the host matrix in hydrofluoric acid, isotactic specificities were higher than those obtained in solution (*mm*/*mr*/*rr* = 25/48/28 for MMA and 39/46/15 for AN, respectively). These were most likely because the adsorbed monomer molecules preformed an isotactic diad placement.

Pyrolyzed poly(AN) included in zeolites was successfully prepared by AN polymerization followed by pyrolysis in the host mesoporous zeolite MCM-41, which has a hexagonal arrangement of linear silicate channels of about 2.7 nm diameter.[185] The obtained polymer would be used as an electronic conductivity material without a doping process. It was also shown that AN was polymerized in Na-Y and Na-β zeolite channels to produce slightly isotactic polymers.[186]

MMA could also be polymerized within the uniform channels of the MCM-41 with a free radical initiator, such as AIBN and BPO, at 100 °C.[187] With MCM-41, the formation of long-lived propagating radicals was also observed by ESR and led to molecular weight control by changing the molar ratio of the initiator to monomer. In contrast, the effects on their tacticity were negligible, most probably because the size of the channels of MAM-41 was too large to induce the confinement effects. MMA was also adsorbed onto various microporous inorganic hosts, including zeolite Na-Y, mordenite, Na-β, and ZSM-5 with pore diameters between 0.51 and 0.76 nm as well as MCM-41 and -48 between 0.3 and 0.35 nm.[188] Although the effects on the tacticity were not discussed, the resultant polymers were confined in the channels and exhibited no glass transition temperature in contrast to the bulk properties of a polymer indicating the interaction between the polymers and internal surface.

More recently, radical polymerizations in porous coordination polymers (PCPs) consisting of metal ions and organic ligands were reported by Kitagawa and Uemura et al., in which the porous materials could create highly ordered channel structures of controllable pore size with dynamic and flexible pores and unique surface potentials.[189] The features of polymerization in PCPs are quite consistent with those of polymerizations in clathrate crystals and porous materials, such as long-lived radical species, space dependence, and regioselectivity.[190,191] For the polymerization of MMA, styrene, and vinyl acetate (VAc), the pore size of the PCPs significantly affected the stereoregularity of the resulting polymers to increase the isotacticity (Table 1).[192] Especially for the VAc polymerization in the framework of $[Zn_2(\text{terephtalate})_2(\text{triethylenediamine})]_n$ (pore size 0.75 × 0.75 nm^2) at 60 °C, the product polymer exhibited not only a rich isotacticity but also a less-branching linear structure (*mm*/*mr*/*rr* = 30/49/21 and M_w/M_n = 1.7). With tunable regularity of the channels, it will be promising to provide further stereoregularity as well as various primary structures,

Table 1. Radical Polymerization in Nanochannels of Porous Coordination Polymers (PCPs)[192]

monomer[a]	pore size, nm^2	M_n	tacticity, *mm*/*mr*/*rr*
styrene	0.75 × 0.75	11 100	17/42/41
styrene	0.57 × 0.57	10 100	19/40/41
styrene	bulk	37 600	16/42/42
MMA	0.75 × 0.75	69 100	8/40/52
MMA	0.57 × 0.57	30 600	10/43/47
MMA	bulk	56 100	5/35/60
VAc	1.08 × 1.08	48 000	22/49/29
VAc	0.75 × 0.75	36 000	30/49/21
VAc	0.57 × 0.57	no polymn	
VAc	bulk	nd	22/50/28

[a] Polymerizations were carried out at 70 °C for 48 h for styrene, at 70 °C for 7 h for MMA, and at 60 °C for 48 h for VAc.

such as molecular weight and copolymer sequence, by creating a highly ordered monomer preorganization inside the PCP channels.

3.1.4. Template Polymerization

In template (matrix) polymerization, the propagation reaction predominantly occurs along or in the vicinity of another polymer chain (template) under its structural and kinetic control through their specific interactions.[193−195] The primary structures including both the chain length and tacticity of a daughter polymer would be inherited through the template macromolecule, where the molecular weight of the daughter polymers is generally higher than that of a corresponding blank polymer and sometimes even higher than that of the template. It is also known that the template tacticity affects the polymerization kinetics.[196]

There have been some reports on the effects of a template on the daughter tacticity, especially for the polymerization of methacrylic acid (MAA) or its polymers as a template. The daughter polymer of MAA obtained in the presence of PEG or PVP as a template in benzene exhibited a slightly syndiotactic specificity.[197] On the other hand, chitosan as the template provided an increase in the isotactic specificity along with the optical activity attributed to the factitious main-chain chirality (see, section 3.2.2), whereas no effect was obtained with the monomeric glucosamine.[198] In the case of the polymerization of *N*-vinylimidazole in the presence of the stereoregular poly(MAA) template, the tacticity of the daughter polymers was different from the blank but independent of the template tacticity.[113,199]

It is well-known that poly(MMA) forms a stereocomplex, in which the inside isotactic polymers were surrounded by a helix of the syndiotactic counterpart via van der Waals interactions.[200,201] Template radical polymerizations of MMA in the presence of another stereoregular poly(MMA) have been attempted in suitable solvents or the solid state.[202−205] In the stereocomplex-induced template polymerization, the effect on the stereospecificity has specifically been obtained only during the early stage of the polymerization, where syndiospecific propagation takes place in the presence of an isotactic polymer and vice versa. More recently, an excellent study on stereocomplex-induced template polymerization was reported by Akashi and Serizawa et al., in which macromolecularly porous ultrathin films fabricated by layer-by-layer assembly were used as the template for the highly efficient stereoregular template polymerization of MMA or MAA.[206−208] Highly stereospecific propagation could occur in the pores, which were prepared by the alternative layer-by-layer assembly of isotactic poly(MMA) and syndiotactic poly(MAA), followed by the extraction of one component from the thin film (Figure 10). In addition to the stereoregularity, the molecular weights of the resulting polymers were also well controlled, which were based on a double- or triple-stranded helical stereocomplex formed between the isotactic and syndiotactic polymers (1:2 in length/length), though the molecular weight distributions became broader. This also indicated the long-lived nature of the growing radicals in such confined media.[209] For example, a thin film of the isotactic poly(MMA) (M_n = 20 900, $M_\mathrm{w}/M_\mathrm{n}$ = 1.3, *mm*/*mr*/*rr* = 96/3/1) as the template afforded a syndiotactic daughter (M_n = 39 100, $M_\mathrm{w}/M_\mathrm{n}$ = 2.0, *mm*/*mr*/*rr* = 0/3/97). The system was also used for the macromolecular pore formed on mesoporous silica gel.[210]

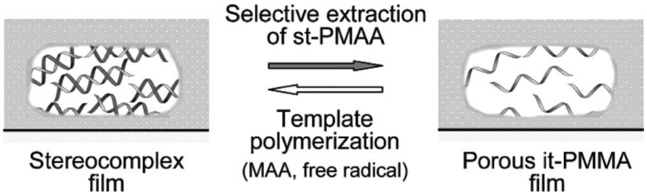


Figure 10. Template stereoregular polymerization of MAA using porous isotactic PMMA film. Reprinted with permission from ref 207. Copyright 2005 American Chemical Society.

3.2. Inherent Stereospecificity in Monomer Structure

In solution polymerization, it is more difficult to provide a stereospecific environment around the growing radical center, because the monomer and growing radical species move freely and diffuse in the reaction media. Therefore, vinyl monomers ordinarily produce polymers with an inherent tacticity specific to their chemical structures. The following section will show the inherent tacticity of common vinyl monomers, as well as the stereospecific radical polymerization of well-designed monomers.

3.2.1. Polymerization of Bulky Monomers

Bulkiness in the monomer structure plays a prominent role in the stereospecificity for radical polymerization in solution. In Bovey's pioneering investigation, it was shown that the tendency to form syndiotactic sequences during the MMA polymerization increases as the temperature is lowered (*mm*/*mr*/*rr* = 5/17/78 at −78 °C).[211,212] Since then, numerous studies on the stereochemistry for the radical polymerization of MMA and related monomers have been done under various conditions.[113,213−218] Selected methacrylic monomers are listed in Figure 11. Now that various methacrylates have been examined in radical polymerization, a wide range of stereoregularity can be available from highly syndiotactic to isotactic polymers (Table 2).[213,216,217,219−225]

Most aliphatic methacrylic polymers formed by radical polymerization have an excess of syndiotactic over isotactic diads (MMA, BM-**1** to BM-**8**), probably due to the steric repulsion among the α-methyl and pendent ester groups of the incoming monomer, growing radical, penultimate, and penpenultimate units in the antistaggered gauche conformations of the planar polymer chain (Figure 12).[112] The syndiotacticity of the aliphatic poly(methacrylates) generally increases with lower polymerization temperature. In addition, the inherent syndiotacticity of the methacrylate polymerizations gradually decreases with the bulkiness of the pendent groups. The stereospecificity in the polymerization of bulkier

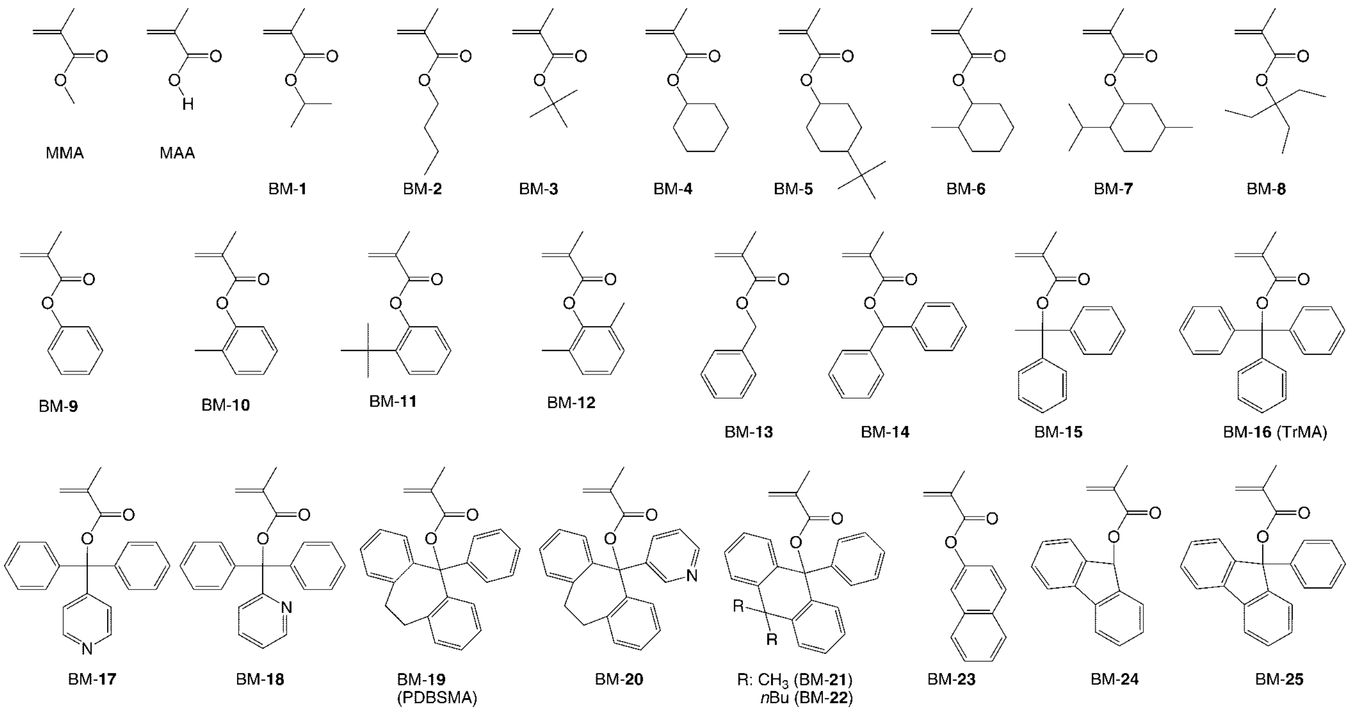


Figure 11. Bulky methacrylate monomers.

Table 2. Tacticity of Poly(methacrylate) Obtained via Radical Polymerization[213,216,217,219−225]

	ester group	temp, °C	solvent	triad tacticity, %		
				mm	*mr*	*rr*
MMA	methyl	60	benzene	3	34	63
MMA	methyl	20	toluene	2	29	69
MMA	methyl	−78	toluene	∼0	11	89
BM-**1**	isopropyl	70	bulk	7	31	62
BM-**2**	*n*-butyl	70	bulk	8	27	65
BM-**3**	*tert*-butyl	60	toluene	3	37	60
BM-**3**	*tert*-butyl	20	toluene	2	33	65
BM-**4**	cyclohexyl	70	benzene	10	35	55
BM-**5**	4-*tert*-butylcyclohexyl	50	benzene	11	35	54
BM-**6**	2-methylcyclohexyl	60	toluene	10	43	47
BM-**7**	menthyl	60	toluene	13	47	40
BM-**8**	1,1-diethylpropyl	50	benzene	14	53	33
BM-**9**	phenyl	60	benzene	9	41	50
BM-**10**	2-methylphenyl	60	benzene	12	45	43
BM-**11**	2-*tert*-butylphenyl	60	benzene	17	53	30
BM-**12**	2,6-dimethylphenyl	60	benzene	20	51	29
BM-**13**	benzyl	60	toluene	7	37	56
BM-**14**	diphenylmethyl	60	toluene	2	41	57
BM-**15**	1,1-diphenylethyl	60	toluene	19	49	32
BM-**16**	triphenylmethyl, $[M]_0 = 0.95$ M	60	toluene	64	24	12
BM-**16**	triphenylmethyl, $[M]_0 = 0.12$ M	60	toluene	98.2	1.7	0.1
BM-**17**	diphenyl-4-pyridylmethyl	60	toluene	76	19	5
BM-**18**	diphenyl-2-pyridylmethyl	60	toluene	86	11	3
BM-**19**	1-phenyldibenzosuberyl	60	toluene	99.9	0.1	0
BM-**20**	1-(3-pyridyl)dibenzosuberyl	60	toluene	>99	<1	0
BM-**21**	10,10-dimethyl-9-phenyl- 9,10-dihydro-9-anthracenyl	60	toluene	>99	<1	0
BM-**22**	10,10-dibutyl-9-phenyl- 9,10-dihydro-9-anthracenyl	60	toluene	91	6	3
BM-**23**	2-naphthyl	50	benzene	14	39	47
BM-**23**	2-naphthyl	50	*n*-hexane	58	24	18
BM-**24**	9-fluorenyl	60	toluene	1	10	89
BM-**25**	9-phenyl-9-fluorenyl	60	toluene	33	49	18

monomers is rather isotactic with the rigidness and bulkiness of the ester group. For example, the *o*-substituted phenyl methacrylates preferred lower syndiotactic propagation as the substituents became bulkier (BM-**9** to BM-**12**).[220]

Methacrylates with extremely bulky substituents, such as a triarylmethyl group (BM-**16** to BM-**22**), give highly isotactic polymers even via free radical solution polymerization.[116] These are most probably due to the inhibition of the planar zigzag conformation of the producing polymer chain by the bulkier group but induce the formation of a helical structure in a gauche-staggered conformation, where all the bulkier pendants are located outside of the central shaft of the helix, and thus the isotacticity is dependent on the bulkiness of the ester group (Figure 13). More precisely, the conformation would slightly deviate from the gauche-staggered position to that with the lowest energy correspond-

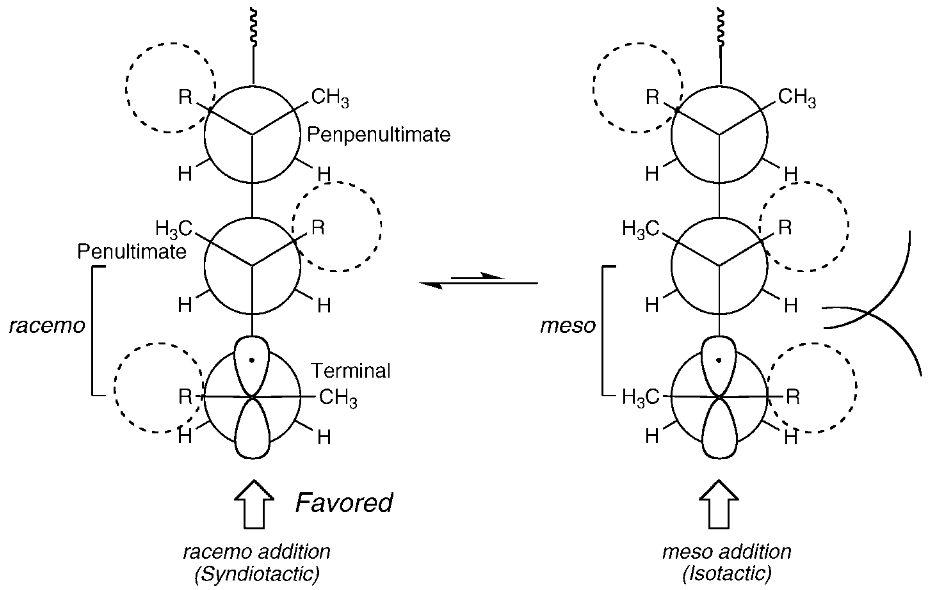


Figure 12. Schematic models of methacrylate polymerization.

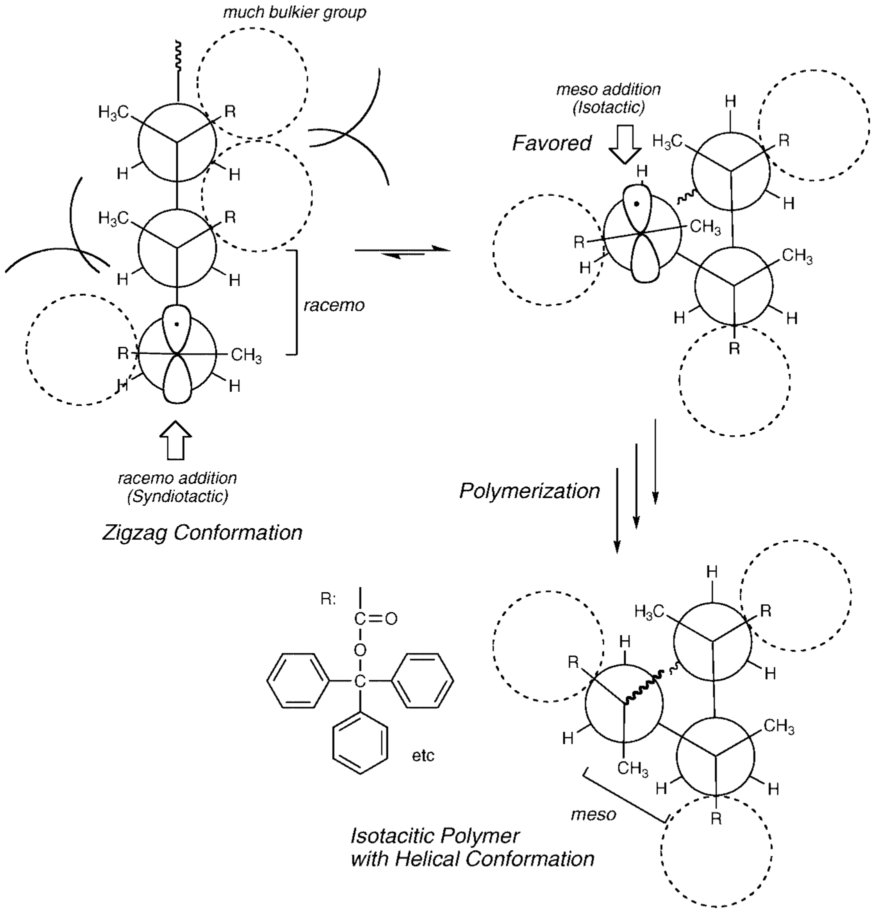


Figure 13. Schematic models of bulky methacrylate polymerization.

ing to a helix with 3.6 monomer units per turn for triphenylmethyl methacrylate (TrMA, BM-**16**).[226] The conformation thus originates from the steric repulsion among several monomer units from the terminus, so the tacticity obtained in the polymerization of the bulky monomers deviates far from the Bernoullian statistics due to the bulkiness of substituents (BM-**9** to BM-**16**).[221,227,228] The radical polymerization of BM-**16** gave a relatively high and tunable isotacticity depending on the polymerization condition, due to the equilibrium between the propagation and depropagation. For example, the polymerization in toluene occurred to give various tacticities depending on the polymerization temperature and monomer concentration; the polymerization at 70 °C ($[M]_0 = 0.18$ M) afforded a very high isotactic specificity of the resulting polymers (*mm*/*mr*/*rr* = 98.1/1.6/0.3), while the polymer obtained at 30 °C exhibited lower isotacticity (*mm*/*mr*/*rr* = 69.9/20.2/9.9).[219] This is most probably caused by the thermodynamic propagation–depropagation equilibrium, which can reconvert a less stable growing polymer terminal with the *r* conformation into the more stable

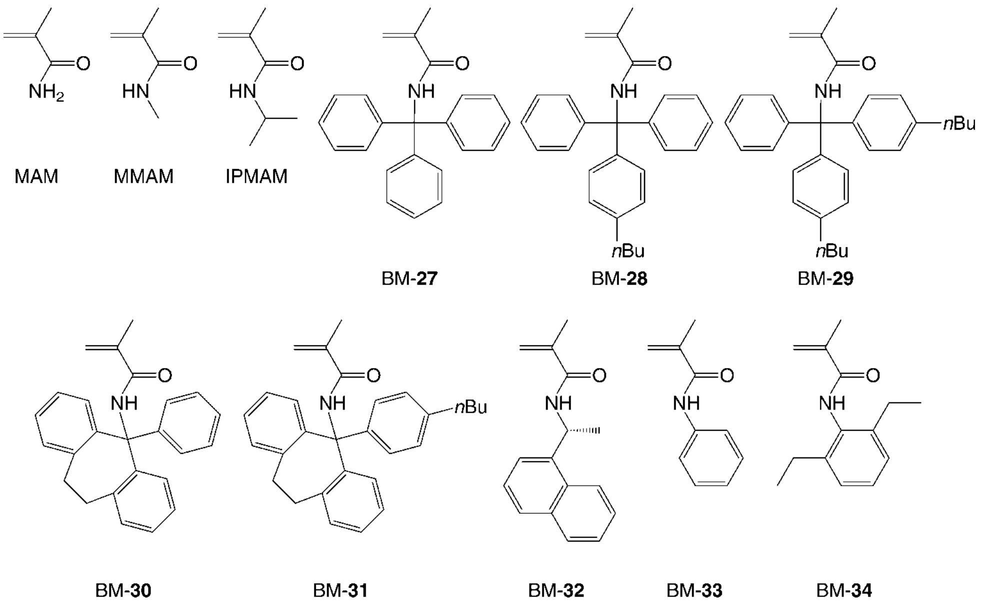


Figure 14. Bulky methacrylamide monomers.

m form especially at a lower monomer concentration. Furthermore, it was also revealed that the instantaneous isotacticity is only governed by the remaining monomer concentration. Similar tendencies to give relatively high isotactic polymers were observed for the polymerization of diphenyl-4-pyridylmethyl (BM-**17**) or diphenyl-2-pyridylmethyl methacrylate (BM-**18**) at 60 °C (*mm*/*mr*/*rr* = 76/19/5 and 86/11/3 for BM-**17** and BM-**18**, respectively).[222]

In contrast, a similar analogue of 1-phenyldibenzosuberyl methacrylate (PDBSMA, BM-**19**) leads to an almost perfect isotactic polymer regardless of the reaction conditions by radical polymerization due to the more rigid group with ethylene-linked aryl groups in toluene at 60 °C (*mm*/*mr*/*rr* = 99.9/0.1/~0).[219,229] 1-(3-Pyridyl)dibenzosuberyl methacrylate (BM-**20**) was also radically polymerized into an almost perfect isotactic polymer.[230] The bulky monomers with methylene-linked aryl groups of 10,10-dimethyl- (BM-**21**) and 10,10-dibutyl-9-phenyl-9,10-dihydro-9-anthracenyl methacrylate (BM-**22**) were similarly examined for their stereospecific radical polymerization.[223] In toluene at 60 °C, BM-**21** resulted in high isotactic selectivity of *mm* > 99% as did the ethylene-linked PDBSMA (BM-**19**), whereas BM-**22** afforded polymers with a slightly lower isotacticity (*mm* = 91%). It is interesting that the isotactic specificity in the BM-**22** polymerization increased upon lowering the temperature (*mm* = 99% at −20 °C), which is the opposite tendency of the thermodynamic control in the TrMA (BM-**16**) polymerization.

Aside from the bulkiness in the pendent groups, it should be noted that methacrylates bearing aromatic groups exhibit a specific feature in the tacticity of the producing polymers dependent on the solvents. This is probably due to the π-stacking interaction or specific interaction between the aromatic ring and growing radicals.[224,231−233] For example, 2-naphthyl methacrylate (BM-**23**) gave an isotactic-rich polymer in *n*-hexane (*mm*/*mr*/*rr* = 58/24/18), whereas that obtained in benzene was rather syndiotactic (*mm*/*mr*/*rr* = 14/39/47). Recently, it was reported that 9-fluorenyl methacrylate (BM-**24**) underwent a highly syndiospecific radical polymerization at 60 °C regardless of the solvents, although the monomer had a relatively bulky pendent group (*mm*/*mr*/*rr* = 1/10/89).[225] In contrast, 9-phenyl-9-fluorenyl methacrylate (BM-**25**) gave much lower stereoregularity via radical polymerization in toluene at 60 °C (*mm*/*mr*/*rr* = 33/49/18), despite its resemblance to BM-**19**.[223]

Originally, the asymmetric polymerization of the bulky triarylmethyl methacrylates had been reported by Okamoto et al. via anionic polymerization with a chiral initiating system, in which an organolithium was employed as an initiator in the presence of chiral ligands such as (−)-sparteine.[116,234,235] Even via a radical process, some bulky methacrylates gave not only an almost perfect isotacticity but also a single-handed helical conformation by chiral free radical initiators, chain transfer agents, or solvents. The polymer of BM-**19** and related derivatives obtained in the asymmetric systems had an almost perfect isotactic main-chain configuration and a prevailing stable one-handed helical conformation exhibiting optical activities.[223,236,237] Among them, the highest optical activity of poly(BM-**19**) was obtained using chiral transfer agents ($[\alpha]_{365}$ = −750°), though lower than that of the anionically polymerized single-handed helical poly(BM-**19**) ($[\alpha]_{365}$ = +1780°). Chiral cobalt catalysts could also mediate the asymmetric polymerization via a dissociation−combination process as in the controlled/living radical polymerization.[238,239] The poly(BM-**19**) obtained with *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-(1*R*,2*R*)-1,2-cyclohexanediaminatocobalt(II) complex showed a higher optical activity with $[\alpha]_{365}$ = +1379°.

Methacrylamides with bulky triarylmethyl substituents (Figure 14), such as *N*-triphenylmethylmethacrylamide (BM-**27**) and its alkylated derivatives (BM-**28** and BM-**29**), were also polymerized via radical polymerization into highly isotactic polymers. Different from the corresponding methacrylates, they have an innate tolerance toward hydrolysis and alcoholysis. Both the poly(BM-**27**) and poly(BM-**29**) obtained via free radical polymerization were nearly 100% isotactic, though the highly stereoregular poly(BM-**27**) was insoluble in any organic solvents.[240] Furthermore, the polymers of BM-**27** and its derivatives obtained in the solvent mixture of (−)-menthol or with the chiral cobalt complex also had specific rotations due to a deviation in the one-handed helix-sense and showed a chiral recognition ability.[241,242] Similar to the methacrylates, *N*-(1-phenyldibenzosuberyl)-methacrylamide (BM-**30**) and its alkylated derivative (BM-**31**) also produced nearly 100% isotactic polymers and its

Table 3. Tacticity Obtained via Radical Polymerization of Monosubstituted Monomers[218,246−250]

	monomer	temperature, °C	solvent	triad tacticity, % *mm*	*mr*	*rr*	diad tacticity, % *m*	*r*
VC	vinyl chloride	90	bulk	28	51	21	54	46
VC	vinyl chloride	20	bulk	33	51	16	59	41
VC	vinyl chloride	−50	bulk	43	44	13	65	35
AN	acrylonitrile	55	DMSO	25	51	24	50	50
AN	acrylonitrile	35	emulsion	27	49	24	52	48
MA	methyl acrylate	40	toluene				52	48
MA	methyl acrylate	−90	toluene				51	49
BM-**35**	trimethylsilyl acrylate	40	toluene				47	53
BM-**35**	trimethylsilyl acrylate	−90	toluene				29	71
BM-**36**	isopropyl acrylate	80	toluene				42	58
BM-**36**	isopropyl acrylate	−105	toluene				24	76
BM-**37**	*tert*-butyl acrylate	60	toluene				46	54
BM-**37**	*tert*-butyl acrylate	−95	toluene				37	63
BM-**38**	triphenylmethyl acrylate	40	toluene				49	51
BM-**39**	1-phenyldibenzosuberyl acrylate	40	toluene				44	56
DMAM	*N*,*N*-methylacrylamide	60	toluene				53	47
BM-**40**	*N*,*N*-diphenylacrylamide	40	toluene				15	85
BM-**41**	*N*,*N*-bis(4-butylphenyl)acrylamide	40	toluene				12	88
VAc	vinyl acetate	40	toluene	22	49	29	47	53
BM-**42**	vinyl pivalate	40	toluene	19	49	37	38	62
BM-**42**	vinyl pivalate	0	emulsion	12	46	42	35	65
BM-**43**	vinyl formate	40	bulk	30	26	44	43	57
BM-**43**	vinyl formate	−20	bulk	27	27	46	40	60
BM-**44**	vinyl benzoate	20	bulk	27	51	22	52	48
BM-**45**	vinyl diphenylacetate	40	toluene	12	46	42	35	65

copolymerization with chiral methacrylamide induced an excess of the one-handed helicity.[243] The random copolymerization of the BM-**27** derivative with other methacrylamides bearing chiral auxiliaries, such as BM-**32**, also led to the prevailing one-handed helicity.[244] *N*-Phenylmethacrylamide (BM-**33**) was polymerized into rather syndiotactic polymers regardless of the polymerization condition (*mm*/*mr*/*rr* = 8/39/53). However, the polymers of its derivatives, such as *N*-(2,6-diethylphenyl)methacrylamide (BM-**34**), prepared in chiral menthols were less soluble and showed optical activities, suggesting the higher stereospecificity though the details are not clear.[245]

In sharp contrast to the above-mentioned vinylidene monomers with an α-methyl group, radical polymerization of the monosubstituted vinyl derivatives has a greater tendency to afford almost atactic polymers regardless of the monomer structure and polymerization temperature (Table 3).[218,246−250] As the substituents in the acrylate become bulkier, the syndiotacticity of the obtained polymers slightly increases contrary to the polymerization of the methacrylates, probably due to the steric repulsion in the antistaggered gauche conformations of the planar polymer chain (Figure 15). Acrylates bearing a bulky substituent, such as a trimethylsilyl or isopropyl group afforded syndiotactic-rich polymers at low temperature (BM-**35** to BM-**37**).[251−253] For example, isopropyl acrylate (BM-**36**) was polymerized at −105 °C to give polymers with a syndiotactic specificity (*m*/*r* = 24/76). Furthermore, the polymer obtained from a

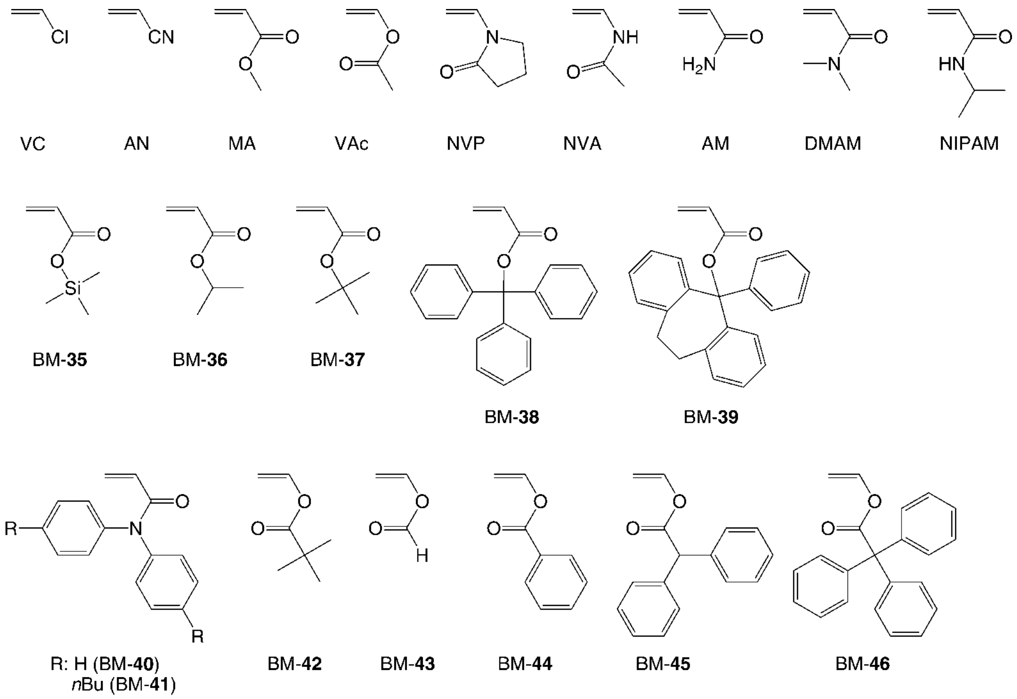


Figure 15. Bulky monosubstituted vinyl monomers.

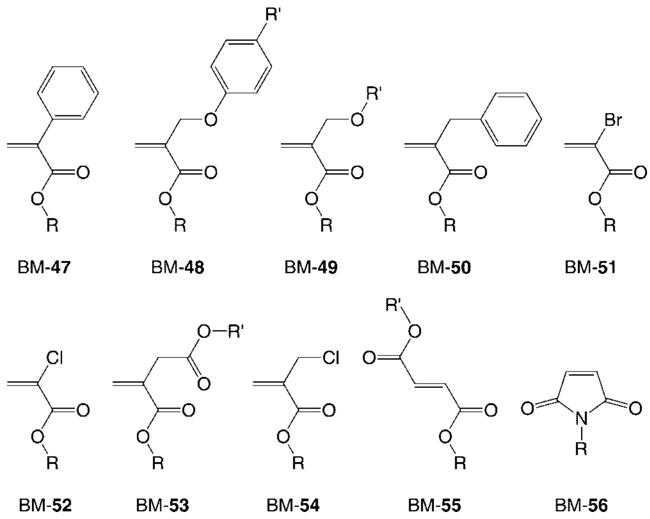


Figure 16. Bulky disubstituted monomers.

much bulkier acrylate showed a slightly syndiotactic specificity even at ambient temperature, that is, for triphenylmethyl acrylate (BM-**38**, *m*/*r* = 49/51) and 1-phenyldibenzosuberyl acrylate (BM-**39**, *m*/*r* = 44/56).[254] The bulky acrylamides, such as *N*,*N*-diphenylacrylamide (BM-**40**) and *N*,*N*-bis(4-butylphenyl)acrylamide (BM-**41**), produced higher syndiotactic polymers than the acrylates via radical polymerization at 40 °C (*m*/*r* = 12/88).[255,256]

Controlling the stereochemistry during the radical polymerization of vinyl esters is especially important because they can be polymerized only via a radical process and converted to poly(vinyl alcohol) by the subsequent hydrolysis. Various bulky vinyl esters were also examined to induce an increase in the syndiotactic specificity (BM-**42** to BM-**46**). The polymerizations of vinyl pivalate (BM-**42**), formate (BM-**43**), and diphenylacetate (BM-**45**) afforded relatively syndiotactic-rich polymers.[257−261] For example, the syndiotactic poly(BM-**42**) was prepared via photoemulsion polymerization at 0 °C and was changed into syndiotactic poly(vinyl alcohol) (*mm*/*mr*/*rr* = 11/49/39) after the hydrolysis. Contrary to acrylates or methacrylate, the bulkier vinyl triphenylacetate (BM-**46**) undergoes little homopolymerization to result in only oligomers, whereas BM-**45** afforded polymers with moderate molecular weights ($M_n \approx 1.0 \times 10^4$) and a higher syndiotactic specificity even at 40 °C (*mm*/*mr*/*rr* = 12/46/42).

The effects of the bulkiness in the α,α-disubstituted acrylate on the tacticity were also studied for a series of monomers, such as α-phenylacrylates (BM-**47**),[262] α-(aryloxymethyl)acrylates (BM-**48**),[263,264] α-(alkoxymethyl)acrylates (BM-**49**),[265,266] α-(benzyl)acrylates (BM-**50**),[267,268] α-bromoacrylates (BM-**51**),[269] α-chloroacrylates (BM-**52**),[270] dialkyl itaconate (BM-**53**),[271] and α-(chloromethyl)acrylate (BM-**54**)[272] (Figure 16). In these cases, however, the radical polymerization tended to give slightly syndiotactic or rather atactic polymers regardless of the bulky substituents in addition to the greater tendency to addition-fragment transfer. It is noteworthy that the γ-ray-induced polymerization of methyl α-(phenoxymethyl)acrylate (BM-**48**; R = CH_3, R′ = H) at 30 °C gave a heterotactic specificity (*mr* ≈ 68%), although the active species was postulated to be an ionic one.[264] The stereospecificity of the radical polymerization of di-*n*-butyl itaconate (BM-**53**; R = R′ = *n*-butyl) had a high temperature dependence, in which highly syndiotactic polymers were obtained at a lower temperature (*mm*/*mr*/*rr* = 0.5/19.0/80.5 at −78 °C), and increasing temperature led to isotactic polymers (*mm*/*mr*/*rr* = 63.6/34.8/1.6 at 120 °C).[271]

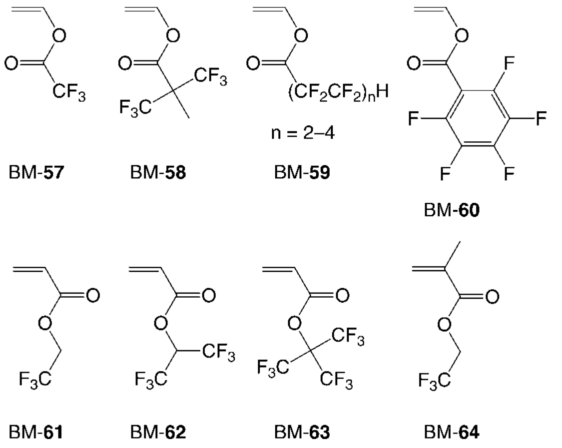


Figure 17. Bulky fluorinated monomers.

Generally, 1,2-disubstituted olefins exhibit little or no tendency to undergo homopolymerizations due to their steric inhibition. However, fumaric acid diesters (BM-**55**) with bulky alkyl substituents were radically homopolymerized to form poly(methylene) derivatives.[273,274] During the propagation, both the meso and racemo addition took place, but the *rr* triad was excluded. For example, diisopropyl fumarate (BM-**55**; R = R′ = isopropyl) produced isotactic-rich polymers at 60 °C in bulk (*mm*/*mr*/*rr* = 55/45/0).[275] In addition, the polymerization proceeded faster and the probability of the meso addition increased as the ester substituents became bulkier.[276,277] Maleimide derivatives (BM-**56**) are also known to produce homopolymers with *threo*-diisotactic and *threo*-disyndiotactic structures via trans addition.[278,279] The asymmetric radical polymerizations of *N*-phenylmaleimide, *N*-cyclohexylmaleimide, and *N*-1-naphthylmaleimide (BM-**56**; R = phenyl, cyclohexyl, and 1-naphthyl, respectively) were examined with a chiral Co(II) complex to result in optical activity of the produced polymers.[280,281]

Not only the steric bulkiness but also a specific electrostatic repulsion in the monomer structure is sometimes an important factor to achieve a unique inherent stereochemistry during radical polymerization (Figure 17). The fluoro-containing vinyl esters such as vinyl trifluoroacetate (BM-**57**), 2,2-bis(trifluoromehyl)propoinate (BM-**58**), perfluoroalkylcarboxylate (BM-**59**), and pentafluorobenzoate (BM-**60**) afforded relatively high syndiotactic polymers by reducing the cohesive intermolecular forces using fluoro-containing substituents.[258,282−284] BM-**58** was polymerized in THF at 0 °C to give prevailing syndiotactic polymers (*mm*/*mr*/*rr* = 9.7/43.3/46.9). A series of fluorinated acrylates was examined for their stereospecific radical polymerization that resulted in a higher syndiotacticity (BM-**61** to BM-**63**). By optimization of the conditions, the racemo contents reached *r* = 81% for the polymerization of 1,1,1,3,3,3-hexafluoro-2-propyl acrylate (BM-**62**).[285] 2,2,2-Trifluoroethyl methacrylate (BM-**64**) gave syndiotactic-rich polymer but almost the same tacticity as that for the corresponding nonfluoro methacrylate (*rr* = 56% at 60 °C).[286]

3.2.2. Monomers with Chiral Auxiliary

The stereochemical control of the vinyl polymerization appears to be a reiteration of the enantioselective insertion reaction between the growing radical and incoming monomers.[287−290]

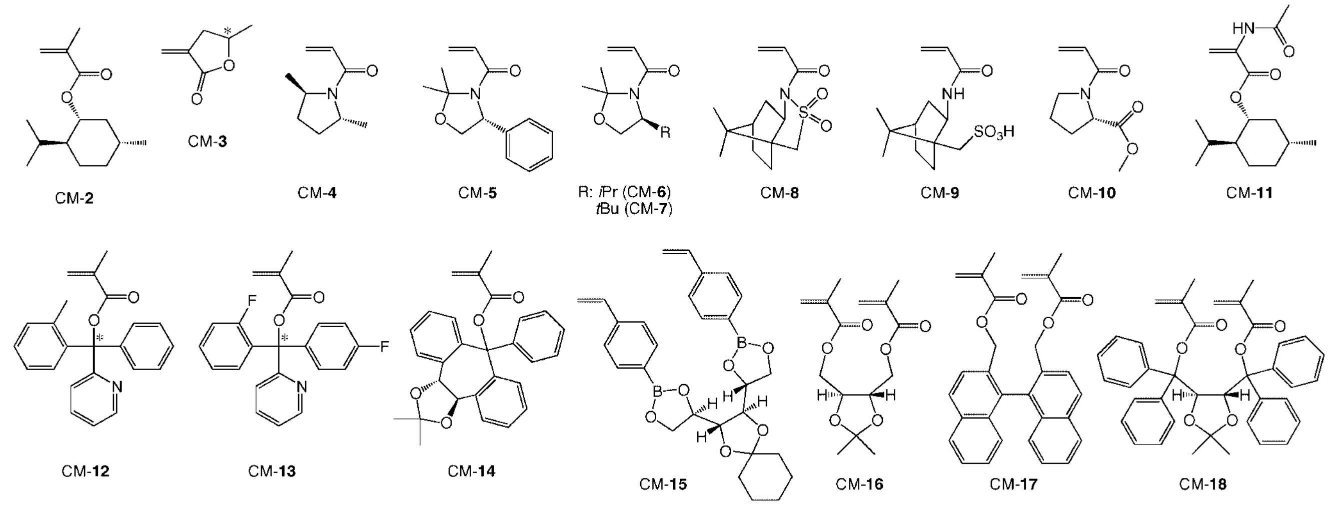


Figure 18. Chiral monomers.

The chirality should be closely related to the tacticity of polymer, because the prostereogenic center of the growing radical would indeed be controlled into continual enantioselective insertions inducing isotactic specificity by the chiral pendent groups attached to the main chain. However, it has been quite difficult to induce isospecific tacticity using chiral vinyl monomers (Figure 18), though it is a promising raw material for asymmetric chiral polymers.[116,291] This is most probably because diastereoselectivity is required for the tacticity control during polymerization. During the polymerization of *d*-, *l*-, or *dl*-menthyl methacrylate (CM-**2**), the tacticity of the resultant polymers hardly changed with the monomer compositions.[292]

Stille et al. reported an example of stereospecific radical polymerization using chirality in a cyclic acrylic monomer. The radical polymerizations of (*RS*)- and (*R*)-α-methylene-γ-methyl-γ-butyrolactone (CM-**3**) were performed at 65 °C with benzoyl peroxide as the initiator. The polymer obtained from the chiral monomer was less soluble than that from the racemic monomer, and a predominantly isotactic propagation for the chiral monomer was also suggested by the ^{13}C NMR spectroscopy.[293]

In the 1990s, it was reported by Porter et al. that the radical polymerization and telomerization of acrylamide with chiral pyrrolidine or oxazolidine (CM-**4** to CM-**7**) proceeded in an isospecific manner (m = 88−92%), in which an enantioselective reaction would take place during every insertion.[294,295] For example, *N*-acryloyl 5(*S*)-*tert*-butyl-2,2-dimethyl-l,3-oxazolidinide (CM-**7**) was polymerized in the presence of a vinyl sulfide as a transfer agent to reduce the molecular weight at 75 °C and then hydrolyzed, which resulted in the isotactic poly(acrylic acid) (m = 88%, *mm*/*mr*/*rr* = 82/12/6). It was explained that the stereocontrol was the result of a facial selectivity during the addition of the monomer to the growing polymer radical because of the steric hindrance caused by the chiral auxiliary. The contribution of the inherent isotacticity due to the bulkiness had not been experimentally verified with the racemic or achiral counterparts. Another cyclic acrylamide with Oppolzer's camphor sultam as a chiral auxiliary (CM-**8**), however, resulted in much lower isotactic polymers (m = 54%), whereas a high stereocontrol was obtained during its radical addition reaction. This indicates the importance of the penultimate group effects during propagation.[296,297] Similar chiral cyclic acrylamides derived from camphorsulfonic acid (CM-**9**) or proline derivatives (CM-**10**) did not exhibit specific tacticities.[293,294] The effects of the chirality and penultimate units on the tacticity and prostereogenic center were also discussed for the radical polymerization of a specific bulky chiral monomer of (−)-menthyl 2-acetamidoacrylate (CM-**11**) along with the monomer conformers.[300]

An optically active and highly bulky phenyl-2-pyridyl-*o*-tolylmethyl methacrylate (CM-**12**) was polymerized with diisopropyl peroxydicarbonate in toluene at 40 °C. The tacticity of the obtained polymers was fairly isotactic (*mm*/*mr*/*rr* = 74/19/7) but almost independent of the enantiomeric excesses in the monomer feed. However, the polymers showed large optical rotations opposite in sign to the rotation of the starting monomer, in which the prevailing in one-handed helix was amplified due to the steric effect of the chiral side group.[301] A similar tendency was observed for the polymerization of another chiral and bulky methacrylate with fluorinated substituents (CM-**13**).[302] Furthermore, the introduction of a chiral auxiliary into the ethylene-linkage of PDBSMA (CM-**14**) resulted in the self-induction of the prevailing one-handed helicity without loss of the highly isotactic specificity.[303]

Since the report by Wulff et al. that the asymmetric cyclopolymerization of distyryl monomers with a chiral linkage (CM-**15**) resulted in main-chain chiral polymers, various divinyl monomers with a chiral template were intensively studied mainly in order to obtain chiral polymers.[114,304,305] As for the tacticity of the obtained polymer with a cyclic structure in the main chain, some dimethacrylic monomers prepared from chiral diols as templates were polymerized via radical polymerization (CM-**16** to CM-**18**).[306−310] In all of the cases, the optical activities were observed in the produced polymers even after their transformation into poly(MMA), probably due to chiral diads from the difunctional monomer in the stereosequences. In contrast, the tacticity obtained via asymmetric cyclopolymerization, even in the case when the degree of cyclization was high, was not highly regulated but was different from that obtained in the polymerization of the corresponding monomeric methacrylate. For example, the cyclopolymerization of dimethacrylate derived from (+)-2,3-*O*-isopropylidene-L-threitol (CM-**16**) at 60 °C resulted in lower syndiotactic polymers than the MMA polymerization (*mm*/*mr*/*rr* = 12/49/39), in which the *mr* value is slightly higher than the Bernoullian statistics (m = 35%, *mm*/*mr*/*rr* = 12/46/42).[306] Most probably, this

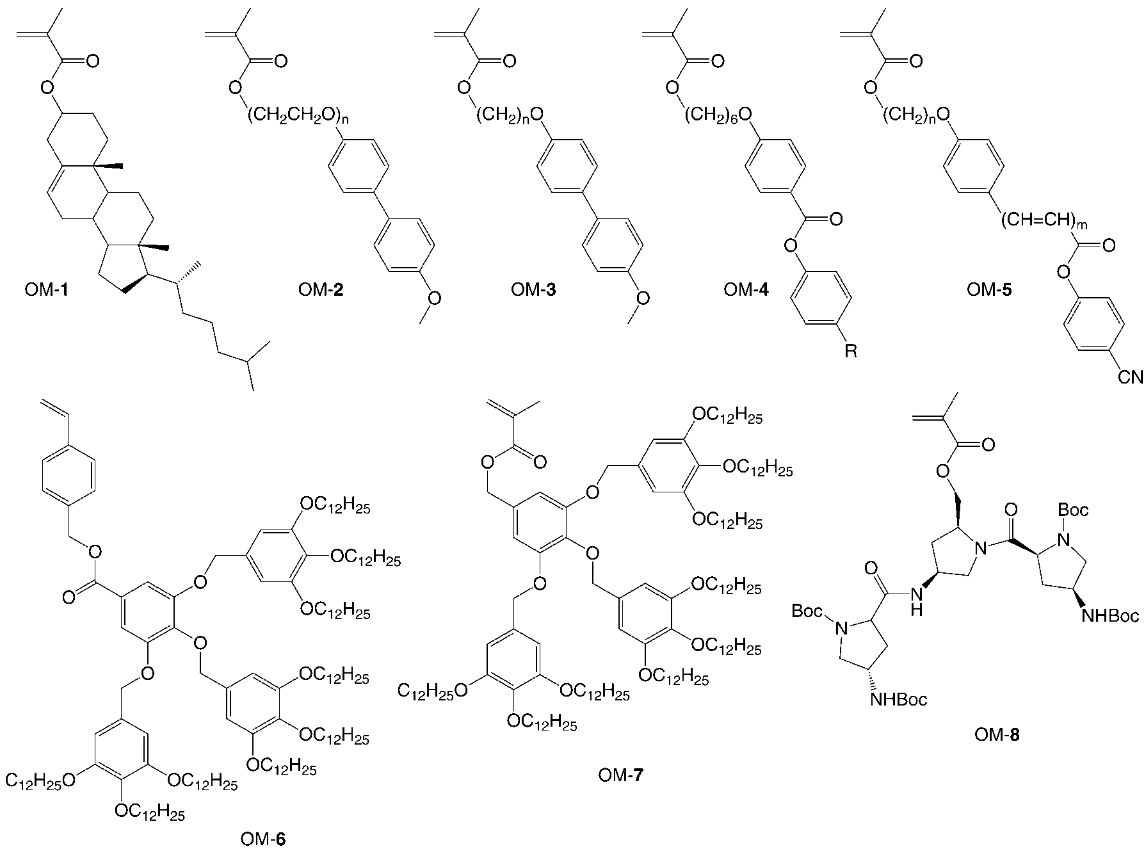


Figure 19. Monomers bearing self-organizable groups.

was attributed not to the chiral template but to the restricted intramolecular cycloaddition compared with the intermolecular propagation, which would be the inherent tacticity for difuncitonal monomers. This tendency was also seen in the cyclopolymerization of dimethacrylates with achiral templates.[311,312] A template with bulky diarylmethyl groups (CM-**18**) also afforded a relatively high isotactic specificity (*mm* ≈ 80%) as in the polymerization of TrMA or PDBSMA regardless of the enantiomer excess in the template.[308,309] An unusual stereospecificity was also suggested for the polymerization of multifunctionalized β-cyclodextrin bearing methacryloyl groups (20.4 per molecule on average).[313]

3.2.3. Monomers with Self-Assembling Group

Polymers with a side-chain mesogen often show a well-organized liquid crystalline mesophase containing a roughly rod-like molecular shape (Figure 19).[314] Many studies of such side-chain liquid crystalline polymers have been reported, where the effects of the tacticity were examined mainly for the mesomorphic property of the product. The tacticity of the producing polymers has been rarely evaluated, although radical polymerizations of such self-organizable monomers would also proceed in an organized and confined medium.

A cholesteryl methacrylate (OM-**1**), which exhibits the characteristic blue-colored cholesteric mesophase, was polymerized at the mesomorphic temperature of 108 °C.[315] Acceleration of the polymerization was observed as in the system for the other side chain liquid crystalline monomers, but there was no significant difference in the tacticity between the polymers obtained in the mesophase and in the isotropic liquid phase. During the polymerization of the methacrylate with a 4′-methoxy-4-biphenylyloxy group as mesogen, various flexible spacers, such as the oligo(ethylene oxide) (OM-**2**) and aliphatic alkyl chain (OM-**3**), have been examined for preparing liquid crystalline polymers, all of which had a prevailing syndiotacticity due to the inherent nature of the methacrylate polymerization. In the case of OM-**2** with oligo(ethylene oxide) as the spacer, the tacticity depended on the length of the spacer.[316] Especially, isotactic specificity increased with decreasing spacer length ($n = 0-4$) probably due to biphenyl−biphenyl interaction at the growing terminus (*mm* = ca. 11−20%), although the polymerizations were even carried out in solution. As for OM-**3** with aliphatic alkyl chains as the spacer, no significant differences in the product tacticity were observed in solution.[317−319] Similarly, the polymerization of methacrylate with the other mesogenic groups, such as phenylbenzoates (OM-**4**) and *p*-alkoxyl cinnamates (OM-**5**), also gave liquid crystalline polymers with unexceptional tacticities even in the mesophase.[320,321]

Dendritic building blocks can also be employed in the construction of supramolecular systems with a complex architecture.[322−324] Percec et al. reported that the polymerization of styrene (OM-**6**) or methacrylate (OM-**7**) with dendrons containing no spacer in the self-assembled state proceeded via a free radical process, where the polymerization was accelerated to give somewhat controlled molecular weights due to the long-lived radical species, similar to the radical polymerization in confined media.[325−327] During the course of their studies, it is interesting that the shape of the produced polymer depended on the chain length. For example, the polymers jacketed with conical dendrons exhibited micellar cubic lattices at low DPs (<20 for OM-**6** and <15 for OM-**7**, respectively), whereas the polymer adopted a cylindrical shape for the longer chain length (DPs > 20 or 15). Although the propagation would occur in a confined medium, the tacticity was not measured. More

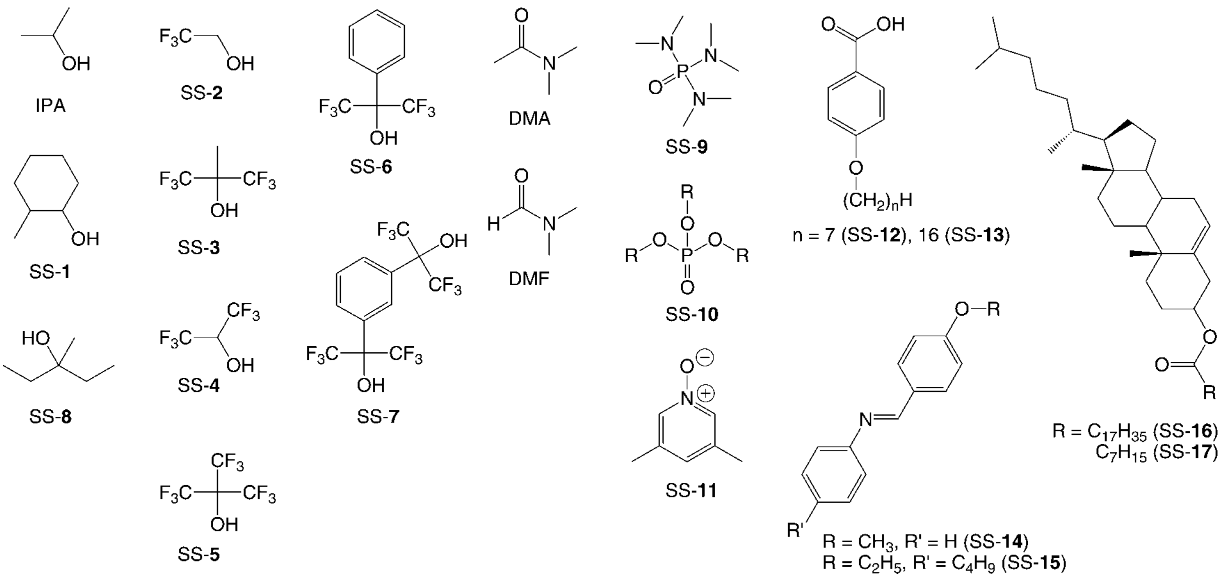


Figure 20. Solvents for stereospecific radical polymerization.

recently, a methacrylate bearing a pendent 4-aminoproline-based second-generation dendron (OM-**8**) was polymerized to afforded polymers with a high rigidness and a right-handed helical sense conformation mainly driven by a dendron/dendron interaction.[328] However, the tacticity of the backbone was not highly regulated but slightly rich in heterotacticity (*mr* ≈ 65%). The molecular dynamics simulations supported the right-handed helicity irrespective of the backbone tacticity, though the polymer with a heterotactic configuration has a more compact structure.

3.3. Stereocontrol by Solvents or Additives

From the viewpoint of versatility and production cost, solvent- or additive-mediated systems might be the most promising solutions to obtain stereospecific polymers. During the past decade, many specific solvents and additives have been found to allow stereospecific radical polymerizations via various interactions with monomers to change their inherent structures. Especially, the metal Lewis acids have also been playing important roles in the stereocontrol of radical polymerization chemistry as well as free radical reactions in organic synthesis.[289,290,329] Various interactions of the solvents or additives such as hydrogen, coordination, and ionic bondings could create stereospecific environments with the incoming monomer and growing terminus in the propagation steps. The present section will focus on the simple and versatile stereospecific radical polymerization via various molecular interactions.

3.3.1. Solvent-Mediated Stereospecific Polymerization

To achieve control of the stereochemistry by specific solvents (Figure 20), the solvents should interact with the pendent groups in the monomer or the generating polymer side chain during the solvation in order to change the inherent structure into an appropriate form for stereospecific environments around the growing chain terminus. While a low temperature or a large amount of the solvent should be required due to the weak interactions, stereospecificity can be attained by steric repulsion between these apparently bulky side groups. However, the inherent value of the tacticity had rarely been changed by usual solvents for the radical polymerization of neutral vinyl monomers, such as the methacrylate and vinyl esters, before the 1990s.[113,330]

In contrast, the tacticity of polymers of methacrylic acid (MAA) or its salts had been known to highly depend on the extent of the hydrogen bonds between the monomer and the solvent.[331] For the polymerization of MAA, the hydrogen bonding of alcohols as solvents to the monomeric acid and growing radical appears to be responsible for the solvent effects on the stereoregularity of the polymer, in which the bigger the monomer−solvent complex, the higher was the syndiotacticity of the producing polymer. For example, the MAA polymerization initiated by cobalt 60 γ-radiation in 2-propanol at −78 °C gave the highest syndiotacticity with *mm*/*mr*/*rr* = 0/5/95.[332] Upon further investigation of the solvents, the MAA polymerization in 2-methylcyclohexanol (SS-**1**) resulted in a high degree of syndiotacticity at 0 °C (*mm*/*mr*/*rr* = 0/18/82).[333] Aprotic amide solvents such as *N*,*N*-dimethylacetamide (DMA) also produced a relatively highly syndiotactic poly(MAA) (*mm*/*mr*/*rr* = 2/30/68) compared with the bulk polymerization at 60 °C (*mm*/*mr*/*rr* = 9/46/45), probably due to suppression of the bimolecular hydrogen bonding interaction between the acids.[334]

More recently, fluorinated alcohols (SS-**1** to SS-**7**) were found to be the most efficient solvents in controlling the stereospecificity of radical polymerizations, even for common neutral vinyl monomers, by Okamoto and Nakano et al.[60,335] A significant increase in the syndiotacticity was first observed for the radical polymerization of vinyl esters.[336,337] While the stereochemistry of the vinyl acetate (VAc) polymerization in acetic acid or methanol was almost the same as that of bulk polymerization, the polymerization in protic fluoroalcohols, such as CF_3CH_2OH (SS-**2**), $(CF_3)_2C(CH_3)OH$ (SS-**3**), $(CF_3)_2CHOH$ (SS-**4**), and $(CF_3)_3COH$ (SS-**5**), resulted in a higher syndiotacticity of the products (Table 4). Among them, SS-**5** was the most effective in enhancing the syndiotactic specificity, and a polymer with a diad *r* of over 70% was obtained when the polymerization took place at −78 °C (*mm*/*mr*/*rr* = 5/45/50). The obtained poly(VAc) was subsequently hydrolyzed into syndiotactic poly(vinyl alcohol), which had a higher melting point (T_m = 269 °C) than the atactic one (225 °C).

Table 4. Stereospecific Radical Polymerization in Fluoroalcohols

			triad tacticity, %			diad tacticity, %		
monomer	solvent or additive	temp, °C	*mm*	*mr*	*rr*	*m*	*r*	ref
VAc	bulk	20	23	49	28	47	53	336, 337
VAc	CH_3OH	20	22	50	28	47	53	336, 337
VAc	CF_3CH_2OH (SS-**2**)	20	20	50	30	45	55	336, 337
VAc	$(CF_3)_2C(CH_3)OH$ (SS-**3**)	20	18	50	32	43	57	336, 337
VAc	$(CF_3)_2CHOH$ (SS-**4**)	20	17	50	33	42	58	336, 337
VAc	$(CF_3)_3COH$ (SS-**5**)	20	13	49	38	38	62	336, 337
VAc	$(CF_3)_3COH$ (SS-**5**)	−78	5	45	50	27	73	336, 337
BM-**42**	bulk	−40	11	48	41	35	65	336, 338
BM-**42**	$(CF_3)_3COH$ (SS-**5**)	−40	21	61	18	51	49	336, 338
BM-**44**	$(CF_3)_2CHOH$ (SS-**4**)	0	33	51	16	59	41	338
NVP	bulk	20	31	29	39	46	54	343
NVP	$(CF_3)_3COH$ (SS-**5**)	−40	19	37	44	37	63	343
NVA	$(CF_3)_2CHOH^a$ (SS-**4**)	−40	25	58	17	54	46	344
MAA	bulk	60	9	46	45	32	68	332
MAA	$(CH_3)_2CHOH$	−78	0	5	95	2	98	332
MAA	2-methylcyclohexanol (SS-**1**)	0	0	18	82	9	91	333
MMA	CH_3OH	20	3	32	66	19	81	345, 346
MMA	$(CF_3)_3COH$ (SS-**5**)	20	1	24	75	13	87	345, 346
MMA	$(CF_3)_3COH$ (SS-**5**)	−98	0	7	93	3	97	345, 346
MMA	$(C_6H_5)C(CF_3)_2OH$ (SS-**6**)	20	1	25	74	13	87	345, 346
MMA	*o*-$C_6H_4[C(CF_3)_2OH]_2$ (SS-**7**)	20	1	22	77	12	88	345, 346
EMA	$(CF_3)_2CHOH$ (SS-**4**)	−40	2	11	87	8	92	345, 346
BM-**3**	toluene	−40	3	23	74	15	85	346
BM-**3**	$(CF_3)_2CHOH$ (SS-**4**)	−40	1	28	71	15	85	346
HEMA	CH_3OH	60	3	34	63	20	80	347
HEMA	$(C_6H_5)C(CF_3)_2OH$ (SS-**6**)	80	7	41	52	28	72	347
HEMA	DMF	0	<1	23	77	12	88	347
MMAM	$(CF_3)_2CHOH$ (SS-**4**)	−78	0	5	95	2	98	349
DMAM	bulk	0				50	50	350
DMAM	$(CF_3)_3COH$ (SS-**5**)	0				63	37	350
DMAM	toluene	−78				77	23	350
NIPAM	toluene	−40	28	53	19	54	46	351
NIPAM	$(CF_3)_3COH^a$ (SS-**5**)	−40	14	75	11	51	49	351, 353
NIPAM	HMPA^a (SS-**9**)	−60				28	72	356−358

[a] Solvent mixture (30−40 vol %) with toluene.

Interestingly, the fluoroalcohol induced a rather heterotactic specificity during the polymerization of slightly bulkier vinyl esters like vinyl pivalate (BM-**42**), propionate, isobutylate, 2,2-dimethylbutylate, or 2,2-dimethylvalerate.[336,338−340] The radical polymerization of BM-**42** in SS-**5** afforded heterotactic-rich polymers at −40 °C (*mm*/*mr*/*rr* = 21/61/18), of which the propagation preferred to alternate between the meso and racemo additions. Furthermore, the polymerization of vinyl benzoate (BM-**44**) in fluoroalcohols gave polymers with a higher isotacticity (*mm*/*mr*/*rr* = 33/51/16) than that in bulk (*mm*/*mr*/*rr* = 27/51/22). On the other hand, its fluorinated derivative (BM-**60**) was polymerized into syndiotactic polymers in SS-**4** at −30 °C (*mm*/*mr*/*rr* = 7/41/52).[284] Whereas the stereochemistry of the VAc polymerization was well-described by a first-order Markov model, the BM-**42** polymerization could be fitted to neither first-order nor second-order models.

The stoichiometry of the interactions between the fluoroalcohol and vinyl ester was evaluated by Job's method by varying the concentration of these components, suggesting that a 1:1 complex is formed.[336] The equilibrium constants for the association were also evaluated to be between 10^0 and 10^1 orders of magnitude, which is consistent with the usual hydrogen bond of protic compounds. Therefore, the stereospecificity of the polymerizations of vinyl esters would be triggered by the hydrogen-bonding interaction between the fluoroalcohol molecules and the ester groups of the monomer and/or the growing species and also by steric repulsion between these apparently bulky side groups depending on the monomer structures (Figure 21). The fluoroalcohol also affected the monomer reactivity ratio in the copolymerization of vinyl esters, as well as the stereospecificity, supporting the steric and monomer activating effects via hydrogen bonding.

Similar to the vinyl esters, vinyl amides, such as *N*-vinylpyrrolidone (NVP) and *N*-vinylacetamide (NVA), are the representatives of the unconjugated monomers that can be polymerized into high molecular weight polymers only by a radical mechanism.[341,342] It was also reported that the acidic and bulky fluoroalcohol SS-**5** led to a higher syndiotacticity at 20 °C (*mm*/*mr*/*rr* = 23/37/40) in the NVP polymerization, while conventional radical polymerization almost led to atactic polymers (*mm*/*mr*/*rr* = 31/30/39).[343] For the NVA polymerization, in contrast, heterotactic-rich polymers were obtained in SS-**4** at −40 °C, whereas another additive of tri-*n*-butyl phosphate increased the syndiotacticity from 25% to 34%.[344]

The fluoroalcohol-mediated stereospecific radical polymerizations were applied to the other methacrylic monomers.[345,346] Methyl (MMA), ethyl (EMA), isopropyl (BM-**1**), and *tert*-butyl methacrylate (BM-**3**) were polymerized in a series of fluorinated alcohols. The effects of the fluoroalcohols to enhance the syndiotactic specificity were observed during the polymerization of MMA and EMA, although the solvents with a bulkier pendent group (BM-**1** and BM-**3**) had negligible effects. The MMA polymerization in SS-**5** at −98 °C achieved the highest syndiotacticity among the radical polymerizations of MMA (*mm*/*mr*/*rr* = 0/7/93). It was also found that the syndiotactic specificity and polymer yield in the MMA polymerization increased even in the presence of

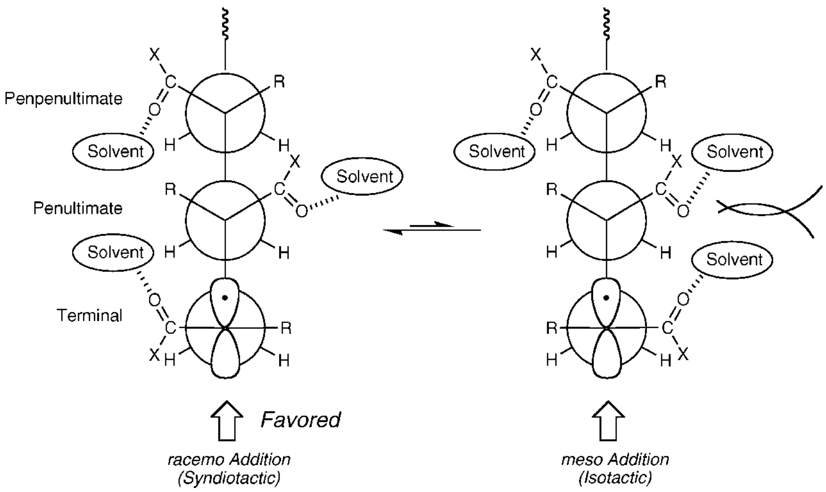


Figure 21. Schematic models for solvent-mediated stereospecific radical polymerization.

catalytic amounts of the fluoroalcohol. In contrast, the hydroxy-functionalized 2-hydroxyethyl methacrylate (HEMA) afforded less syndiotactic polymers in $(C_6H_5)C(CF_3)_2OH$ (SS-**6**).[347] However, an aprotic amide solvent, such as *N*,*N*-dimethylformamide (DMF) and DMA, effectively induced the syndiospecific radical polymerization via the characteristic hydrogen-bonding interaction between the hydroxyl group in the monomer and the aprotic solvent.

For the polymerization of (meth)acrylamides, the effects of the solvent were also examined for stereospecificity induction. In the radical polymerization of methacrylamides, such as *N*-methylmethacrylamide (MMAM), syndiotactic-rich polymers were generated under various conditions inherent to the α-methyl group and similar to the methacrylate polymerization.[348] Among them, SS-**4** also had the highest effect on the syndiospecificity to form highly syndiotactic poly(MMAM) at −78 °C (*mm*/*mr*/*rr* = 0/5/95).[349] The highly syndiotactic polymer exhibited a clear melting point, which indicates a change in the morphology from amorphous to crystalline due to the stereoregularity.

The polymerization of *N*,*N*-disubstituted acrylamides like *N*,*N*-dimethylacrylamide (DMAM) and *N*,*N*-dephenylacrylamide (BM-**40**) were carried out under various conditions. It was revealed that DMAM gives an isotactic-rich polymer in most cases, whereas BM-**40** produced a syndiotactic polymer. Although the fluoroalcohols also worked for these polymerizations, other solvents were more effective: poly(DMAM) with diad isotacticity (*m*) of 77% was obtained in toluene at −78 °C and poly(BM-**40**) with a diad syndiotacticity (*r*) of 93% was obtained in THF at −98 °C at a low monomer concentration. The obtained syndiotactic polymer could also be converted into poly(MA).[350]

The specific interaction of the fluoroalcohol was used for the radical polymerization of *N*-substituted acrylamide, such as *N*-isopropylacrylamide (NIPAM) and *N*-*tert*-butoxycarbonylacrylamide (BocAM), which are functional monomers for thermo-responsive polymers and protected poly(acrylamide)s, respectively.[351−353] Heterotactic specificity was also observed during the polymerization of NIPAM in the fluoroalcohol similar to those of BM-**42** and NVA. NIPAM was polymerized in the presence of a large amount of SS-**5** at −40 °C to afford polymers with a slightly higher syndiotacticity of the diad sequence (*m*/*r* = 42/58) than that in the absence of SS-**5** (*m*/*r* = 46/54), in which the tacticity was determined by ^{1}H NMR. Detailed analyses by ^{13}C NMR, however, showed that the polymer obtained with the fluoroalcohol had a higher heterotactic sequence (*mm*/*mr*/*rr* = 14/75/11), while an almost atactic polymer was produced in its absence (*mm*/*mr*/*rr* = 28/53/19).[351,353] On the other hand, BocAM was polymerized in SS-**5** and SS-**4** at −40 °C into syndiotactic- (*mm*/*mr*/*rr* = 11/44/45) and heterotactic-rich polymers (*mm*/*mr*/*rr* = 16/63/21), respectively. These polymers were successfully converted to poly(acrylamide) by the subsequent deprotection of the Boc group.[352] For the NIPAM polymerization, it was reported that not only the fluorinated alcohol but also simple aliphatic alcohols induce the stereospecific radical polymerization. The syndiotactic specificity was induced by adding simple alkyl alcohols, such as 3-methyl-3-pentanol (SS-**8**), in toluene/methylcyclohexane mixture at −60 °C (*m*/*r* = 27/73). In this system, it was proposed that the alcohol compound coordinates both to the N−H proton and to the C=O oxygen, where the former works to induce the syndiotactic specificity and the latter to accelerate the polymerization reaction.[354,355]

In contrast to the hydrogen-bonding interaction of the carbonyl group in the vinyl ester or methacrylate with acidic fluoroalcohols, the hydrogen atom in the acrylamide molecules could also form a hydrogen bond with Lewis bases. A variety of systems for the stereospecific radical polymerization of NIPAM have been reported in which the tacticity of the producing polymers was controlled by Lewis bases as solvents or additives. Upon addition of hexamethylphosphoramide (HMPA, SS-**9**), the syndiotacticity of the resultant poly(NIPAM) increased with the concentration of SS-**9**, and higher syndiotactic polymers were obtained in toluene at −60 °C with the ratio of $[\text{SS-}\mathbf{9}]_0/[\text{NIPAM}]_0 = 5$ (*m*/*r* = 28/72).[356−358] SS-**9** and the above-mentioned SS-**8** were also used for a series of polymerizations of *N*-alkylacrylamides, such as *N*-methyl-, *N*-*n*-propyl-, *N*-benzyl-, and *N*-(1-phenylethyl)acrylamide.[359] Although the racemo contents of the produced polymers gradually increased with the bulkiness of the N-substituents without the additives, SS-**9** induced higher syndiotactic specificities for all the monomers than those in the alcohol. Various additives, such as alkylphosphates (SS-**10**) and pyridine *N*-oxides, were also employed for the radical polymerization of NIPAM, though their effect on the stereospecificity was lower than that of SS-**8** and SS-**9**.[360−364] Among them, it is interesting that the isotactic polymers were obtained upon the addition of tri-*n*-butyl phosphate (SS-**10**; R = *n*Bu) at −80 °C (*m*/*r* = 57/43)[360] or pyridine *N*-oxide especially derived from 3,5-dimethylpyridine (SS-**11**) at −60 °C (*m*/*r* = 68/32).[363,364]

Host−guest interaction offers the opportunity of polymerization in an unusual solvent. Due to the polar hydrophilic outer shell and relatively hydrophobic cavity of cyclodextrins (H-**10** in Figure 8), they are able to build host−guest complexes by the inclusion of suitable hydrophobic monomers. It also turned out that the complexed hydrophobic monomers can be successfully polymerized as apparent hydrophilic forms via free radicals even in homogeneous aqueous media.[365] An enantiomer selective polymerization of menthyl methacrylate was implied in the presence of β-CD in water to produce an optically active polymer.[366] In aqueous media, AN was polymerized into slightly higher isotactic polymers in the presence of β-CD (*mm*/*mr*/*rr* = 32/49/19) than in the absence (*mm*/*mr*/*rr* = 16/48/36).[367] Styrene complexes with β-CD were also polymerized in water to afford somewhat syndiotactic polymers, which is a different tendency from the polymers obtained in the solid-state inclusion polymerization (see section 3.1.2).[368]

The liquid crystalline state derived from solvents could provide a confined or organized mesophase media with anisotropic diffusion to the polymerization system and may produce a specific preorientation of the monomers.[314] The effects of the mesophase on tacticity were first investigated for the polymerization of 4-carboxyphenyl methacrylate in the nematic and smectic phases using the lattice of *p*-(heptyloxy)benzoic acid (SS-**12**) and *p*-(cetyloxy)benzoic acid (SS-**13**), respectively.[369] In both cases, the increases in isotacticity were observed during the early stage of the polymerization, while the tacticity values of the producing polymers became close to that obtained in the isotropic solution as the polymerization proceeded. Various alkyl methacrylates were also polymerized in liquid crystalline solvents with nematic, smectic, and cholesteric phases using *N*-(4-methoxyphenylmethylene)phenylamine (SS-**14**), *N*-(4-ethoxyphenylmethylene)-4- butylphenylamine (SS-**15**), and cholesteryl octadecanoate (SS-**16**).[370] While no significant effects were observed for the MMA polymerization, methacrylates with aliphatic alkyl chains underwent slightly isotactic specific polymerizations in the mesomorphic phase, in which the polymers formed in the smectic and nematic phases had a higher isotacticity than those in the cholesteric one. For example, *n*-octyl methacrylate produced polymers with the highest meso contents in the smectic phase of SS-**16** (*mm*/*mr*/*rr* = 31/29/40). There were also several reports on MMA polymerization in other liquid crystalline solvents.[371,372] In the cholesteric phase of cholesteryl caprylate (SS-**17**), the polymerization afforded a slightly lower syndiotactic poly(MMA) (*mm* = 12.9%).

3.3.2. Lewis Acid-Mediated Stereospecific Polymerization

Lewis acids of certain metal salts can coordinate to the carbonyl groups in polar monomers, sometimes forming a complex via a coordinative bond to change the reactivity of the monomers.[373−376] In 1957, Bamford et al. first reported that LiCl accelerates the polymerization of AN.[377] They pointed out that the interaction of the lithium cation with a pendent nitrile group resulted in increased polymerization rate and molecular weight of the produced polymer. Furthermore, it is also well-known that such complexation between a Lewis acid and a polar conjugated vinyl monomer sometimes leads to an alternating cross-propagation in the copolymerization.[375,378]

As for the tacticity control, Lewis acids have also proved effective additives for stereospecific radical polymerization. In the early studies, it had been reported that the effect on the stereochemistry by adding a small amount of zinc chloride ($ZnCl_2$) was negligible for the radical polymerization of MMA, while the addition dramatically accelerated the polymerization.[379] From the 1960s, however, the effects of a large amount of $ZnCl_2$ on the stereoregularity of the radical polymerization of MMA were studied under various conditions.[380−382] For examples, Otsu et al. reported that the polymerization of MMA in 70% $ZnCl_2$ at 100 °C, in which the concentration of $ZnCl_2$ was much higher than that of the monomer ($[MMA]_0/[ZnCl_2]_0 = 1.10/9.60$ M), gave a lower syndiotactic poly(MMA) (*mm*/*mr*/*rr* = 15/42/43).[380] The poly(MMA) obtained from the viscous 1:1 complex of the monomer and $ZnCl_2$ also had a slightly higher isotacticity (*mm*/*mr*/*rr* = 13/39/48) than that in the absence of the Lewis acid (*mm*/*mr*/*rr* = 5/37/58).[381] All the triad sequences of poly(MMA) produced in these systems were fairly close to the calculated values, assuming that the stereochemistry of the polymerizations roughly obeys the Bernoullian statistics and, in a more precise sense, the first-order Markovian.

Matsumoto et al. also employed magnesium bromide ($MgBr_2$) as an additive for the radical polymerization of MMA.[383] With $MgBr_2$, the polymerization also produced a slightly lower syndiotactic poly(MMA) (*rr* = 55−65%). Furthermore, greater effects of the Lewis acid on the tacticity were observed on the solid surface of the magnesium bromide that was partly insoluble in the polymerization system (*mm*/*mr*/*rr* = 8/39/53). They suggested a postulated mechanism for the stereospecific propagation during radical polymerization, in which the meso propagation would be preferred by a bidentate chelation of the Lewis acid and pendent groups, whereas a monodentate interaction would lead to a racemo addition due to the steric repulsion (Figure 22).

Many further improvements of the Lewis acid-mediated selectivity in tacticity of the radically produced polymers were achieved with rare earth metal triflates [$Mt(OTf)_3$; Mt = Y, Sc, Yb, etc.; OTf = OSO_2CF_3]. Okamoto and Habaue et al. reported that with $Mt(OTf)_3$, which might strongly interact with the pendent groups of the polymer terminus or the monomer, the catalytic stereospecific radical polymerizations of methacrylates and (meth)acrylamides prevailed in an isospecific manner (Table 5).[60,384,385] These are known as unique Lewis acids characterized by strong Lewis acidity, large ionic radii of the central metal, high coordination numbers, and tolerance toward protic solvents and water.[386] These characteristics must have allowed the stereospecific polymerization most likely via a “multiple” coordination, though the detailed mechanism had not yet been clarified.

The first discovery of the $Mt(OTf)_3$-mediated stereospecific radical polymerization was reported for the radical polymerization of α-(alkoxymethyl)acrylate (BM-**49**) with $Sc(OTf)_3$.[387] In the presence of $Sc(OTf)_3$, the tangled coordination of the Lewis acid with both the pendent carbonyl and alkoxyl groups would produce isospecific propagation (*mm*/*mr*/*rr* = 50/38/12) whereas almost only atactic polymers were obtained in the absence of the Lewis acid (*mm*/*mr*/*rr* = 30/48/22). More interestingly, during the polymerization of α-(alkoxymethyl)acrylate, another Lewis acid, such as $ZnBr_2$, induced the opposite tendency in the stereospecificity to give syndiotactic polymers (*mm*/*mr*/*rr* = 9/40/51).[388,389] In addition, a possible heterotacticity was obtained upon the addition of an amino alcohol (2-aminoethanol) as a ligand to $ZnBr_2$ (*mm*/*mr*/*rr* = 21/57/22), of

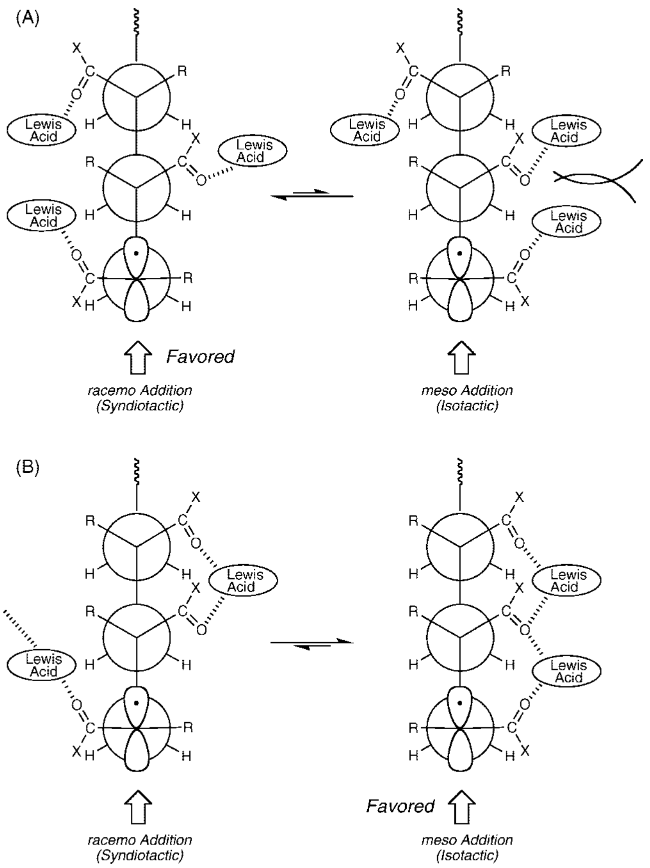


Figure 22. Schematic models for Lewis acid-mediated stereospecific radical polymerization.

which the propagation alternatingly took place between the meso and racemo additions.[390] Mt(OTf)$_3$ was also used for the polymerization of another α-substituted acrylate of di-*n*-butyl itaconate (DBI) that resulted in a slight effect on the stereospecificity but suppression of the intramolecular transfer reaction.[391]

For the methacrylate polymerization, Sc(OTf)$_3$ was the most effective among the various rare earth triflates and the syndiotacticity of the resultant poly(MMA) decreased with the concentration of Sc(OTf)$_3$, and almost only the atactic poly(MMA) could be obtained even by a radical polymerization (*mm*/*mr*/*rr* = 22/47/31).[392] In this case, only catalytic amounts of Sc(OTf)$_3$ were required to induce the stereospecificity. On the basis of an NMR analysis, the interaction of the Lewis acid with MMA proved stronger than that with the produced poly(MMA) chain. Thus, the Lewis acid most probably forms a complex with one or more monomers to accelerate the propagation, and then the Lewis acid would be released from the polymer chain to form a complex with another monomer again in order to achieve the stereoeffects with catalytic amounts of Sc(OTf)$_3$.

As for the radical polymerization of acrylamides and methacrylamides, much greater effects of Mt(OTf)$_3$ were obtained, in which a small catalytic amount of the Lewis acid also resulted in tacticity control as high as that obtained in ionic and coordinating polymerizations.[384,385,393] This is probably because the Lewis acids would more tightly interact with the amide groups in the monomers than that of the carboxyl ester version. For the radical polymerization of unsubstituted or *N*-alkyl acrylamides, a highly isospecific radical polymerization proceeded with various Mt(OTf)$_3$, especially in protic solvents, such as methanol and water, though the isospecificity of the produced polymers also depended on the central metals of the Lewis acid, solvents, and polymerization temperatures.

In the polymerization of the unsubstituted acrylamide (AM) or *N*,*N*-dimethyl acrylamide (DMAM), Yb(OTf)$_3$ formed the highest meso contents at 0 °C in methanol (*m*/*r* = 80/20 and 88/12 for AM and DMAM, respectively).[393,394] In contrast, for the radical polymerization of NIPAM, Y(OTf)$_3$ and Lu(OTf)$_3$ are the most effective triflates for the production of highly isotactic polymers in methanol at −20 °C (*m*/*r* = 92/8).

Among the various acrylamides, NIPAM has attracted much attention in the biomedical field because the aqueous solution of its polymer and the hydrogel have a thermoresponsive ability with a coil-to-globule transition around body temperature. The lower critical solution temperature (LCST) of poly(NIPAM) critically depended on the tacticity, in which the transition temperature decreased as the isotacticity of the chain increased, and polymers with an isotacticity higher than 70% are insoluble in water.[395] Along with the above-mentioned solvent- or additive-mediated stereospecific radical polymerizations, a series of poly(*N*-alkylacrylamide)s with different tacticities are now available, that is, from syndiotactic to isotactic (*m* = 27−92%) and heterotactic (*mr* = 75%). Their transition behaviors are just beginning to be studied.[353,396−399]

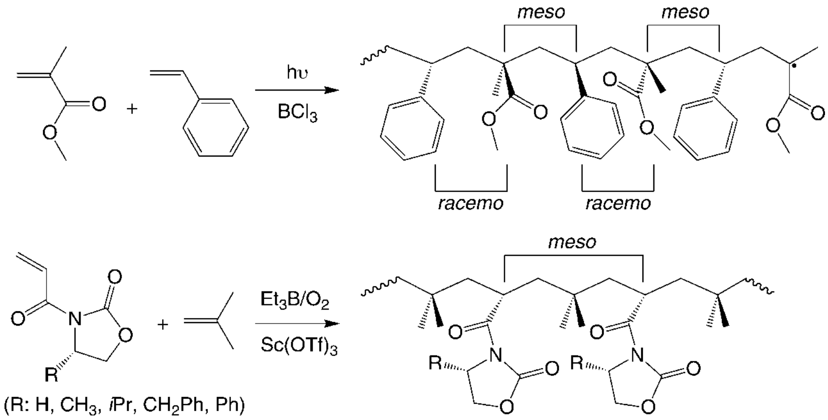
In the presence of Mt(OTf)$_3$, methacrylamides were also polymerized into isotactic-rich polymers despite the fact that they generally tend to generate rather syndiotactic polymers in its absence due to the α-methyl group as in the methacrylate polymerization.[394,400,401] A series of methacrylamides were examined for the stereocontrol by Mt(OTf)$_3$, including unsubstituted methacrylamide (MAM), *N*-methylmethacrylamide (MMAM), *N*-isopropylmethacrylamide (IPMAM), *N*-*tert*-butylmethacrylamide, and *N*-phenylmethacrylamide. For example, IPMAM produced polymers with high meso contents in the presence of Yb(OTf)$_3$ in methanol at −20 °C (*mm*/*mr*/*rr* = 67/29/4), whereas syndiotactic polymers were obtained in the absence of the Lewis acid (*mm*/*mr*/*rr* = ∼0/20/80). The LCST behavior of poly(IPMAM) was also investigated and showed variable transition temperatures depending on the tacticity from ca. 40 °C (syndiotactic, *rr* = 80%) to 30 °C (isotactic, *mm* = 67%).[400] The stereospecific radical polymerization was further applied for the optically active methacrylamides bearing a bulky chiral auxiliary under various conditions using Yb(OTf)$_3$ and Y(OTf)$_3$.[402,403] The tacticity influenced the intramolecular hydrogen bond formation, the higher order structure, and the chiral recognition ability, which would show a different ability as the chiral stationary phase for HPLC resolution of the various racemates upon subsequent immobilization on silica gel.

Similar effects of Lewis acids for enhancing the isospecificity was reported for the radical polymerization of acrylonitrile and VAc with fairly large amounts of Mg or Co halides, in which the Lewis acids form almost 1:1 complexes with the monomers.[404,405] Under such conditions, the monomer−Lewis acid complex somewhat forms a confined medium of geometrically regulated space created by monomer/host molecular complexes in a heterogeneous slurry condition. The poly(acrylonitrile) and poly(VAc) obtained with MgCl$_2$ or MgBr$_2$ were highly isotactic (*mm*/*mr*/*rr* = 67/25/8 and 65/27/8, respectively). In contrast, a slight effect of the Lewis acids upon the radical solution polymerization of vinyl

Table 5. Lewis Acid-Mediated Stereospecific Radical Polymerization of Acrylic Monomers [$CH_2{=}C(R^1)CO(R^2)$]

							triad tacticity, %			diad, %		
monomer	R^1	R^2	Lewis acid	$[\text{Lewis acid}]_0/[\text{monomer}]_0$	temp, °C	solvent	*mm*	*mr*	*rr*	*m*	*r*	ref
MMA	$-CH_3$	$-OCH_3$	None		60	toluene	3	34	63	20	80	392
MMA	$-CH_3$	$-OCH_3$	$MgBr_2$	0.05	80	benzene	8	41	51	29	71	383
MMA	$-CH_3$	$-OCH_3$	$Sc(OTf)_3$	0.20	60	toluene	14	46	40	37	63	392
MMA	$-CH_3$	$-OCH_3$	$Sc(OTf)_3$	0.375	60	toluene	21	48	31	45	55	392
BM-**49**	$-CH_2OCH_3$	$-OCH_2Ph$	None		30	CH_2Cl_2	30	48	22	54	46	387
BM-**49**	$-CH_2OCH_3$	$-OCH_2Ph$	$Sc(OTf)_3$	0.12	30	CH_2Cl_2	50	38	12	69	31	387
BM-**49**	$-CH_2OCH_3$	$-OCH_2Ph$	$ZnBr_2$	0.10	30	CH_2Cl_2	9	40	51	29	71	388, 389
BM-**49**	$-CH_2OCH_3$	$-OCH_2Ph$	$ZnBr_2$/ligand [a]	0.10	30	CH_2Cl_2	21	57	22	50	50	390
AM	H	$-NH_2$	None		0	CH_3OH	22	49	29	46	54	393, 394
AM	H	$-NH_2$	$Sc(OTf)_3$	0.10	0	CH_3OH	40	43	17	62	38	393, 394
AM	H	$-NH_2$	$Yb(OTf)_3$	0.10	0	CH_3OH	65	29	6	80	20	393, 394
DMAM	H	$-N(CH_3)_2$	None		0	CH_3OH				49	51	393, 394
DMAM	H	$-N(CH_3)_2$	$Yb(OTf)_3$	0.10	0	CH_3OH				88	12	393, 394
DMAM	H	$-N(CH_3)_2$	$Lu(OTf)_3$	0.10	0	CH_3OH				85	15	393, 394
NIPAM	H	$-NH\textit{i}Pr$	None		60	$CHCl_3$				45	55	393, 394
NIPAM	H	$-NH\textit{i}Pr$	$Y(OTf)_3$	0.08	60	$CHCl_3$				62	38	393, 394
NIPAM	H	$-NH\textit{i}Pr$	None		60	CH_3OH				45	55	393, 394
NIPAM	H	$-NH\textit{i}Pr$	$Sc(OTf)_3$	0.08	60	CH_3OH				62	38	393, 394
NIPAM	H	$-NH\textit{i}Pr$	$Y(OTf)_3$	0.08	60	CH_3OH				80	20	393, 394
NIPAM	H	$-NH\textit{i}Pr$	$Yb(OTf)_3$	0.08	60	CH_3OH				82	18	393, 394
NIPAM	H	$-NH\textit{i}Pr$	$Lu(OTf)_3$	0.08	60	CH_3OH				84	16	393, 394
NIPAM	H	$-NH\textit{i}Pr$	$Y(OTf)_3$	0.21	−20	CH_3OH				92	8	393, 394
MMAM	$-CH_3$	$-NHCH_3$	None		60	CH_3OH	2	29	69	16	84	400, 401
MMAM	$-CH_3$	$-NHCH_3$	$Yb(OTf)_3$	0.10	60	CH_3OH	46	44	10	68	32	400, 401
IPMAM	$-CH_3$	$-NH\textit{i}Pr$	None		60	CH_3OH	1	31	68	16	84	400, 401
IPMAM	$-CH_3$	$-NH\textit{i}Pr$	$Yb(OTf)_3$	0.10	60	CH_3OH	63	33	4	80	20	400, 401
IPMAM	$-CH_3$	$-NH\textit{i}Pr$	$Yb(OTf)_3$	0.10	−20	CH_3OH	67	29	4	82	18	400, 401

[a] Ligand, 2-aminoethanol.



CM-**17**

Figure 23. Stereospecific alternating copolymerization with Lewis acids.

esters was reported. The relatively weak Lewis acid of Al(O*t*Bu)$_3$ was most effective for the syndiotactic polymerization of vinyl acetate (*mm*/*mr*/*rr* = 17/47/36) and vinyl pivalate (*mm*/*mr*/*rr* = 14/48/38).[406]

As for the copolymerization, in which a complexation between Lewis acids and conjugated monomers gives an alternating fashion, the Lewis acid could also play a role in controlling the stereospecificity (Figure 23).[407] During the copolymerization of styrene and MMA, $ZnCl_2$ afforded alternating but almost atactic copolymers, in which the triad cotacticities determined by NMR showed *mm*/*mr*/*rr* = 29/44/27 for the MMA center.[408,409] In contrast, alternating copolymers with a high coheterotacticity were obtained with excess amounts of BCl_3 at −95 °C, of which the cotacticities were *mm*/*mr*/*rr* = 1/89/10 and 4/85/11 for the MMA- and styrene-centered triads, respectively.[410] For this polymerization, a ternary molecular complex of the three components consisting of two monomers and one Lewis acid was proposed, in which the syndiotactic addition took place from the styrene unit to MMA, and the MMA unit favored isotactic addition to the styrene.[409,411] *N*-Acryloyl imides bearing bulky and chiral oxazolidinone auxiliaries were copolymerized with isobutene in the presence of Lewis acids to form an alternating copolymer. Among the various Lewis acids, $Sc(OTf)_3$ led to highly isotactic alternating copolymers of the phenyl or benzyl oxazolidinone acrylamide and isobutene at −40 °C (*m*/*r* = 95/5).[288,412]

3.3.3. Ionic Bonding or Interaction

A strong ionic bonding interaction can form an ionic pair of a monomer and its counterions to change the reactivity and apparent bulkiness of the original acidic or basic monomer. There have also been reports on the stereospecific radical polymerizations of the monomer salts (Figure 24). Especially, the polymerization of MAA has been extensively studied in its form of organic onium salts or metal salts, as well as the template polymerization as already described.

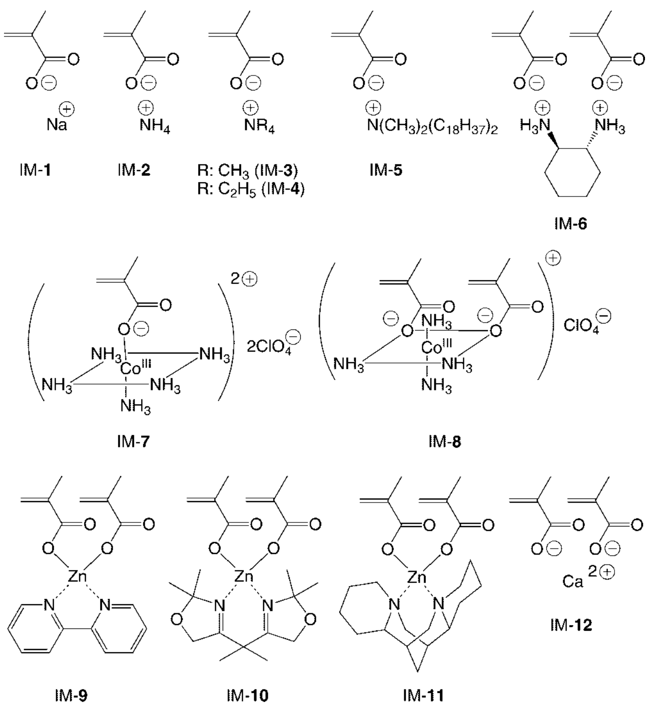


Figure 24. Ionic monomers for stereospecific radical polymerization.

Bovey first found that during the polymerization of MAA, syndiotactic propagation is favored at a higher pH with the sodium cation (IM-**1**), presumably because Coulombic repulsion between the negatively charged monomer and negatively charged growing polymer radicals increases the free energy of activation for the isotactic monomer placement.[413] In 1972, Kabanov et al. polymerized MAA in the presence of various neutralizing agents or metal salts in aqueous solution in the pH range of 2−12 and pointed out that the nature of the countercation affects the stereochemistry and kinetics due to the ion pairs formed between the ionized terminal units of the growing ends and cations.[414,415] With H_4N^+ as the countercation at pH = 8.8 (IM-**2**), a highly syndiotactic poly(MAA) was obtained at 60 °C (*rr* = 82−84%).

Tetraalkylammonium salts of MAA (IM-**3** and IM-**4**) were also examined for the syndiospecific radical polymerization in water. Both these monomers were polymerized with potassium persulfate in water at 60 °C to afford polymers with a relatively high syndiotacticity (*mm*/*mr*/*rr* = 5/15/80). Furthermore, tetraethylammonium methacrylate (IM-**4**) gave a highly syndiotactic polymer even at 5 °C (*mm*/*mr*/*rr* = 0.3/7.7/92).[416] As the alkyl chain in the ammonium becomes longer, the solubility of the monomer in water decreases to form micelles or vesicles, which would be a kind of confined media as described in section 3.1. Dioctadecyldimethylammonium methacrylate (IM-**5**) forms vesicles in water under ultrasonication, which were directly polymerized into predominantly syndiotactic polymers (*mm*/*mr*/*rr* = 2/22/76 at 30 °C).[417] MAA forms a 2:1 salt or complex with divalent amines and was polymerized in the presence of various amine compounds including 1,2-diaminocyclohexane (IM-**6**).[117] Contrary to the above-mentioned results in enhancing the syndiotacticity, the IM-**6** with diamine provided an increase in the isotactic specificity in $CHCl_3$ at 60 °C (*mm*/*mr*/*rr* = 16/49/35), which is similar to the template polymerization of MAA in the presence of chitosan.[198]

Metal salts or complexes of MAA were also examined for stereospecific polymerization. Cobalt(III) complexes of methacrylatopentaammine (IM-**7**) and *cis*-dimethacrylatotetraammine (IM-**8**) with the perchlorate anion were polymerized at pH 3 or 7 in the presence of a redox initiator system at 30 °C in water to induce an increase in isotactic specificity (*mm*/*mr*/*rr* = 23/38/39 for the former).[418] Coupled with various bidentate nitrogen ligands (IM-**9** to IM-**11**), divalent zinc(II) salts of MAA were also employed for the homopolymerization and copolymerization with MAA. Among them, the zinc dimethacrylate with 2,2′-isopropylidenebis(4,4-dimethyl-2-oxazoline) (IM-**10**) or (−)-sparteine (IM-**11**) afforded polymers with a somewhat specific feature, whereas that with 2,2′-bipyridine (IM-**9**) showed no significant effects.[419] The zinc dimethacrylate with (−)-sparteine (IM-**11**) was also employed for the copolymerization with various common monomers to give copolymers with an optical activity similar to the copolymerization of chiral divinyl compounds.[420] Recently, it was reported that the divalent calcium(II) salt of MAA (IM-**12**) could be polymerized into isotactic-rich polymers by the judicious choice of solvents.[421] The polymerization of IM-**12** was performed in a toluene/DMF mixture at 60 °C to afford polymers with a high isotacticity (*mm*/*mr*/*rr* = 65/29/6), which is consistent with the fact that the steric configuration of the polyanion from isotactic poly(MAA) is more favorable during the chelation with divalent cations than that from the syndiotactic one.[422]

3.3.4. Multiple Hydrogen Bonding Interactions

Multiple hydrogen bonding plays crucial roles in forming well-designed natural molecules and also in determining the secondary and tertiary structures of natural macromolecules. The interaction of the multiple hydrogen bonds would be much greater than those of the aforementioned specific solvents or additives such as bulky fluoroalcohols, which can form a single hydrogen bond with the polar substituents in the monomer units. For template polymerization, a number of hydrogen bonding sites were put on the template polymer chains to induce a stereospecificity, while some special polymerization conditions are required for high stereospecificity (in section 3.1).

An efficient stereospecific radical polymerization is mediated by the multiple hydrogen-bonding interactions of a low molecular weight mediator for well-designed acrylamide with an array composed of a DAD sequence (MH-**1**), where D and A denote the proton donor and acceptor sites, respectively (Figure 25).[423] Upon the addition of a cyclic imide as a mediator with the complementary ADA sequence (MH-**2** and MH-**3**), the syndiotacticity increased from *r* = 43% to 72% even at 60 °C in $CHCl_3$. The effective induction can be ascribed to the strong association constant ($K \approx 6 \times 10^2$) via the triple hydrogen bonding, which is about 10^2 times greater than those of the solvents and about 10^1 times greater than those of Lewis acids.

Recently, it was found that a divalent alcohol of diethyl tartrate (MH-**4**) induces a higher syndiotacticity in the radical polymerization of DMAM.[424,425] In the presence of the titrate and at a low monomer concentration (0.1 mol/L), poly(DMAM) with *r* = 69% was obtained in toluene at −60 °C. Interestingly, the syndiotacticity of the obtained polymer depended on the enantiomeric excess of the titrate; the racemic titrate gave a lower syndiotactic specificity than the corresponding D- or L-enantiomer. The NMR analysis suggested that a DMAM monomer and a tartrate formed a 1:1 complex through double hydrogen bonding, although the interactions at the growing chain ends were still unclear.

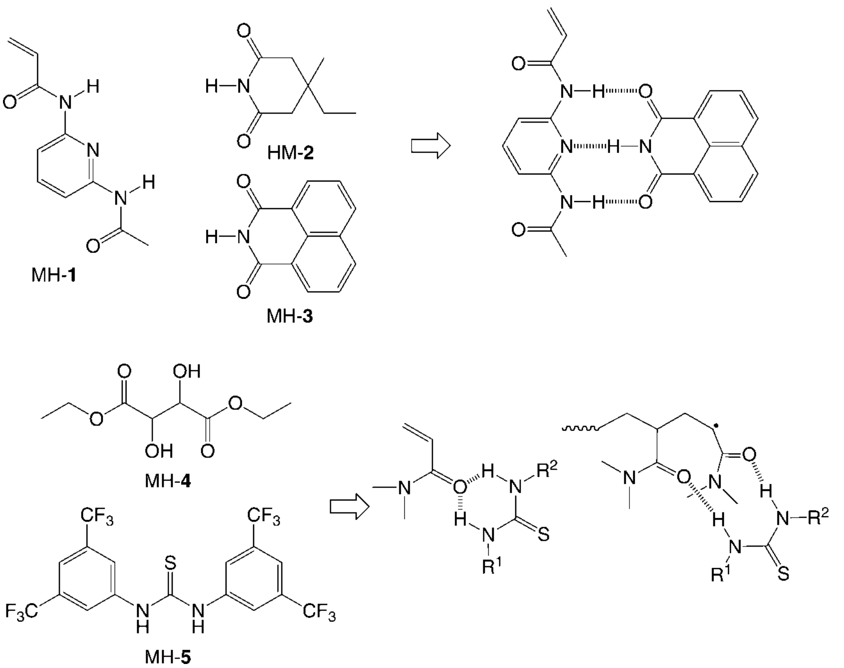


Figure 25. Multiple hydrogen-bonding interactions for stereospecific radical polymerization.

On the other hand, thiourea derivatives, which have been utilized as host molecules for molecular recognition[426,427] as well as organocatalysts for organic reactions,[428,429] were also examined for the stereospecific radical polymerization of acrylamides via multiple hydrogen-bonding interactions between the additives and the monomers or the growing polymer termini.[430] Among the various thioureas, moderately bulky monothioureas possessing one or two 3,5-bis(trifluoromethyl)phenyl substituents (MH-**5** and MH-**6**) proved effective for higher isotacticity of DMAM ($m = 74\%$) and NIPAM ($m = 68\%$) than achieved in their absence ($m = 55$ and 48% for DMAM and NIPAM, respectively) in CH_2Cl_2 at −78 °C. The ^1H NMR analysis of mixtures of the thioureas with DMAM or its dimer both indicated 1:1 interactions, of which the association constant was estimated from 10^1 to 10^2, and the multiple hydrogen-bonding interactions at the growing terminus would contribute to the isotactic specificity similar to the polymerizations with multiple coordinating Lewis acids like $Mt(OTf)_3$.

4. Stereospecific Living Radical Polymerization

Stereospecific living radical polymerization requires controlled/living chain growth with a stereospecificity via a radical mechanism. Analogous to the chiral catalysts or initiators in coordination or anionic stereospecific living polymerizations,[431] one of the apparently promising strategies might be to use chiral living catalysts[99−104] or regulating agents,[80−84] which would induce controlled/living radical propagation as well as stereospecific chain growth via a possible interaction with the propagating radical species. However, as described above for several attempts, no tacticity control was achieved by this approach most probably because the chiral counterparts might be located too far away from the monomer addition reaction site as well as because of the difficulty in controlling tacticity by enantioselective insertion.

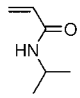
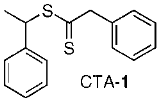
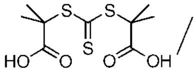
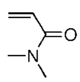
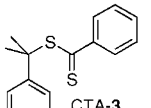
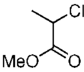
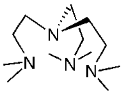
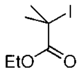
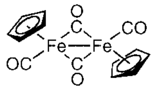
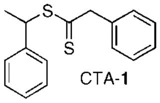
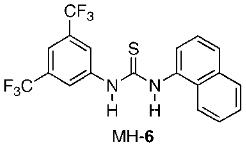
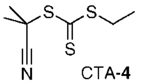
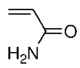
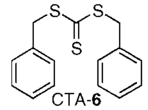
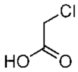
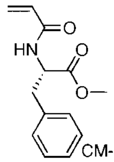
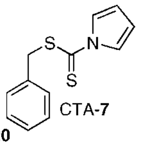
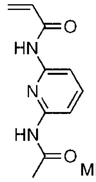
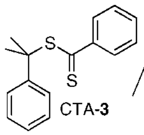
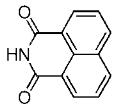
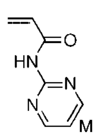
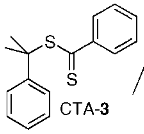
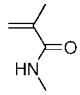
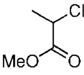
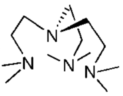
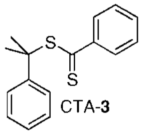
More direct effective methods have now been developed by using various combinations of the controlled/living radical polymerization and stereospecific radical polymerization so that one of the components would not disturb the other control. Effective controlled/living radical polymerizations for the combination include metal-catalyzed living radical polymerization or ATRP, RAFT, iodine-transfer radical polymerization, etc., which can work for molecular weight control even in polar solvents, in the presence of Lewis acids, or for specially designed monomers for stereospecific radical polymerizations.[61−63] The applicable monomers are acrylamides, methacrylamides, methacrylates, vinyl esters, and vinyl amides, and all possess polar carbonyl groups, by which the monomers or the chain ends interact with the polar solvents or added Lewis acids for the induction of stereospecificity. This part will deal with such stereospecific living radical polymerizations from the viewpoint of the types of monomers and then its application to the synthesis of stereoblock and stereogradient polymers.

4.1. Acrylamides and Methacrylamides

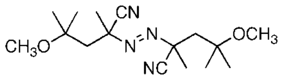
As stated above, controlled/living radical polymerization of acrylamide derivatives has been achieved by various systems including metal-catalyzed living radical polymerization or ATRP, RAFT, etc. In addition, tacticity control has also been attained by using Lewis acid or polar compound additives and polar solvents, which can strongly interact with the amide groups via coordination or hydrogen-bonding interaction to influence the stereochemistry during the propagation. Thus, dual control of the molecular weight and tacticity during acrylamide polymerizations has been attained by various combinations (Table 6), in which each component does not disturb the other control.

Stereospecific controlled/living radical polymerization was first reported for *N*-isopropylacrylamide (NIPAM) with RAFT polymerization in the presence of a Lewis acid additive in methanol/toluene at 60 °C.[432] The addition of $Y(OTf)_3$ to the RAFT polymerization of NIPAM with 1-phenylethyl phenyldithioacetate (CTA-**1**) increased not only the polymerization rate, but also the isotacticity of the polymers ($m = 83\%$) most probably due to the complexation of the Lewis acid to the monomer or around the growing

Table 6. Stereospecific Living Radical Polymerization of Acrylamides and Methacrylamides

Monomer	Initiating System	Mediator	*m* / *r*	M_w/M_n	M_n	ref
	 CTA-**1** / AIBN	$Y(OTf)_3$ $Yb(OTf)_3$ $Sc(OTf)_3$	83 / 17 84 / 16 67 / 33	1.76 1.72 1.57	27 800 25 400 27 200	395, 432, 433
		$Y(OTf)_3$ $Sc(OTf)_3$	60 / 40 64 / 36	1.30 1.29	30 000 34 000	397
	 CTA-**2** / AIBN	$Y(OTf)_3$	–	1.46	4 200	434 | 436
	 CTA-**3** / AIBN	$Y(OTf)_3$	86 / 14	1.10	10 100	437
	 / CuCl + 	$Y(OTf)_3$ $Yb(OTf)_3$	86 / 14 86 / 14	1.13 1.13	5 600 4 700	437
	 / 	$Y(OTf)_3$ $Yb(OTf)_3$	82 / 18 78 / 22	1.87 1.87	9 900 10 000	438
	 CTA-**1** / V-70*	 MH-**6**	64 / 36	1.34	14 000	430
	 CTA-**4** / V-70*		64 / 36	1.18	14 000	
	 CTA-**6** / *hν*	$Y(OTf)_3$	70 / 30	1.24	50 600	440, 441
	 / CuCl + TMEDA	$Y(OTf)_3$ $AlCl_3$	71 / 29 76 / 24	1.58 1.03	123 000 52 280	442, 443
 CM-**20**	 CTA-**7** / AIBN	$Y(OTf)_3$ $Yb(OTf)_3$	68 / 32 66 / 34	1.55 1.59	18 000 18 000	444
 MH-**1**	 CTA-**3** / AIBN	 (MH-**3**)	32 / 68	1.34	25 500	423
 MH-**7**	 CTA-**3** / AIBN	$(CF_3)_2C(Ph)OH$ (SS-**6**)	45 / 55	–	28 000	445
	 / CuCl + 	$Y(OTf)_3$ $Yb(OTf)_3$	*mm* / *mr* / *rr* 36 / 45 / 19 43 / 42 / 14	1.10 1.11	15 100 10 900	446
	 CTA-**3** / AIBN	$Y(OTf)_3$	45 / 44 / 10	1.19	8 000	446

V-70* 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile)



polymer terminus as observed for the Lewis-acid mediated stereospecific radical polymerization without the RAFT agents.[393,394] The molecular weights increased in direct proportion to the monomer conversion and well agreed with the calculated value assuming that one polymer chain was formed from one molecule of CTA-**1**. A similar simultaneous control was achieved with other metal triflates, such as $Yb(OTf)_3$ and $Sc(OTf)_3$, and CTA-**1**. The tacticity was changed by the central metal species and its concentration. Thus, isotactic-rich poly(NIPAM) with controlled molecular weights can be obtained by combination of the RAFT polymerization with the Lewis-acid-mediated isospecific polymerization. However, the MWDs were relatively broad ($M_w/M_n = 1.5-1.7$) in comparison to those obtained by the RAFT polymerization without the Lewis acids ($M_w/M_n = 1.3-1.5$), which was attributed to the very fast propagation in the presence of the Lewis acid or some decomposition of the RAFT termini caused by the Lewis acid.[433] A slight decrease in the isotacticity along with the monomer conversion was observed, which was ascribed to the decreased concentration of the effective Lewis acid for the propagation site along with the polymerization.

Such dual control of the molecular weight and the stereoregularity enabled the synthesis of a series of poly(NIPAM) polymers with similar molecular weights ($M_n = 37000 \pm 3000$, $M_w/M_n = 1.2-1.3$) but with different tacticities ($m = 45-72\%$) in order to investigate the effects of tacticities on the phase separation temperature of the aqueous solution of poly(NIPAM), which is known as a water-soluble temperature-responsible polymer with LCST around 32−34 °C for the atactic polymers.[395] An increase in the isotacticity apparently decreased the solubility, where the cloud point (T_c) of a 1.0 wt % solution decreased from 31 to 17 °C with the increasing isotacticity ($m = 45-66\%$), and a further increase finally made the polymer ($m = 72\%$) insoluble in water. Furthermore, with the increasing m value, the transition curve became broad and the hysteresis also became larger. These results indicate that the properties of poly(NIPAM) can be tuned by the tacticity during the controlled radical polymerization. A more detailed study on the phase diagram for poly(NIPAM) prepared by the same system revealed that the phase boundary curve also shifted to a lower temperature with the increasing isotactic content.[397] A further modulation of the thermoresponsive properties can be possible by changing the molecular weights and the terminal groups based on the living nature of the polymerizations.

A trithiocarbonate (CTA-**2**), which can work as a bifunctional RAFT agent, was also effective in controlling the molecular weights of poly(NIPAM) even in the presence of $Y(OTf)_3$ to yield isotactic-rich polymers ($m = 70-80\%$) in methanol/toluene at 60 °C though the tacticity was not measured.[434] The stereospecific living radical polymerization with CTA-**1** and CTA-**2** can be used for the synthesis of the AB- and ABA-type stereoblock poly(NIPAM), respectively, as will be shown later.[433−436]

Similar and various approaches to dual control were also reported for *N*,*N*-dimethylacrylamide (DMAM).[437] The first system for this monomer was reported for the combination of the RAFT agent (CTA-**3**; cumyl dithiobenzoate) and $Y(OTf)_3$ in methanol at 60 °C, in which isotactic-rich polymers ($m = 86\%$) with controlled molecular weights ($M_n = 10\,100$, $M_w/M_n = 1.10$) were obtained under the optimized conditions. The copper-based ATRP with methyl 2-chloropropionate/CuCl/tris[2-(dimethylamino)ethyl]amine (Me_6-TREN) was also combined with metal triflates [$Y(OTf)_3$, $Yb(OTf)_3$] in methanol at 30 °C to give similar isotactic-rich polymers with controlled molecular weights, while the polymerizations stopped below 50% due to the loss of activity of the copper catalyst in the presence of the Lewis acids.[437] A nitroxide-mediated polymerization (NMP) of DMAM with *N-tert*-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide (SG1) was also investigated in the presence of $Y(OTf)_3$ in *n*BuOH at 110 °C but failed in its control due to a higher temperature needed for NMP or the reaction of the Lewis acid with the nitroxide/alkoxyamine.

In contrast to the copper ATRP in the presence of metal triflates, a highly active iron(I)-catalyzed living radical polymerization with ethyl 2-iodoisobutyrate and $[FeCp(CO)_2]_2$ induced almost quantitative conversion of DMAM even in the presence of $Y(OTf)_3$ or $Yb(OTf)_3$ in toluene/methanol at 60 °C without any loss in activity to achieve simultaneous control.[438] However, the MWDs were broader due to the very fast propagation in the presence of the Lewis acids. In addition, some contribution of the iodine-transfer process was suggested for such systems containing the carbon−iodine dormant terminals.[439] The isotacticity obtained from stereospecific living radical polymerization with Fe(I)/$Y(OTf)_3$ was slightly higher than that obtained for stereospecific nonliving radical polymerization with AIBN/$Y(OTf)_3$, suggesting that the interconversion between the dormant and radical species would have some effects on the stereospecificity by the Lewis acid. All these effective systems for the dual control in the DMAM polymerizations were utilized for preparing atactic-*b*-isotactic polymers by just adding $Y(OTf)_3$ during the controlled/living radical polymerization,[437,438] which will be described later.

Another method for the dual control for DMAM was reported using the hydrogen-bonding interaction caused by the thiourea additives like MH-**6** in conjunction with the RAFT agents (CTA-**1** and CTA-**4**) in CH_2Cl_2 at 20 °C.[430] A relatively low temperature and a high concentration of the thiourea additive were necessary for the stereochemical control due to the relatively weak interaction between the additive and the monomer in comparison to the metal triflates. Although the isotacticity was lower ($m = 64\%$) than that obtained in the presence of the rare-earth metal triflates, almost no decrease in the molecular weight control was observed ($M_w/M_n = 1.1-1.3$) compared with that obtained with the RAFT polymerization in the absence of the additives. This combination can be regarded as a metal-free stereospecific living radical polymerization of acrylamides.

Unsubstituted acrylamide (AM) was also polymerized in the presence of $Y(OTf)_3$ coupled with a trithiocarbonate (CTA-**6**) as a photoiniferter under UV-irradiation in methanol at 40 °C.[440,441] Upon increase of the concentration of $Y(OTf)_3$, the meso content increased from 47% to 70% along with a slight broadening of the MWDs ($M_w/M_n = 1.24$). This study also suggested the formation of stereogradient polymers, in which the isotacticity gradually increased with increasing conversion, as will be discussed later. A copper-ATRP of AM with chloroacetic acid/CuCl/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) was also coupled with $Y(OTf)_3$ in water to give isotactic-rich poly(AM) ($m = 71\%$) with a relatively broad MWD ($M_w/M_n = 1.58$) and a much higher M_n than the calculated value.[442] However, a higher isotacticity ($m = 76\%$) and a narrower MWD ($M_w/M_n = 1.03$) were reported when $AlCl_3$ was used instead of $Y(OTf)_3$ in water irrespective of the low monomer conversion (≤2%) and low initiation efficiency (<1%). The working mechanism of $AlCl_3$ in water was not known because it was most probably hydrolyzed in water. This polymerization was further applied for surface-initiated polymerization of acrylamide from a 1-chloropropyltrichlorosilane unit attached to a silicon wafer in the presence of CuCl/TMEDA, $AlCl_3$, and chloroacetic acid as a free initiator in water.[443] Some effects of the stereoregularity of the grafted chains on the contact angle and thickness were discussed.

Other acrylamide derivatives with specific substituents were also examined for their stereospecific living radical polymerization. An acrylamide containing an L-phenylalanine moiety (CM-**20**) was polymerized in the presence of a dithiocarbamate-type RAFT agent (CTA-**7**) and rare-earth metal triflates in 1,4-dioxane at 60 °C to yield isotactic-rich polymers ($m = 66-68\%$) with controlled molecular weights and similar relatively broad MWDs ($M_w/M_n = 1.5-1.6$).[444] The T_g of the isotactic-rich polymers was higher than that of the atactic one [$T_g = 87.2$ °C ($m = 62\%$), 82.1 °C ($m = 49\%$)]. The effects of the tacticity on the specific rotations of the polymers with the chiral substituents were also studied.

A different approach to dual control was reported for another acrylamide possessing a designed multiple hydrogen bonding site with an array of DAD sequences (MH-**1**), in which additives with the complementary ADA sequence (MH-**3**) were added to the RAFT polymerization with CTA-**3** in $CHCl_3$ at 60 °C.[423] The relatively bulky cyclic imide (MH-**3**) was very effective in increasing the syndiotacticity even at 60 °C due to the strong triple hydrogen bonding without producing any significant damage to the molecular weight control ($r = 68\%$, $M_w/M_n = 1.34$). A similar acrylamide (MH-**7**) with a pyrimidinyl substituent, which may have a double hydrogen bonding site, was polymerized in a bulky fluoroalcohol [$(CF_3)_2C(Ph)OH$, SS-**6**] at 60 °C in the presence of the same RAFT agent (CTA-**3**) to give more or less syndiotactic polymers ($r = 55\%$) with controlled molecular weights, although the MWDs were not measured due to the poor solubility of the polymers in organic solvents.[445]

In contrast to a wide variety of dual controlled systems for acrylamides, there are not many for the α-methyl-substituted acrylamides, that is, methacrylamides, partially due to the lack of relevant suitable controlled/living radical polymerizations of the monomers. There is the only one report for MMAM using copper ATRP with methyl 2-chloropropionate/CuCl/Me_6TREN in methanol at 25 °C in conjunction with metal triflates, such as $Y(OTf)_3$ or $Yb(OTf)_3$.[446] The obtained polymers showed narrow MWDs ($M_w/M_n = 1.1$) as well as a higher isotacticity ($mm = 36-43\%$) than that in the absence of the rare-earth metal triflates ($mm = 6\%$, $rr = 70\%$) although the molecular weights were higher than the calculated values. The RAFT polymerization with CTA-**3** in methanol at 60 °C in the presence of $Y(OTf)_3$ also gave a higher isotacticity ($mm = 45\%$) and a narrow MWD ($M_w/M_n = 1.19$) irrespective of the higher M_n.

4.2. Methacrylates and Acrylates

In contrast to almost no efficient stereocontrolled systems for acrylates of a lower coordination ability than acrylamides, the stereospecific radical polymerization of methacrylates, which possess the α-methyl substituent, can be attained by adding Lewis acids or using polar solvents as mentioned above. Furthermore, the controlled/living radical polymerizations of methacrylates have been achieved by a variety of initiating systems including the metal-catalyzed living radical polymerization or ATRP and RAFT polymerizations. Thus, the judicious choice of these combinations has enabled the dual control of the molecular weight and tacticity during the methacrylate polymerizations (Table 7).

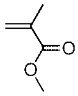
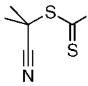
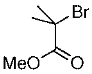
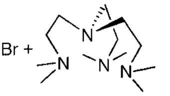
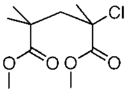
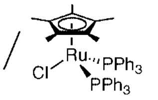
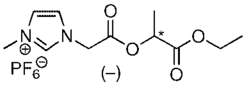
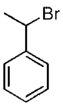
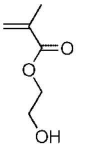
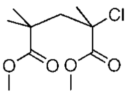
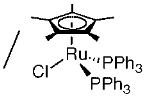
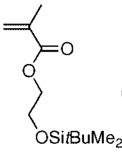
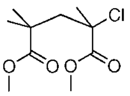
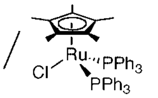
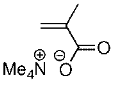
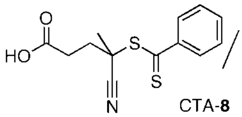
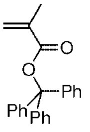
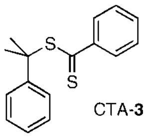
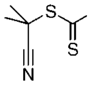
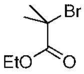
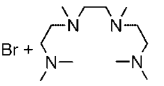
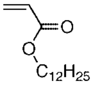
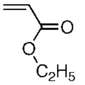
The first attempt at simultaneous control for MMA was reported for combinations of $Sc(OTf)_3$, which is effective for stereospecific radical polymerization,[392] and dithiobenzoate (CTA-**3**)-mediated RAFT polymerization or copper(I)- or iron(II)-catalyzed ATRP.[446] However, these combinations gave only limited control mainly due to the decomposition of the dithiobenzoate moiety or the deactivation of the Cu or Fe catalysts induced by the added Lewis acid. However, a significant improvement was achieved using trithiocarbonate (CTA-**4**) as a RAFT agent in the presence of $Sc(OTf)_3$ in benzene at 60 °C, where relatively narrow MWDs ($M_w/M_n = 1.31$) and an increased isotacticity ($m = 34\%$, $mm/mr/rr = 12/44/44$) were attained.[447,448] This was attributed to the higher stability of the trithiocarbonate RAFT agents than dithiobenzoates in the presence of Lewis acids, similar to its higher stability to the hydrolysis.

Polar solvents for stereospecific radical polymerization seem more compatible with the late transition-metal catalysts for living radical polymerizations than the Lewis acids, which may cause deactivation of the metal catalyst or decomposition of the carbon−halogen terminus. A bulky fluoroalcohol, such as $(CF_3)_2CHOH$ (SS-**4**), which is effective for syndiospecific radical polymerization of MMA at a low temperature,[345,346] was thus employed for the ATRP of MMA with ethyl 2-bromoisobutyrate/CuBr/Me_6TREN at −20 and −78 °C.[449] Highly syndiotactic poly(MMA)s with narrow MWDs were obtained ($rr = 75\%$, $M_w/M_n = 1.17$ at −20 °C; $rr = 84\%$, $M_w/M_n = 1.31$ at −78 °C) although the M_n values were higher than the calculated values. The addition of $CuBr_2$ improved the molecular weight control especially during the early stage of the polymerization.[450]

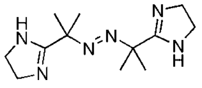
A series of ruthenium catalysts [$RuCl_2(PPh_3)_3$, $Ru(Ind)Cl(PPh_3)_2$, $Ru(Cp^*)Cl(PPh_3)_2$] were also employed for MMA in conjunction with a series of bulky fluoroalcohols [$(CF_3)_3COH$ (SS-**5**), $(CF_3)_2C(Ph)OH$ (SS-**6**), m-$C_6H_4[C(CF_3)_2OH]_2$ (SS-**7**)]. One of the advantages of the ruthenium catalysts in such alcoholic solvents is expected to be their high stability to these solvents due to the low oxophilicity of ruthenium.[451] Among the various ruthenium complexes, $Ru(Cp^*)Cl(PPh_3)_2$ was the most effective in giving the narrowest MWD ($M_w/M_n = 1.07$) in $(CF_3)_3COH$ and $(CF_3)_2C(Ph)OH$, which were also efficient in enhancing the syndiotacticity to $rr = 80\%$ and 77%, respectively, at 0 °C.[347]

Nonchiral and chiral ionic liquids were also employed as another type of polymerization media for the possible stereocontrolled radical polymerization of MMA in conjunction with AIBN/$CuCl_2$/bipy, which would induce the reverse ATRP polymerization for molecular weight control, at 90 °C.[452] A very slight increase in the isotacticity was reported for the chiral ionic liquid ($mm/mr/rr = 8.3/37.2/54.5$) compared with the nonchiral one ($mm/mr/rr = 7.2/36.6/56.3$), suggesting that the asymmetric environments of the chiral ionic liquids may influence the microstructure of the polymers, although the detailed mechanism was not clarified. A similar effect of a chiral ionic liquid on increase in

Table 7. Stereospecific Living Radical Polymerization of Methacrylates and Acrylates

Monomer	Initiating System	Mediator	mm / mr / rr	M_w/M_n	M_n	ref
	 CTA-**4** /AIBN	Sc(OTf)$_3$	12 / 44 / 44	1.31	78 900	447, 448
	 /CuBr + 	(CF$_3$)$_2$CHOH (SS-**4**)	0.9 / 23.7 / 75.4 0.5 / 15.8 / 83.7	1.17 1.31	13 100 13 400	449, 450
	 / 	(CF$_3$)$_3$COH (SS-**5**) (CF$_3$)$_2$C(Ph)OH (SS-**6**)	0.4 / 19.7 / 79.9 0.7 / 22.7 / 76.6	1.07 1.07	10 900 9 300	347
	AIBN / CuCl$_2$ + bipy		8.3 / 37.2 / 54.5	1.21	15 400	452
	 /YbI$_2$	YbI$_2$	2.9 / 28.7 / 68.4	1.24	3 300	454
	 / 	MeOH DMF DMA (CF$_3$)$_2$C(Ph)OH (SS-**6**)	3.1 / 33.5 / 63.4 0.6 / 22.8 / 76.6 1.1 / 23.1 / 75.8 6.0 / 40.8 / 53.2	1.31 1.16 1.12 1.24	31 800 24 100 26 800 24 600	347
	 / 	(CF$_3$)$_2$C(Ph)OH (SS-**6**)	0.9 / 21.9 / 77.2	1.14	8 200	455
 IM-**3**	 CTA-**8** /VA-061*	None	2 / 21 / 77	1.17	21 700	448
 BM-**16**	 CTA-**3** /AIBN	None	63 / 25 / 12	1.59	9 500	456
	 CTA-**4** /AIBN	None	64 / 24 / 12	1.55	10 400	
	 /CuBr + 	None	52 / 30 / 18	1.17	38 200	457
	CHI$_3$ / Na$_2$S$_2$O$_4$ + pTsNa + NaHCO$_3$	None	m / r 25 / 75	–	23 400	458
	CHI$_3$ / Na$_2$S$_2$O$_4$ + pTsNa + NaHCO$_3$	None	45 / 55	–	14 000	459

VA-061* 2,2'-azobis[2-(2-imidazolin-2-yl)propane]



isotacticity was reported for the copper ATRP of methyl acrylate, while the detailed data about the molecular weights and tacticity were not shown.[453]

An interesting result of dual control was reported using YbI$_2$, which might serve as a metal catalyst for living radical polymerization as well as a mediator for stereospecific radical polymerization.[454] The MMA polymerizations were carried out with 1-phenylethyl bromide/YbI$_2$ at 90 °C to give polymers with controlled molecular weights (M_w/M_n = 1.24) and a slightly higher syndiotacticity (*mm*/*mr*/*rr* = 3/29/68) than that obtained by AIBN at 90 °C (*mm*/*mr*/*rr* = 7/40/52). The effect of the rare-earth metal iodide on the tacticity was opposite to that of the triflate [Yb(OTf)$_3$],[393] which increased the isotacticity similar to Sc(OTf)$_3$.

A hydroxy-functionalized monomer, 2-hydroxyethyl methacrylate (HEMA), underwent special solvent effects on the tacticity, which were different from those observed for the alkyl methacrylate.[347] The polymerization of HEMA in MeOH gave almost the same tacticity (*mm*/*mr*/*rr* = 3/34/63) as that for poly(MMA) obtained in a typical organic solvent like toluene, while aprotic solvents, such as DMF and DMA, increased the syndiotacticity (*mm*/*mr*/*rr* = 1/23/76) of poly(HEMA) at 0 °C. In addition, a bulky fluoroalcohol [$(CF_3)_2C(Ph)OH$ (SS-**6**)] decreased the syndiotacticity and resulted in a slight increase of the isotacticity at 60 °C (*mm*/*mr*/*rr* = 6/41/53), which is the opposite effect on the tacticity of poly(MMA). All the poly(HEMA)s obtained with $Ru(Cp^*)Cl(PPh_3)_2$ in various solvents had controlled molecular weights and narrow MWDs, indicating again that the ruthenium catalyst is highly compatible with these solvents. Such specific tacticities for HEMA were attributed to the special hydrogen bonding interaction originating from the hydroxyl groups in the HEMA units. In contrast to HEMA, silyl-protected HEMA [2-(*tert*-butyldimethylsilyoxy)ethyl methacrylate; tBuMe$_2$SiHEMA] without the free OH functions gave syndiotactic-rich polymers (*mm*/*mr*/*rr* = 1/22/77) in the bulky fluoroalcohol at 0 °C similar to MMA, and dual control was also achieved with the ruthenium-based initiating systems.[455]

Controlled/living radical polymerization of a special monomer that gives a specific stereoregularity originating from the nature of the substituent can result in polymers with a controlled molecular weight as well as a special stereoregularity. An ammonium salt monomer, tetramethylammonium methacrylate (IM-**3**), was thus polymerized by the RAFT polymerization with a water-soluble RAFT agent (CTA-**8**) in water at 45 °C to give syndiotactic-rich polymers (*mm*/*mr*/*rr* = 2/21/77) with controlled molecular weights ($M_w/M_n = 1.17$).[448] Alkali metal salt methacrylates (IM-**1**; Na, K, Cs) were also polymerized in the presence of the RAFT agents to result in similar syndiotactic-rich polymers with narrow MWDs ($M_w/M_n \approx 1.1$), while the syndiotacticities were lower [*rr* = 75% (Na), 69% (K), 72% (Cs)] than that with the ammonium salt. The increased syndiospecificity was attributed to the mutual repulsion between the ionic carboxylate groups during the propagation.

In contrast to most methacrylates, a highly bulky monomer, triphenylmethyl methacrylate (BM-**16**), can afford isotactic-rich polymers even by radical polymerizations, as described above.[219] The RAFT polymerization of BM-**16** with CTA-**3** and CTA-**4** gave controlled molecular weights although the MWDs were broader ($M_w/M_n \approx 1.5$) than those for MMA due to the slow addition−fragmentation process for the bulky monomer.[456] The polymers obtained in the later stage of the polymerization at 60 °C possessed a high isotacticity (*mm* = 64%) although the tacticity was dependent on the monomer concentration and the polymerization temperature. The unique dependence of the tacticity on the monomer concentration can be applied to the synthesis of stereogradient polymers by combining them with the living radical polymerization as discussed later. A copper ATRP with ethyl 2-bromoisobutyrate/CuBr/1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) was also employed for TrMA to give predominantly isotactic polymers (*mm*/*mr*/*rr* = 52/30/18) with controlled molecular weights ($M_w/M_n = 1.17$).[457]

Irrespective of the absence of effective sterocontrolled methods for common acrylates, an interesting result for some tacticity control was reported for the single electron transfer/degenerative chain transfer (SET/DT) living radical polymerization of lauryl and ethyl acrylates in water near ambient temperatures.[458,459] In these polymerizations, the initiating radical species was generated via a single electron transfer to CHI_3 from SO_2^-, originating from $Na_2S_2O_8$, to induce the living radical polymerization via degenerative transfer to the C−I polymer terminus. Although the MWDs were relatively broad ($M_w/M_n \approx 2$), the M_n values increased in direct proportion to the monomer conversion. The poly(acrylates) with a long alkyl chain (C_{12}) obtained at 35 °C were predominantly syndiotactic (*r* = 75%),[458] while the shorter substituent (C_2) gave a slightly higher syndiotactic content (*r* = 55%) than that obtained in the free radical polymerization (*r* = 52%) at the same temperature (25 °C).[459] However, the mechanism for the syndiospecific propagation was not clarified.

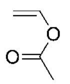
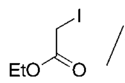
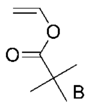
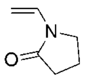
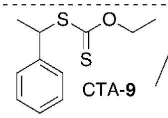
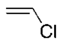
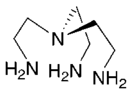
4.3. Vinyl Esters, Vinyl Amides, and Vinyl Chloride

In contrast to the conjugated acrylic monomers, the controlled/living radical polymerization of unconjugated monomers, such as vinyl esters, vinyl amides, and vinyl chloride, has been more difficult due to several factors including the less reactive dormant bond, the highly active radical species, the head-to-head linkages, etc. However, there are now several effective systems for controlling the molecular weights of these monomers, most of which are based on degenerative chain-transfer mechanisms. As for the stereochemical control, bulky fluoroalcohols proved effective for the syndiospecific radical polymerization of vinyl acetate (VAc) at a low temperature.[336] Partly because of the difficulty in the living radical polymerization, only a few examples of dual control of the molecular weight and tacticity were reported for vinyl esters and vinyl amides (Table 8).

The iodine-transfer radical polymerization, which is one of the first effective systems for controlling the molecular weight of poly(VAc),[460] was thus employed in conjunction with the fluoroalcohol-mediated stereospecific radical polymerization for simultaneous control.[461] The polymerization of VAc was carried out with V-70 in the presence of ethyl iodoacetate in several fluoroalcohols [$(CF_3)_3COH$ (SS-**5**), $(CF_3)_2C(Ph)OH$ (SS-**6**), m-$C_6H_4[C(CF_3)_2OH]_2$ (SS-**7**)] at 20 °C to give the syndiotactic-rich polymers (*r* ≈ 60%) with narrower MWDs ($M_w/M_n = 1.2-1.4$) than those obtained in the bulk iodine-transfer radical polymerization. This was attributed to the increased regiospecificity in the fluoroalcohols, where the head-to-head linkage decreased from 1.2% in bulk to 0.8%. The higher head-to-tail regiospecificity diminished the contents of the less reactive primary C−I terminus, which results in broadening of the MWDs due to the difficulty in the activation to the growing radical species. Thus, the fluoroalcohol enhanced not only the stereospecificity but also the molecular weight control due to the increased regiospecificity.

A bulky vinyl ester, vinyl pivalate (BM-**42**), was also employed for obtaining syndiotactic-rich poly(vinyl alcohol) segments in block copolymers with styrene (St).[462] The polymerization of BM-**42** was initiated by AIBN in the presence of CCl_4 as a chain transfer agent or telomer in ethyl acetate at 60 °C to give syndiotactic-rich polymers (*r* = 59%) with controlled chain-end groups (CCl_3− and −Cl), although precise molecular weight control was difficult by this system because the chloride terminus cannot be reversibly activated.

Table 8. Stereospecific Living Radical Polymerization of Vinyl Esters, Vinyl Amides, and Vinyl Chloride

Monomer	Initiating System	Mediator	*m* / *r*	M_w/M_n	M_n	ref
	 / V-70	m-$C_6H_4[C(CF_3)_2OH]_2$ $(CF_3)_2C(Ph)OH$ $(CF_3)_3COH$	41.0 / 59.0 41.3 / 58.7 39.6 / 60.4	1.20 1.36 1.31	8 000 5 000 7 100	461
 BM-**42**	CCl_4 / AIBN	None	41 / 59	1.57	4 760	462
	 CTA-**9** / AIBN	$(CF_3)_3COH$	40 / 60	1.28	12 600	343
	CHI_3 / Cu^0 + 	None	38 / 62	1.59	11 100	465, 466

However, another terminus, the CCl_3-end, was used as the initiating group for the copper ATRP of styrene with CuCl/bipy that resulted in the VAc-*b*-St copolymers. The saponified block copolymers containing higher syndiotactic poly(vinyl alcohol) blocks showed a lower critical micelle concentration than the atactic blocks due to the poor solubility of the syndiotactic segment in water.

A representative vinyl amide, NVP, can be polymerized only via a radical mechanism similar to VAc, and its polymer possesses a unique combination of chemical, physicochemical, and biological properties due to the presence of the amide group. This monomer was also polymerized in a bulky fluoroalcohol [$(CF_3)_3COH$ (SS-**5**)] at 20 °C to give syndiotactic-rich polymers (r = 60%) via hydrogen-bonding interactions.[343] Molecular weight control was achieved by the RAFT polymerization with xanthate (CTA-**9**) as a reversible chain-transfer agent ($M_w/M_n = 1.28$). The effects of the tacticity and the molecular weight on T_g were investigated for a series of poly(NVP)s with different tacticities and molecular weights prepared by RAFT polymerization in $(CF_3)_3COH$. The T_g value decreased from 174 to 165 °C for almost the same molecular weight polymers ($M_w \approx 2 \times 10^4$) with increasing syndiotacticity between r = 53% and 63%.

Living radical polymerization of VC, one of the representatives of unconjugated or nonactivated vinyl monomers, has now been achieved by the Cu(0)-based system, where Cu(0) generates the initiating radical species from CHI_3 via SET to induce the living radical polymerization via a degenerative iodine transfer mechanism.[463−466] The poly(VC) obtained in water at 25 °C had not only a controlled molecular weight but also a higher syndiotacticity (r = 62%) than that obtained by the free radical polymerization (r = 56%) at the same temperature.[465] The stereochemistry obtained by the SET-living radical polymerization deviated from the Bernoullian statistics and could be fit to the first-order Markovian while the poly(VC) obtained by the free radical polymerization exhibited only a slight deviation from the Beroullian one. A similar higher syndiotacticity was also observed in the nontransition metal-catalyzed living radical polymerization of VC initiated from CHI_3 in the presence of $Na_2S_2O_8$ in water at 25 °C.[466] However, the reason for the relatively high syndiotacticity in these living radical polymerizations is yet to be elucidated.

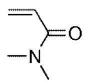
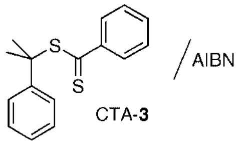
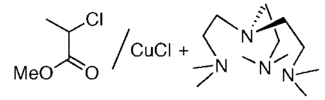
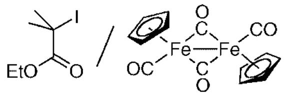
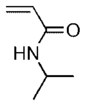
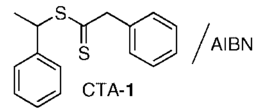
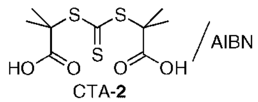
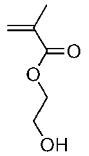
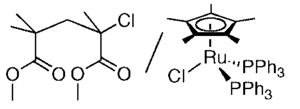
4.4. Stereoblock and Stereogradient Polymers

Stereochemical control during living propagation can lead to the synthesis of unique stereocontrolled polymers, such as stereoblock and stereogradient polymers. For the former polymers, the stereoregularity abruptly changes at a certain position in the chain, while for the latter, the stereochemistry gradually varies along a chain. Such well-defined stereocontrolled polymers can be obtained only by stereospecific living polymerization and are expected as novel homopolymer-based materials because different properties can be bestowed on the homopolymer chain in a controlled manner by the change in the tacticities. More specifically, isotactic−atactic stereoblock polyolefins prepared by coordination polymerizations show elastomeric properties due to the significant differences in the melting temperatures (T_m) of each segment.[431] In contrast, reports on the synthesis of stereogradient polymers are very scarce for all the vinyl addition polymerizations including ionic and coordination polymerizations.[467−469]

4.4.1. Stereoblock Polymers

Stereoblock polymers can be prepared by suddenly changing the tacticity during the living polymerization. A stereoblock polymer prepared by the stereospecific living radical polymerization was first reported for the atactic−isotactic poly(DMAM) by RAFT or ATRP in conjunction with Lewis acid additives (Table 9).[437] For example, into the polymerization media, in which DMAM was polymerized with CTA-**3**/AIBN in MeOH at 60 °C to give atactic polymers with a controlled molecular weight and end-groups via the RAFT mechanism, was added $Y(OTf)_3$ when the DMAM conversion reached 43% (M_n = 5300, M_w/M_n = 1.1). After the addition of $Y(OTf)_3$, isospecific propagation occurred and resulted in atactic-*b*-isotactic poly(DMAM) (M_n = 13 800, M_w/M_n = 1.21), in which the meso contents immediately changed from 55% to 86% at the blocking point. A similar one-pot synthetic procedure was also applied for the copper ATRP to give the stereoblock polymers [M_n = 12 400 (atactic) + 4600 (isotactic), M_w/M_n = 1.16], although the second polymerization seemed to stop around 60% due to the loss of the catalytic activity of Cu(I) in the presence of $Y(OTf)_3$.

Table 9. Stereoblock Polymers by Stereospecific Living Radical Polymerization

Monomer	Initiating System	Mediator	(*m*/*r*) or (*mm*/*mr*/*rr*) M_n	M_w/M_n	ref
	 CTA-**3**	None + Y(OTf)$_3$	*atactic – isotactic* (55/45) – (86/14) 5 300 – 8 500	1.21	437
		None + Y(OTf)$_3$	*atactic – isotactic* (55/45) – (84/16) 12 400 – 4 600	1.16	437
		None + Y(OTf)$_3$	*atactic – isotactic* (53/47) – (81/19) 7 000 – 3 700	1.72	438
	 CTA-**1**	None + Y(OTf)$_3$	*atactic – isotactic* (47/53) – (86/14) 4 500 – 17 600 10 400 – 15 100 13 200 – 10 700	 2.09 1.84 1.65	433
	 CTA-**2**	None + Y(OTf)$_3$	*isotactic – atactic – isotactic* 2 000 – 40 000 – 2 000 2 000 – 28 000 – 2 000 5 000 – 28 000 – 5 000 5 000 – 70 000 – 5 000	 1.29 1.29 1.20 1.31	434, 435, 436
		Y(OTf)$_3$ + None	*atactic – isotactic – atactic* 12 000 – 5 000 – 12 000 12 000 – 10 000 – 12 000	 1.32 1.37	
		DMA + (CF$_3$)$_2$C(Ph)OH	*syndiotactic – atactic* (1/23/76) – (7/41/52) 19 700 – 17 500	1.53	347

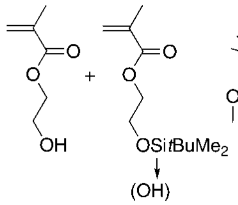
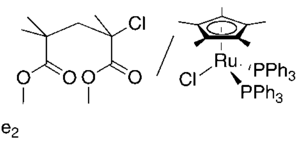
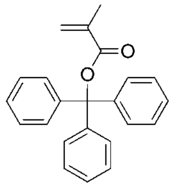
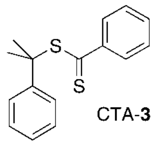
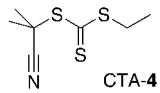
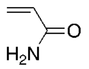
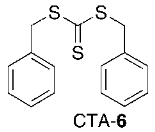
The highly active iron(I)-catalyzed living radical polymerization of DMAM was also employed for the synthesis of similar atactic-*b*-isotactic polymers.[438] Upon the addition of Y(OTf)$_3$ in methanol to the atactic living radical polymerization of DMAM with ethyl 2-iodoisobutyrate/[FeCp(CO)$_2$]$_2$/I$_2$ in toluene at 60 °C, the reaction was accelerated and induced almost quantitative consumption of the monomer to result in the stereoblock poly(DMAM) [M_n = 7040 (atactic) + 10 700 (isotactic), M_w/M_n = 1.72] consisting of atactic- (m = 53%) and isotactic-rich (m = 81%) blocks. The broadening of the MWDs after the addition of Y(OTf)$_3$ was ascribed to the fast propagation in the presence of the Lewis acid.

A similar approach was also valid for the synthesis of the stereoblock poly(NIPAM). To the RAFT polymerization of NIPAM with CTA-**1**/AIBN in toluene/methanol at 60 °C was added Y(OTf)$_3$ at varying monomer conversions (16−51%) to prepare a series of the atactic-*b*-isotactic polymers possessing various block lengths of atactic (m = 47%) or isotactic (m = 83−86%) segments and almost the same total chain lengths [M_n(total) = 22 100−25 500; M_n(atactic) = 4500−13 200].[433] The solubility of the stereoblock polymers in water was apparently dependent on the isotactic block lengths. The stereoblock polymer with a shorter isotactic block formed an emulsion in water, while the longer one was insoluble due to the low solubility of the isotactic-rich poly(NIPAM).

The synthesis and properties of the stereotriblock poly(NIPAM) were reported using bifunctional trithiocarbonate RAFT agents (CTA-**2**) coupled with Y(OTf)$_3$ in toluene/methanol at 60 °C.[434−436] The atactic and isotactic macro-RAFT agents of poly(NIPAM), which were prepared from CTA-**2** in the absence and presence of Y(OTf)$_3$, respectively, were employed for the block polymerization with and without the Lewis acid to give a series of isotactic-*b*-atactic-*b*-isotactic and atactic-*b*-isotactic-*b*-atactic polymers, respectively. Although the tacticities of each block were not measured, the meso contents of the isotactic blocks were supposed to be around 70−80%. When these polymers were dispersed in water, the isotactic-*b*-atactic-*b*-isotactic polymers formed flower-like micelles, while the atactic-*b*-isotactic-*b*-atactic ones generated branched micelle structures due to the differences in the solubility of the atactic and isotactic segments in water.[436] The formation of a clear gel at room temperature was also reported for the isotactic-*b*-atactic-*b*-isotactic poly(NIPAM) at a high concentration of the polymers (≥45 g/L).[435]

As for the methacrylate-based stereoblock polymers, syndiotactic-*b*-atactic poly(HEMA) was prepared by changing the solvents and temperatures for the ruthenium-catalyzed living radical polymerization.[347] The living radical polymerization of HEMA with Ru(Cp*)Cl(PPh$_3$)$_2$ was first conducted in DMA at 0 °C to give syndiotactic-rich polymers with narrow MWDs (M_w/M_n = 1.18) and C−Cl dormant termini, which were isolated and then employed as a macroinitiator for the second living radical polymerization with Ru(Cp*)Cl(PPh$_3$)$_2$ in (CF$_3$)$_2$C(Ph)OH (SS-**6**) at 80 °C to result in the stereoblock poly(HEMA) [M_n = 19 700 (syndiotactic) + 17 500 (atactic), M_w/M_n = 1.53] consisting of syndiotactic-rich (*mm*/*mr*/*rr* = 1/23/76) and atactic (*mm*/*mr*/*rr* = 7/41/52) blocks.

Table 10. Stereogradient Polymers by Stereospecific Living Radical Polymerization

Monomer	Initiating System	Mediator	Tacticity	M_n	M_w/M_n	ref
		$(CF_3)_2C(Ph)OH$	rr: 62% → 77% rr: 55% → 63%	19 800 21 700	1.25 1.27	455
BM-**16** (TrMA) ↓ (MMA)	CTA-**3** /AIBN	None	mm: 55% → 100%	9 500	1.59	456
	CTA-**4** /AIBN	None	mm: 55% → 100%	10 400	1.55	
	CTA-**6** /hv	$Y(OTf)_3$	mm: 86% ← 30% → 86%	50 600	1.24	441

4.4.2. Stereogradient Polymers

The requirement for the synthesis of stereogradient polymers is to gradually change the stereospecificity during the living polymerization. There are now a few reports on the synthesis using the stereospecific living radical polymerization (Table 10). The first method is based on the use of two monomers with different reactivities and stereospecificities for living radical polymerization.[455] In this system, an equimolar mixture of HEMA and *t*BuMe$_2$SiHEMA was polymerized with $Ru(Cp^*)Cl(PPh_3)_2$ in $(CF_3)_2C(Ph)OH$ (SS-**6**) at 0 or 60 °C, in which HEMA has a higher reactivity and produces lower syndiospecific sequences than *t*BuMe$_2$SiHEMA. The copolymerization led to about a two-times faster consumption of HEMA and resulted in gradient copolymers, in which the HEMA contents gradually decreased and the *t*BuMe$_2$SiHEMA gradually increased along with the polymerization. The subsequent removal of the protected silyl groups in the *t*BuMe$_2$SiHEMA units resulted in stereogradient homopolymers of HEMA with controlled molecular weights ($M_w/M_n = 1.2-1.3$) and a gradual increase in syndiotacticity along the chain depending on the temperatures [*rr* = 62→77% (0 °C), 55→63% (60 °C)].

Another strategy owes to the spontaneous gradual change in the stereospecificity depending on the monomer concentration during controlled/living radical polymerization.[456] The RAFT polymerization of a very bulky methacrylate, BM-**16**, was carried out with CTA-**3** or CTA-**4** in the presence of AIBN in toluene at 60 °C to give polymers with controlled molecular weights ($M_n \approx 10\,000$, $M_w/M_n = 1.5-1.6$). As the polymerization proceeded, the isotacticity gradually increased from 55% to 100% resulting isotactic-rich stereogradient polymers. This was caused by the propagation–depropagation equilibrium, which can convert a less thermodynamically stable growing terminus with the racemo conformation into the more stable meso form. The equilibrium became more dominant at a lower monomer concentration, in which the propagation became slower. Another equilibrium between the dormant and the radical chain end via the RAFT process enabled continuous chain growth of almost all the polymer chains throughout the monomer consumption to generate stereogradient polymer chains with controlled molecular weights. The polymers can be easily converted to stereogradient poly(MMA) after hydrolysis followed by methylation.

Another spontaneous formation of stereogradient microstructures was reported for the photoinitiated controlled/living radical polymerization of acrylamide with CTA-**6** as a bifunctional trithiocarbonate photoiniferter and $Y(OTf)_3$ as an additive for the stereochemical modulation in methanol at 40 °C under UV irradiation.[441] Although the detailed polymer structure and the mechanism were not clarified, the polymers seemed to have isotactic-*grad*-atactic-*grad*-isotactic sequences, in which the *mm* contents varied between 30% and 86%.

5. Conclusions

This paper has provided a comprehensive review of the dual control of molecular weight and tacticity by stereospecific living radical polymerization after surveying the fields of controlled/living radical polymerization and stereospecific radical polymerization. Stereospecific living radical polymerization has grown by merging the two fields together over the past several years. Although the simultaneous controls are not perfect and have not reached the levels reported in ionic or coordination counterparts, the radical system apparently yielded unprecedented well-defined polymers especially from polar acrylamides and methacrylates, which are not suitable for ionic or coordination polymerizations, as well as vinyl esters and amides, which cannot be polymerized by other mechanisms. In addition, its tolerance and versatility owing to the radical character has enabled the relatively easy synthesis of stereoblock and stereogradient polymers, which are regarded as interesting polymeric materials based on a single monomer component. For attaining a higher level of control, the advent of a new strategy for controlling the radical polymerization would be necessary. Furthermore, stereochemical control during the controlled/living radical polymerization of hydrocarbon monomers such as styrene and dienes would be a remaining and challenging problem, in contrast to the large variety of stereospecific and living radical polymerizations of polar monomers that can interact with solvents or additives. The developments would definitely contribute to further progress in not only polymeric materials based on a finely controlled architecture[470] but also commercial polymer production in the future.

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