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Review

Stereoregulation in Living Radical Polymerization

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ABSTRACT: This perspective article reviews the recent developments in stereoregulation in living radical polymerization of various polar vinyl monomers including methacrylates, acrylamides, vinyl esters, and vinyl amides. The stereoregulation should rely on an added Lewis acid, a polar solvent, or a multiple hydrogen-bonding additive, which can interact with the polar groups around the growing polymer terminal and/or of the monomer to induce the stereospecific chain growth, while the living or controlled chain growth is governed by a metal catalyst or a reversible chain transfer agent. The stereospecific living radical polymerization is thus achievable by the judicious combination of the stereocontrollable additive or solvent and the living radical polymerization catalyst or mediator. This methodology is relatively easily applied to the precise synthesis of stereoblock or stereogradient polymers, in which the stereochemistry of the enchainment is abruptly or gradually changed, respectively. This review also discusses other possible approaches to the simultaneous control using chiral metal catalysts or mediators for living radical polymerization or by utilizing a physically confined nanospace for the controlled and stereospecific chain growth.

Introduction

One of the ultimate goals for polymer chemists is to develop a synthetic macromolecule with a well-defined molecular weight, a high stereoregularity, and a controlled monomer sequence for the creation of functional polymers that may rival a nature-synthesized macromolecule with a perfectly ordered structure. The control of the molecular weights in synthetic polymers dates back to the birth of the living polymers of styrene in anionic polymerizations,[1] while the stereocontrol for the advent of isotactic polypropylene prepared by coordination polymerizations,[2] both of which have recently celebrated their 50th anniversaries. These controlled polymerizations have led to significant developments in synthetic polymers for various polymeric materials, which exert their excellent properties depending on their controlled structures such as block copolymer by living anionic polymerizations and stereoregular polyolefins by stereospecific coordination polymerizations.[3,4]

In contrast to these controlled ionic and coordinative polymerizations, radical polymerization had long been considered unsuitable for precise polymer synthesis due to the highly reactive free radical species that induces the uncontrolled rapid chain propagation without stereoselectivity and undergoes inevitable termination via radical−radical coupling and disproportionation.[5,6] However, radical polymerization has been one of the most efficient synthetic methods, especially for a massive amount of commercially available polymers due to the versatility of the polymerizable vinyl monomers and the robust nature of the polymerizations to water or moisture and polar and ionic compounds. This feature offers a significant contrast to that of the ionic and coordination polymerizations, which are highly affected by the monomer substituents and sensitive to a small amount of polar impurities. Therefore, the advent of efficient

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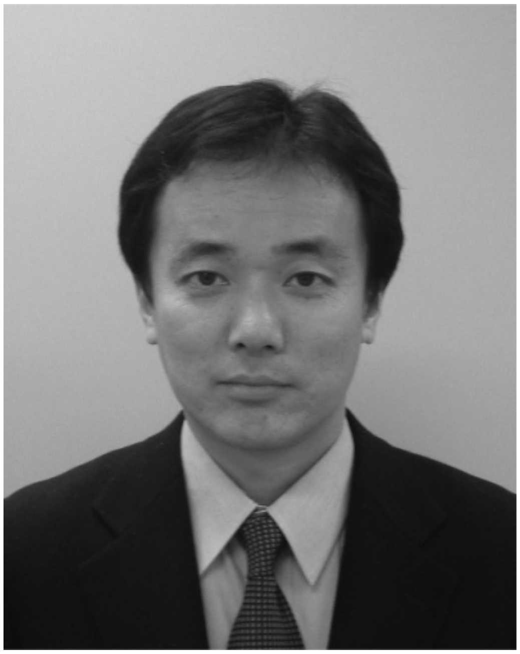
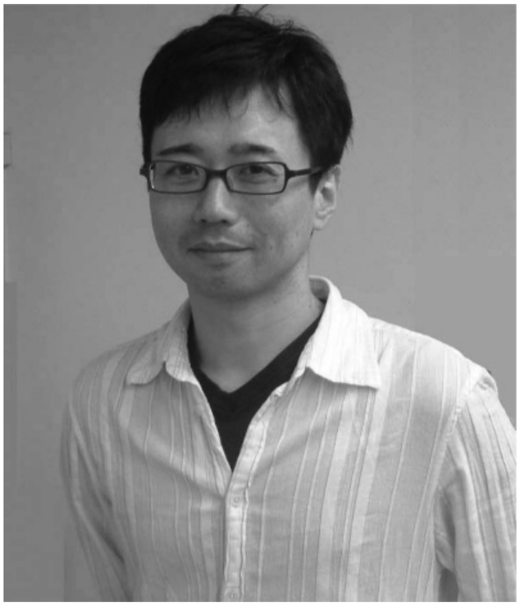


Masami Kamigaito was born in 1965 in Nagoya, Japan. He received his B.S. (1988), M.S. (1990), and Ph.D. (1993) degrees in polymer chemistry from Kyoto University under the direction of Professor Toshinobu Higashimura. After conducting postdoctoral research with Professor Mitsuo Sawamoto, he joined the faculty of Kyoto University in 1995, where he was promoted to Associate Professor in 1999. In 2003, he moved to Nagoya University as Associate Professor working with Professor Yoshio Okamoto and was promoted to Professor in 2004. During 1997−1998, he was a visiting scientist at Stanford University working with Professor Robert M. Waymouth. He is the recipient of the 1999 Award for the Encouragement of Research in Polymer Science of the Society of Polymer Science, Japan, and the 2001 Arthur K. Doolittle Award of the ACS PMSE Division. His research interests include controlled radical and cationic polymerizations, the development of new polymerizations, and their applications to the precision polymer synthesis.

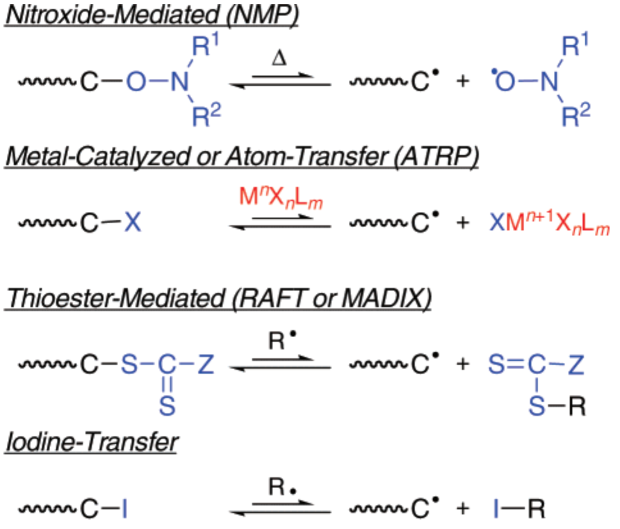
methods for taming radical polymerizations into controlled ones has long been required for the further development of functional polymeric materials by controlling the primary polymer structure.[7]

However, this decade has witnessed great progress in the controlled/living radical polymerizations, which can regulate the molecular weights of the polymers from a wide variety of monomers including nonpolar and polar, conjugated and unconjugated monomers, such as styrenes, dienes, methacrylates, acrylates, acrylamides, acrylonitrile, vinyl esters, vinyl amides, etc.[5,6,8] The initiating systems are widely varied and categorized into nitroxide-mediated polymerizations (NMP),[9,10] metal-catalyzed living radical polymerizations or atom transfer radical polymerizations (ATRP),[11−13] reversible addition−fragmentation chain-transfer (RAFT)[14] polymerizations or macromolecular designs via the interchange of xanthate (MADIX),[15] and others.[16−19] They all rely on a common concept, in which the reactive growing radical species is transiently and reversely converted into the dormant state via the formation of the covalent terminal (Scheme 1). These methods have now been used for the synthesis of a significant variety of architecture-controlled polymers such as end-functionalized, block, graft, and star polymers and their combined structural polymers and further applied to hybrid materials with natural or biopolymers, inorganics or ceramics, metals, etc. The advent of living radical polymerization is thus opening a new era of functional materials based on the controlled polymer structures.



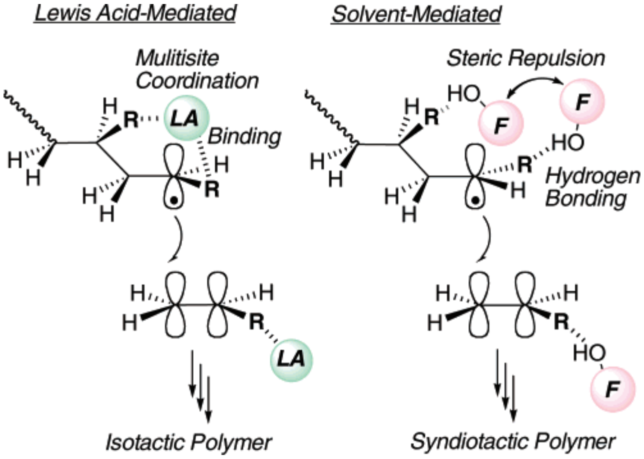
Kotaro Satoh was born in 1972 in Osaka, Japan. He received his B.S. (1995), M.S. (1997), and Ph.D. (2000) degrees in polymer chemistry from Kyoto University. His doctoral study was on the discovery of cationic polymerization systems in aqueous media under the direction of Professor Mitsuo Sawamoto. During 2000−2004, he worked for Tsukuba Research Laboratories, of Kuraray Co Ltd., as a researcher to develop a novel thermoplastic elastomer via living anionic polymerization. In 2004, he moved to the Graduate School of Engineering, Department of Applied Chemistry, of Nagoya University, as an Assistant Professor working with Professor Masami Kamigaito and was promoted to Associate Professor in 2007. His research interests include exploring precision polymerization systems as well as developments of new polymer materials by means of addition polymerizations.

Scheme 1. Living Radical Polymerizations Based on the Interconversion between the Dormant and Radical Species



The stereochemical control in radical polymerization has also been considered more difficult due to the lack of efficient methods for providing an asymmetric coordination environment around the propagating radical species. Although one solution for this problem is the use of a solid-based reaction field as in the inclusion[20,21] and topochemical[22] polymerizations and another is to design the monomers by adding bulky[23] or chiral auxiliary[24] substituents, there are limitations of the monomers and reaction conditions. However, recent years within this decade also witnessed more general methods applicable to

Scheme 2. Stereospecific Radical Polymerizations Mediated by Lewis Acid or Polar Solvent



various polar monomers, such as methacrylates, acrylamides, vinyl esters, and vinyl amides, in which polar solvents or added Lewis acids interact with the polar substituents of the monomers and/or around the propagating radical species to induce the stereospecific chain growth via coordination (Scheme 2).[25]

This short review focuses on the recent developments involving stereoregulation in living radical polymerization for the simultaneous control of the molecular weight and the tacticity during the radical polymerizations.

Attempts To Control Stereochemistry by Chiral Metal Catalysts or Chiral Nitroxides

Although the earliest studies on living radical polymerizations showed that the polymers obtained by using achiral metal complexes and mediators have similar tacticities to those obtained in free radical polymerizations using conventional azo- or peroxy-initiators,[26−28] the possibility of the stereochemical control using chiral catalysts or mediators has been expected since the advent of living radical polymerizations. It is based on some suggestions that the living radical propagation may occur via a "radical cage complex" or a "radical within the coordination sphere", which was proposed for the controlled radical addition reactions catalyzed by transition metal complexes.[29] Indeed, the stereochemistry during the ruthenium-catalyzed radical addition reaction between a halide and an olefin can be controlled by a chiral ruthenium complex to give the adduct with a moderate enantiomeric excess, which might be due to the fact that the radical is confined in the coordination sphere of the ruthenium complex.[29] Alternatively, some potential effect of the rate of the intermittent activation on stereoselectivity was discussed on the basis of the simulation.[30]

Several chiral ruthenium,[31] copper,[32−34] and molybdenum[35] complexes have thus been prepared, isolated in some cases, and employed for the living radical polymerizations of methyl methacrylate (MMA), methyl acrylate (MA), and styrene in order to examine the effects of the chiral catalysts on the tacticity of the produced polymers (Figure 1), though chiral induction during the radical addition reaction was confirmed only for a series of chiral ruthenium complexes.[29,31] All these chiral metal complexes basically enabled the molecular weight control while a broader molecular weight distribution (MWD) was observed with some complexes most probably due to slow interconversion between the dormant and the radical species. However, all the polymers showed a stereochemistry similar to that obtained in conventional radical polymerizations.[36] This may suggest that the chiral metal catalyst may be located too far away from the monomer addition reaction site to influence the stereochemistry of the monomer enchainment.[37] Similar results were also obtained with chiral nitroxide mediators, which had no effects on the tacticity of the resulting polymers.[38−40] On the basis of these results and other mechanistic studies of the controlled/living radical polymerizations,[8,41] it may be reasonable to regard that the growing radical species is basically free from the "counter radical" during the monomer addition. Furthermore, it may also be appropriate to assume that the chiral Ru(II)-mediated asymmetric radical addition reaction is not due to the confined radical species in the chiral coordination sphere but only originated from the chirality of the Ru(III) species that returns the halogen to the adduct radical species to form the 1:1 adduct on the C−X bond formation. Alternatively, if one can provide a special trick to the metal catalysts or the mediators such that they remain in the vicinity of the growing radical species or the incoming monomer, stereocontrol might be possible. However, such a situation has not been attained; thus, other practical methods might be suited for accomplishing the stereochemical control during the living radical polymerizations.[42,43]

Lewis-Acid-Mediated Stereocontrol in Living Radical Polymerization

In contrast to other living ionic or coordination polymerizations, one of the most significant features of the living radial polymerizations is their tolerance to functionalities including polar groups such as alcohols, amines, acids, ions, and others while the appropriate choice of the systems is needed for precise control of the molecular weight depending on the functional groups. This suggests that a robust living radical polymerization can hopefully occur even in a polar solvent or in the presence of a Lewis acid to achieve the molecular weight control in addition to the stereocontrol exerted by the solvent or the added Lewis acid. This strategy is based on how to efficiently combine the stereocontrollable solvents or agents and living radical catalysts or mediators, so that one of the components should not disturb the control by the other.

The stereospecific living radical polymerization by the combined system was first reported for the RAFT polymerization of *N*-isopropylacrylamide (NIPAM) in the presence of lanthanide triflate [$Y(OTf)_3$, $Yb(OTf)_3$] (Figure 2).[44−46] It has been reported that such a strong Lewis acid with a high coordination number and relatively large atomic radius induces isospecific chain growth in conventional radical polymerization of (meth)acrylamides and methacrylates due to the multisite coordination to the carbonyl groups around the growing polymer terminal and the monomer.[47,48] The Lewis acid was then employed in conjunction with a RAFT agent for the simultaneous control of the molecular weight and the tacticity to give poly(NIPAM) with controlled molecular weights, relatively narrow MWDs ($M_w/M_n = 1.3{-}1.8$), and predominantly isotactic contents ($m \sim 0.8$). The efficient dual control is due to the effective interaction of the Lewis acid with the amide moieties around the polymer terminal and/or the incoming monomer even in the presence of the thioester group as well as the rapid interconversion between the dormant thioster terminal and the growing radical species even in the presence of the added Lewis acid. This system can permit the synthesis of a series of poly(NIPAM)s with different tacticities, but with almost the same molecular weight and a narrow MWD just by changing the amount of the Lewis acid and keeping the same monomer/initiator ratio, which cannot be directly obtained by the stereospecific living anionic or coordination polymerizations of the same amide monomer due to the presence of the amide

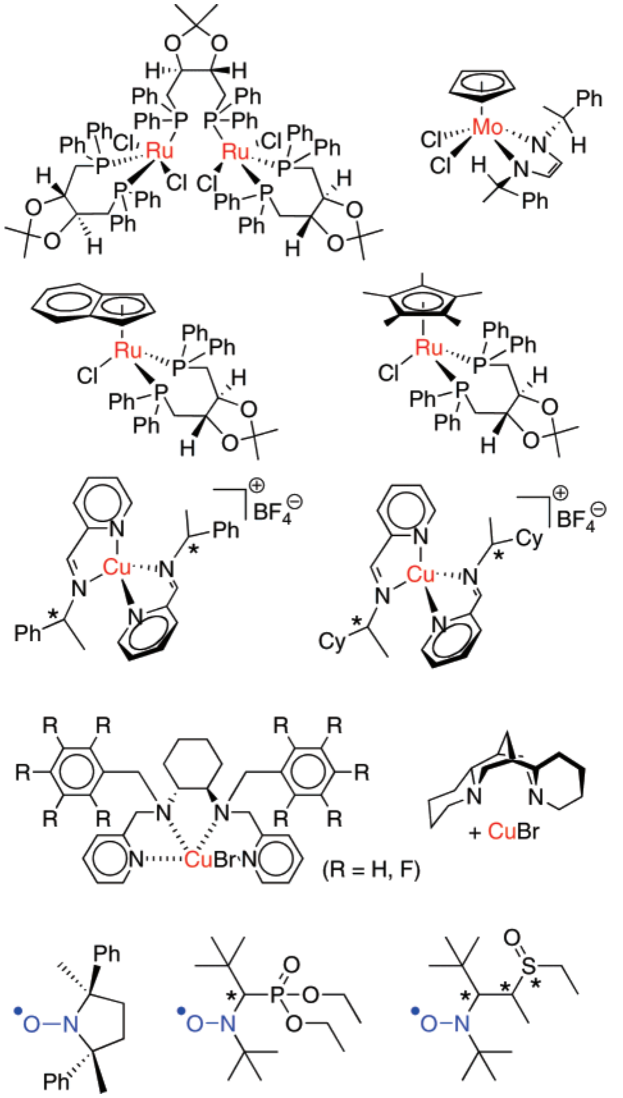


Figure 1. Chiral metal complexes and nitroxides employed for living radical polymerizations.

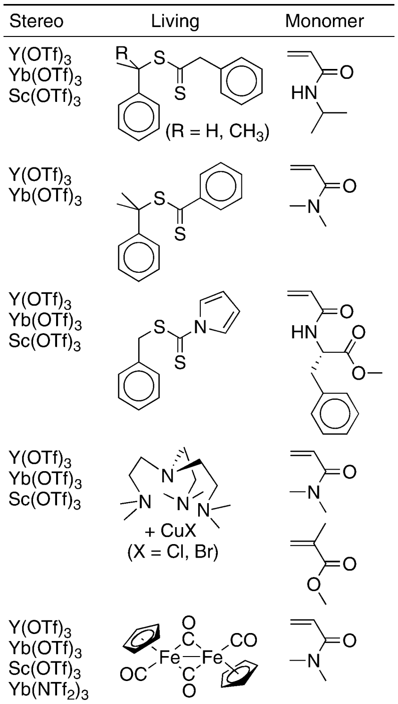


Figure 2. Lewis-acid-mediated stereoregulation in living radical polymerizations.

proton. The subsequent analysis of a series of the poly(NIPAM) aqueous solutions have revealed that the phase separation (T_{PS}) decreases from 31 to 17 °C with the increasing isotacticity from $m = 45$ to 66% without changing the molecular weight ($M_n = 34\,000-40\,000$), which would be interesting as thermoresponsive polymeric materials with variable responsive temperatures for biomedical applications.[46]

The combination of the metal triflate [$Y(OTf)_3$, $Yb(OTf)_3$, $Sc(OTf)_3$] with the RAFT agent was also effective for the simultaneous dual control for other acrylamides, such as *N*,*N*-dimethylacrylamide (DMAA)[49] and an acrylamide with the L-phenylalanine moiety,[50] to give isotactic-rich ($m = 0.6-0.8$) polymers with a narrow MWD ($M_w/M_n = 1.1-1.8$).

In contrast, when the metal triflate is combined with the transition-metal-catalyzed living radical polymerization or ATRP, a careful choice of the transition metal complex seems necessary for completing the polymerization. The combination of the nitrogen-ligand-based copper catalyst with $Y(OTf)_3$ produced the isotactic poly(DMAA) with controlled molecular weights while the polymerization stopped below a 60% monomer conversion most probably due to the coordination of the metal triflate to the nitrogen-based ligand followed by the deactivation of the copper catalyst.[49] Similarly, a loss of the molecular weight control and/or the inhibition were observed in the Cu-catalyzed ATRP of MMA by the addition of another Lewis acid, $Sc(OTf)_3$,[51] which is a good mediator for producing the isotactic-rich PMMA. In contrast, an iron complex without such basic ligands, $[FeCp(CO)_2]_2$, did not lose the catalytic activity even in the presence of $Y(OTf)_3$ and induced the quantitative and rapid polymerization of DMAA to give the isotactic poly(DMAA) with controlled molecular weights.[52] These results indicate that the judicious design or choice of the transition-metal catalysts is necessary for completing the isospecific living radical polymerization in the presence of the Lewis acid.

The Lewis acid can thus generally mediate the isospecific living radical polymerization of acrylamides in the presence of RAFT agents without significant unfavorable interactions between the metal triflate and the thioester moiety, while it deteriorates most of the transition metals for the metal-catalyzed living radical polymerizations or ATRP.

Polar-Solvent-Mediated Stereocontrol in Living Radical Polymerization

A bulky fluoroalcohol like $(CF_3)_3COH$ and $(CF_3)_2CHOH$ was reported to be effective for the syndiospecific radical polymerization of ester-type monomers, such as vinyl acetate (VAc) and MMA, as mentioned above.[53,54] The highly acidic bulky alcohol coordinates to the ester functions around the growing polymer terminal and/or of the monomer to cause steric repulsion around the growing polymer terminal, resulting in a syndiospecific chain growth. To achieve the syndiotactic propagation in living radical polymerization, a variety of living systems were examined for these ester monomers in the fluoroalcohols.

The syndiospecific living radical polymerization based on the polar solvent was first reported for the copper-catalyzed ATRP of MMA in $(CF_3)_2CHOH$ at a temperature below −20 °C (Figure 3).[55,56] This study showed that the fluoroalcohol enhanced not only the syndiotacticity but also the molecular weight control in the CuBr/Me_6TREN-catalyzed ATRP of MMA, in contrast to the broader MWDs obtained in toluene,

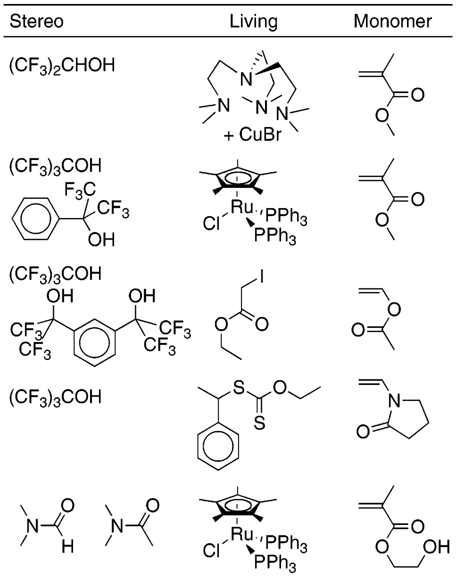


Figure 3. Polar-solvent-mediated stereoregulation in living radical polymerizations.

THF, and MeOH, which suggested some interaction between the copper catalyst and the fluoroalcohol. Lowering the polymerization temperature to −78 °C further increased the syndiotacticity ($rr = 0.84$) while keeping a narrow MWD ($M_w/M_n \sim 1.3$).

A series of ruthenium complexes [$RuCl_2(PPh_3)_3$, Ru(Ind)Cl(PPh_3)$_2$, and RuCp*Cl(PPh_3)$_2$] generally proved effective in the syndiospecific living radical polymerization of MMA even in various fluoroalcohols including $(CF_3)_3COH$, $(CF_3)_2C(Ph)OH$, and *m*-$C_6H_4[C(CF_3)_2OH]_2$.[57] The best control was attained with RuCp*Cl(PPh_3)$_2$ in $(CF_3)_2C(Ph)OH$ at 0 °C to give the polymers with a narrow MWD ($M_w/M_n = 1.08$) and a high syndiotacticity ($rr = 0.77$).

The fluoroalcohol-mediated stereospecific control is also compatible with the molecular weight control via degenerative chain-transfer processes such as iodine-transfer radical polymerizations and RAFT/MADIX. The combination of the iodine-transfer system with a fluoroalcohol was employed for VAc,[58] which can be polymerized only by a radical mechanism to give a precursor polymer [poly(VAc)] for poly(vinyl alcohol). Although the control of molecular weight was compromised by $(CF_3)_2CHOH$ in the iodine-transfer radical polymerization probably due to the abstraction of hydrogen in the $(CF_3)_2CH$ group, simultaneous control was achieved with the other tertiary fluoroalcohols. Especially, in *m*-$C_6H_4[C(CF_3)_2OH]_2$, a narrow MWD ($M_w/M_n \sim 1.2$) as well as a syndiotactic selectivity ($r = 0.59$) was attained in the presence of $CH_2I(CO_2Et)$ at 20 °C. Another additional control was accompanied in the fluoroalcohols, in which the head-to-head enchainment, inherent to the VAc radical polymerization, was suppressed (1.2% in bulk or methanol vs 0.8% in the fluoroalcohols) to enhance the regiospecificity. The decrease in the head-to-head propagation also worked for a decrease in the formation of the primary $-CH(OAc)CH_2-I$ terminal, which has a lower reactivity than $-CH_2-CH(OAc)-I$ via the normal head-to-tail propagation, to result in a better molecular weight control for the iodine-transfer radical polymerization of VAc. Therefore, the iodine-transfer radical polymerization of VAc in the fluoroalcohols controlled the molecular weight, stereospecificity, and regiospecificity. This leads to advanced properties of the poly(vinyl alcohol) because the enhanced stereoregularity increases the T_m and the decrease of the head-to-head enchainment helps the thermal stability.

A fluoroalcohol was also employed for the RAFT/MADIX polymerization of *N*-vinylpyrrolidone (NVP),[59] another representative unconjugated vinyl monomer, which can be converted into high-molecular-weight polymers only via a radical pathway similar to VAc. The dual control was achieved with a xanthate as a degenerative chain transfer agent in $(CF_3)_3COH$ to afford a narrow MWD ($M_w/M_n \sim 1.2$) and a high syndiotacticity ($r = 0.60$). A series of poly(NVP)s with varying molecular weights and tacticities were obtained and were submitted for further analysis of their thermal properties. The T_g of poly(NVP) increased from 165 to 180 °C with the increasing molecular weights or the decreasing syndiotacticity at least between $r = 0.53$ and 0.63, which may be beneficial for changing the properties of poly(NVP) as biocompatible materials.

Alternative solvents for the stereospecific radical polymerization include aprotic polar solvents such as DMF, DMA, DMSO, and HMPA for the particular monomers that possess protic hydrogens, such as alcoholic and amide protons.[57,60] A hydroxy-functionalized methacrylate, 2-hydroxyethyl methacrylate (HEMA), was polymerized in DMF and DMA to give the syndiotactic polymers while the fluoroalcohols had adverse effects on the tacticity.[57] The RuCp*Cl(PPh_3)$_2$-catalyzed living radical polymerization of HEMA was attainable in DMF at 0 °C to give the syndiotactic-rich poly(HEMA) with controlled molecular weights ($rr = 0.77$ and $M_w/M_n \sim 1.1$). This allows the further development in the solvent-mediated stereospecific living radical polymerization without using special and expensive fluoroalcohols.

Therefore, the polar solvent-mediated stereospecific radical polymerizations are more compatible with various living radical polymerizations, such as metal-catalyzed living radical polymerization or ATRP, iodine-transfer radical polymerization, and RAFT/MADIX, than the Lewis-acid mediated ones most probably due to the stability of the metal catalysts and/or the dormant species in such polar solvents.

Multiple-Hydrogen-Bonding-Mediated Stereocontrol in Living Radical Polymerization

The solvent-mediated stereospecific radical polymerization should be carried out at a low temperature (≤20 °C) for attaining a high stereospecificity due to the relatively weak association ($K = 10^{-1}-10^{0}$) between the monomer and the solvent, which usually relies on the single hydrogen-bonding interaction. The use of a stronger interaction based on the multiple hydrogen bonding between a monomer and an additive would be more effective for the stereocontrol at a higher temperature. A designed acrylamide monomer with an array of DAD sequences, where D and A denote the proton-donor and -acceptor sites, was then polymerized at 60 °C in the presence of a cyclic imide additive with the complementary ADA sequence in conjunction with a RAFT system to give the syndiotactic polymers with a narrow MWD ($r \sim 0.7$ and $M_w/M_n \sim 1.3$) (Figure 4).[61] The stereocontrol was due to the high association constant ($K = 6 \times 10^{2}$) via the triple hydrogen bonding. This suggests that the more sophisticated construction of hydrogen-bonding-mediated systems may lead to the further precise control of the stereochemistry in radical polymerizations.

Outcomes of Stereospecific Living Radical Polymerization: Stereoblock and Stereogradient Polymers

A meaningful application of the stereospecific and living chain growth for a precision polymer synthesis is to prepare special polymers that can be synthesized only by the stereospe-

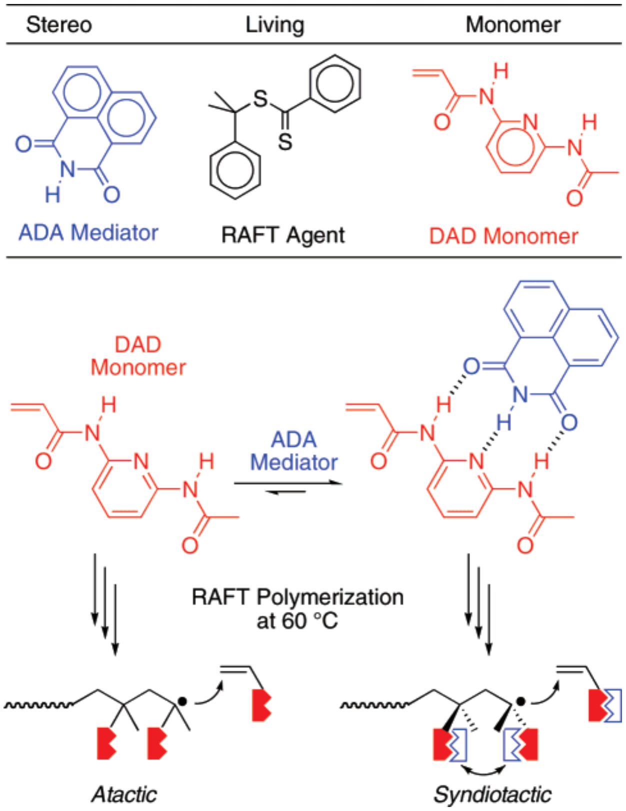


Figure 4. Mutiple hydrogen bonding for stereoregulation in living radical polymerizations.

cific living polymerizations. One of the representatives is a stereoblock polymer, in which the tacticity abruptly changes at a certain position in the chain, while another is a rather novel polymer, i.e., a stereogradient polymer, in which the tacticity continuously varies along the chain (Figure 5).

The successful synthesis of stereoblock polymers was first reported in the RAFT polymerization of DMAA in the presence of Y(OTf)$_3$.[49] This strategy is based on the first living radical polymerization without the Lewis acid additive, in which the atactic ($m = 0.55$) living polymer segments are formed, followed by the addition of the Lewis acid that subsequently induces the isotactic chain growth ($m = 0.86$) to give the atactic−isotactic block poly(DMAA). This method is very attractive and easy, and just based on the addition of Y(OTf)$_3$ during the living radical polymerization, and can be also applicable to the RAFT polymerization of NIPAM[45] as well as the iron-catalyzed living radical polymerization of DMAA.[52] These polymers are interesting as new polymeric materials because each segment has different thermal or physical properties such as T_{sp} and T_g depending on the tacticity.

The synthesis of stereogradient polymers is based on the stereospecific living radical copolymerization of two monomers with different stereospecificities and reactivities.[62] A ruthenium catalyst [RuCp*Cl(PPh$_3$)$_2$] was employed for the copolymerization of HEMA and a silyl-capped HEMA [(*tert*-butyldimethylsilyl)-HEMA (SiHEMA)] in a fluoroalcohol [(CF$_3$)$_2$C(Ph)OH]. The former was copolymerized faster than the latter and underwent the atactic chain growth while the latter grew via the syndiospecific propagation. This resulted in a gradient increase in the syndiotacticity along the chain (e.g., from 0.62 to 0.77 at 0 °C). The subsequent hydrolysis of the silyl group resulted in the first synthesis of a stereogradient poly(HEMA) with controlled chain lengths ($M_w/M_n \sim 1.2$). Further progress in the stereogradient polymers is expected in terms of the synthetic methods and their properties as new polymeric materials.

Confined Nanospace for Stereoregulation in Radical Polymerization

Another quite different strategy for controlling radical polymerization is to utilize a confined nanospace as a physically restricted reaction field for the suppression of the radical−radical termination between the polymer chains and for the stereochemical control exerted by the surrounding “nanovessel”. Such a specific reaction field can be constructed by soft materials like organic compounds or polymers and/or hard materials such as silica and metal ions.[20,21,63,64]

A mesoporous silica-based zeolite (27 Å diameter) was employed for the radical polymerization of MMA with BPO, in which a long-lived radical species was observed to result in the moderate molecular weight control though the stereochemistry of the main chain was not changed.[65] A recent advance in this field has been accomplished by the use of a well-designed narrower nanometer-sized space composed of transition-metal ions and organic bridging ligands.[66] This channel can be characterized by the controllable pore size (4−20 Å) and the flexibility of the pores, which may be tunable depending on the monomers. A long-lived growing radical species of styrene polymers was also confirmed by ESR, achieving the moderate molecular weight control ($M_w/M_n \sim 1.6$).[67] Such a channel can also be utilized for the site-selective radical polymerization of divinylbenzenes to give the linear polymers without cross-linking.[68] A more rational design of the porous materials may lead to the stereospecific chain growth during the radical polymerization.

Another recent remarkable result of the simultaneous control was obtained for the template radical polymerizations of methacrylic monomers [MMA or methacrylic acid (MAA)].[69−71] In these polymerizations, highly iso- or syndiotactic methacrylic polymers ($mm > 0.9$ or $rr > 0.9$) with controlled molecular weights were obtained via the interaction with the complementary template syndio- or isotactic-methacrylic polymers originally prepared by the stereospecific living anionic polymerizations. The template polymerization thus enabled the precise and simultaneous control of the molecular weight and the tacticity by the template polymer. The key point for the template polymerization is the preparation of ultrathin films composed of double-strand helical or van der Waals contacted stereocomplex nanostructures by the layer-by-layer assembly method followed by the selective extraction of a single component to form the stereocomplex films, which becomes a specific nanospace for the stereospecific and living chain growth.

Summary and Outlook

In summary, stereoregulation in living radical polymerization is possible by the additional use of Lewis acid additives or polar solvents besides the living radical polymerization catalysts or mediators because the counterpart radical species is most probably located too far away from the growing radical species to induce the stereospecific monomer addition. However, the added Lewis acid or polar solvent can efficiently work for the stereospecific chain growth via coordination to the polar groups of the monomers and/or around the growing polymer terminal without reducing the molecular weight control by the living radical polymerization catalysts or mediators when a judicious combination is selected. This is in sharp contrast to other stereospecific living ionic or coordination polymerizations, in which the counterion or the metal catalyst plays a dual role for

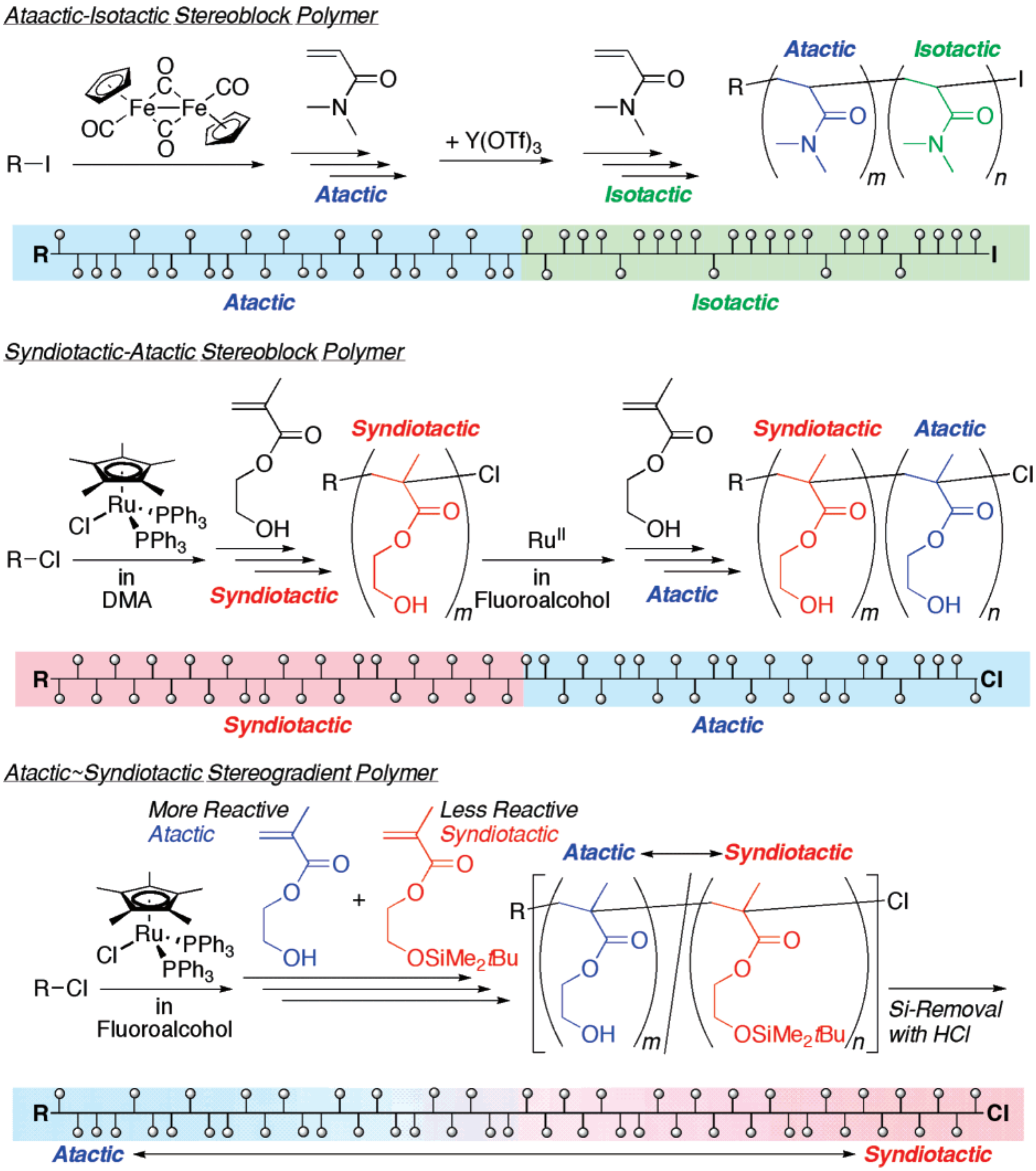


Figure 5. Stereoblock and stereogradient polymers prepared by stereoregulation in living radical polymerizations.

both controls. However, from another viewpoint, the stereoregulation in living radical polymerization can be modulated by changing the compounds or the amounts of the stereochemical mediators while maintaining the molecular weight control because both controls are basically independent. This further leads to the relatively facile synthesis of stereoblock and stereogradient polymers due to the modulation. Although a variety of polar vinyl monomers can undergo a stereospecific chain growth in living radical polymerizations, the degree of the stereochemical control is still lower than those in the stereospecific living coordination polymerizations. A different strategy for stereoregulation in radical polymerization would be necessary for further developments in terms of the stereoregularity and versatility of the applicable monomers including less polar monomers such as styrenes.

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