Stereospecific Living Radical Polymerization of Designed Bulky Monomers

モノマーの嵩高さの設計による

立体特異性リビングラジカル重合系の開発

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Contents

General Introduction

Background

Control of the Primary Structure of Polymers

Polymer properties are generally affected by the primary structure of polymers, including polymer chain length, or molecular weight, stereoregularity, terminal groups, and monomer sequences (Figure 1).   Naturally occurring macromolecules, such as proteins and nucleic acids, possess excellent properties and functions mainly originating from their perfectly ordered structures.[1]   In contrast, general synthetic polymers have distributions in their structures, which are inherent to the synthetic methods.   Therefore, one of the ultimate goals for polymer chemists is to develop a synthetic polymer with a perfectly-defined primary structure that may rival a nature-synthesized macromolecule. Owing to a huge number of precedent researches on controlling the primary structures of synthetic polymers, the chain length and stereoregularity have now been controlled by living polymerizations and stereospecific or stereoregular polymerizations, respectively. Although the controls are still not perfect in comparison to those of natural macromolecules, these controlled polymerizations have led to significant progress in various polymeric materials based on their controlled primary structures.[2,3]
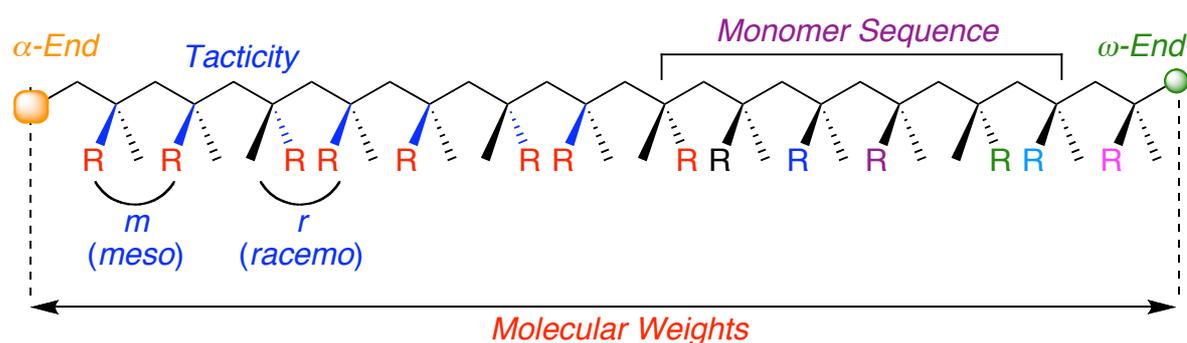


Figure 1.   Primary Structure of Polymers

Living Polymerization

Living polymerization is defined as a chain-growth polymerization without side reactions such as termination and chain transfer reactions to enable the precision control of

molecular weights and their distributions of the resulting polymers (Figure 2). In this polymerization, one initiator generates one polymer chain via living chain growth, where the molecular weight can be controlled by ratio of the consumed monomer to the initiator. Since Szwarc first discovered living anionic polymerization of styrene in 1956,[4] many kinds of living polymerizations via cationic,[5–7] coordination,[8–10] group-transfer,[11] ring-opening,[12] and ring-opening metathesis,[13] mechanisms have been developed by an appropriate design of the reaction systems. These remarkable progresses in living polymerizations have enabled the synthesis of various well-defined polymers, such as block, gradient, end-functionalized, graft, star, and more complicated polymers.[14]
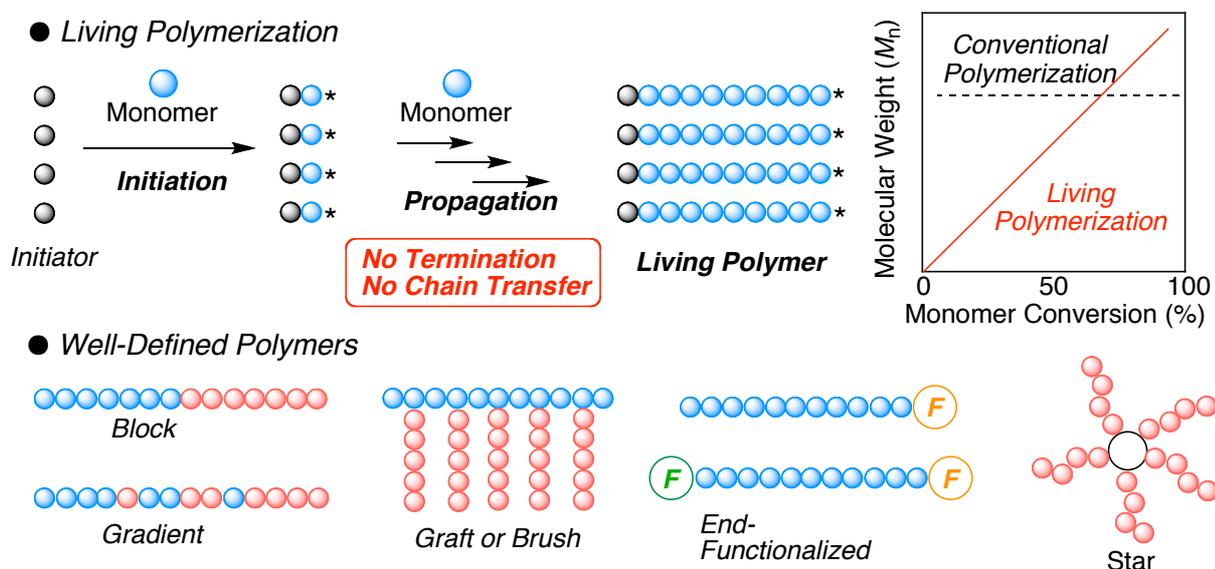
Figure 2. Living Polymerization and Well-Defined Polymers by Living Polymerization

Living Radical Polymerization

Radical polymerization is one of the most efficient methods in both industry- and laboratory-scale polymer synthesis, because of many advantages, such as wide variety of monomers, mild reaction conditions, and tolerance to polar groups. However, it was considered difficult to achieve living radical polymerization due to the highly reactive free radical species that undergoes inevitable bimolecular termination via radical–radical coupling

and disproportionation.[15,16] Irrespective of such a view, possibility of living radical polymerization was first suggested by the "iniferter" systems that Otsu et al. proposed in the 1980s.[16] From 1990s, a large variety of living radical polymerizations have been reported, which include nitroxide-mediated polymerization (NMP),[18–20] metal-catalyzed living radical polymerization or atom transfer radical polymerization (ATRP),[21–23] and reversible addition-fragmentation chain transfer (RAFT) polymerization[24] (Scheme 1). All of them are based on a common concept, reversible capping of the growing radical species to form a dormant species. The fast interchange reaction can control the chain growth by giving almost the same chance for propagation to all the polymer chains. Furthermore, the equilibrium can reduce the concentration of radical species to diminish the probability of termination reactions. Among various living radical polymerizations, RAFT polymerization can be used for a variety of monomers by simply adding an appropriate RAFT agent.

● *Nitroxide-Mediated Polymerization (NMP)*

● *Metal-Catalyzed Living Radical Polymerization or ATRP*

● *RAFT (Reversible Addition-Fragmentation Chain Transfer) Polymerization*
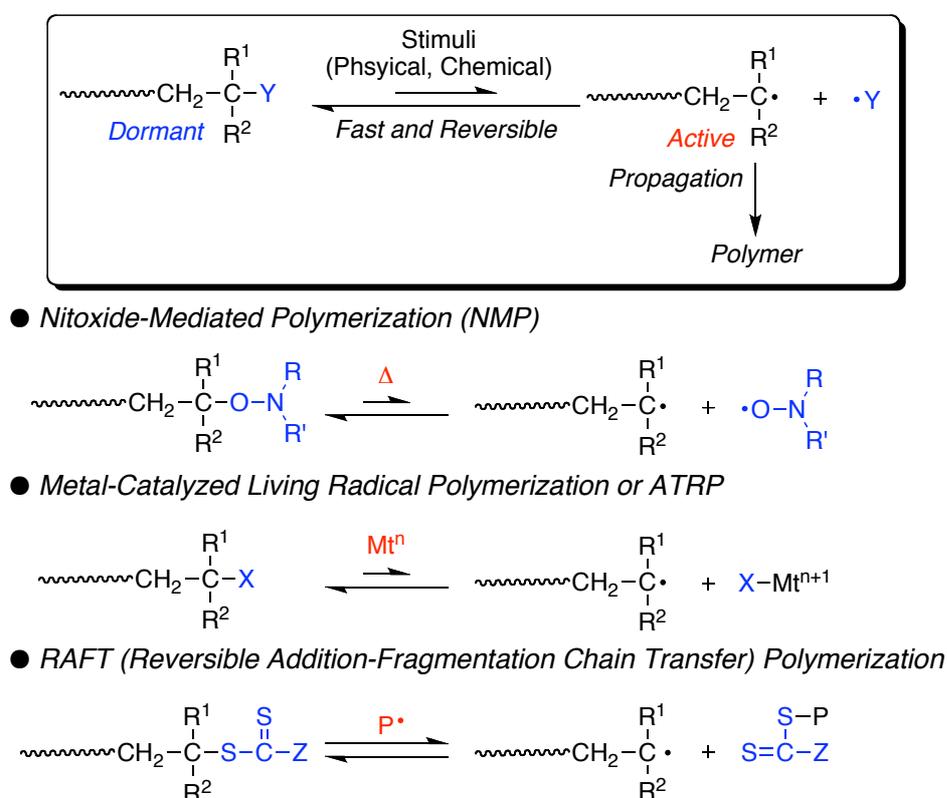
Scheme 1. Various Living Radical Polymerizations Based on Reversible Activation of Dormant Species into Radical Species

Stereospecific Radical Polymerization

Stereoregularity affects various polymer properties, such as glass transition temperature, melting point, solubility, crystallinity, and mechanical strength. With one preceding discovery of stereoregular poly(vinyl ether) by Schikdknecht et al. in 1947,[25] the pioneering work on stereospecific polymerization by Natta led to the synthesis of isotactic polypropylene using coordination polymerization.[26] Since the discovery, a large number of stereospecific polymerizations have been reported in coordination[27,28] and anionic[29] polymerizations.

In sharp contrast to the coordination and ionic polymerizations, the control of stereochemistry in radical polymerization has been much more difficult because of the "free" and neutral carbon radical species that cannot be regulated by electronic interactions, unlike ionic propagating species in ionic polymerizations. However, recent developments in stereospecific radical polymerization have allowed the control of the stereoregularity by several methods, based on bulky substituents in monomer structure,[30,31] and solvents or additive.[32−34] The solvent- or additive- mediated stereochemical control can be achieved by the interaction with pendent polar groups and/or growing terminus during the propagation steps via hydrogen bonding or coordination (Figure 3). However, these stereochemical controls are still inferior to those achieved in coordination of α-olefins or anionic polymerization of methacrylic monomers.
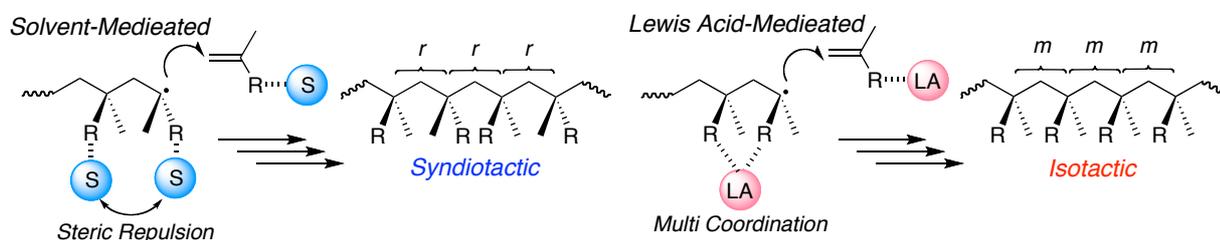

Figure 3. Stereochemical Control via Solvent- or Additive- Meditated Systems

Stereospecific Living Radical Polymerization

Along with the progresses in controlling the molecular weights by living radical polymerizations and stereochemistry by stereospecific radical polymerizations, the simultaneous control of both. Molecular weights and tacticities has been reported by a judicious combination of the two controlled polymerizations, in which both controlling systems should be properly selected so that the controlling components do not disturb each other (Figure 4).[35–39] These combinations are easily applied to the synthesis of novel types of stereocontorolled polymers like stereoblock or stereogradient polymers, whose tacticity is abruptly or gradually changed along with the chain, respectively.
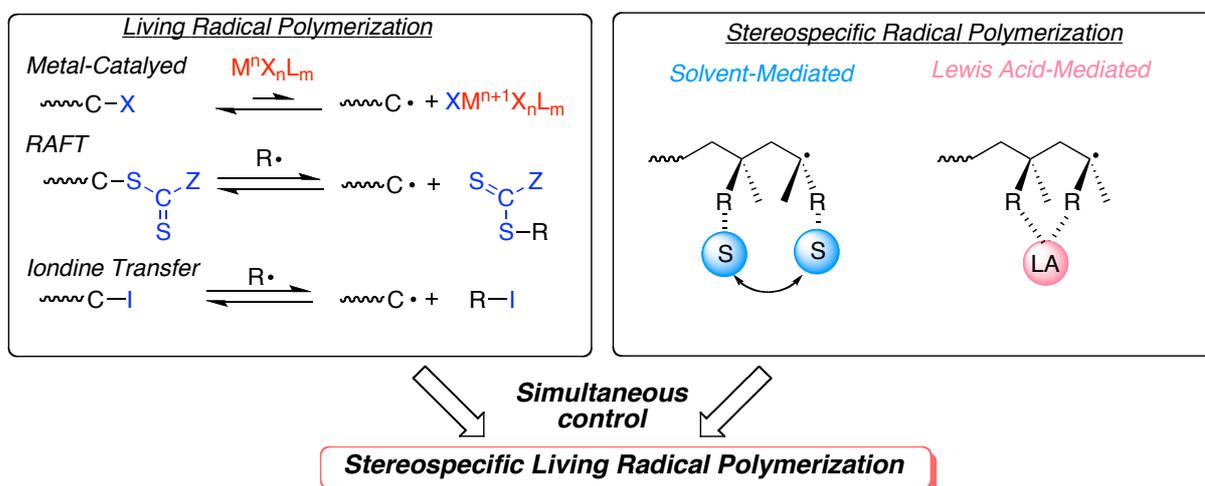

Figure 4. Stereospecific Living Radical Polymerization

Radical Polymerization of Bulky Monomer

Bulkiness in monomers often plays an important role in dictating the stereochemistry of the resulting polymers even in radical polymerizations.[30,31,40] For example, a variety of methacrylates with different substituents have been synthesized and radically polymerized under various conditions to produce a series of poly(methacrylate)s with various tacticities, ranging from syndiotactic-rich to highly isotactic enchainment. The tacticity is mainly governed by the bulkiness of the substituents.[35d] Specifically, usual alkyl

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methacrylates, such as methyl methacrylate (MMA), form predominantly syndiotactic polymers (*rr* ~ 65%) due to the steric repulsion among the α-methyl and ester groups of incoming monomer, growing radical, and penultimate units, which prefer the racemo conformation (Figure 5). The syndiotacticity gradually decreases with increasing bulkiness of the pendent groups.[30,31] Further increasing the bulkiness using tirarylmethyl groups, results in highly isotatcitic polymers with a rigid helical conformation. Triphenylmethyl (trityl) methacrylate (TrMA) is radically polymerized to give a relatively high isotactic (*mm* = 64–98%) polymers, the tacticity of which somewhat depends on the polymerization condition.[31b] In contrast, a similar analogue of 1-phenydibenzosuberyl methacrylate (PDBSMA) leads to an almost perfect isotactic polymer (*mm* = 99%)[31b] regardless of reaction conditions because of the more rigid group with ethylene-linked aryl groups.
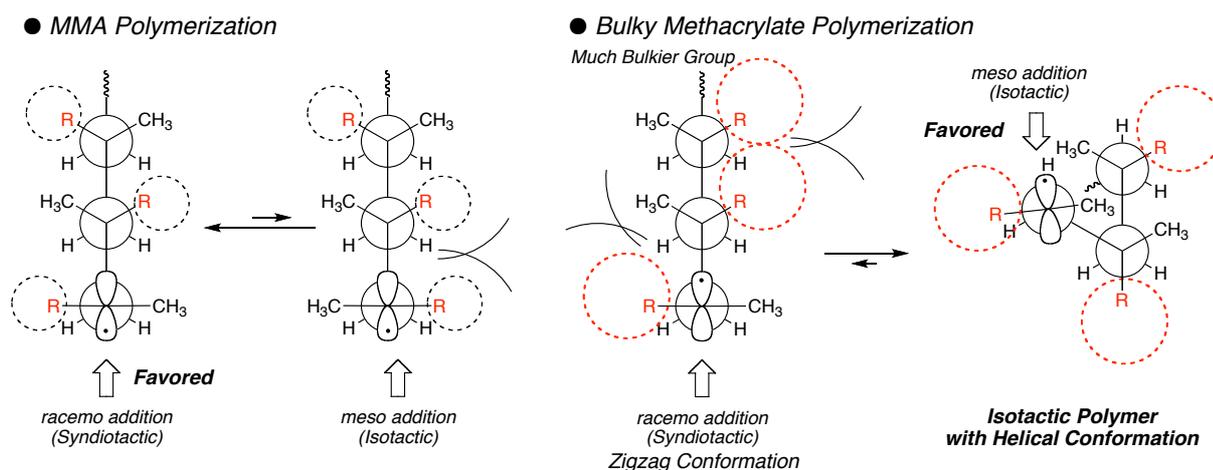

Figure 5.   Conformation in Methacrylate Polymerization

Objectives

Considering these backgrounds, the author focused on bulky monomers, especially bulky methacrylates, which could result in novel controlled polymer structures by developing the stereospecific living radical polymerizations. Although it had been revealed that bulkiness in methacrylate monomers plays an important role on dictating the stereochemistry of the resulting polymers, the living radical polymerization of bulky methacrylates, such as

TrMA, was not attained.   In addition, the bulky methacrylates that can give stereoregular polymers were limited to triarylmethyl-based monomers whereas a different type of bulky substituents could be a candidate for controlling the stereochemistry of the resulting polymer. The author thus decided to investigate stereospecific living radical polymerization of designed bulky methacrylate monomers for the synthesis of novel controlled polymers by formulating the following two objectives:

(1) Stereospecific Living Radical polymerization of Bulky Triarylmethyl Methacrylates for Novel Stereogradient Polymers

(2) Design and Polymerization of Novel Bulky Silyl Methacrylates for Stereoregular Protected Poly(methacrylic Acid)s

(1) Stereospecific Living Radical Polymerization of Bulky Triarylmethyl Methacrylates for Novel Stereogradient Polymers

The first objective of this study was to synthesize stereogradient polymers by controlled/living radical polymerization of a bulky methacrylate, TrMA.   For this, the author investigated RAFT homopolymerization of TrMA that accompanies a spontaneous and gradual increase of isospecificity along with monomer consumption.   Furthermore, for the synthesis of from-syndiotactic-to-isotactic stereogradient polymers, RAFT copolymerization of two monomers with different reactivities and stereospecificities were examined using a combination of a bulky methacrylate, which propagates via isotactic enchainment, and methacrylic acid, which gives syndiotactic-rich polymers.

(2) Design and Polymerization of Novel Bulky Silyl Methacrylates for Stereoregular Protected Poly(methacrylic Acid)s

The second objective of this study was to design novel bulky silyl methacrylates

and to develop stereospecific and asymmetric polymerization for stereoregular poly(methacrylic acid)s protected with silyl groups. The author focused his attention on changing the tacticity of poly(methacrylic acid)s by radically polymerizing a series of silyl methacrylates with varying bulkiness of the substituent and simply deprotecting them. Furthermore, the author also investigated asymmetric radical or anionic polymerization of an extremely bulky silyl methacrylate, tris(trimethylsilyl)silyl methacrylate (TTMSSMA), for the synthesis of optically active polymers.

Outline of This Study

The present thesis consists of two parts: **Part I** (Chapter 1–2) deal with the synthesis of stereogradient polymers by RAFT (co)polymerization of bulky triarylmethyl methacrylates. **Part II** (Chapter 3–4) presents the design and stereospecific polymerization of novel silyl methacrylates by using a series of silyl groups with different bulkiness for the synthesis of protected poly(methacrylic acid)s with various tacticities.

In Part I, *Chapter 1* focuses on the controlled/living radical homopolymerization of TrMA for the synthesis of novel stereogradient polymers (Scheme 2). The monomer was polymerized with several RAFT agents to achieve controlled/living radical polymerization under various conditions at varying the temperatures and monomer concentrations. Cumyl dithiobenzoate (CDB) and trithiocarbonate-type compounds, which are effective for controlling radical polymerization of usual alkyl methacrylates, similarly induced the controlled/living radical polymerization of TrMA. More interestingly, as the polymerization proceeded, the isotacticity gradually increased to give the isotactic stereogradient polymers spontaneously. It was suggested that the gradual increase of isotaciticity is caused by polymerization-depolymerization equilibrium which makes the thermodynamically stable isotactic enchainment more prevailing in this case along with the decrease of monomer concentration. In addition, controlled/living chain growth via RAFT polymerization works for the formation of gradient structures along the chain. Block copolymerization with MMA

was further examined to obtain novel stereoblock copolymers with syndiotactic and isotactic-stereogradient segments.
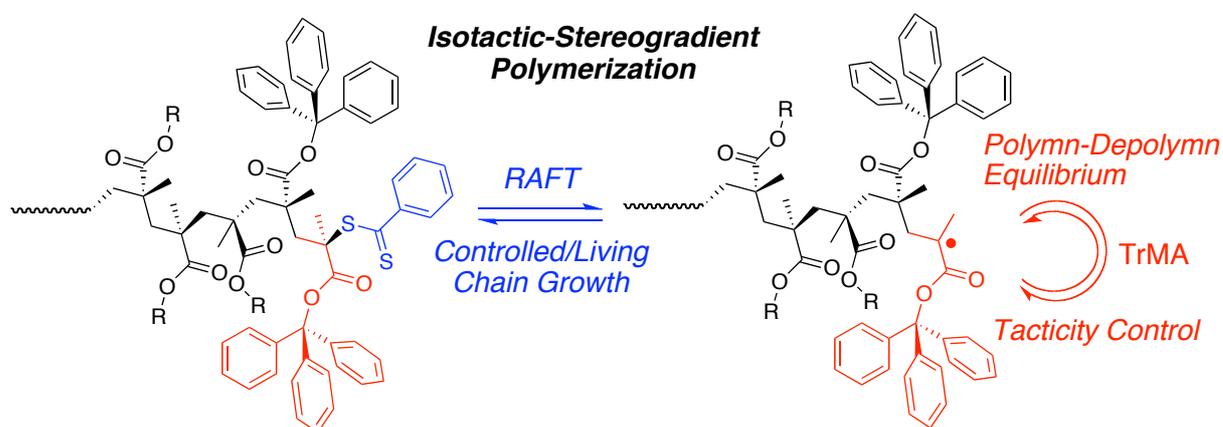

Scheme 2.   Stereogradient Polymers Formed by RAFT Polymerization of TrMA

Chapter 2 discusses the synthesis of from-syndiotactic-to-isotactic stereogradient polymers by RAFT copolymerization of bulky triarylmethyl methacrylates, such as TrMA and PDBSMA, and methacrylic acid (MAA), which propagate via isotactic and syndiotactic-rich enchainment, respectively (Scheme 3).   The reactivity of the acid monomer, MAA, depends on the polarity of the solvents due to the hydrogen-bonding interaction: In toluene, MAA was polymerized faster than TrMA while both monomers were consumed almost at the same rate in 1,4-dioxane.   In both solvents, the molecular weights of the copolymers increased with monomer conversion, indicating that controlled/living radical copolymerization proceeded.   The tacticity of the polymers obtained in toluene gradually changed form *mm* = 11% to nearly 100% along with the polymerizations, whereas the copolymers obtained in 1,4-dioxane resulted in nearly atactic enchainment (*rr*/*mr*/*mm* ~ 38/49/13) throughout the polymerizations monomer.   A similar from-sydiotactic-to-isotactic tereogradient copolymer was also obtained by RAFT copolymerization of PDBSMA and MAA in toluene, where the isotacticity changed from *mm* = 14% to nearly 100%.
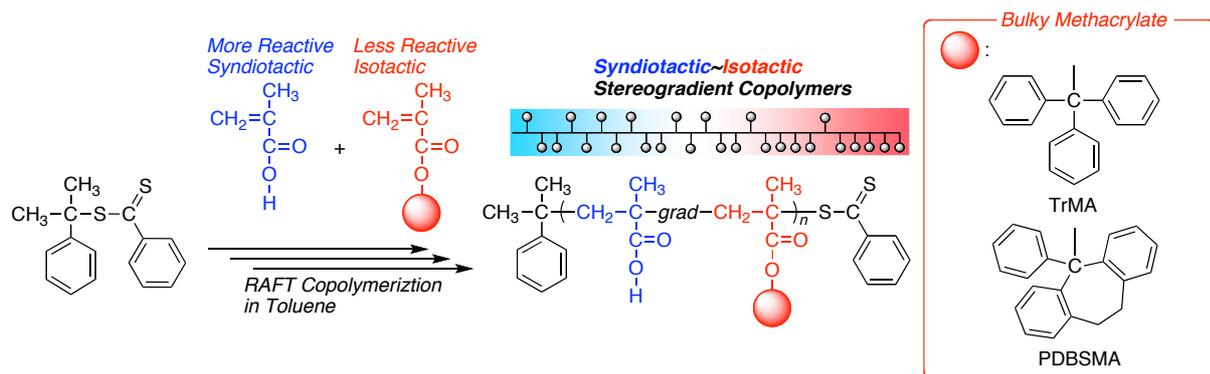
Scheme 3. From-Syndiotactic-to-Isotactic Stereogradient Methacrylic Polymers by RAFT Copolymerization of Methacrylic Acid and Its Bulky Esters.

Chapter 3 is directed to the design and stereospecific radical polymerization of a series of silyl methacrylates [$CH_2=C(CH_3)CO_2SiR_3$] with varying bulkiness in their silyl substituent [R_3Si: Me_3Si, Et_3Si, Me_2tBuSi, iPr_3Si, Ph_2tBuSi, Ph_3Si, and $(Me_3Si)_3Si$] for the synthesis of protected poly(methacrylic acid)s with various tacticities (Scheme 4). The tacticity was heavily dependent on the bulkiness, where the isotacticity increased with increasing the bulkiness. Thus, a series of PMAAs with various tacticities ranging from syndiotactic-rich (rr = 74%; Me_2tBuSi) to atactic (mr = 50%; iPr_3Si) and highly isotactic [mm = 93%; $(Me_3Si)_3Si$] enchainment were obtained by conventional radical polymerization of the silyl methacrylates followed by simple deprotection of the silyl groups. Especially, an extremely bulky silyl methacrylate, TTMSSMA, resulted in a high isotacticity, which is comparable to those for bulky triarylmethyl methacrylates, such as TrMA and PDBSMA. Thus, another bulky substituent, a supersilyl group, which is structurally quite different from a series of precedent triarylmethyl substituents, has proved similarly effective in dictating highly isotactic propagation most probably via the helical polymer conformation. The RAFT polymerization of these silyl methacrylates was achieved by CDB and was applied to the synthesis of novel stereoblock polymers, such as stereo triblock PMAA consisting of syndiotactic-rich, atactic, and isotactic-stereogradient segments.

Silyl Group

CH₃
−Si−CH₃
CH₃
TMS

CH₂CH₃
−Si−CH₂CH₃
CH₂CH₃
TES

CH₃ CH₃
−Si−C−CH₃
CH₃ CH₃
TBDMS

CH₃   CH₃
   CH   CH₃
−Si−CH
       CH₃
CH₃ CH₃
TIPS

        CH₃
−Si−C−CH₃
        CH₃
TBDPS

−Si
TPS

        CH₃ CH₃
CH₃−Si
             CH₃
−Si−Si−CH₃
             CH₃
      Si
CH₃ CH₃
      CH₃
TTMSS

● *Stereospecific Radical Polymerization*

CH₃
CH₂=C
C=O
O
Si

Silyl Methacrylate

→ **Radical Polymn**

$+$CH₂−C$+_n$
CH₃
C=O
O
Si

Protected PMAA

● *syndiotactic-rich*
  TMS
  TBDMS
  TES
● *atactic*
  TIPS
  TBDPS
  TPS
● *isotactic*
  TTMSS

→ **Deprotection**

$+$CH₂−C$+_n$
CH₃
C=O
OH

PMAA with Various Tacticities (mm = 3–93%)

● *Stereospecific RAFT Polymerization*

CH₃
CH₃−C−S−C
         S

Silyl Methacrylate

→ **RAFT Polymn**

CH₃
CH₃−C$+$CH₂−C$+_n$−S−C
                CH₃   S
                C=O
                O
                Si

Silyl Methacrylate

→ **RAFT Block Copolymn**

Stereoblock PMAA

Controlled Molecular Weight Controlled Tacticity

Scheme 4. Stereospecific RAFT Polymerization of Various Silyl Methacrylates for Stereo- and Molecular Weight-Controlled Poly(methacrylic Acid) and Its Ester

Chapter 4 deals with possibility of asymmetric radical or anionic polymerization of the bulky silyl methacrylate, TTMSSMA (Scheme 5). The anionic and radical process. Asymmetric anionic polymerization with 9-fluorenyllithium (Fl-Li) as an initiator in the presence of a chiral ligand, (–)-spartaine [(–)-Sp] was carried out to afford inosoluble polymers almost quantitatively (>90%). The resulting polymers in a solid state exhibited characteristic diffusion reflection circular dichroism (DRCD). The tacticitity of the poly(TTMSSMA)s obtained with the Fl-Li/(–)-Sp system was measured after converted to poly(MMA) and proved highly isotactic (*mm* = 99%). These results indicated the poly(TTMSSMA) had a prevailing one-handed helical conformation in the solid state.
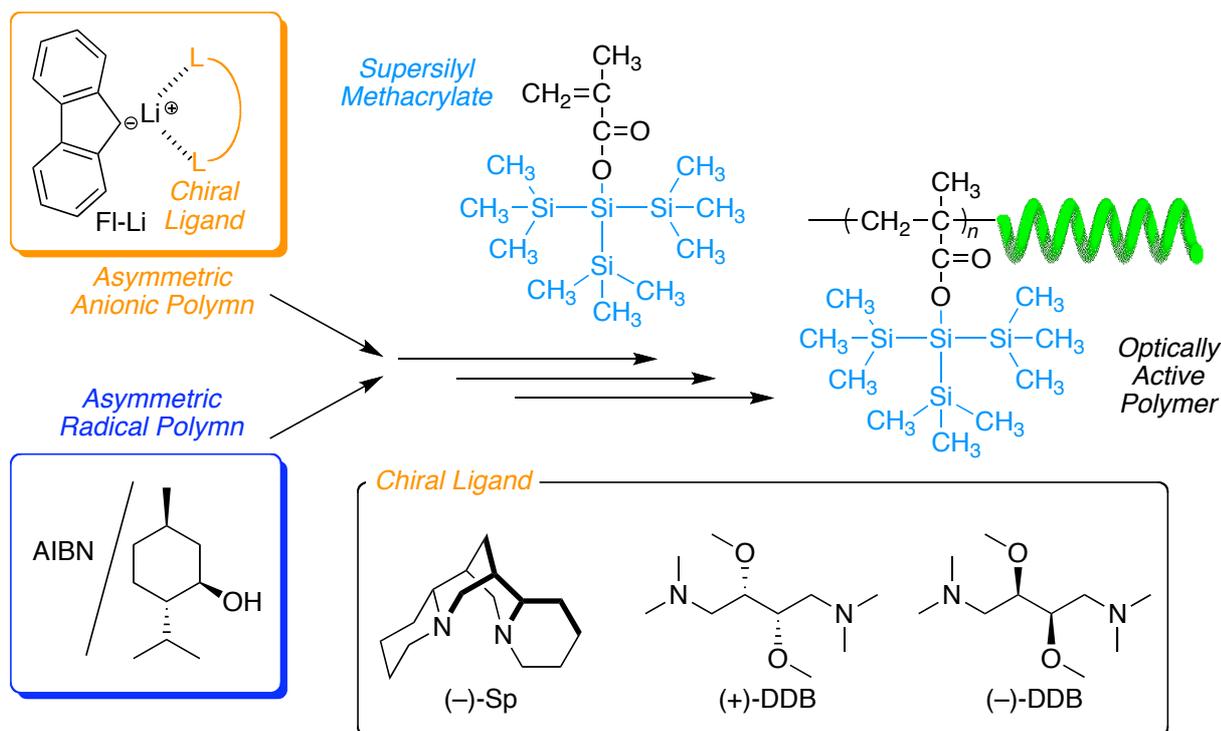
Scheme 5. Asymmetric Anionic or Radical Polymerization of Bulky Silyl Methacrylate

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Part I

Stereospecific Living Radical Polymerization of

Bulky Triarylmethyl Methacrylates

for Novel Stereogradient Polymers

Chapter 1

Setereogradient Polymers Formed by RAFT Polymerization of Bulky Triphenylmethyl Methacrylate

Abstract

A bulky methacrylate, triphenylmethyl methacrylate, was polymerized with RAFT agents to give stereogradient polymers, in which the isospecificity increases spontaneously with the decreasing monomer concentration via polymerization-depolymerization equilibrium. Block copolymerization with methyl methacrylate further resulted in stereoblock copolymers with syndiotactic and isotactic-stereogradient segments.

Introduction

The stereochemistry of monomer additions can be recorded on a living polymer chain because the chain continues its growth throughout the polymerization process. If the stereochemistry of the monomer addition can be changed during the living polymerization, it will be reflected accordingly in the changes in the tacticity along the chain. However, unless the chain is living, the products will only be mixtures of the polymer chains with different tacticities and various chain lengths.

A stereogradient polymer is defined as a polymer in which the tacticity gradually varies along the chain, and is of interest because of the continuous changes in its physical and thermal properties. This type of stereocontrolled polymer is rather new, with only a few examples reported to date;[1–3] this is partly because the synthetic methodology requires both living and stereospecific polymerization and also requires a steady change in the stereospecificity.

A methacrylate monomer with extremely bulky pendant groups, such as triphenylmethyl (TrMA) and its analogues, undergoes anionic polymerization to give highly isotactic polymers.[4,5] Furthermore, asymmetric anionic polymerizations with chiral initiators afford optically active polymers with a stable one-handed helical conformation,[6,7] which are commercialized as a chiral support for HPLC.[8] Even radical polymerizations generate isotactic-rich polymers because of steric repulsion between the bulky ester groups of an incoming monomer and of the growing chain end, which results in a rigid helical conformation of the polymer chain maintained by the bulky substituents, although the isotacticity is slightly lower than for anionic polymerizations.[4] The isotacticity (*mm*) of poly(TrMA) obtained by radical polymerization ranges from 64% to 99% and is dependent on the monomer concentrations, temperatures, and solvents, which is most probably due to changes in the kinetic and thermodynamic control.[9] In particular, the isotacticity increases with the decreasing monomer concentration, which suggests the possibility of preparing stereogradient polymers by giving the chains a living nature (Scheme 1). In this chapter, the author reports the controlled/living radical

polymerization[10] of TrMA by using RAFT agents with varying monomer concentrations and temperatures for the spontaneous formation of the stereogradient polymers.
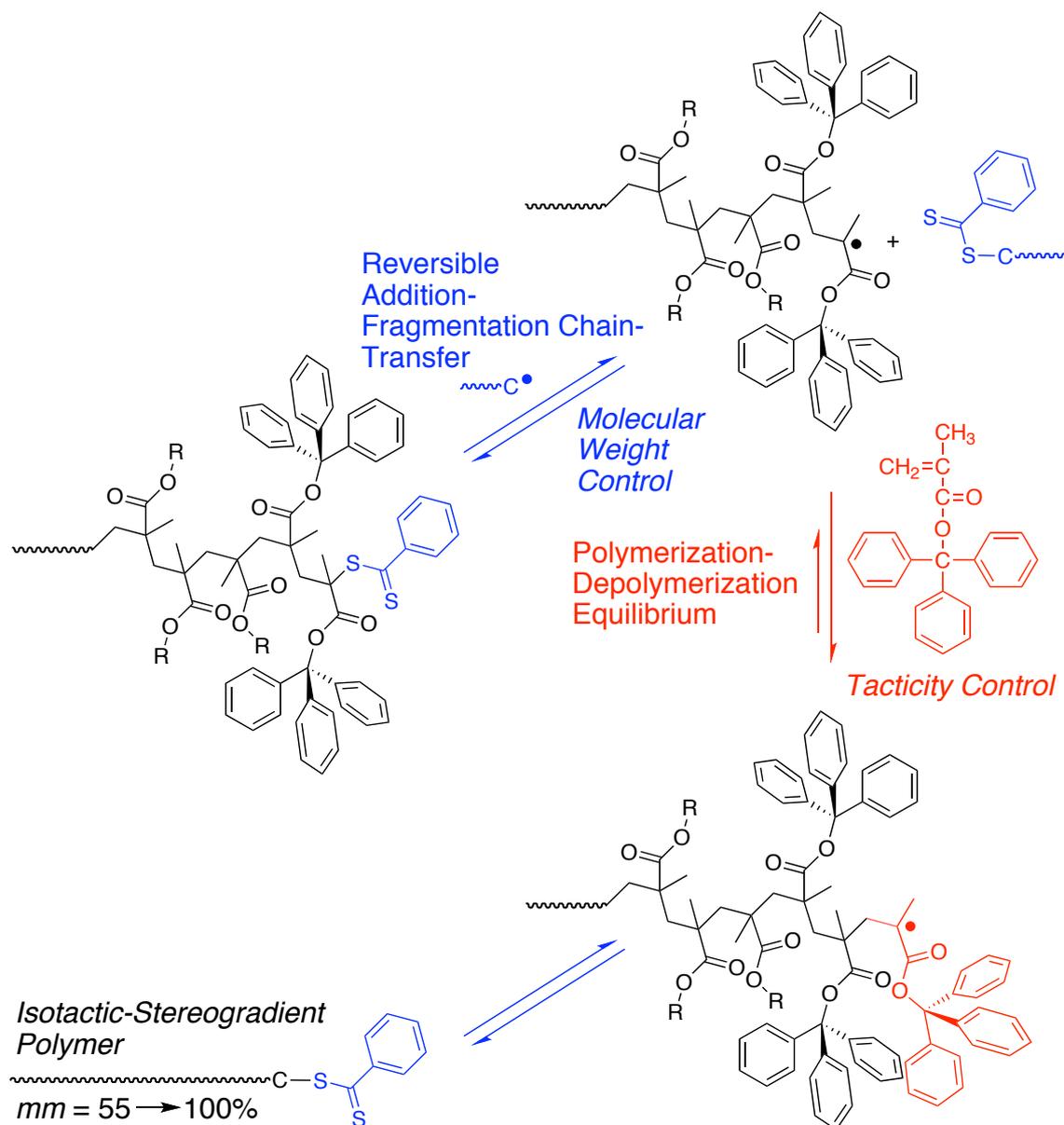
Scheme 1. Stereogradient Polymer by RAFT Polymerization of Triphenylmethyl Methacrylate

Experimental Section

Materials

2,2'-Azobis(isobutyronitrile) (AIBN) (Kishida, >99%) was purified by recrystallization from methanol. 2,2'-azo-bis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) (Wako, >95%) and Et$_2$O solution (Aldrich, 2.0 M) of trimethylsilyldiazomethane were used as received. TrMA was prepared from methacrylic acid and triphenylmethyl chloride and purified by recrystallization as reported.[11] MMA (TCI, >99%) and 1,2,3,4-tetrahydronaphthalene (Wako, 97%) were distilled from calcium hydride under reduced pressure before use. Toluene was distilled over sodium benzophenone ketyl and bubbled with dry nitrogen over 15 minutes just before use. Cumyl dithiobenzoate (CDB) was synthesized according to the literature.[12]

Synthesis of *S*-2-Cyano-2-propyl *S'*-Ethyl Trithiocarbonate (CPETC)

The synthesis of CPETC was conducted similar to that of the *S'*-methyl or *S'*-dodecyl analogues reported by Rizzardo et al.[13] The details are as follows: *S*-ethyl trithiocarbonate (59.3 g, 0.37 mol) was prepared from ethane thiol (27.0 mL, 0.37 mol), sodium hydride (60% in oil) (16.0 g, 0.40 mol), and carbon disulfide (24.0 mL, 0.40 mmol). Into a suspension of sodium *S*-ethyl trithiocarbonate in diethyl ether (760 mL), portions of solid iodine (47.9 g, 0.19 mol) were added under stirring at room temperature. After 1 h, the solution was filtrated to remove sodium iodide, washed with an aqueous solution of sodium thiosulfate to remove excess iodine and water, dried over sodium sulfate, and evaporated to give bis[(ethylthio)thiocarbonyl]disulfide (32.8 g, 119 mmol).

Bis[(ethylthio)thiocarbonyl]disulfide (18.1 g, 65.9 mmol) thus obtained was dissolved in ethyl acetate (400 mL) and mixed with AIBN (22.8 g, 139 mmol). The solution was heated to reflux for 18 h. After evaporation, the crude product was purified by column chromatography on silica gel with *n*-hexane/ethyl acetate (20/1) as an eluent. CPETC (12.8 g, 47% yield) was obtained as red-orange liquids. ^{1}H NMR (CDCl$_3$, rt): δ 1.36 (t, 3H, SCH$_2$C*H$_3$*), 1.88 (s, 6H,

C(C*H*$_3$)$_2$CN), 3.35 (q, 2H, SC*H*$_2$CH$_3$).

Synthesis of *S*-2-Cyano-4-methoxy-4-methyl-2-pentyl *S'*-Ethyl Trithiocarbonate (CMMETC)

The synthesis of CMMETC was conducted similar to the synthesis of CPETC by replacing AIBN with V-70. Bis[(ethylthio)thiocarbonyl]disulfide (16.5 g, 60.9 mmol) and V-70 (25.0 g, 81.1 mmol) were dissolved in ethyl acetate (235 mL), and heated to 30 °C under stirring for 18 h. After evaporation, the crude product was purified by column chromatography on silica gel with *n*-hexane/ethyl acetate (5/1) as an eluent. CMMETC (6.69 g, 21% yield) was obtained as red-orange liquids. ^{1}H NMR (CDCl$_3$, rt): δ 1.27 and 1.45 (ds, 6H, C(C*H*$_3$)$_2$OMe), 1.36 (t, 3H, SCH$_2$C*H*$_3$), 1.97 (s, 3H, C(C*H*$_3$)CN), 2.05 and 2.67 (dd, 2H, C*H*$_2$CMe$_2$OMe), 3.21 (s, 3H, CMe$_2$OC*H*$_3$), 3.34 (q, 2H, SC*H*$_2$CH$_3$).

Polymerization

Polymerization was carried out by the syringe technique under dry argon or nitrogen in sealed glass tubes. A typical example for polymerization of TrMA with CDB/AIBN is given below: in a 50 mL round-bottomed flask were placed TrMA (10.0 mmol; 3.28 g), toluene (4.9 mL), 1,2,3,4-tetrahydronaphthalene (0.55 mL) as an internal standard, and toluene solutions of AIBN (0.50 mL, 0.05 mmol) and CDB (1.0 mL, 0.10 mmol) at room temperature. The total volume of the reaction mixture was 10.0 mL. Immediately after mixing, the solution was evenly charged in 6 glass tubes and the tubes were sealed by flame under nitrogen atmosphere. The tubes were immersed in thermostatic oil bath at 60 °C. In predetermined intervals, the polymerization was terminated by the cooling of the reaction mixtures to −78 °C. Monomer conversion was determined from the concentration of residual monomer measured by ^{1}H NMR with 1,2,3,4-tetrahydronaphthalene as an internal standard (for 48 h, 86% conv.). The quenched reaction solutions were evaporated to dry to give poly(TrMA).

For analysis, the obtained poly(TrMA) was converted into poly(MMA) by acid-hydrolysis of the trityl group followed by methylation with trimethylsilyldiazomethane, as follows:[10,14] a portion of the obtained poly(TrMA) (260.5 mg) was dispersed in CH_3OH (20 mL) containing a small amount of hydrochloric acid (11 M; 1 mL) and the solution was refluxed for 12 h. After concentrating it by evaporation, the product was washed with Et_2O and dried in vacuo at room temperature overnight to give the poly(methacrylic acid) (68.2 mg, 99.8% yield). The poly(methacrylic acid) was dissolved in 10 mL of a toluene/CH_3OH mixture (4/1 vol) and then an Et_2O solution of trimethylsilyl diazomethane (2.0 M, 1.25 mL) was added. After 12 h, the methylation was quenched by adding a small amount of acetic acid. The mixture was washed with distilled water and evaporated to dryness under reduced pressure, and then vacuum-dried to give poly(MMA) (82.0 mg, ~100% yield, M_n = 9300, M_w/M_n = 1.61). Polymer samples for NMR analysis were carefully fractionated by preparative SEC (column: Shodex K-2002) to be free from low molecular weight compounds without loss of MMA oligomers if present.

Measurements

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 55 °C on a Varian Gemini 2000 or a JEOL ECS-400 spectrometer, operating at 400 and 100 MHz for ^1H and ^{13}C, respectively. The triad tacticity of the polymer were determined by the area of the a-methyl protons at 0.8–1.3 ppm in the ^1H NMR spectrum or carbonyl C=O carbons at 175–180 ppm in the ^{13}C NMR spectrum of the side chain. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the product polymers were determined by size-exclusion chromatography (SEC) in $CHCl_3$ at 40 °C on two polystyrene gel columns [Shodex K-805 (pore size: 20–1000 Å; 8.0 mm i.d. × 30 cm) × 2; flow rate 1.0 mL/min] connected to Jasco PU-2080 precision pump and a Jasco RI-2031 detector. The columns were calibrated against 7 standard poly(MMA) samples (Shodex; M_p = 1990–1950000; M_w/M_n = 1.02–1.09).

The normalized chain length (NCL) is defined as the relative polymer chain length at a

certain conversion to those at final conversions.   The isotactic contents (mm_{inst}) for a certain part in the chains were calculated by the following equation:

$$mm_{inst} = d(mm_{cum} \times \text{NCL})/d(\text{NCL})$$

where mm_{cum} is best fitted to a curve from the plots of the cumulative triad isotacticity determined by NMR against the normalized chain length or monomer conversion.

Results and Discussion

1. RAFT Polymerization of TrMA

TrMA was first polymerized by using AIBN in the presence of cumyl dithiobenzoate (CDB)[15] at 60 °C.   The polymerization smoothly occurred and proceeded at almost the same rate for methyl methacrylate (MMA) under the same conditions (Figure 1A).   The SEC of the poly(TrMA) showed broad and bimodal molecular weight distributions (MWDs) (dotted SEC curves in Figure 1C) due to the aggregation of the rigid and less soluble polymers,[16] which were then converted into poly(MMA) by acid-hydrolysis of the trityl group followed by methylation with trimethylsilyldiazomethane.   The obtained poly(MMA) showed unimodal SEC curves, and the number-average molecular weights (M_n) increased with the conversion and were very close to the calculated values (Figure 1B).   Slightly broader MWDs suggest a slower addition-fragmentation process for this bulky monomer.   Trithiocarbonate-type RAFT agents also enabled a similar molecular weight control (Figure 2B).   Thus, the controlled/living radical polymerization of TrMA was attained using these RAFT agents.

The tacticites of the polymers were determined by the ^{1}H or ^{13}C NMR spectra of the PMMAs converted from poly(TrMA) (Figure 3).   All the polymers showed a predominant isotacticity, which increased with the consumption of TrMA.   The entire or cumulative triad isotacticity (mm_{cum}) obtained for each conversion increased from approximately 55% to 65%.   Figure 2 shows a plot of the mm_{cum} value against the normalized chain length, that is, the chain length of
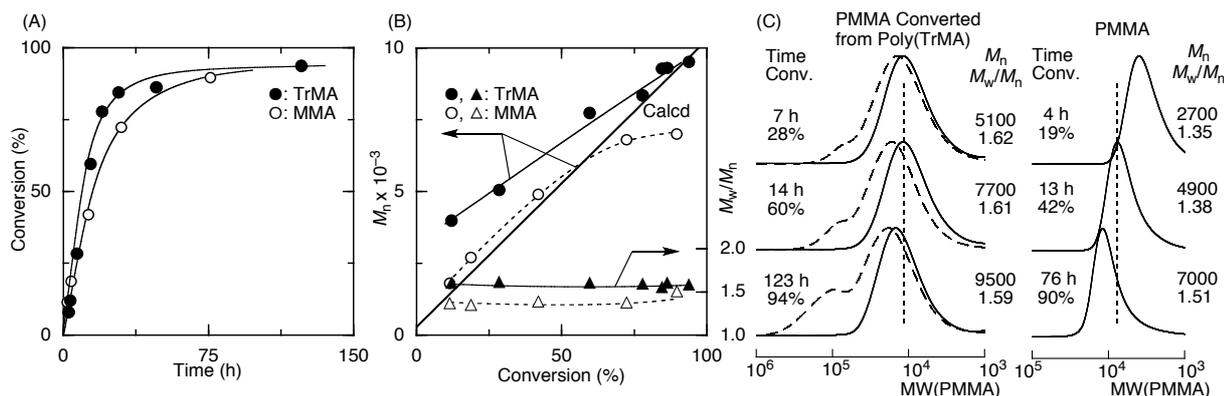
Figure 1. (A) Time-conversion curves, (B) M_n and M_w/M_n, and (C) SEC curves of obtained in the RAFT polymerization of TrMA (●, ▲) and MMA (○, △) with AIBN/CDB in toluene at 60 °C: [Monomer]$_0$ = 1.0 M; [CDB]$_0$ = 10 mM; [AIBN]$_0$ = 5.0 mM. The diagonal line indicates the calculated M_n assuming the formation of one polymer chain per CDB molecule. The dotted SEC curves are elution diagrams of poly(TrMA).
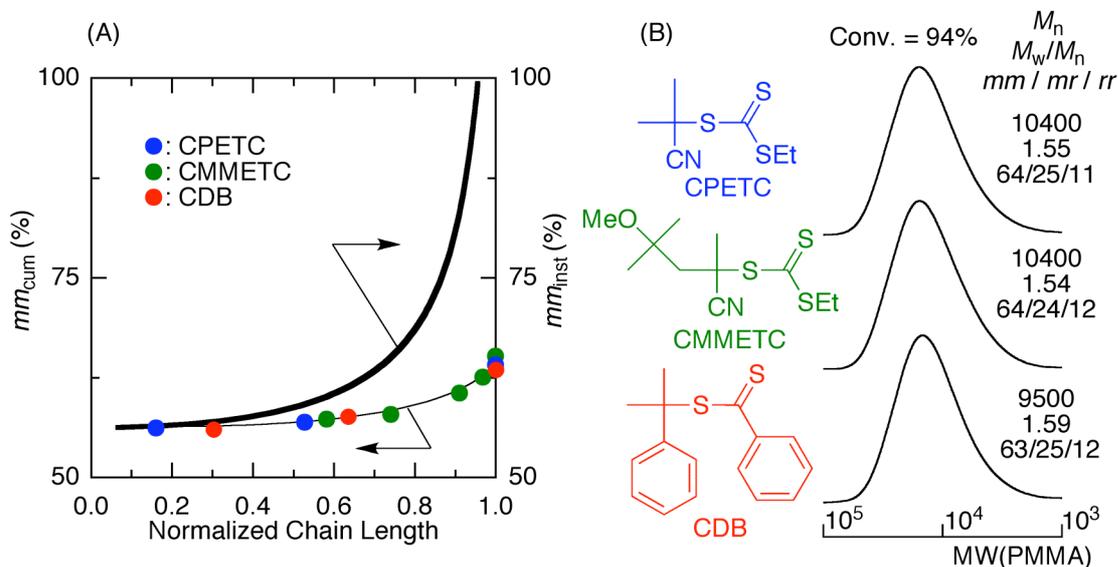

Figure 2. (A) Dependences of cumulative and instantaneous *mm* triad contents on the normalized chain length and (B) SEC curves of poly(MMA) from the RAFT polymerizations of TrMA in toluene at 60 °C: [TrMA]$_0$ = 1.0 M. [RAFT Agent]$_0$ = 10 mM, [AIBN]$_0$ = 5.0 mM; RAFT agent: 2-cyanoprop-2-yl ethyl trithiocarbonate (CPETC) (●), 2-cyano-4-methoxy-4-methylpentan-2-yl ethyl carbonotrithioate (CMMETC) (●), and CDB (●).

the polymers obtained for each conversion relative to those at the final conversion. The mm_{cum} values depended on the monomer conversion, but almost independent of the structure of the RAFT agents. The isotactic contents (mm_{inst}) for a certain part in the chains were then calculated from the differential increase in the mm_{cum} versus the chain length. The instantaneous values of the isotacticity (mm_{inst}) gradually increased with the normalized chain lengths from 55% to finally over 95% (Figure 2A), indicating the formation of the isotactic-rich stereogradient polymers. This means that a decrease in the monomer concentration changes the propagation into a more isotactic enchainment.
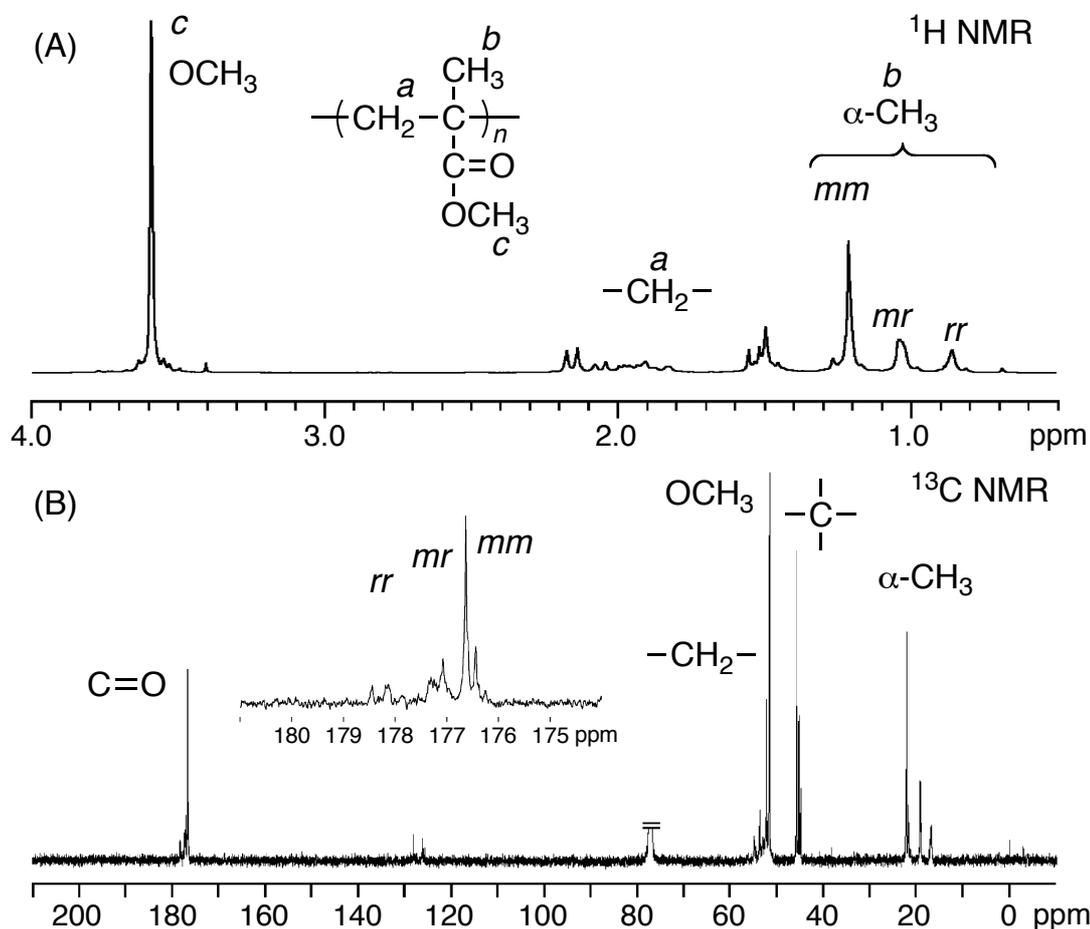
Figure 3. ^{1}H (A) and ^{13}C NMR (B) spectra (CDCl₃, 55 °C) of PMMA converted from poly(TrMA) obtained in the same experiment as for Figure 1.

2. RAFT Polymerization of TrMA under Various Conditions

For analyzing the reaction mechanism, the RAFT polymerization of TrMA was carried out under various conditions by changing initial monomer concentration and temperature.

The effects of the monomer concentration were investigated on the polymerization with CDB in toluene at 60 °C. Upon decreasing the initial monomer concentrations, polymerizations became slower and the final conversions became lower (Figure 4A). However, the final monomer concentrations reached almost the same value (60–70 mM) independent of the initial concentrations, which indicated the presence of the equilibrium monomer concentration for such a bulky monomer even at 60 °C.[17] In all cases, the molecular weights increased with the conversion, showing that the molecular weight control is achievable irrespective of the monomer concentrations (Figure 5A). The mm_{inst} also increased with an increase in the monomer conversion and was higher for a lower initial monomer concentration at the same monomer conversion (Figure 5B). The mm_{inst} was then plotted versus the remaining monomer concentration (Figure 4B). They were almost on the same line, which gradually increased with a
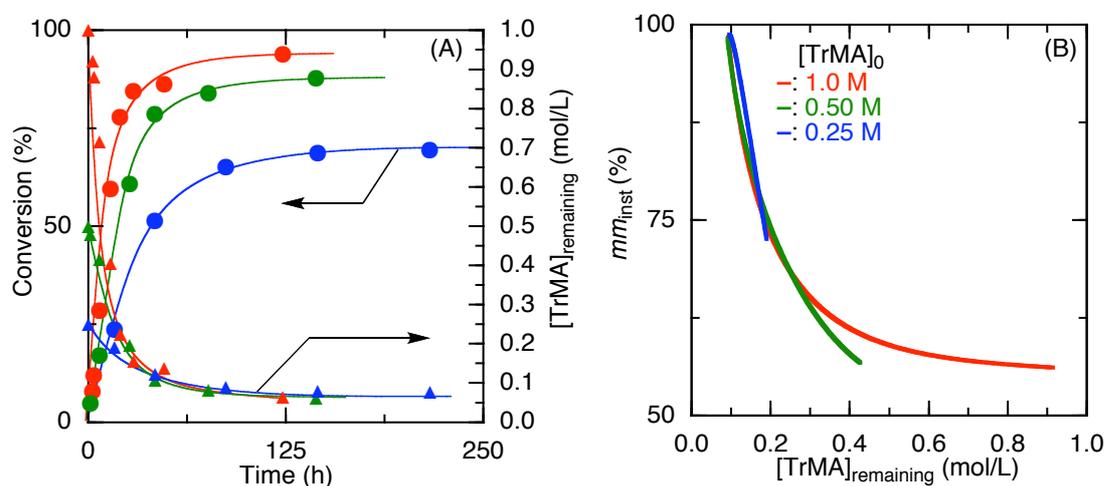

Figure 4. Effects of initial monomer concentrations on the accessible conversion (A) and instantaneous *mm* triad contents (B) in the RAFT polymerizations of TrMA in toluene at 60 °C: $[TrMA]_0$ = 1.0 (●, ▲, −) 0.50 (●, ▲, −), and 0.25 (●, ▲, −) M; $[TrMA]_0/[CDB]_0/[AIBN]_0$ = 100/1/0.5.
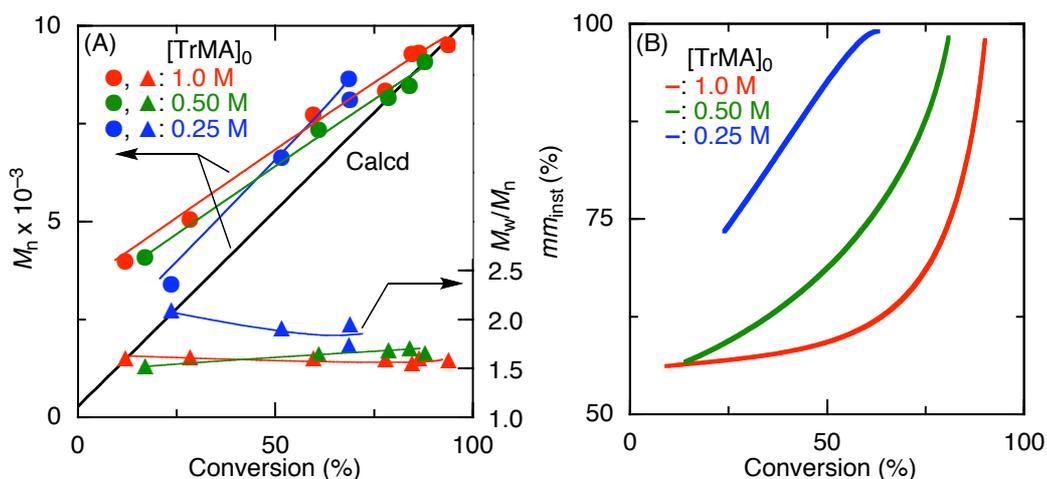
Figure 5. Effects of initial monomer concentrations on the molecular weights (A) and instantaneous *mm* triad contents (B) in the RAFT polymerizations of TrMA in toluene at 60 °C: $[TrMA]_0$ = 1.0 (●, ▲, –) 0.50 (●, ▲, –), and 0.25 (●, ▲, –) M; $[TrMA]_0/[CDB]_0/[AIBN]_0$ = 100/1/0.5.

decrease in the instantaneous monomer concentration. These results indicate that the tacticity is governed by the remaining monomer concentration.

The effects of the temperature were also examined on the polymerizations. Upon raising the temperature, the initial rate increased while the conversions reached plateaus at lower values most probably becoming close to the ceiling temperature at this monomer concentration. The mm_{inst} increased with temperature (Figure 6). These results suggest that lowering the monomer concentration or increasing the polymerization temperature makes the formation of the more thermodynamically stable isotactic propagating chain ends more favorable via the reversible polymerization–depolymerization equilibrium.

The polymerization–depolymerization equilibrium was further examined by increasing the temperature during the polymerization. We thus first conducted the RAFT polymerization at 60 °C and suddenly increased the temperature to 80 °C when the conversion reached 70%. Upon increasing the temperature, the monomer conversion decreased and reached a constant

around 60% (Figure 7). The molecular weights also decreased and became constant while the molecular weight distributions became broader. This also supports the presence of the polymerization–depolymerization equilibrium via the reversible formation of the growing radical species.
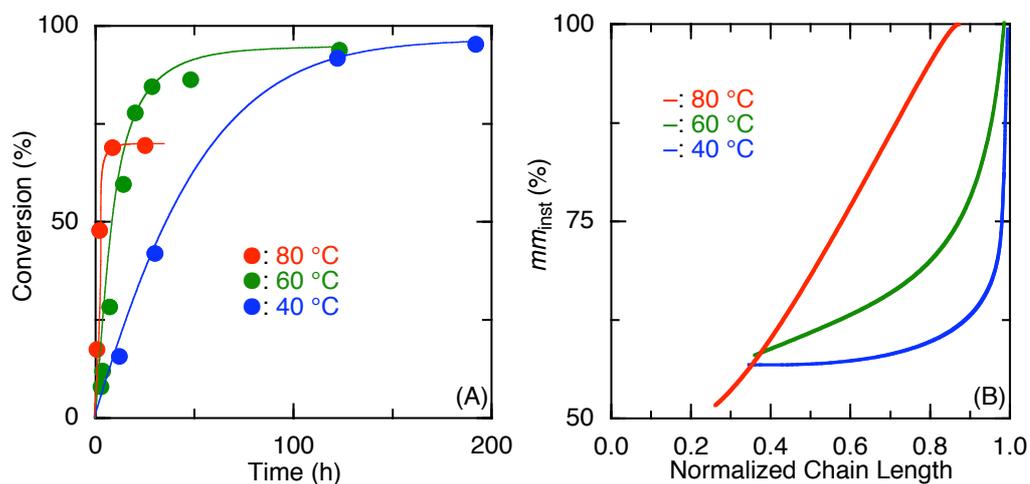

Figure 6. Effects of polymerization temperature on the final accessible monomer conversions and tacticities of the obtained polymer in the RAFT polymerization of TrMA in toluene: $[TrMA]_0$ = 1.0 M; $[CDB]_0$ = 10 mM; $[AIBN]_0$ = 5.0 mM at 80 (red filled circle and line), 60 (green), and 40 °C (blue).
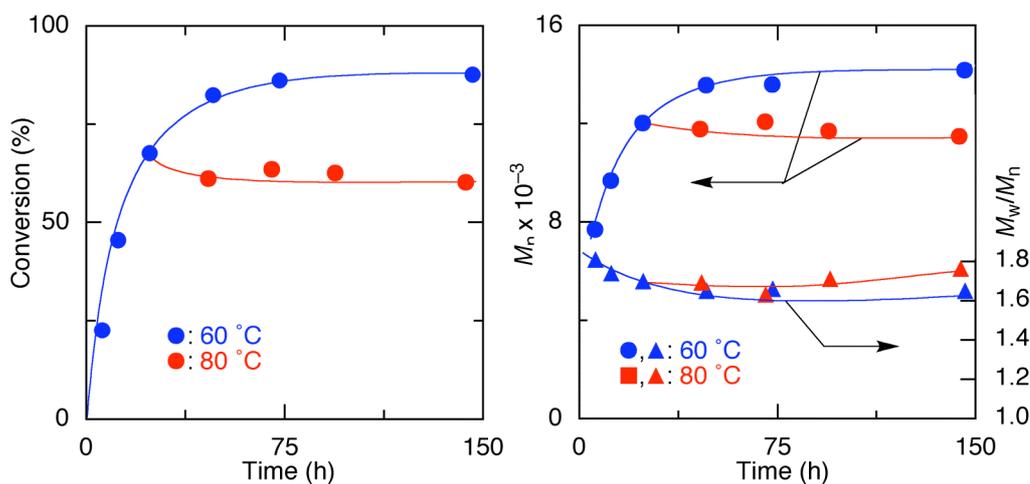

Figure 7. RAFT polymerization of TrMA with increasing the temperature during the polymerization in toluene at 60–80 °C: $[TrMA]_0$ = 0.50 M; $[CPETC]_0$ = 5.0 mM; $[AIBN]_0$ = 2.5 mM.

Table 1. RAFT Polymerization of TrMA at Various Temperatures[a]

temp. (°C)	RAFT Agent	$[TrMA]_0$ (M)	time (h)	conv (%)[b]	$[M]_{eq}$ (mM)[c]	M_n[d]
40	CPETC	0.25	209	90.1	25	9600
40	CPETC	0.50	144	95.3	23	11200
60	CDB	1.0	123	93.8	62	9500
60	CDB	0.50	144	87.8	61	9100
60	CDB	0.25	220	69.6	76	8600
60	CPETC	1.0	58	93.6	64	10400
80	CDB	1.0	25	72.8	272	7100
100	CDB	1.0	1	7.8	922	–
100	CPETC	1.0	2	6.3	937	–

[a] Polymerization conditions: $[TrMA]_0/[RAFT\ Agent]_0/[AIBN]_0 = 100/1.0/0.5$, in toluene. [b] Determined by ^1H NMR. [c] Calculated from $[TrMA]_0$ and monomer conversion. [d] By SEC of poly(MMA) converted from poly(TrMA).

We then measured the final accessible monomer conversions by varying the temperatures (40–100 °C) and the initial monomer concentrations (0.25–1.0 M) to obtain the equilibrium monomer concentration ($[M]_{eq}$) at each temperature (Table 1). We thus plotted the logarithmic monomer concentrations versus the reciprocal of the temperatures (Figure 8). The plot showed a good linear relationship, which indicated the propagation–depropagation equilibrium for this a-substituted bulky monomer. The enthalpy (ΔH_p) and entropy (ΔS_p) for the polymerizations of TrMA were calculated from this linear plot ($\ln[M]_{eq} = \Delta H_p/RT - \Delta S_p/R$) and obtained as follows: $\Delta H_p = -60.4$ kJmol^{-1}, $\Delta S_p = -160.5$ Jmol^{-1}K^{-1}.[18] The enthalpy is almost the same as those for the other methacrylates [ΔH_p(MMA) $= -56$ kJmol^{-1}, ΔH_p(ethyl methacrylate) $= -60$ kJmol^{-1}] while the entropy is higher [ΔS_p(MMA) $= -118$ Jmol^{-1}K^{-1}, ΔS_p(ethyl methacrylate) $= -124$ Jmol^{-1}K^{-1}] probably due to the rigid main-chain conformation of poly(TrMA).[19] The linear plot also gave the ceiling temperature of TrMA at $[M]_0 = 1.0$ M: $T_c = 104$ °C. This is also reasonable because almost no polymers were obtained at 100 °C for $[M]_0 = 1.0$ M.

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$$\ln [M]_{eq} = \Delta H_p/RT - \Delta S_p/R$$
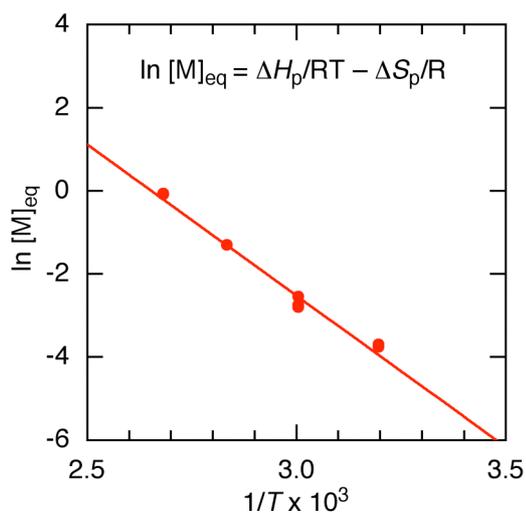
Figure 8. Dependences of equilibrium monomer concentration ($[M]_{eq}$) on temperature in the RAFT polymerizations of TrMA in toluene.

3. Synthesis of Stereoblock Polymers

We further utilized the unique isotactic-rich stereogradient RAFT polymerization for a block copolymerization to synthesize another novel stereocontrolled polymer. Thus we first polymerized MMA with CDB to prepare the syndiotactic-rich living poly(MMA) with RAFT moieties at the chain ends and then employed it as a macroinitiator for the RAFT polymerization of TrMA (Figure 9). After the copolymerization, we converted the trityl substituent into a methyl group and obtained the homopoly(MMA) with narrow MWDs. Figure 5 also shows the cumulative and instantaneous *mm* contents versus the normalized chain length. The isotacticity was abruptly changed at the blocking point, after which it gradually increased along the chain. The differential spectrum of these polymers also indicates the formation of the isotactic-rich segments in the second polymerization (cumulative *mm*/*mr*/*rr* = 61/26/13, Figure 10). These show the formation of the stereoblock PMMA[20] with syndiotactic and isotactic-stereogradient segments.
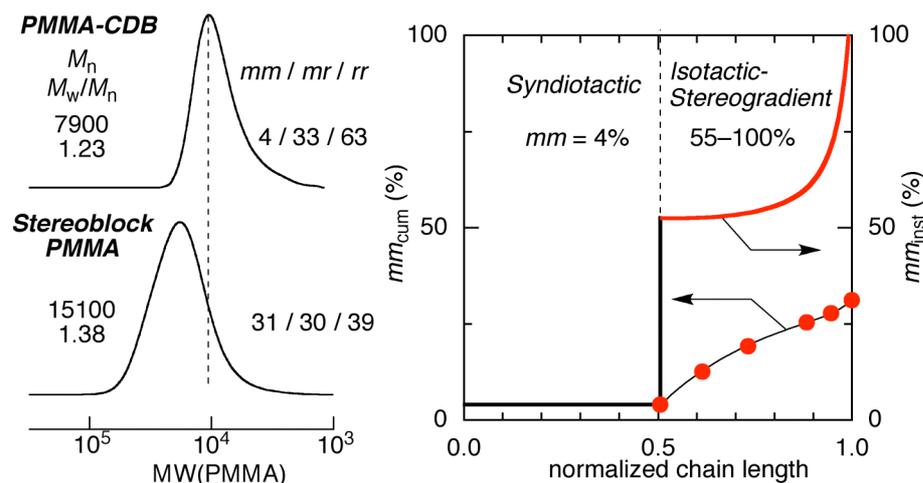
Figure 9. Stereoblock PMMA obtained from the RAFT block copolymerization of MMA and TrMA in toluene at 60 °C. For PMMA macro RAFT agent: $[MMA]_0 = 7.0$ M; $[CDB]_0 = 35$ mM; $[AIBN]_0 = 5.0$ mM, for poly(MMA-*b*-TrMA): $[TrMA]_0 = 1.0$ M; $[PMMA–CDB]_0 = 12$ mM; $[AIBN]_0 = 6.0$ mM.
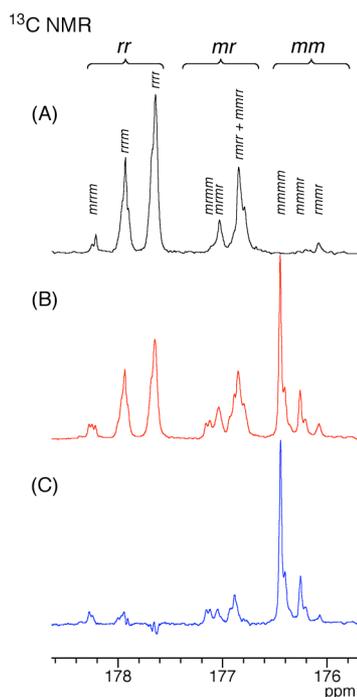

Figure 10. ^{13}C NMR spectra (CDCl$_3$, 55 °C) (for the carbonyl region) of PMMA from the RAFT block copolymerization of MMA and TrMA (the same experiment as for Figure 9): (A) syndiotactic PMMA as a macro RAFT agent, (B) syndiotactic and isotactic-stereogradient PMMA converted from poly(MMA-*b*-TrMA), and (C) their difference spectrum with adjusting y scaling depending on the comonomer compositions (MMA/TrMA = 50.5/49.5).

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Conclusion

In conclusion, the author has demonstrated the formation of stereogradient polymers by the RAFT polymerization of bulky triphenylmethyl methacrylate, in which the isospecificity gradually increased with a decrease in the monomer concentrations. This is caused by the propagation–depropagation equilibrium, which can convert a less stable growing polymer terminal with the *r* conformation into the more stable *m* form especially at a lower monomer concentration. Further studies are now directed to the controlled/living radical copolymerization of bulky methacrylates with other monomers for the synthesis of novel stereocontrolled polymers.[21]

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21. The synthesis of highly isotactic poly(methacrylates) with controlled molecular weights was attempted whereby the TrMA concentration was kept low by slow monomer addition from a syringe pump, but it was experimentally difficult to attain appropriate conditions mainly because of a very slow polymerization under the equilibrium monomer concentration.

Chapter 2

From-Syndiotactic-to-Isotactic Setereogradient Polymers by RAFT Copolymerization of Methacrylic Acid and Its Bulky Methacrylates

Abstract

The synthesis of stereogradient polymers with tacticities that vary from predominantly syndiotactic to highly isotactic was investigated by reversible addition-fragmentation chain transfer (RAFT) copolymerization of bulky methacrylates, such as triphenylmethyl methacrylate (TrMA) and 1-phenyldibezosuberyl methacrylate (PDBSMA) and methacrylic acid (MAA) in both no-polar and polar solvents. The MAA monomer showed increased reactivity in toluene because of hydrogen bonding and was consumed slightly faster than TrMA or PDBSMA. However, the RAFT copolymerization of TrMA and MAA in 1,4-dioxane resulted in consumption of both monomers at the same rate. The copolymers can be easily converted to homopoly(MAA) by the acid hydrolysis of the bulky groups and converted further to poly(methyl methacrylate) by methyl esterification using trimethylsilyldiazomethane to analyze the molecular weights and tacticity. The molecular weights of the polymers obtained in both solvents increased with monomer conversion, which indicates that controlled/living radical copolymerization proceeded irrespective of the solvents. ^{13}C NMR analyses of the polymers revealed that stereogradient polymers were produced in toluene, in which the tacticity changed from mm = 11% to nearly 100%, whereas the copolymers obtained in 1,4-dioxane resulted in nearly atactic enchainment ($rr/mr/mm \approx 38/49/13$), independent of monomer conversion. A similar stereogradient copolymer was also obtained by RAFT copolymerization of PDBSMA and MAA in toluene, where the isotacticity changed more gradually from mm = 14% to nearly 100%.

Introduction

Stereogradinet polymers are a new class of polymers in which the tacticity continuously changes from one chain end to the other. Such polymers may exhibit special properties or functions that originated from gradual changes in the physical or chemical properties along the polymer chain. They can principally be obtained by the combination of living and stereospecific polymerizations, where the stereospecificity gradually changes with the consumption of monomers or with chain growth. Although there have been several reports of syntheses based on the copolymerization of racemic mixtures, on the use of two monomers[1–4] that possess different reactivities and stereoselectivities, or on homopolymerization that accompany a gradual change of stereospecificities along with monomer consumption,[5,6] general synthetic strategies for targeting stereogradient polymers have not yet been established.

Radical polymerization is one of the most robust synthetic methods for vinylic monomers because of the highly reactive propagating radical species. Nonetheless, the control of stereospecificity is difficult due to the "free" and neutral carbon radical species that cannot be regulated by electronic interactions, unlike ionic propagating species with counterions in ionic polymerizations. Although several methods have now been adapted to allow for a degree of stereochemical control of radical species using additives that can interact with pendant polar groups,[7–9] these methods still fall short of the high degree of stereochemical control found in coordination or ionic polymerization reactions. The use of steric interactions around the propagating chain ends dose work for controlling stereospecificity to some extent, even in radical polymerizations, and the bulkienss of monomers can largely affect the tacticity of the resulting polymers.[10–25] In particular, radical polymerization of methacrylic acid esters with very bulky pendant groups, such as triphenylmethyl methacrylate (TrMA)[14,15] and 1-phenyldibezosuberyl methacrylate (PDBSMA),[17–19] gives highly isotactic polymers, whose chains take on a rigid, helical conformations

Living polymerization has also been difficult for radical polymerization because of the

bimolecular termination between the neutral propagating radical species.[26,27] However, tremendous developments in controlled/living radical polymerizations[28–34] based on reversible capping of the growing radical species to form a dormant state have recently been reported. Some of these methods are both versatile and robust and permit the synthesis of finely controlled macromolecular architectures. Furthermore, judicious combinations of stereospecific and living radical polymerizations have enabled the simultaneous control of both the stereospecificity and the molecular weight of the resulting polymers.[2,6,35–39] We have been investigating stereospecific living radical polymerizations and have found several effective combinations for the simultaneous control of molecular weight and tacticity.[35,36] These combinations have allowed us to produce novel polymers, including stereoblock and stereogradient polymers.

As the first synthesis of stereogradient polymers by stereospecific living radical polymerization,[2] we copolymerized two monomers, 2-hydroxyethyl methacrylate (HEMA) and the silyl-capped HEMA [2-(*tert*-butyldimethylsilyl)oxyethyl methacrylate] (SiHEMA), by ruthenium-catalyzed living radical polymerization. The latter monomer exhibits lower reactivity and higher syndiospecificity than the former monomer in $(CF_3)_2C(Ph)OH$. Subsequent deprotection of the silyl group afforded stereogradient homopoly(HEMA), in which the triad syndiotactic (*rr*) content gradually increased from 62% to 77%.

The author has also synthesized stereogradient polymers by relying on the spontaneous and gradual change in the stereospecificity that results from varying the monomer concentration during the controlled/living radical polymerization of a single monomer, TrMA in Chapter 1.[6] The bulky monomer was thus polymerized using a reversible addition-fragmentation chain transfer (RAFT) process to result in stereogradient polymers; the triad isotacticity of the polymers gradually increased with decreasing monomer concentration (*mm* = 55–100%). The author has shown that the stereogradient structure is a result of the propagation–depropagation equilibrium, which can convert a less thermodynamically stable growing terminus with a *racemo* conformation into the more stable *meso* form. The stereogradient structure is more pronounced

with decreasing monomer concentration during the polymerization.

In Chapter 2, the author combined both of the above strategies to synthesize novel stereogradient polymers with more widely varying tacticities using controlled/living radical polymerizations.   Herein, the author has copolymerized methacrylic acid (MAA) and its bulky esters, including TrMA and PDBSMA, by the RAFT method to obtain stereogradient copolymers. These polymers were then converted into the stereogradient poly(MAA) or poly(methyl methacrylate) (PMMA), in which the tacticity varied from predominantly syndiotactic to isotactic enchainment (Scheme 1).   By judicious choice of the copolymerization conditions, including solvent choice, monomer feed ratios, and monomer choice, the spontaneous formation of syndiotactic–isotactic stereogradient polymers was achieved by RAFT copolymerization.   More specifically, when MAA and the bulky methacrylates were copolymerized in the non-polar solvent toluene, stereogradient polymers that varied from syndiotactic to isotactic (mm = 11–100%) enchainment were efficiently produced.
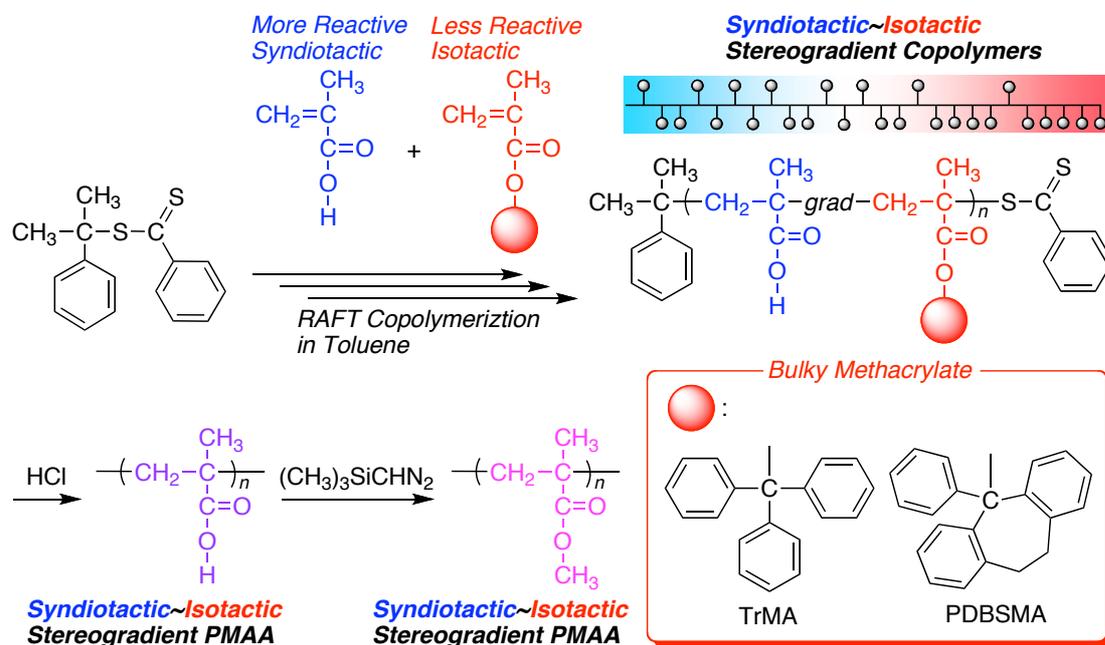
Scheme 1.   Synthesis of Stereogradient Polymers by Stereospecific Controlled/Living Radical Copolymerization of Bulky Methacrylates and Methacrylic Acid

Experimental section

Materials

α,α-Azobis(isobutyronitrile) (AIBN) (Kishida, >99%) was purified by recrystallization from methanol. TrMA[40] and PDBSMA[19] were prepared as reported. MAA (Tokyo Kasei; >99%) was distilled under reduced pressure before use. MMA (Tokyo Kasei, >99%) was distilled from calcium hydride under reduced pressure before use. Toluene and 1,4-dioxane were distilled over sodium benzophenone ketyl and bubbled with dry nitrogen over 15 minutes just before use. Cumyl dithiobenzoate (CDB) was synthesized according to the literature.[41] Et$_2$O solution (Aldrich, 2.0 M) of trimethylsilyldiazomethane, which is known as a stable compound in contrast to diazomethane,[42] was used as received.

General Procedure for RAFT Copolymerization of TrMA and MAA

Polymerization was carried out by the syringe technique under dry argon or nitrogen in sealed glass tubes. A typical example for copolymerization of TrMA and MAA with CDB/AIBN is given below: in a 50 mL round-bottomed flask were placed toluene (5.40 mL), TrMA (4.41 mL of 1.36 M solution in toluene), MAA (0.51 mL, 6.01 mmol), 1,2,3,4-tetrahydronaphthalene (0.48 mL) as an internal standard, and toluene solutions of AIBN (0.60 mL of 100 mM solution in toluene) and CDB (0.60 mL of 200 mM solution in toluene) at room temperature. The total volume of the reaction mixture was 12.0 mL. Immediately after mixing, the solution was evenly charged in 6 glass tubes and the tubes were sealed by flame under nitrogen atmosphere. The tubes were immersed in thermostatic oil bath at 60 °C. In predetermined intervals, the polymerization was terminated by the cooling of the reaction mixtures to −78 °C. Monomer conversion was determined from the concentration of residual monomer measured by ^{1}H NMR with 1,2,3,4-tetrahydronaphthalene as an internal standard (150 h, 88% for TrMA and 100% for MAA, respectively). The quenched reaction solutions were evaporated to dry to give poly(MAA-*grad*-TrMA).

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For analysis, the obtained poly(MAA-*grad*-TrMA) was converted into PMMA by acid-hydrolysis of the trityl group followed by methylation with trimethylsilyldiazomethane, as follows: a portion of the obtained poly(MAA-*grad*-TrMA) (396mg) was dispersed in CH_3OH (20 mL) containing a small amount of hydrochloric acid (11 M; 1 mL) and the solution was refluxed for 12 h.   After concentrating it by evaporation, the product was washed with Et_2O and dried in vacuo at room temperature overnight to give the poly(methacrylic acid) (156 mg, 96% yield). The poly(methacrylic acid) was dissolved in 10 mL of a toluene/CH_3OH mixture (4/1 vol) and then an Et_2O solution of trimethylsilyldiazomethane (2.0 M, 2.50 mL) was added.   After 12 h, the methylation was quenched by adding a small amount of acetic acid.   The mixture was washed with distilled water and evaporated to dryness under reduced pressure, and then vacuum-dried to give PMMA (182 mg, 96% yield, M_n = 10100, M_w/M_n = 1.63).   Polymer samples for NMR analysis were fractionated by preparative SEC (column: Shodex K-2002) to be free from low molecular weight compounds without loss of MMA oligomers if present.

Measurements

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 55 °C on a JEOL ECS-400 spectrometer, operating at 400 and 100 MHz for ^1H and ^{13}C, respectively.   The triad tacticity of the polymer was determined by the area of the α-methyl protons at 0.8–1.3 ppm in the ^1H NMR spectrum or carbonyl C=O carbons at 175–180 ppm in the ^{13}C NMR spectrum of the side chain. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the product polymers were determined by size-exclusion chromatography (SEC) in $CHCl_3$ at 40 °C on two polystyrene gel columns [Shodex K-805 (pore size: 20–1000 Å; 8.0 mm i.d. × 30 cm) × 2; flow rate 1.0 mL/min] connected to Jasco PU-2080 precision pump and a Jasco RI-2031 detector. The columns were calibrated against 7 standard PMMA samples (Shodex; M_p = 1990–1950000; M_w/M_n = 1.02–1.09).

The normalized chain length is defined as the relative polymer chain length at a certain

conversion to those at final conversions. The TrMA contents ($F_{inst,TrMA}$) and the isotactic contents (mm_{inst}) for a certain part in the chains were calculated by the following equation:

$$F_{inst,TrMA} = d(F_{cum,TrMA} \times total\ conv.)/d(total\ conv.)$$

$$mm_{inst} = d(mm_{cum} \times total\ conv.)/d(total\ conv.)$$

where $F_{cum,TrMA}$ and mm_{cum} are best fitted to a curve from the plots of the cumulative triad isotacticity determined by NMR against the total conversion or normalized chain length.

Results and Discussion

RAFT Homopolymerization of TrMA and MAA

Prior to the copolymerizations, the author investigated the controlled/living homopolymerizations of MAA and TrMA using cumyl dithiobenzoate (CDB) as the RAFT agent in non-polar (toluene) and polar (1,4-dioxane) aprotic solvents.

The RAFT polymerization of MAA was performed with CDB in the presence of AIBN as the radical reservoir at 60 °C. The reactivity of MAA was highly dependent on the solvent; its consumption rate in toluene was significantly higher than that in 1,4-dioxane (Figure 1).
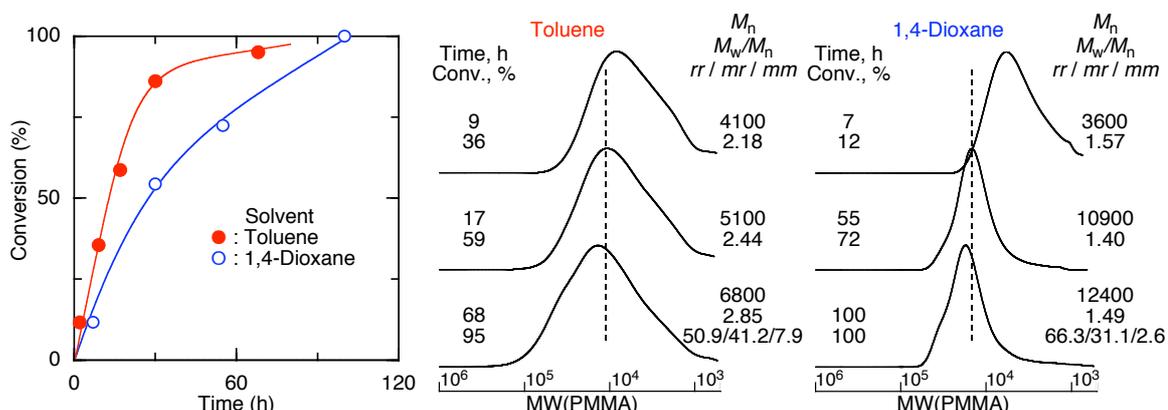

Figure 1. RAFT homopolymerization of MAA with CDB/AIBN in toluene (red) or 1,4-dioxane (blue) at 60 °C: $[MAA]_0 = 1.0$ M; $[CDB]_0 = 10$ mM; $[AIBN]_0 = 5.0$ mM. SEC curves: poly(MMA) converted from the obtained poly(MAA).

This result is consistent with previous studies on the solvent effects in the free radical polymerization of MAA, in which intermolecular hydrogen bonding of MAA induces the high

reactivity observed in non-polar solvents such as toluene.[43]   To evaluate the molecular weights

and tacticity of the products, the obtained poly(MAA) was then converted into PMMA by

esterification using trimethylsilyldiazomethane.[6,44]   In both cases, the number-average molecular

weights (M_n) of the converted polymers increased with monomer conversion, which indicates that

the RAFT polymerization of MAA proceeded in controlled fashion, irrespective of the solvent.

The molecular weight distribution (MWD) of the polymer obtained in toluene was broader than

that obtained in 1,4-dioxane, probably because of the lower solubility of poly(MAA) in the

non-polar solvent.   The tacticity of the PMMA was then determined by ^{13}C NMR analysis.   As

is often observed in the free radical polymerization of methacrylic acid and other typical

methacrylates, the tacticity of the obtained polymers was predominantly syndiotactic.   Their

syndiotacticity also depended on the solvent: the poly(MAA) obtained in toluene (rr = 50%) was

less syndiotactic than that obtained in 1,4-dioxane (rr = 66%).   These results indicate that the

intermolecular hydrogen bonding of MAA affected not only the reactivity during the RAFT

polymerization but also the tacticity of the resultant polymers.[45]

In contrast to MAA, the TrMA polymerizations proceeded smoothly at almost the same

rate in both solvents (Figure 2).   As previously reported, SEC analysis of the obtained

poly(TrMA) showed broad and bimodal MWDs because of the aggregation of the rigid and

less-soluble polymers.[40]   Thus, the obtained poly(TrMA) was similarly converted into PMMA

by acid hydrolysis of the trityl group, followed by methyl esterification.   Irrespective of the

reaction solvents, the SEC curves of the converted polymers became unimodal after the

treatments.   Furthermore, the M_n values increased in proportion to the monomer conversion and

were similar to the calculated values, assuming that one RAFT agent generates one polymer chain.

The slightly broad MWDs were probably due to the slower addition-fragmentation process during

the bulky TrMA polymerization, as discussed in previous work.[6]
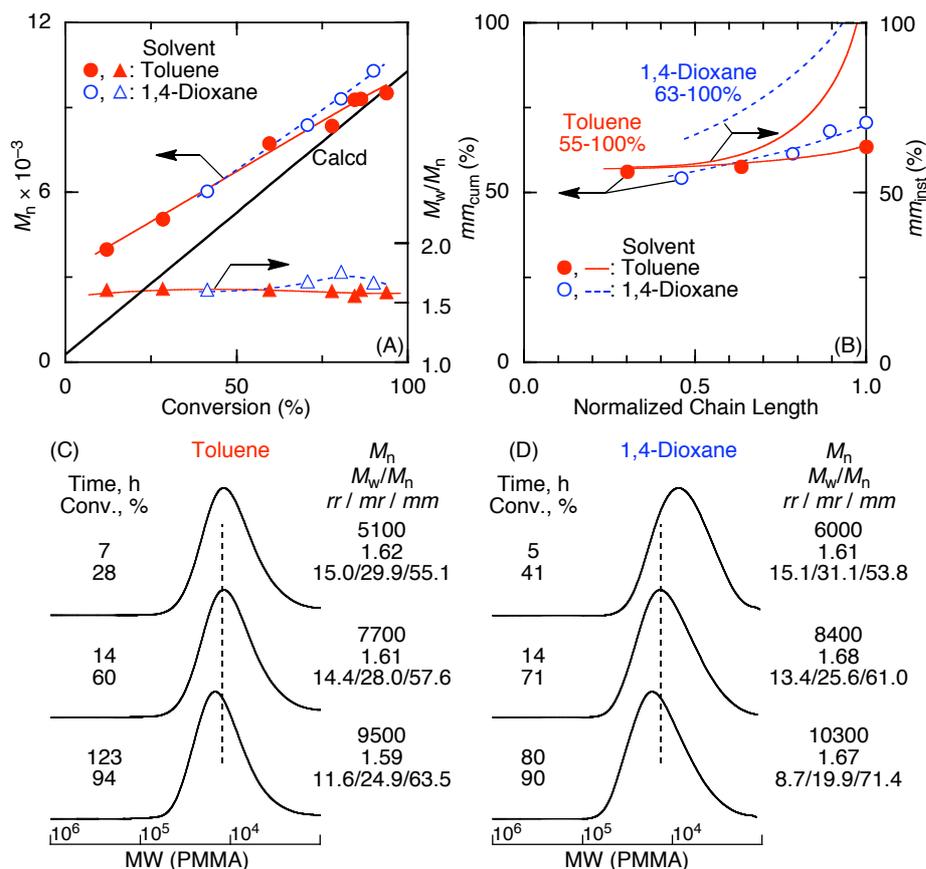
Figure 2. RAFT homopolymerization of TrMA with CDB/AIBN in toluene (red) or 1,4-dioxane (blue) at 60 °C: $[\text{TrMA}]_0 = 1.0$ M; $[\text{CDB}]_0 = 10$ mM; $[\text{AIBN}]_0 = 5.0$ mM. (A) M_n and M_w/M_n values of poly(MMA) converted from the obtained poly(TrMA) vs monomer conversion of TrMA. The diagonal bold line indicates the calculated M_n assuming the formation of one living polymer per CDB molecule. (B) Dependences of cumulative and instantaneous isotacticity (*mm*) contents on the normalized chain length in the RAFT polymerization of TrMA. (C) and (D) SEC curves of poly(MMA) converted from poly(TrMA) obtained in toluene and 1,4-dioxane, respectively.

The polymers obtained in 1,4-dioxane also exhibited isotactic-rich stereogradient structures, with the cumulative triad isotacticity (mm_{cum}) varying more gradually than that observed in toluene (Figure 2B). These results suggest that the polymerization–depolymerization equilibrium also depends on the polarity of the solvent.

Thus, controlled/living radical homopolymerizations of TrMA and MAA were attained using the RAFT method to afford polymers with controlled molecular weights. Furthermore, isotactic-rich stereogradient enchainment was achieved for TrMA, and syndiotactic-rich stereostatic enchainment was achieved for MAA, where the steric structures of the resulting polymers were observed to be somewhat dependent on the reaction solvent.

Stereogradient polymers by RAFT copolymerization of TrMA and MAA

For the synthesis of stereogradient polymers varying from predominantly syndiotactic to isotactic domains, the RAFT copolymerization of TrMA and MAA was performed using the CDB/AIBN system at 60 °C in either toluene or 1,4-dioxane (Figure 3).
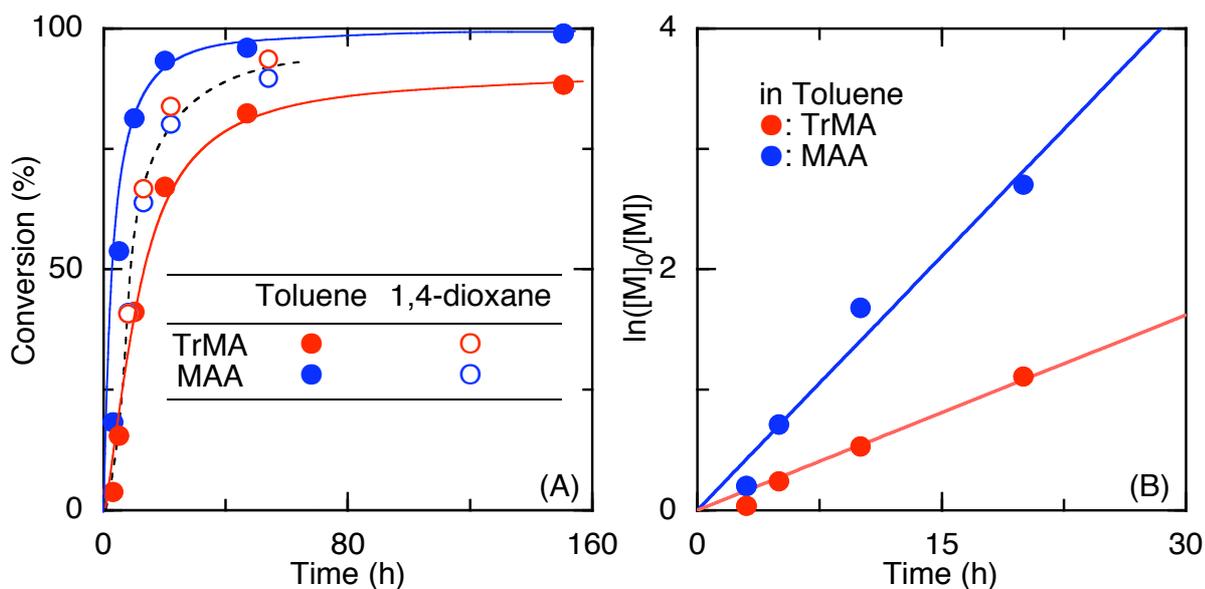
Figure 3. (A) Time-conversion curves and (B) first-order kinetic plots for the RAFT copolymerization of TrMA and MAA with CDB/AIBN in toluene (solid lines) or 1,4-dioxane (dashed line) at 60 °C: $[TrMA]_0 = [MAA]_0 = 0.50$ M; $[CDB]_0 = 10$ mM; $[AIBN]_0 = 5.0$ mM.

Irrespective of the solvent choice, the copolymerizations proceeded efficiently to produce the copolymers. As was observed in the homopolymerizations, the reactivity of MAA was clearly affected by the polarity of the solvent during the copolymerization with TrMA. Whereas the

two monomers were simultaneously consumed at the same rate in 1,4-dioxane, the consumption

of MAA was faster than that observed for TrMA in toluene (Figure 3A). A similar tendency has

been previously reported for the free radical copolymerization of MMA and MAA.[46] Figure 3B

shows the first-order plots for the RAFT copolymerization of MAA and TrMA in toluene, where

the initial slope for the MAA consumption was 2.5 times greater than that for TrMA. This result

indicates that a copolymer with a higher MAA content was formed at the initial stage of the

copolymerization and that the content of TrMA gradually increased as the reaction proceeded.

After the trityl ester groups in the obtained copolymers were hydrolyzed by acid, the

resulting homopoly(MAA) was further converted to PMMA by methylation with

trimethylsilyldiazomethane to analyze the molecular weights and tacticity. Figure 4 shows the

M_n, MWDs, and SEC curves of the PMMA obtained from copolymers of TrMA and MAA in

toluene and 1,4-dioxane. Irrespective of the solvent, the SEC curves were unimodal and shifted

to higher molecular weights as the copolymerizations proceeded. The M_n of the obtained

polymers increased in direct proportion to the total monomer conversions and was similar to the

calculated values, assuming that one molecule of the RAFT agent generates one polymer chain.

These results indicate that the radical copolymerization of TrMA and MAA proceeded in a

controlled manner using CDB as the RAFT agent.

As expected from these results on the copolymerization rates and the molecular weights,

gradient copolymers of MAA and TrMA were spontaneously formed during RAFT

copolymerization in toluene, whereas random copolymers of TrMA and MAA were obtained in

1,4-dioxane. Figure 5 shows a plot of the cumulative TrMA contents ($F_{TrMA,cum}$) in the produced

copolymers against the normalized chain length, i.e., the ratio of chain length at a given

conversion to the full chain length at final conversion. The $F_{TrMA,cum}$ values of the copolymers

obtained in toluene increased from approximately 20% to 50% (filled circles in Figure 5),

whereas the $F_{TrMA,cum}$ values in 1,4-dioxane were almost constant, at approximately 50% (open

circles), throughout the copolymerization. The instantaneous TrMA contents ($F_{TrMA,inst}$) for a
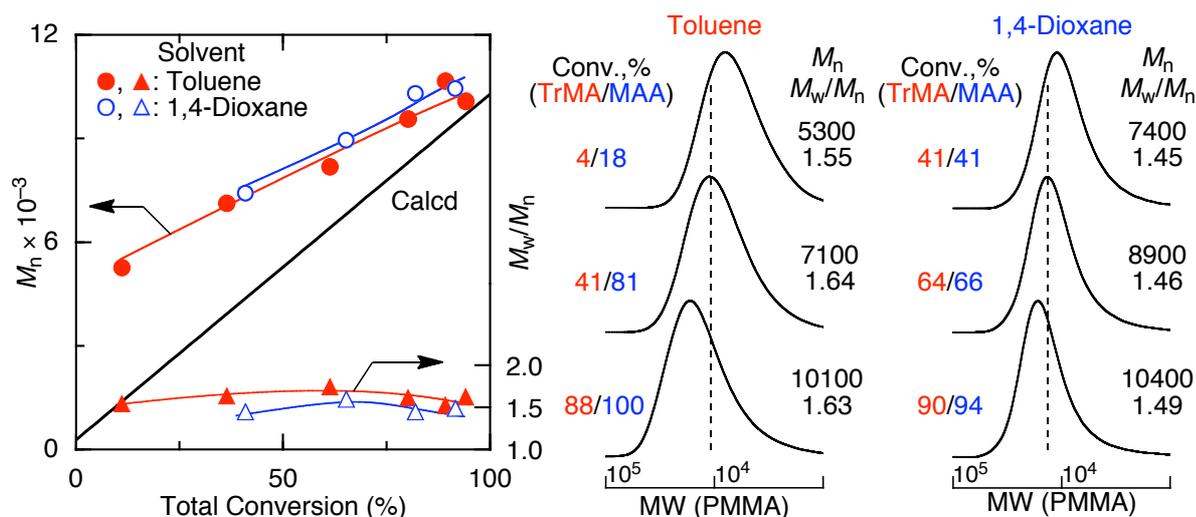
**Figure 4.** M_n, M_w/M_n, and SEC curves of poly(MMA) converted from the copolymers, which were obtained in the RAFT copolymerization of TrMA and MAA with CDB/AIBN in toluene (red) or 1,4-dioxane (blue) at 60 °C: $[TrMA]_0 = [MAA]_0 = 0.50$ M; $[CDB]_0 = 10$ mM; $[AIBN]_0 = 5.0$ mM.
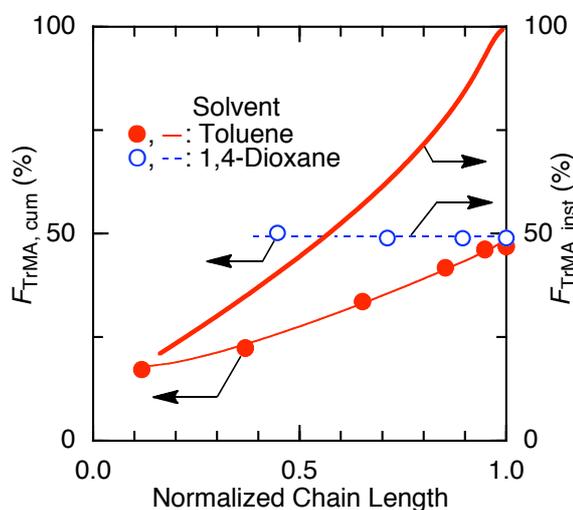

Figure 5. Dependences of cumulative ($F_{TrMA,cum}$) and instantaneous ($F_{TrMA,inst}$) TrMA contents on the normalized chain length in the RAFT copolymerization of TrMA and MAA with CDB/AIBN in toluene (red) or 1,4-dioxane (blue) at 60 °C: $[TrMA]_0 = [MAA]_0 = 0.50$ M; $[CDB]_0 = 10$ mM; $[AIBN]_0 = 5.0$ mM.

certain part of the polymer chain were then calculated from the differential increase in the $F_{TrMA,cum}$ value. The $F_{TrMA,inst}$ in toluene was then estimated to change gradually from 20% to 100% (bold line in Figure 5). Thus, the spontaneous formation of gradient copolymers in toluene was proved, with a gradually increasing TrMA content observed along the polymer chain.

The tacticity of the obtained polymers was investigated using ^{13}C NMR spectroscopy by analyzing the resonances of the carbonyl carbons in PMMA obtained from the RAFT copolymerizations of TrMA and MAA in toluene and 1,4-dioxane (Figure 6A). The tacticity of
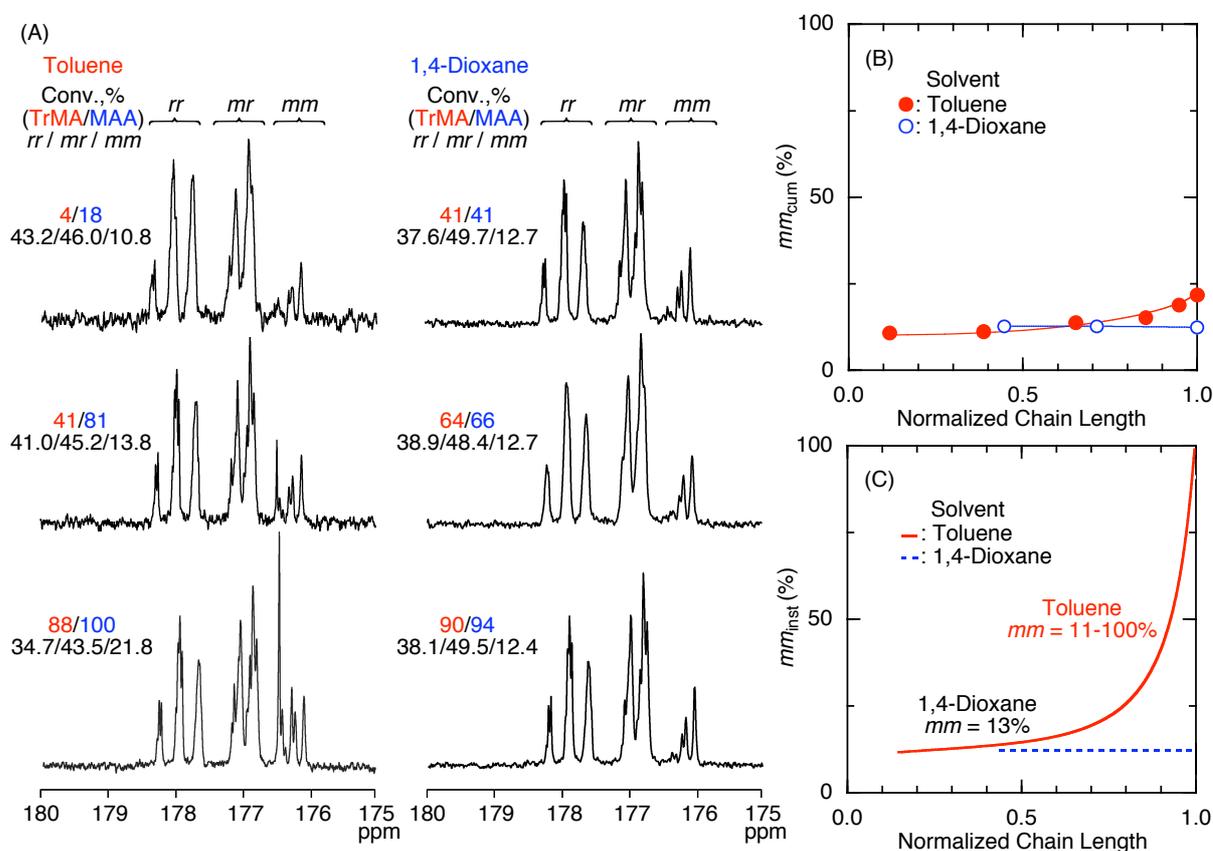

Figure 6. ^{13}C NMR spectra (CDCl$_3$, 55 °C) of poly(MMA) converted from the obtained copolymers (A), dependences of cumulative (B) and instantaneous (C) isotacticity (*mm*) contents on the normalized chain length in the RAFT copolymerization of TrMA and MAA with CDB/AIBN in toluene (red) or 1,4-dioxane (blue) at 60 °C: [TrMA]$_0$ = [MAA]$_0$ = 0.50 M; [CDB]$_0$ = 10 mM; [AIBN]$_0$ = 5.0 mM.

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the polymers obtained in 1,4-dioxane were nearly constant (*rr*/*mr*/*mm* ~ 38/49/13) during the copolymerizations because both monomers were consumed at the same rate in 1,4-dioxane, irrespective of their differing stereospecificities. Furthermore, the importance of the propagation–depropagation equilibrium step observed for the polymerization of TrMA was absent in the random copropagation of TrMA with the less-bulky MAA monomer under the reaction conditions. In contrast, the polymer obtained in toluene exhibited a gradual change in tacticity. The peak intensities related to the triad tacticity changed as the copolymerization proceeded, with the isotactic content increasing from 11% to 22%. More specifically, although the polymers formed at lower monomer conversion were syndiotactic rich (*rr*/*mr*/*mm* ~ 43/46/11), they became nearly atactic (*rr*/*mr*/*mm* ~ 35/43/22) as the reaction progressed. Figure 6B plots the cumulative triad isotacticity values (mm_{cun}) of the polymers obtained at each conversion as a function of the normalized chain length of the polymers. In toluene, the mm_{cum} values of the polymers gradually increased from 11% to 22% as the copolymerization proceeded. Furthermore, the instantaneous triad isotacticity (mm_{inst}) values, which were calculated from the differential increase in the mm_{cum} values, significantly varied from 11% to near 100% (Figure 6C). Thus, RAFT copolymerization of TrMA and MAA proved effective in producing controlled/living copolymers with spontaneous gradients in monomer composition as well as polymers with varying tacticity in their main chain structure.

These results indicate that the key factors for obtaining polymers with steeply graded structures not only include the different reactivities and stereospecificities of the monomers, TrMA and MAA, but also include changes in the monomer concentrations during the copolymerizations. At an early stage of copolymerization in toluene, the more reactive MAA is predominantly consumed to generate syndiotactic-rich enchainment. As the copolymerization proceeds, the less-reactive TrMA is incorporated into the copolymer to form isotactic-rich enchainment. Finally, when MAA is completely consumed and the concentration of TrMA becomes sufficiently low, substantial homopropagation of TrMA induces a gradual increase in

isotacticity via propagation–depropagation equilibrium at the growing terminus, as was reported for TrMA homopolymerization.[6]   Along with the continuous and gradual changes in the monomer composition and stereochemistry, the reversible interconversion between the growing radical species and the stable RAFT terminus enables stereogradient propagation from syndiotactic to isotactic in each polymer chain in a controlled/living fashion.

RAFT Copolymerization of TrMA and MAA under Various Conditions

In an attempt to optimize the conditions for preparing various stereogradient polymers, the RAFT copolymerization of MAA and TrMA was investigated under various conditions by changing monomer feed ratios and temperature (Table 1).

The effects of the initial monomer ratio were examined for the RAFT copolymerization of TrMA and MAA in toluene, including ratios of $[TrMA]_0/[MAA]_0 = 1/1$, $3/1$, and $1/3$ (Table 1, entries 1–3, respectively).   In all cases, MAA was consumed faster than TrMA.   The molecular weights of the products increased as the copolymerizations progressed, although the MWDs became broader at higher MAA concentration (Figures 7–9).   The gradient structures, both in monomer composition and in stereospecificity, were confirmed by increases in the TrMA incorporation ratio and the triad isotacticity determined by ^1H and ^{13}C NMR spectroscopies, respectively.   As the initial feed ratio of TrMA was increased, greater $F_{TrMA,cum}$ and $F_{TrMA,inst}$ values were observed at all conversions.   The mm_{cum} and mm_{inst} values also depended on the initial feed ratios of TrMA, whereas the isotacticity increased with normalized chain length in all cases.

Table 1. RAFT Copolymerization of Bulky Methacrylates (M$_1$) and Methacrylic Monomers (M$_2$)[a]

entry	M$_1$	M$_2$	[M$_1$]$_0$/[M$_2$]$_0$	temp., °C	time, h	conv. (M$_1$/M$_2$), %[b]	total conv., %[b,c]	M$_n$[d]	M$_w$/M$_n$[d]	F$_{M_1, cum}$, %[e]	F$_{M_1, inst}$, %[f]	mm$_{cum}$, %[g]	mm$_{inst}$, %[h]
1	TrMA	MAA	1/1	60	3	3/18	11	5300	1.55	17	–	11	–
					10	41/81	61	7100	1.64	34	58	14	18
					150	88/100	94	10100	1.63	47	99	22	100
2	TrMA	MAA	3/1	60	5	37/16	21	5100	1.59	58	58	20	20
					24	63/100	46	7400	1.68	59	68	21	30
					58	88/100	91	10300	1.62	73	100	35	100
3	TrMA	MAA	1/3	60	3	3/20	16	3800	1.88	5	–	6	–
					10	25/68	57	7500	1.98	11	20	9	7
					123	77/100	94	8000	1.94	20	100	11	100
4	TrMA	MAA	1/1	40	7	5/19	12	3800	1.73	22	–	11	–
					38	35/76	56	8500	1.87	32	37	14	20
					216	90/100	95	10300	1.63	47	100	22	100
5	TrMA	MAA	1/1	80	0.17	6/13	12	5200	1.58	32	–	9	–
					1.5	39/95	67	6600	1.67	29	n.d.	10	n.d.
					12	49/100	74	6300	1.62	33	n.d.	13	n.d.
6[i]	TrMA	MAA	1/1	60	8	41/41	41	7400	1.45	51	50	12	13
					13	64/66	65	8900	1.46	49	50	13	13
					54	90/94	92	10400	1.49	51	49	13	13
7	TrMA	MMA	1/1	60	12.5	23/23	23	5400	1.33	50	50	15	15
					24	55/51	53	7900	1.36	51	51	15	15
					116	>99/>99	>99	10400	1.39	50	50	15	15
8[i]	PDBSMA	MAA	1/1	60	4	15/34	24	5500	1.67	30	–	12	–
					16	48/76	62	8200	1.61	39	54	18	27
					83	87/98	93	8800	1.69	47	100	27	100

[a] Polymerization conditions: [M$_1$]$_0$ + [M$_2$]$_0$ = 1.0 M, [CDB]$_0$ = 10 mM, [AIBN]$_0$ = 5.0 mM in toluene. [b] Determined by ^{1}H NMR. [c] Total conv. = ([M$_1$]$_0$ × conv.(M$_1$) + [M$_2$]$_0$ × conv.(M$_2$))/([M$_1$]$_0$ + [M$_2$]$_0$) [d] The number-average molecular weight (M_n) and distribution (M_w/M_n) were determined by size-exclusion chromatography. [e] Cumulative M$_1$ content ($F_{M_1, cum}$) = [M$_1$]$_0$ × conv.(M$_1$)/([M$_1$]$_0$ × conv.(M$_1$) + [M$_2$]$_0$ × conv.(M$_2$)). [f] Instantaneous content M$_1$ content ($F_{M_1, inst}$) = d($F_{M_1, cum}$ × total conv.)/d(total conv.) [g] Cumulative triad isotacticity (mm_{cum}) was determined by ^{13}C NMR. [h] Instantaneous triad isotacticity (mm_{inst}) = d(mm_{cum} × total conv.)/d(total conv.) [i] In 1,4-dioxane. [j] [M$_1$]$_0$ = [M$_2$]$_0$ = 0.30 M, [CDB]$_0$ = 6.0 mM, [AIBN]$_0$ = 3.0 mM in toluene.
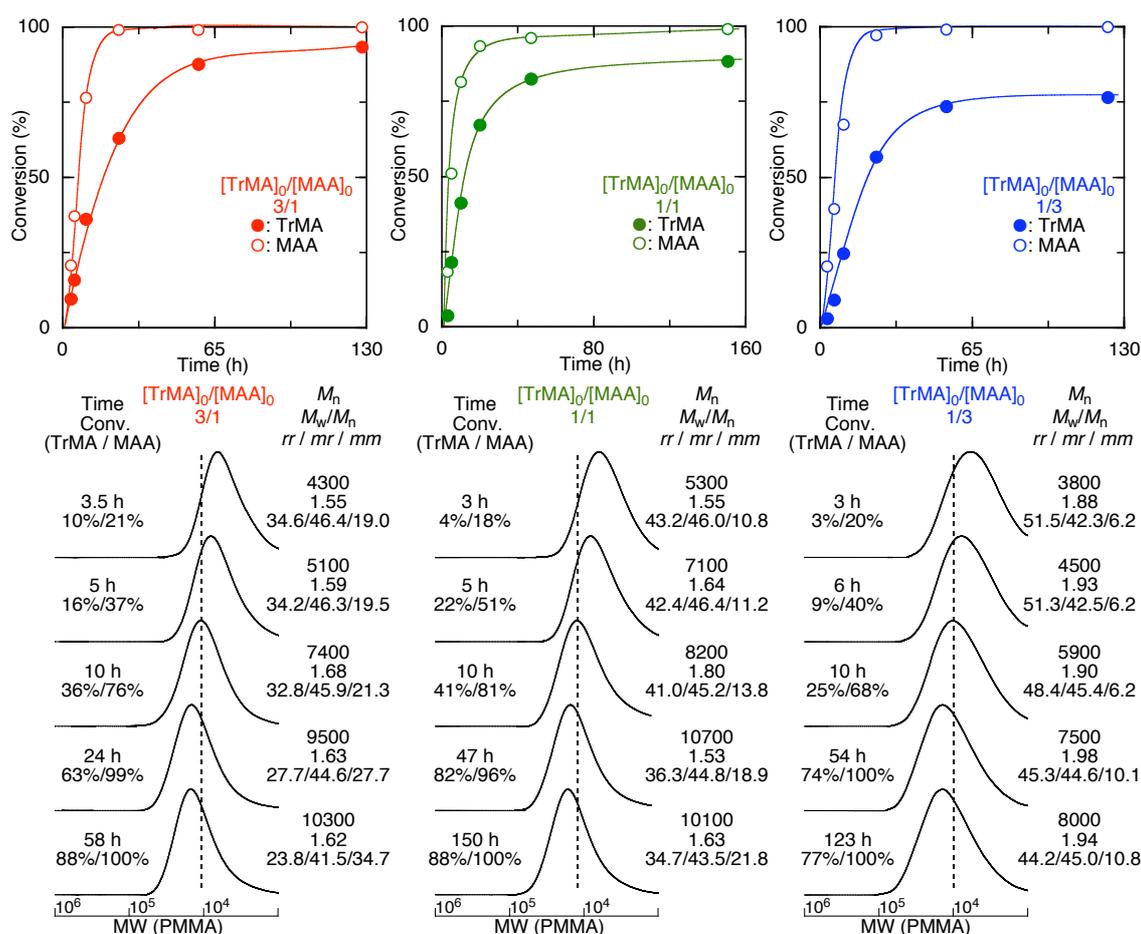
Figure 7. Effects of initial charge ratio of TrMA and MAA on the RAFT copolymerization of TrMA and MAA with CDB/AIBN in toluene at 60 °C: $[TrMA]_0 + [MAA]_0 = 1.0$ M; $[CDB]_0 = 10$ mM; $[AIBN]_0 = 5.0$ mM; $[TrMA]_0/[MAA]_0 = 3/1$ (red), 1/1 (green), or 1/3 (blue). SEC curves: poly(MMA) converted from the obtained copolymers.
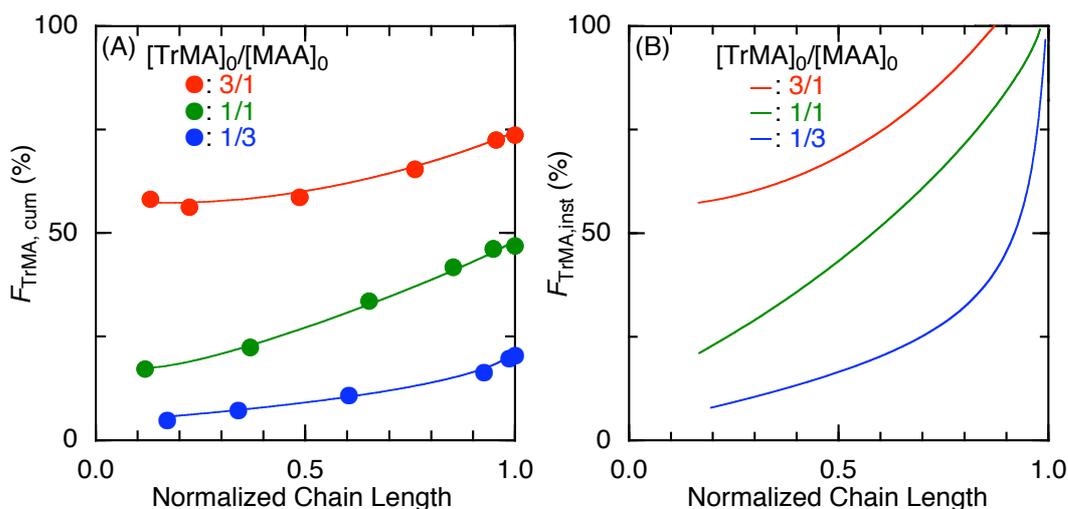
Figure 8. Effects of initial charge ratio of TrMA and MAA on the dependences of cumulative (A) and instantaneous (B) TrMA contents on the normalized chain length in the RAFT copolymerization of TrMA and MAA with CDB/AIBN in toluene at 60 °C: $[TrMA]_0 + [MAA]_0 = 1.0$ M; $[CDB]_0 = 10$ mM; $[AIBN]_0 = 5.0$ mM; $[TrMA]_0/[MAA] = 3/1$ (red), 1/1 (green), or 1/3 (blue).
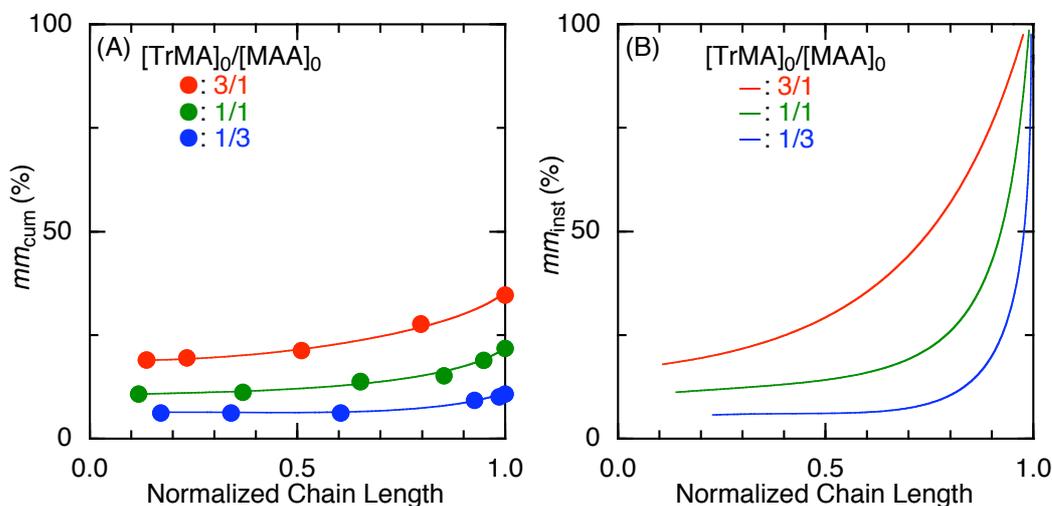
Figure 9. Effects of initial charge ratio of TrMA and MAA on the dependences of cumulative (A) and instantaneous (B) *mm* contents on the normalized chain length in the RAFT copolymerization of TrMA and MAA with CDB/AIBN in toluene at 60 °C: $[TrMA]_0 + [MAA]_0 = 1.0$ M; $[CDB]_0 = 10$ mM; $[AIBN]_0 = 5.0$ mM; $[TrMA]_0/[MAA]_0 = 3/1$ (red), 1/1 (green), or 1/3 (blue).

The RAFT copolymerization of TrMA and MAA was also performed at various temperatures to investigate the effects (entries 1, 4, and 5). The copolymerization proceeded faster at the higher temperature, in which much faster consumption of MAA was observed than that of TrMA with the reaction temperature raising. In addition, the consumption of TrMA ceased around 50% at 80 °C, where the copolymerization was uncontrolled to result in the copolymers with almost constant M_n. In contrast, acceptable level of the control was achievable at 40 °C to give the stereogradient copolymers similar to those at 60 °C. These were due to the thermodynamic propagation-depropagation equilibrium in the TrMA polymerization, which is more pronounced at a higher temperature (Figures 10–12).
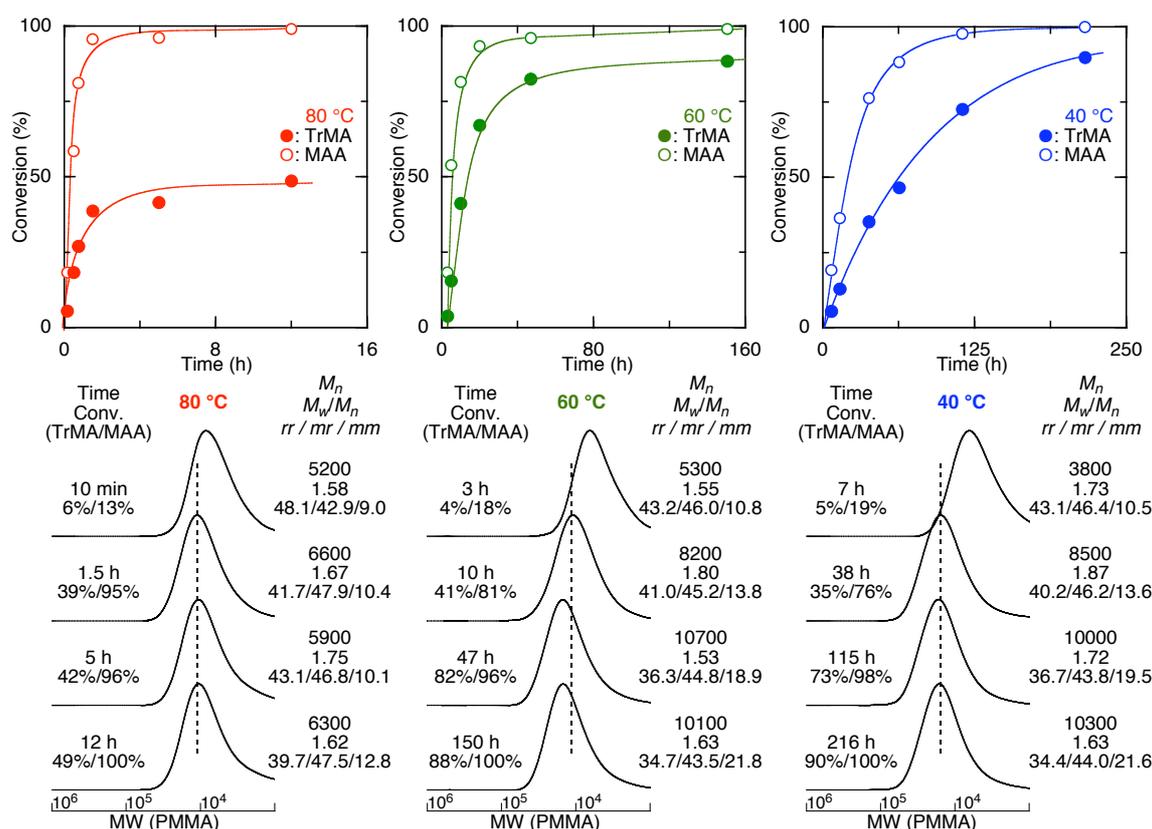
Figure 10. RAFT copolymerization of TrMA and MAA with CDB/AIBN at various temperature: $[TrMA]_0 = [MAA]_0 = 0.50$ M; $[CDB]_0 = 10$ mM; $[AIBN]_0 = 5.0$ mM in toluene at 80 (red), 60 (green), or 40 °C (blue). SEC curves: poly(MMA) converted from the obtained copolymers.
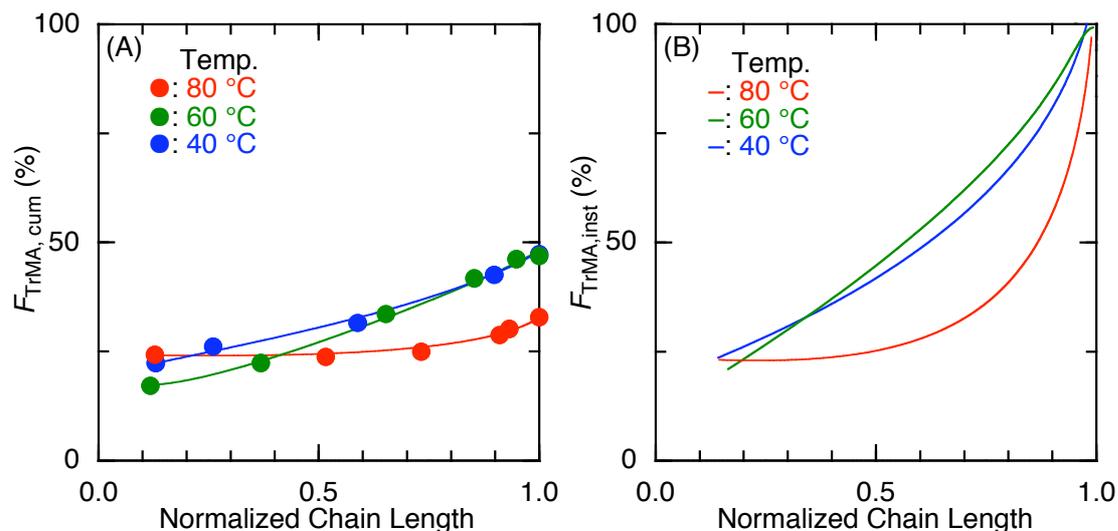
Figure 11. Effects of polymerization temperature on the dependences of cumulative (A) and instantaneous (B) TrMA contents on the normalized chain length in the RAFT copolymerization of TrMA and MAA with CDB/AIBN at various temperature: $[TrMA]_0 = [MAA]_0 = 0.50$ M; $[CDB]_0 = 10$ mM; $[AIBN]_0 = 5.0$ mM in toluene at 80 (red), 60 (green), or 40 °C (blue).
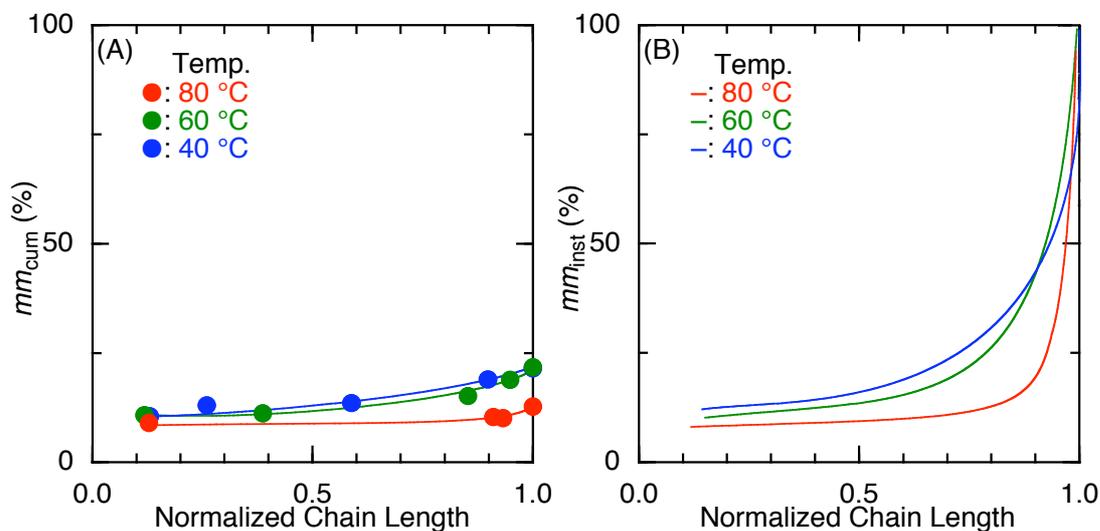
Figure 12. Effects of polymerization temperature on the dependences of cumulative (A) and instantaneous (B) *mm* contents on the normalized chain length in the RAFT copolymerization of TrMA and MAA with CDB/AIBN at various temperature: $[TrMA]_0 = [MAA]_0 = 0.50$ M; $[CDB]_0 = 10$ mM; $[AIBN]_0 = 5.0$ mM in toluene at 80 (red), 60 (green), or 40 °C (blue).

Stereogradient Polymers by RAFT Copolymerization of Other Methacrylates

Other combinations of bulky methacrylates with less-bulky methacrylic monomers were also examined. In the RAFT copolymerization of bulky (TrMA) and less-bulky methacrylates (MMA) with CDB in toluene, the two monomers were simultaneously consumed at almost the same rate to give copolymers with controlled molecular weights (entry 7 in Table 1). Although narrower MWDs were obtained with MMA as the comonomer because of the high solubility of the PMMA units in toluene, the triad isotacticity was constant throughout the copolymerization (*mm* = 15%). This behavior is similar to that of the TrMA/MAA copolymerization in 1,4-dioxane, where almost no differences in the monomer reactivities were observed. In addition, a similar tacticity was obtained in anionic copolymerization of TrMA and MMA.[47]

A bulkier methacrylate, PDBSMA, which is known to produce more highly isotactic polymers via radical homopolymerization independent of the monomer concentration and conversion,[17] was also used for the synthesis of similar stereogradient polymers. The RAFT copolymerization of PDBSMA was thus examined with MAA using CDB as the RAFT agent (entry 8). As was observed in the copolymerization of TrMA and MAA, PDBSMA was consumed more slowly than MAA in toluene to afford copolymers with controlled molecular weights. This result suggests the spontaneous formation of gradient copolymers. The isotacticity, which was measured using ^{13}C NMR of the converted PMMA, increased with monomer conversion, with the mm_{inst} increasing from 14% to 100% (Figure 13). The curvature of the plot was less pronounced than that observed for TrMA, which is due to the fact that PDBSMA gives consistently higher isotacticity independent of the monomer concentration. The effects of the initial charge ratio of PDBSMA and MAA were also examined and showed results similar to those observed for TrMA and MAA (Figures 14–16). Thus, the thermodynamic propagation–depropagation process, which is essential for stereogradient homopolymerization of TrMA, is not necessarily required for the formation of syndiotactic–isotactic stereogradient polymers in this copolymerization, probably because PDBSMA induces highly isotactic

enchainment relative to the syndiotactic-rich enchainment of MAA and is copolymerized with MAA at appropriately different rates.
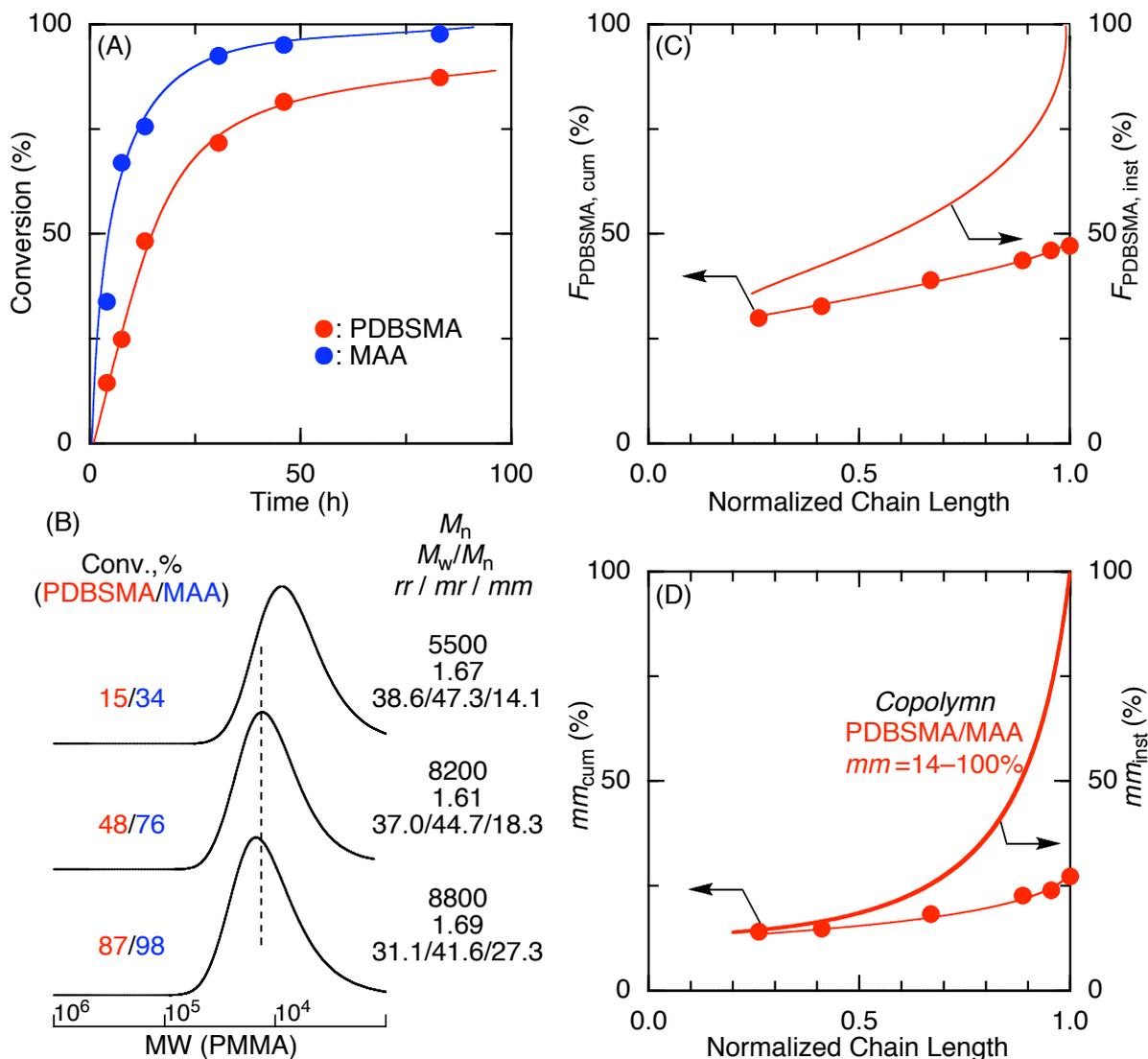

Figure 13. RAFT copolymerization of PDBSMA and MAA with CDB/AIBN in toluene at 60 °C: $[PDBSMA]_0 = [MAA]_0 = 0.30$ M; $[CDB]_0 = 6.0$ mM; $[AIBN]_0 = 3.0$ mM. (A) Time-conversion curves for the RAFT copolymerization. (B) SEC curves of poly(MMA) converted from the obtained copolymers. (C) Dependences of cumulative ($F_{PDBMSA,cum}$) and instantaneous ($F_{PDBMSA,inst}$) PDBMSA contents on the normalized chain length in the RAFT copolymerization. (D) Dependences of cumulative and instantaneous isotacticity (mm) contents on the normalized chain length in the RAFT copolymerization.
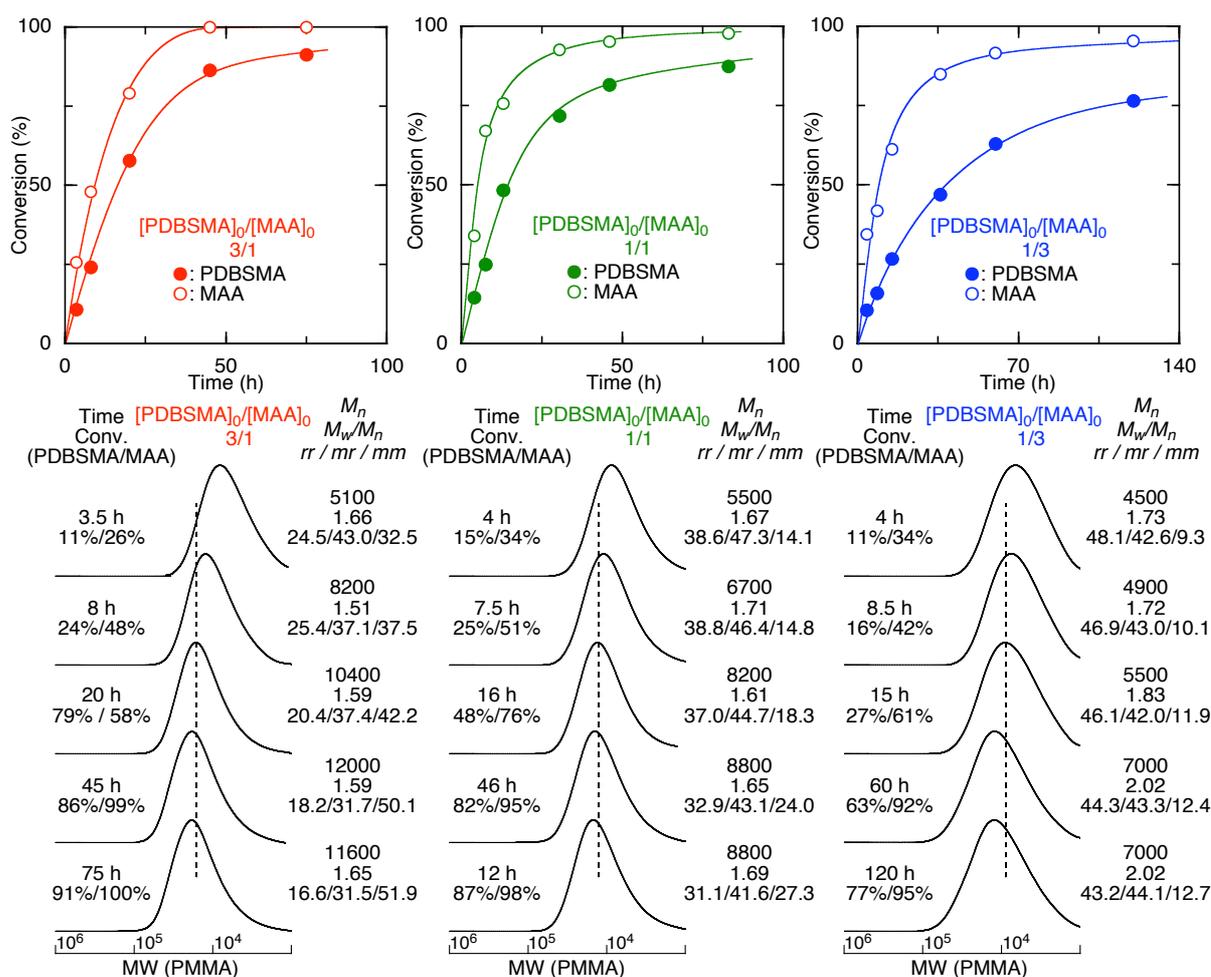
Figure 14. Effects of initial charge ratio of PDBSMA and MAA on the RAFT copolymerization of PDBSMA and MAA with CDB/AIBN in toluene at 60 °C: $[PDBSMA]_0+[MAA]_0 = 0.60$ M; $[CDB]_0 = 6.0$ mM; $[AIBN]_0 = 3.0$ mM; $[PDBSMA]_0/[MAA]_0 = 3/1$ (red), 1/1 (green), or 1/3 (blue). SEC curves: poly(MMA) converted from the obtained copolymers.
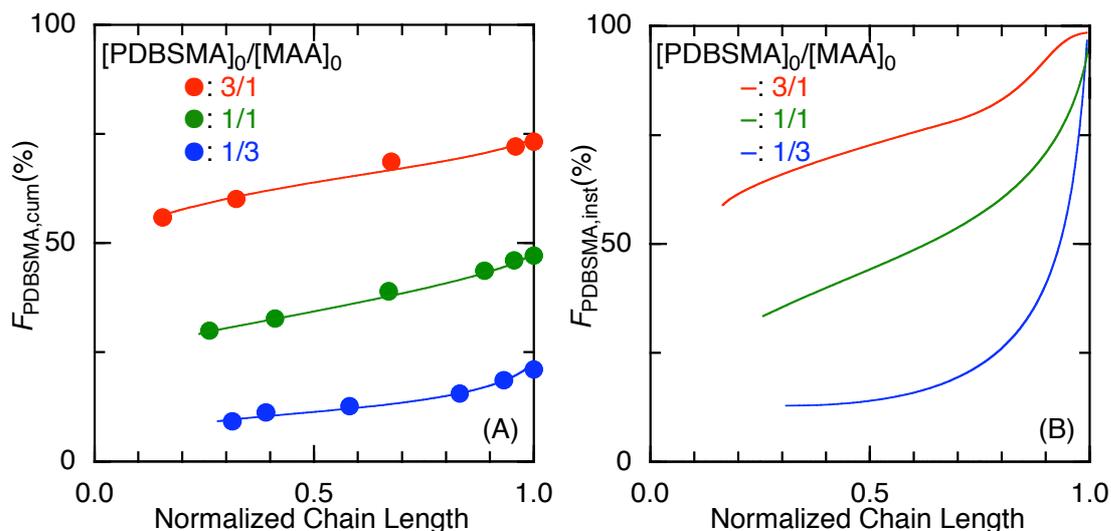
**Figure 15.** Effects of initial charge ratio of PDBSMA and MAA on the dependences of cumulative (A) and instantaneous (B) PDBSMA contents on the normalized chain length in the RAFT copolymerization of PDBSMA and MAA with CDB/AIBN in toluene at 60 °C: $[PDBSMA]_0+[MAA]_0 = 0.60$ M; $[CDB]_0 = 6.0$ mM; $[AIBN]_0 = 3.0$ mM; $[PDBSMA]_0/[MAA]_0 = 3/1$ (red), 1/1 (green), or 1/3 (blue).
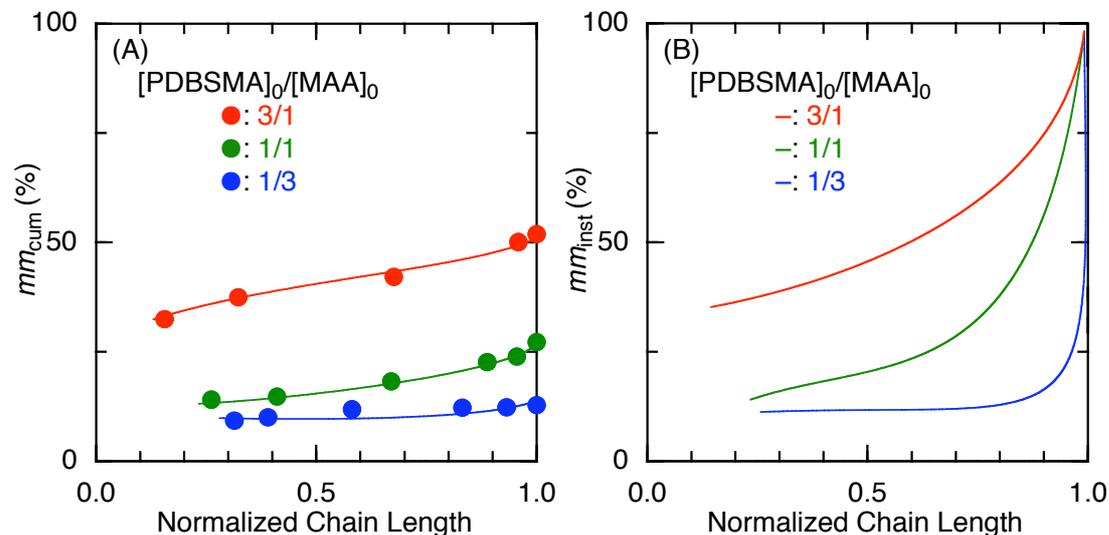

Figure 16. Effects of initial charge ratio of PDBSMA and MAA on the dependences of cumulative (A) and instantaneous (B) *mm* contents on the normalized chain length in the RAFT copolymerization of PDBSMA and MAA with CDB/AIBN in toluene at 60 °C: $[PDBSMA]_0+[MAA]_0 = 0.60$ M; $[CDB]_0 = 6.0$ mM; $[AIBN]_0 = 3.0$ mM; $[PDBSMA]_0/[MAA]_0 = 3/1$ (red), 1/1 (green), or 1/3 (blue).

Conclusion

This study demonstrated the spontaneous formation of syndiotactic–isotactic stereogradient polymers by RAFT copolymerization of bulky methacrylates, such as TrMA and PDBSMA, with MAA.   Toluene was the solvent of choice to induce the desired reactivity of MAA both in the homopolymerizations and copolymerizations, probably due to intermolecular hydrogen-boning interactions in MAA.   With the differing reactivities and stereospecificities of TrMA and MAA, the isotacticity of the resultant copolymer gradually increased from 11% to nearly 100% along the polymer chain.   The reported method can be applied to the synthesis of various stereogradient poly(MAA)s or polymethacrylates by postpolymerization modification.

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Part II

Design and Polymerization of

Novel Bulky Silyl Methacrylates

for Stereoregular Protected Poly(methacrylic Acid)s

Chapter 3

Stereospecific Free Radical and RAFT Polymerization of Bulky Silyl Methacrylates for Stereo- and Molecular Weight-Controlled Poly(methacrylic acid)

Abstract

A series of silyl methacrylates [CH_2=$C(CH_3)CO_2SiR_3$] with varying silyl group bulkiness [R_3Si: Me_3Si, Et_3Si, Me_2tBuSi, iPr_3Si, Ph_2tBuSi, Ph_3Si, and $(Me_3Si)_3Si$] was synthesized and radically polymerized to efficiently give soluble polymers with the exception of the highly bulky tris(trimethylsilyl)silyl methacrylate (TTMSSMA), which resulted in insoluble polymers. All the polymers can easily be converted into poly(methacrylic acid) (PMAA) via acid- or fluoride-induced deprotection of the silyl groups and further into poly(methyl methacrylate) (PMMA) via methylation with trimethylsilyl diazomethane for the analysis of molecular weight and tacticity. The tacticity was dependent on the bulkiness of the silyl substituents; the isotacticity increased with increasing bulkiness. Thus, a series of PMAAs with various tacticities ranging from syndiotactic-rich (rr = 74%; Me_2tBuSi) to atactic (mr = 50%; iPr_3Si) and highly isotactic [mm = 93%; $(Me_3Si)_3Si$] enchainment was obtained by conventional radical polymerization of silyl methacrylates followed by simple post-reactions. The high isotacticity and insolubility of poly(TTMSSMA) suggested the formation of helical polymers as in the polymerization of similarly bulky triarylmethyl methacrylate. Reversible addition fragmentation chain-transfer (RAFT) polymerization also worked for these silyl methacrylates, which resulted in well-defined polymers with controlled molecular weights and various tacticities. RAFT polymerization was further applied to the synthesis of novel stereoblock polymers, such as stereo-triblock PMAA that consisted of syndiotactic-rich, atactic, and isotactic-stereogradient segments.

Introduction

Silyl groups are among the most frequently used protective groups for alcoholic protons and can similarly be used for protecting carboxylic acidic protons in their silyl ester forms.[1] Various silyl groups have been prepared and adapted for the realization of selective deprotection reactions of silyl ethers because the reactivity of the Si–O bond is strongly affected by the steric and electronic properties of the silyl moiety. However, silyl groups were not employed to induce diastereoselective reactions until an extremely bulky tris(trimethylsilyl)silyl group, known as the hypersilyl, sisyl, or supersilyl group,[2] was used for diastereoselective [2+2] cyclizations and Mukaiyama aldol reactions of the silyl enol ethers by Yamamoto et al.[3]

Even in polymer chemistry, silyl groups have been extensively used as protecting groups for the functional moieties (OH, NH_2, CHO, $COCH_3$, COOH, and C≡CH) of various monomers and initiators, mainly in ionic polymerizations,[4,5] where these functional groups induce termination or chain-transfer reactions with the ionic propagating species. In addition, silyl groups have also been employed as part of the initiating system for inducing living or controlled polymerization, such as in group transfer polymerization,[6] where the silylated propagating species induces a kind of chemoselective propagation reaction by diminishing the side reactions. However, silyl groups have rarely been used for stereoselective or stereospecific polymerizations, in which their steric properties can be used for stereochemical control, except for a few reports on the free-radical polymerization of 2-silyl-substituted 1,3-butadiene derivatives, where the alkoxysilyl substituents affect the microstructure of the resulting polydienes.[7]

In vinyl polymerizations, including radical polymerizations, bulkiness in monomers often plays an important role in dictating the stereochemistry of the resulting polymers.[8] A variety of alkyl methacrylates with different substituents have been synthesized and radically polymerized under various conditions to produce a series of poly(alkyl methacrylate)s with various tacticities, ranging from syndiotactic-rich to highly isotactic enchainment. The tacticity is mainly governed by the bulkiness of the substituents.[9] Specifically, usual alkyl methacrylates, such as methyl

methacrylate (MMA), form predominantly syndiotactic polymers (*rr* ~ 65%), and the syndiotacticity gradually decreases with increasing bulkiness of the pendent groups. Upon further increasing the bulkiness,[10,11] an extremely bulky methacrylate, triphenylmethyl (trityl) methacrylate (TrMA), gives highly isotactic (*mm* = 76–98%) polymers, even in common organic solvents such as toluene, at 60°C, probably due to the helical conformation imposed by the highly bulky substituent. Although Kitayama and Hatada reported stereospecific anionic polymerization of trimethylsilyl methacrylate at low temperature,[12] there have been no studies focusing on the stereospecific radical polymerization of a series of various silyl methacrylates with different bulkiness. In addition, trimethylsilyl and its related silyl methacrylates have been synthesized[13–16] and homo- or co-polymerized radically or anionically, which were particularly directed to photo-resist applications as precursors of PMAA moieties.[17,18]

In this study, we investigated the radical polymerization of a series of silyl methacrylates [$CH_2=C(CH_3)CO_2SiR_3$] with varying degrees of bulkiness in their silyl substituent [R_3Si: Me_3Si, Et_3Si, Me_2tBuSi, iPr_3Si, Ph_2tBuSi, Ph_3Si, and $(Me_3Si)_3Si$] and examined the effect of stereospecificity on the radical polymerization (Scheme 1). The author focused his attention on changing the tacticity of poly(methacrylic acid)s from syndiotactic-rich to highly isotactic enchainment by radically polymerizing a series of silyl methacrylates and simply deprotecting them. Among the various silyl methacrylates, particular attention was paid to the synthesis and polymerization of the novel bulky monomer supersilyl methacrylate (TTMSSMA), which is a different type of bulky methacrylate from the series of triarylmethyl methacrylates previously listed that undergoes a similar isospecific radical polymerization. Furthermore, the author investigated reversible addition-fragmentation chain transfer (RAFT) polymerizations[19] of these silyl methacrylates for simultaneous control of the molecular weight and the tacticity. The synthesis of stereoblock poly(methacrylic acid) (PMAA) and poly(methyl methacrylate) (PMMA) by block copolymerization of silyl methacrylates with different substituents and subsequent simple post-reactions was also investigated.
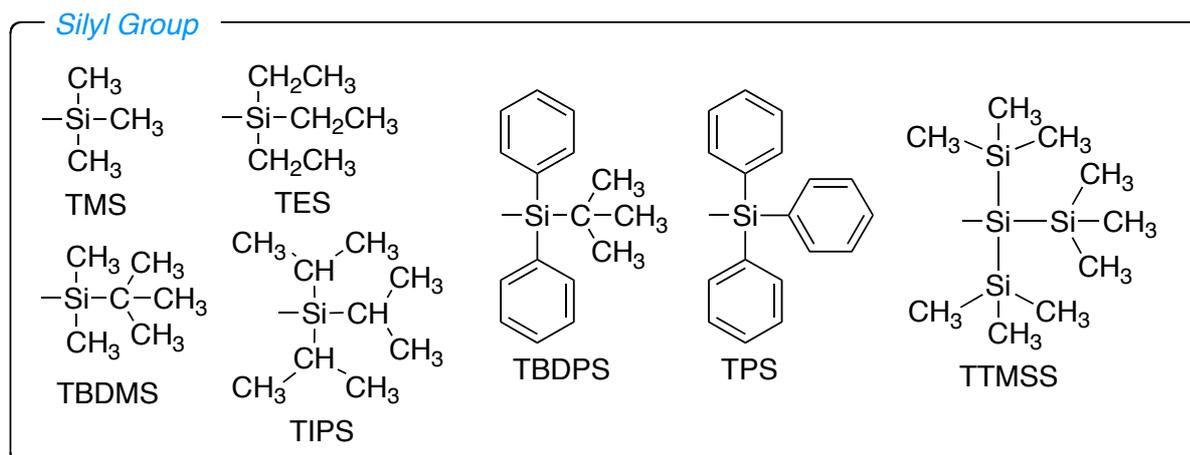
Silyl Group

TMS

TES

TBDMS

TIPS

TBDPS

TPS

TTMSS

● **Stereospecific Radical Polymerization**

Silyl
Methacrylate

**Radical
Polymn**

Protected
PMAA

● *syndiotactic-rich*
TMS
TBDMS
TES

● *atactic*
TIPS
TBDPS
TPS

● *isotactic*
TTMSS

Deprotection

PMAA with
Various Tacticities
(mm = 3–93%)

● **Stereospecific RAFT Polymerization**

*Silyl
Methacrylate*

**RAFT
Polymn**

Controlled Molecular Weight
Controlled Tacticity

*Silyl
Methacrylate*

**RAFT
Block
Copolymn**

*Stereoblock
PMAA*
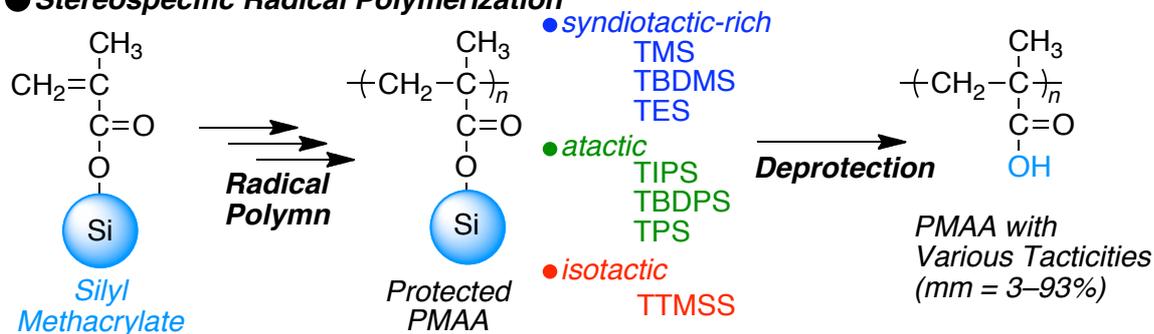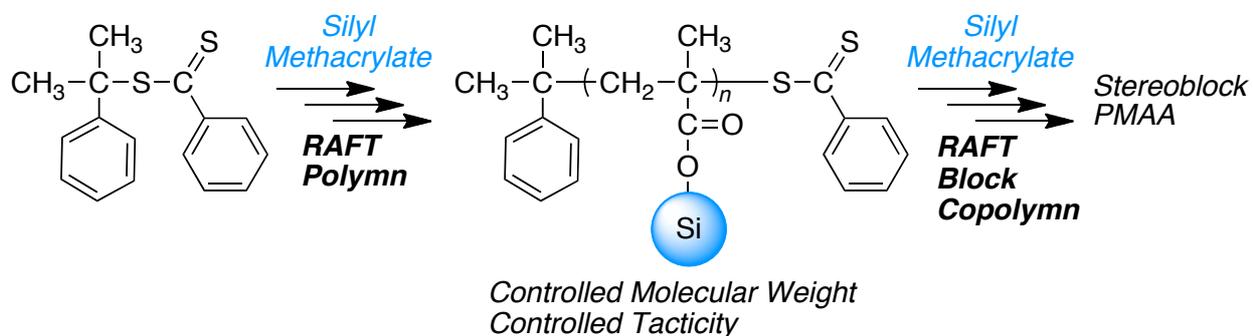
Scheme 1. Stereospecific RAFT Polymerization of Various Silyl Methacrylates for Stereo- and

Molecular Weight-Controlled Poly(methacrylic Acid) and Its Ester

Experimental Section

Materials

α,α-Azobis(isobutyronitrile) (AIBN) (Kishida, >99%) was purified by recrystallization from methanol. 2,2'-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) (Wako, >95%) was purified by washing dry acetone and drying under reduced pressure. Trimethylsilyl methacrylate (TMSMA) (Aldrich) and 1,2,3,4-tetrahydronaphthalene (Wako, 97%) were distilled from calcium hydride under reduced pressure before use. Toluene was distilled over sodium benzophenone ketyl and bubbled with dry nitrogen over 15 minutes just before use. Cumyl dithiobenzoate (CDB) was synthesized according to the literature.[20] Trimethylsilyl diazomethane (Aldrich, 2.0 M in Et$_2$O), tetrabutylammonium fluoride (TBAF) (Aldrich, 1.0 M in THF), sodium methacrylate (Aldrich, 99%), *tert*-butyldimethylsilyl chloride (TCI, >98%), triethylsilyl chloride (TCI, >97%), triisopropylsilyl chloride (TCI, >95%), *tert*-butyldiphenylsilyl chloride (TCI, >95%), triphenylsilyl chloride (TCI, >95%), tris(trimethylsilyl)silyl chloride (Aldrich, 97%), phenothiazine (Kishida, 98%) and 2,6-di-tert-butyl-*p*-cresol (TCI, >99%) was used as received.

Synthesis of Silyl Methacrylates

A series of silyl methacrylates were synthesized by a simple reaction between sodium methacrylate and silyl chlorides in the presence of 2,6-di-*tert*-butyl-*p*-cresol or phenothiazine as an inhibitor for radical polymerization in dry THF as follows. The reaction was carried out by the use of a syringe technique under a dry nitrogen atmosphere in an oven-dried glass tube equipped with three-way stopcocks. Each silyl methacrylate was synthesized as follows.

tert-Butyldimethylsilyl Methacrylate (TBDMSMA)

TBDMSMA was synthesized by the reaction between the sodium methacrylate and *tert*-butyldimethylsilyl chloride (TBDMS–Cl).[21] Sodium methacrylate (16.8 g, 0.155 mol) was dispersed in dry THF (86.0 mL) in the presence of 2,6-di-*tert*-butyl-*p*-cresol (34.2 mg, 0.155

mmol). In to the suspension, 2.78 M TBDMS–Cl solution (51.0 mL, 0.142 mol) was add dropwise at 0 °C over a period of 30 min under stirring. After stirring at ambient temperature for additional 24 h, the solution was evaporated, washed with *n*-hexane and filtrated to remove sodium chloride. After evaporation, the crude product was obtained and purified by distillation from calcium hydride under reduced pressure. TBDMSMA was thus obtained as colorless liquid (15.6 g, 55%, b.p.: 52 °C/533 Pa). ^{1}H NMR (CDCl$_3$, r.t.): δ 0.30 (s, 6H, Si(C*H*$_3$)$_2$C(CH$_3$)$_3$), 0.96 (s, 9H, Si(CH$_3$)$_2$C(C*H*$_3$)$_3$), 1.92 (dd, 3H, CH$_2$=C–C*H*$_3$), 5.56 (m, 1H, cis C*H*$_2$=C–CH$_3$), 6.09 (m, 1H, trans C*H*$_2$=C–CH$_3$). ^{13}C NMR (CDCl$_3$, r.t.): δ −4.8 (Si(*C*H$_3$)$_2$C(CH$_3$)$_3$), 17.8 (Si(CH$_3$)$_2$*C*(CH$_3$)$_3$), 18.5 (CH$_2$=C–*C*H$_3$), 25.7 (Si(CH$_3$)$_2$C(*C*H$_3$)$_3$), 126.1 (*C*H$_2$=C–CH$_3$), 137.9 (CH$_2$=*C*–CH$_3$), 167.7 (*C*O$_2$Si(CH$_3$)$_2$C(CH$_3$)$_3$).

Triethylsilyl Methacrylate (TESMA)

Synthesis of TESMA was conducted in a similar way to that of TBDMSMA by replacing TBDMS–Cl with triethylsilyl chloride (TES–Cl). Sodium methacrylate (17.9 g, 0.166 mol) was dispersed in dry THF (92.6 mL) in the presence of 2,6-di-*tert*-butyl-*p*-cresol (36.6 mg, 0.166 mmol). In to the suspension, 2.70 M TES–Cl solution (25.3 mL, 0.149 mol) was add dropwise at 0 °C over a period of 30 min under stirring. After stirring at ambient temperature for additional 18 h, the solution was evaporated, washed with *n*-hexane and filtrated to remove sodium chloride. After evaporation, the crude product was obtained and purified by distillation from calcium hydride under reduced pressure. TESMA was obtained as colorless liquid (17.9 g, 60%, b.p.: 77 °C/666 Pa). ^{1}H NMR (CDCl$_3$, r.t.): δ 0.76-0.84 (q, 6H, Si(C*H*$_2$CH$_3$)$_3$), 0.93-1.03 (t, 9H, Si(CH$_2$C*H*$_3$)$_3$), 1.93 (dd, 3H, CH$_2$=C–C*H*$_3$), 5.58 (m, 1H, cis C*H*$_2$=C–CH$_3$), 6.11 (m, 1H, trans C*H*$_2$=C–CH$_3$). ^{13}C NMR (CDCl$_3$, r.t.): δ 4.7 (Si(*C*H$_2$CH$_3$)$_3$), 6.7 (Si(CH$_2$*C*H$_3$)$_3$), 18.5 (CH$_2$=C–*C*H$_3$), 126.1 (*C*H$_2$=C–CH$_3$), 137.7 (CH$_2$=*C*–CH$_3$), 167.7 (*C*O$_2$Si(CH$_2$CH$_3$)$_3$).

Triisopropylsilyl Methacrylate (TIPSMA)

Synthesis of TESMA was conducted in a similar way to that of TBDMSMA by replacing TBDMS–Cl with triisopropylsilyl chloride (TIPS-Cl). Sodium methacrylate (12.3 g, 0.114 mol) was dispersed in dry THF (65.4 mL) in the presence of 2,6-di-*tert*-butyl-*p*-cresol (20.5 mg, 0.114 mmol). In to the suspension, 2.87 M TIPS–Cl solution (36.3 mL, 0.104 mol) was add dropwise at 0 °C over a period of 30 min under stirring. After stirring at ambient temperature for additional 25 h, the solution was evaporated, washed with *n*-hexane and filtrated to remove sodium chloride. After evaporation, the crude product was obtained and purified by distillation from calcium hydride under reduced pressure. TIPSMA was obtained as colorless liquid (14.1 g, 57%, b.p.: 78 °C/533 Pa). ^{1}H NMR (CDCl$_3$, r.t.): δ 1.04-1.09 (s, 18H, Si(CH(CH_3)$_2$)$_3$), 1.21-1.39 (m, 3H, Si(CH(CH$_3$)$_2$)$_3$), 1.95 (dd, 3H, CH$_2$=C–CH_3), 5.59 (m, 1H, cis CH_2=C–CH$_3$), 6.14 (m, 1H, trans CH_2=C–CH$_3$). ^{13}C NMR (CDCl$_3$, r.t.): δ 12.1 (Si(CH(CH$_3$)$_2$)$_3$), 17.9 (Si(CH(CH$_3$)$_2$)$_3$), 18.6 (CH$_2$=C–CH$_3$), 126.1 (CH$_2$=C–CH$_3$), 137.8 (CH$_2$=C–CH$_3$), 167.4 (CO$_2$Si(CH(CH$_3$)$_2$)$_3$).

tert-Butyldiphenylsilyl Methacrylate (TBDPSMA)

Synthesis of TBDPSMA was conducted in a similar way to that of TBDMSMA by replacing TBDMS–Cl with *tert*-butyldiphenylsilyl chloride (TBDPS–Cl). Sodium methacrylate (10.6 g, 98.1 mmol) was dispersed in dry THF (55.0 mL) in the presence of phenothiazine (0.195 g, 98.1 mmol). In to the suspension, 2.88 M TBDPS–Cl solution (30.7 mL, 88.4 mmol) was add dropwise at 0 °C over a period of 30 min under stirring. After stirring at ambient temperature for additional 72 h, the solution was evaporated, washed with *n*-hexane and filtrated to remove sodium chloride. After evaporation, the crude product was obtained and purified by distillation from calcium hydride under reduced pressure. TBDPSMA was obtained as colorless liquid (20.1 g, 70%, b.p.: 120 °C/40 Pa). ^{1}H NMR (CDCl$_3$, r.t.): δ 1.10 (s, 9H, SiPh$_2$C(CH_3)$_3$), 1.96 (dd, 3H, CH$_2$=C–CH_3), 5.64 (m, 1H, cis CH_2=C–CH$_3$), 6.25 (m, 1H, trans CH_2=C–CH$_3$),

7.32-7.42 (m, 6H, *m, p*-Ar*H*), 7.62-7.68 (d, 4H, *o*-Ar*H*). ^{13}C NMR (CDCl$_3$, r.t.): δ 18.7 (CH$_2$=C–*CH$_3$*), 19.4 (SiPh$_2$*C*(CH$_3$)$_3$), 27.1 (SiPh$_2$C(*CH$_3$*)$_3$), 126.7 (*CH$_2$*=C–CH$_3$), 127.9, 130.1, 132.0, and 135.5 (phenyl), 137.7 (CH$_2$=*C*–CH$_3$), 166.6 (*C*O$_2$SiPh$_2$C(CH$_3$)$_3$).

Triphenylsilyl Methacrylate (TPSMA)

Sodium methacrylate (10.1 g, 0.102 mol) was dispersed in dry THF (56.8 mL) in the presence of phenothiazine (20.3 mg, 10.2 mmol).   In to the suspension, 0.832 M triphenylsilyl chloride solution (102 mL, 0.849 mol) was add dropwise at 0 °C over a period of 30 min under stirring.   After stirring at ambient temperature for additional 48 h, the solution was evaporated, washed with *n*-hexane and ethyl acetate, and filtrated to remove sodium chloride.   After evaporation, the obtained crude product was purified by recrystallization in *n*-hexane (20.3 g, 70%).   And then the crude TPSMA (12.0 g) product was purified by column chromatography on silica gel with CHCl$_3$ as an eluent.   TPSMA was obtained as white solid (7.71 g, 64%). ^{1}H NMR (CDCl$_3$, r.t.): δ 2.00 (m, 3H, CH$_2$=C–C*H$_3$*), 5.67 (m, 1H, cis C*H$_2$*=C–CH$_3$), 6.31 (m, 1H, trans C*H$_2$*=C–CH$_3$), 7.32-7.42 (m, 9H, *m, p*-Ar*H*), 7.63-7.69 (d, 6H, *o*-Ar*H*). ^{13}C NMR (CDCl$_3$, r.t.): δ 18.5 (CH$_2$=C–*CH$_3$*), 127.2 (*CH$_2$*=C–CH$_3$), 128.1, 130.7, 132.4, and 135.8 (phenyl), 137.4 (CH$_2$=*C*–CH$_3$), 167.0 (*C*O$_2$SiPh$_3$).

Tris(trimethylsilyl)silyl Methacrylate (TTMSSMA)

Sodium methacrylate (7.32 g, 67.7 mmol) was dispersed in dry THF (37.7 mL) in the presence of phenothiazine (135 mg, 0.677 mmol).   In to the suspension, 0.834 M tris(trimethylsilyl)silyl chloride solution (67.8 mL, 56.4 mmol) was add dropwise at 0 °C over a period of 30 min under stirring.   After stirring at ambient temperature for additional 2 h, the solution was evaporated, washed with *n*-hexane, and filtrated to remove sodium chloride.   After evaporation, the crude product was obtained purified by distillation with calcium hydride under reduced pressure.   TTMSSMA was obtained as colorless liquid (11.0 g, 56%, b.p.: 106 °C/133

Pa). ^{1}H NMR (CDCl$_3$, r.t.): δ 0.22 (s, 27H, Si(Si(C*H*$_3$)$_3$)$_3$), 1.91 (m, 3H, CH$_2$=C–C*H*$_3$), 5.55 (m, 1H, cis C*H*$_2$=C–CH$_3$), 6.00 (m, 1H, trans C*H*$_2$=C–CH$_3$). ^{13}C NMR (CDCl$_3$, r.t.): δ 0.01 (Si(Si(*C*H$_3$)$_3$)$_3$), 18.9 (CH$_2$=C–*C*H$_3$), 125.5 (*C*H$_2$=C–CH$_3$), 137.6 (CH$_2$=*C*–CH$_3$), 169.3 (*C*O$_2$Si(Si(CH$_3$)$_3$)$_3$).

General Procedure for Conventional Radical Polymerization

Polymerization was carried out by the syringe technique under dry argon or nitrogen in sealed glass tubes. A typical example for polymerization of TBDMSMA with AIBN in toluene is given below. In a 50 mL round-bottomed flask were placed toluene (4.65 mL), TBDMSMA (1.61 mL, 7.00 mmol), 1,2,3,4-tetrahydronaphthalene (0.39 mL) as an internal standard, and toluene solutions of AIBN (0.35 mL of 100 mM solution in toluene) and at room temperature. The total volume of the reaction mixture was 7.0 mL. Immediately after mixing, aliquots (1.0 mL each) of the solution were distributed via a syringe into baked glass tubes, which were then sealed by flame under nitrogen atmosphere. The tubes were immersed in thermostatic oil bath at 60 °C. In predetermined intervals, the polymerization was terminated by the cooling of the reaction mixtures to −78 °C. Monomer conversion was determined from the concentration of residual monomer measured by ^{1}H NMR with 1,2,3,4-tetrahydronaphthalene as an internal standard (30 h, 93%). The quenched reaction solutions were evaporated to dry to give poly(TBDMSMA).

General Procedure for RAFT Polymerization

RAFT Polymerization was carried out by the syringe technique under dry argon or nitrogen in sealed glass tubes. A typical example for polymerization of TBDMSMA with AIBN in the presence of CDB is given below: in a 50 mL round-bottomed flask were placed toluene (3.98 mL) as an internal standard, TBDMSMA (1.38 mL, 6.00 mmol), and toluene solutions of AIBN (0.30 mL of 100 mM solution in toluene) and CDB (0.34 mL of 178 mM solution in

toluene) at room temperature. The total volume of the reaction mixture was 6.0 mL. Immediately after mixing, the solution was evenly charged in 6 glass tubes and the tubes were sealed by flame under nitrogen atmosphere. The tubes were immersed in thermostatic oil bath at 60 °C. In predetermined intervals, the polymerization was terminated by the cooling of the reaction mixtures to −78 °C. Monomer conversion was determined from the concentration of residual monomer measured by ^{1}H NMR with toluene as an internal standard (32 h, 96%). The quenched reaction solutions were evaporated to dry to give poly(TBDMSMA).

Transformation of Poly(silyl Methacrylate) into Poly(methacrylic Acid) and Poly(methyl Methacrylate)

The obtained poly(silyl methacrylate)s were converted into poly(methacrylic acid) (PMAA) and poly(methyl methacrylate) (PMMA). A typical example for poly(TBDMSMA) by acid-hydrolysis of the silyl group is as follows: a portion of the obtained poly(TBDMSMA) (216 mg, M_n = 30600, M_w/M_n = 2.77) was dispersed in CH_3OH (20 mL) containing a small amount of hydrochloric acid (11 M; 1 mL) and the solution was refluxed for 24 h. After concentrating it by evaporation, the product was washed with Et_2O and dried in vacuo at room temperature overnight to give the PMAA (75.5 mg, 98% yield). For poly(TMSMA) and poly(TESMA), hydrolysis reaction was continued for 24 h. For poly(TIPSMA) and poly(TBDPSMA), hydrolysis reaction was continued for 72 h.

PMAA thus obtained was dissolved in 10 mL of a toluene/CH_3OH mixture (4/1 vol) and then an Et_2O solution of trimethylsilyl diazomethane (2.0 M, 2.50 mL) was added. After 12 h, the methylation was quenched by adding a small amount of acetic acid. The mixture was washed with distilled water and evaporated to dryness under reduced pressure, and then vacuum-dried to give PMMA (84.8 mg, 85% yield, M_n = 23500, M_w/M_n = 3.13).

In contrast, the silyl groups in poly(TPSMA) and poly(TTMSSMA) were deprotected by TBAF. A typical example for poly(TTMSSMA) by deprotection of the silyl group followed by

methylation with trimethylsilyl diazomethane is as follows: a portion of the obtained poly(TTMSSMA) (494 mg) was freeze-dried with benzene and an THF solution of TBAF (1.0 M, 5.00 mL) was added dropwise at 0 °C over a period of 10 min under stirring. The solution was stirring at 40 °C for additional 24 h. The deprotection was quenched by adding methanol (5.00 mL). After concentrating it by evaporation, the product was dissolved in 20 mL of a toluene/CH$_3$OH mixture (4/1 vol) and then an Et$_2$O solution of trimethylsilyl diazomethane (2.0 M, 5.00 mL) was added. After 12 h, the methylation was quenched by adding a small amount of acetic acid. The mixture was washed with distilled water and evaporated to dryness under reduced pressure, and then vacuum-dried to give PMMA containing a small amount of the residual silyl fluoride (159 mg, $M_n = 34900$, $M_w/M_n = 3.10$).

Polymer samples for NMR analysis were fractionated by preparative size-exclusion chromatography (SEC) (column: Shodex K-2002) to be free from low molecular weight compounds without loss of MMA oligomers if present.

Measurements

Monomer conversion was determined from the concentration of residual monomer measured by ^{1}H NMR spectroscopy with 1,2,3,4-tetrahydronaphthalene or toluene as an internal standard. ^{1}H NMR spectra for monomer conversion were recorded in CDCl$_3$ at 25 °C on a Varian Mercury 300 spectrometer, operating at 300 MHz. ^{1}H and ^{13}C NMR spectra of the obtained polymers were recorded in CDCl$_3$ at 55 °C on a JEOL ECS-400 spectrometer, operating at 400 and 100 MHz for ^{1}H and ^{13}C, respectively. The triad tacticity of the polymer was determined by the area of the a-methyl protons at 0.8–1.3 ppm in the ^{1}H NMR spectrum or carbonyl C=O carbons at 175–180 ppm in the ^{13}C NMR spectrum of the side chain. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the product polymers were determined by SEC in CHCl$_3$ at 40 °C on two polystyrene gel columns [Shodex K-805 (pore size: 20–1000 Å; 8.0 mm i.d. × 30 cm) × 2; flow rate 1.0 mL/min] connected to

Jasco PU-2080 precision pump and a Jasco RI-2031 detector. The columns were calibrated against 8 standard PMMA samples (Shodex; M_p = 875–1950000; M_w/M_n = 1.02–1.09). The glass-transition temperature (T_g: midpoint of the transition) of the polymers was recorded on Q200 differential scanning calorimetry (TA Instruments Inc.). Certified indium and sapphire were used for temperature and heat flow calibration. For poly(silyl methacrylate)s and PMMA, samples were firs heated to 180 °C at 10 °C/min, equilibrated at this temperature for 5 min, and cooled to –50 °C at 10 °C/min. After being held at this temperature for 5 min, the sample was then reheated to 180 °C at 5 °C/min. All T_g values of poly(silyl methacrylate)s and PMMA were obtained from the second scan, after removing the thermal history. For PMAAs, samples were first heated to 160 °C at 10 °C/min for mainly removing moisture, equilibrated at this temperature for 5 min, and cooled to –50 °C at 10 °C/min. After being held at this temperature for 5 min, the sample was then reheated to 300 °C at 5 °C/min to form the anhydride structure of PMAA, and cooled to –50 °C at 10 °C/min. After being held at this temperature for 5 min., the sample was reheated again to 300 °C at 5 °C/min to obtain T_g of the anhydro-PMAA.

Results and Discussion

Free Radical Polymerization of Various Silyl Methacrylates

A series of silyl methacrylates of varying bulkiness was polymerized with AIBN in toluene at 60 °C (entries 1, 3, 5, 7, 9, 10, and 13 in Table 1). All of the silyl methacrylates were efficiently polymerizable via a radical mechanism, but the reactions were slower for TIPSMA and TBDPSMA (Figure 1). All the polymers were soluble in organic solvents except for the one derived from TTMSSMA (entry 13), which, possessing an extremely bulky tris(trimethylsilyl)silyl group, was insoluble. Its lack of solubility was probably due to its rigid helical structure, which is similar to the structures of other bulky triarylmethyl methacrylates such as TrMA and 1-phenlydibenzosuberyl methacrylate (PDBSMA).[22]
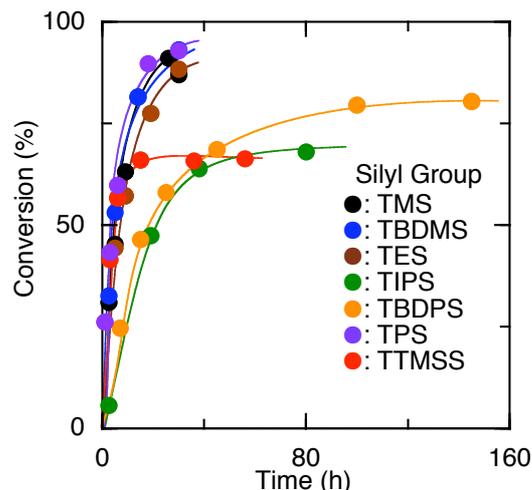
Figure 1. Time-conversion curves for the free radical polymerization of various silyl methacrylates with AIBN in toluene at 60 °C: [silyl methacrylate]$_0$ = 1.0 M; [AIBN]$_0$ = 5.0 mM.

The resulting poly(silyl methacrylate)s were analyzed by ^{1}H NMR spectroscopy (Figure 2) after purification by preparative SEC to remove any residual monomers. The spectra showed the characteristic signals of each proton in the main chain and in the silyl substituents, which indicated the formation of poly(silyl methacrylate)s. However, the tacticities of several polymers were difficult to determine from the α-methyl protons in the ^{1}H NMR spectra because of incomplete separation of the signals or overlap with other alkyl protons in the pendent groups.

Instead, the tacticities of the polymers were determined by ^{13}C NMR spectroscopy of the PMMAs obtained from the conversion of the poly(silyl methacrylate)s via a facile acid- or TBAF-induced deprotection of the silyl groups followed by methylation with trimethylsilyl diazomethane. Although poly(TTMSSMA) was not soluble in any solvent (see above), the deprotection reaction using TBAF to remove the bulky silyl groups proceeded smoothly and resulted in soluble PMAA, which was further converted to PMMA for the determination of molecular weight and tacticity. Figure 3 shows the ^{13}C NMR spectra of the carbonyl carbons of the PMMAs obtained from various poly(silyl methacrylate)s. As is evident from the differences in the spectral patterns, the stereospecificity was heavily dependent on the original silyl substituents,

Table 1. Free Radical Polymerization of Various Silyl Methacrylates[a]

entry	silyl group	temp (°C)	time (h)	conv[c] (%)	poly(silyl methacrylate)			converted PMMA[f]			
					M_n[d]	M_w/M_n[d]	T_g[e] (°C)	M_n[d]	M_w/M_n[d]	$rr/mr/mm$[g]	T_g[e] (°C)
1	TMS	60	30	87	28200	2.42	90	26700	2.41	63.7/31.6/4.7	124
2[b]	TBDMS	20	72	92	46100	2.47	140	38800	2.82	73.5/23.5/3.0	126
3	TBDMS	60	30	93	30600	2.77	146	23500	3.13	67.4/29.3/3.3	122
4	TBDMS	80	24	89	17000	2.39	137	13600	2.53	63.7/31.7/4.6	118
5	TES	60	30	88	30900	2.42	74	26700	2.41	59.5/36.2/4.3	120
6[b]	TIPS	20	580	88	28000	2.00	115	20600	2.08	29.1/49.0/21.9	100
7	TIPS	60	80	68	18000	2.08	87	11300	2.21	31.4/50.6/18.3	102
8	TIPS	80	14	34	8300	1.99	91	6500	1.91	32.5/49.7/17.8	95
9	TBDPS	60	145	80	23400	2.99	131	16200	2.37	35.9/49.9/14.2	107
10	TPS	60	30	93	32800	4.17	161	40400	2.41	46.6/44.9/8.5	116
11[b]	TTMSS	20	280	93	n.d.[h]	n.d.[h]	–	50700	2.96	8.4/9.5/82.1	56
12	TTMSS	40	80	90	n.d.[h]	n.d.[h]	–	92000	2.94	4.3/6.2/89.5	58
13	TTMSS	60	56	66	n.d.[h]	n.d.[h]	–	34900	3.10	1.4/5.2/93.4	54
14	TTMSS	80	56	8	n.d.[h]	n.d.[h]	–	–	–	–	–

[a] [silyl methacrylate]$_0$ = 1.0 M, [AIBN]$_0$ = 5.0 mM, in toluene. [b] [silyl methacrylate]$_0$ = 1.0 M, [V-70]$_0$ = 5.0 mM, in toluene. [c] By ^{1}H NMR. [d] By SEC using PMMA standard. [e] By DSC. [f] PMMA converted from the poly(silyl methacrylate). [g] By ^{13}C NMR. [h] Insoluble polymer.
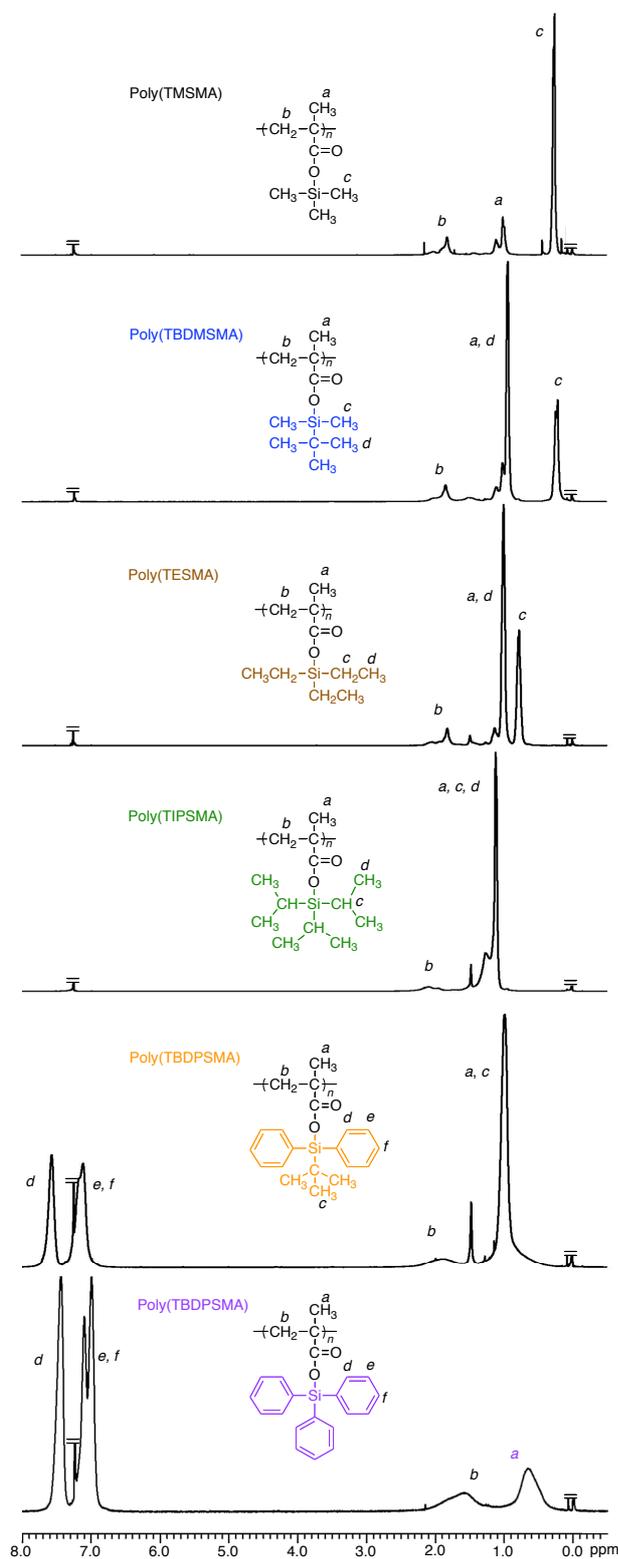
Figure 2. ^{1}H NMR spectra of (CDCl$_3$, 55 °C) of poly(silyl methacrylate)s obtained in the free radical polymerizations of various silyl methacrylates in toluene at 60 °C: [silyl methacrylate]$_0$ = 1.0 M; [AIBN]$_0$ = 5.0 mM.
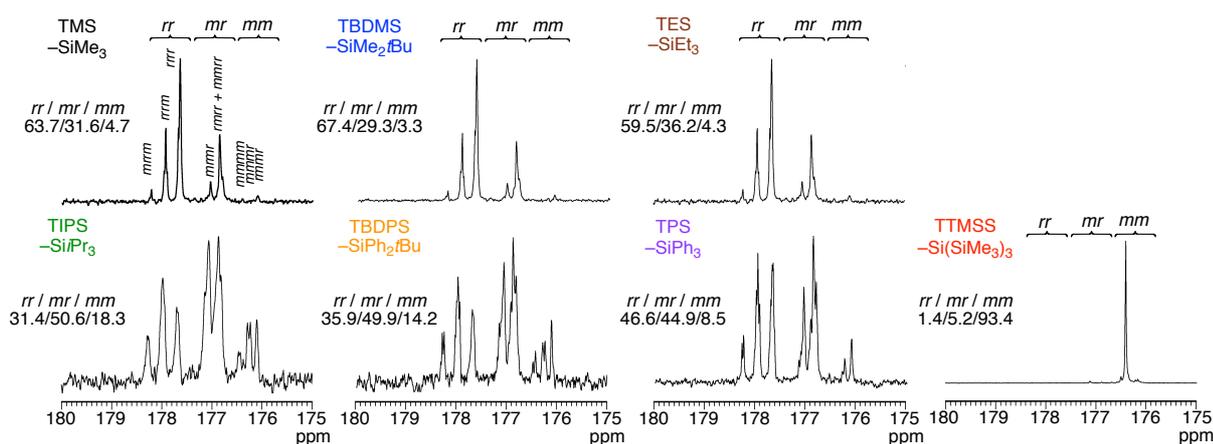
Figure 3. ^{13}C NMR spectra (CDCl$_3$, 55 °C) of poly(MMA)s converted from the poly(silyl methacrylate)s obtained in the free radical polymerization of various silyl methacrylates in toluene at 60 °C: [silyl methacrylate]$_0$ = 1.0 M; [AIBN]$_0$ = 5.0 mM.

where the isotactic index, *mm*, varied from 3.0% to 93.4%. Specifically, polymers that originally bore relatively less-bulky substituents, such as TMS (entry 1) and TES (entry 5), were predominantly syndiotactic (*rr* = 63.7% and 59.5%, respectively), as were poly(alkyl methacrylate)s, such as PMMA, obtained under similar conditions.[23] Even with an apparently bulky protecting group, TBDMS, a similar syndiotactic rich polymer (*rr* = 67.4%) was obtained (entry 3). However, upon a further increase in the bulk of the trialkylsilyl substituent with the triisopropylsilyl (TIPS) group, a nearly atactic polymer (*mr* = 50.6%) was formed (entry 7). The use of phenyl groups on the silyl substituent similarly decreased the syndiotacticity and resulted in almost atactic polymers, as observed for TBDPS (*rr* = 35.9% in entry 9) and TPS (*rr* = 46.6% in entry 10). However, the effects of these bulky substituents were, in general, smaller than those obtained with alkyl methacrylates: 1,1-diethylpropyl (R–: Et$_3$C–) resulted in a nearly atactic polymer (*rr/mr/mm* = 33/53/14), and triphenylmethyl (R–: Ph$_3$C–) gave an isotactic-rich (*rr/mr/mm* = 12/24/64) structure under similar conditions,[10,11b] whereas their silyl versions, i.e., triethylsilyl (Et$_3$Si–) and triphenylsilyl (Ph$_3$Si–), resulted in a syndiotactic-rich (*rr/mr/mm* = 59.5/36.2/4.3) and an atactic (*rr/mr/mm* = 46.6/44.9/8.5) polymer, respectively. The smaller effect of the silyl versions on the tacticities can be ascribed to the longer silyl ester (Si–O) bond relative to the alkyl (C–O) bond, where the substituent is located away

from the propagation chain end.[8]

In contrast, the novel silyl methacrylate with the extremely bulky TTMSS group led to high isotactic enchainment (*mm* = 93.4% in entry 12), probably because of the steric repulsion between the TTMSS groups of an incoming monomer and the growing chain end. This high enchainment led to a rigid helical conformation of the main chain, which is similar to that in the highly isospecific radical polymerization of triarylmethyl methacrylate.[10,11,24] The low solubility of the resulting poly(TTMSSMA) also suggests that the rigid helical conformation is due to the bulky substituent.

Figure 4 shows the triad tacticities, *mm*, *mr*, and *rr*, of the poly(silyl methacrylate)s plotted against the probabilities or contents of the *meso* diads (P_m) calculated by triad tacticities. Theoretical lines for Bernoullian statistics [$mm = P_m^2$, $mr = 2P_m(1-P_m)$, $rr = (1-P_m)^2$] are indicated as solid lines in the figure, and the plots are within the bounds, except for TPS and TTMSS.
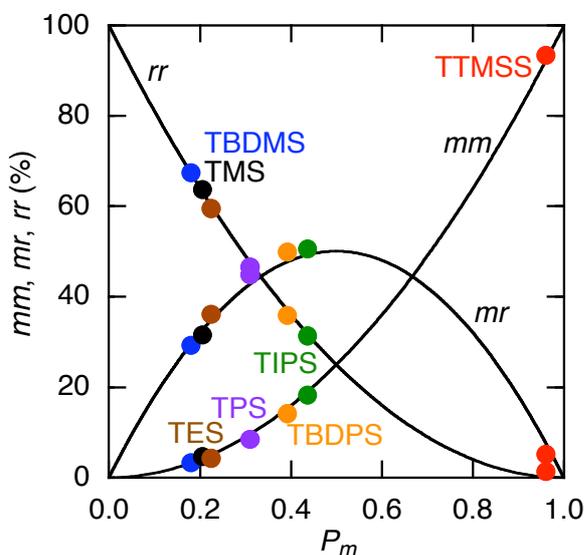
Figure 4. The probabilities or contents of isotactic (*mm*), heterotactic (*mr*), and syndiotactic (*rr*) triads as a function of P_m, the probabilities or contents of the *meso* diads in the radical polymerization of various silyl methacrylates in toluene at 60 °C. P_m was calculated according to the following equation, $P_m = mm + mr/2$, by using the observed *mm* and *mr* values. The solid lines indicate the theoretical lines for Bernoullian statistics.

These results indicate that radical polymerizations of silyl methacrylates mostly proceeded via the Bernoullian model, where the last monomer unit at the end of the propagating chain is important in determining the polymer stereochemistry, as is the case in the radical polymerizations of alkyl methacrylates.[25,26]

Thus, PMAA and PMMA with various stereoregularities that range from syndiotactic-rich to atactic and finally isotactic enchainment were synthesized by simply changing the bulkiness of the silyl substituents on the monomer during conventional radical polymerizations. Furthermore, highly isotactic PMAA can be prepared by using supersilyl group as the protecting group for methacrylic acid and subsequently performing a facile deprotecting reaction.

The effect of polymerization temperature on the tacticity was also examined by changing the temperature from 20 to 60 or 80 °C for several typical silyl monomers: TBDMSMA, TIPSMA, and TTMSSMA, which generate syndiotactic-rich, atactic, and isotactic structures, respectively. In the polymerization of TBDMSMA, as the temperature decreased, the syndiotacticity increased from 63.7% to 73.5% (entries 2–4 in Table 1), which is similar to what has been observed for alkyl methacrylates such as MMA.[27,28] However, TIPSMA resulted in nearly identical atactic polymers (*rr/mr/mm* ~ 30/50/20) over the same temperature range (entries 6–8). In contrast, the isotacticity of poly(TTMSSMA) increased from 82.1% to 93.4% when the temperature was increased from 20 to 60 °C (entries 11–13). However, the final accessible monomer conversion decreased in the highest temperature range; almost no polymers were obtained at 80 °C (entry 14). A similar effect of temperature on tacticity and monomer conversion has been reported for the radical polymerization of the bulky methacrylate, TrMA, and the effect of the polymerization-depolymerization equilibrium was not neglected near the ceiling temperature.[8,29]

The dependency of the tacticity on the temperature was analyzed in greater detail by the use of Fordham plots[30] for the polymerizations of TBDMSMA, TIPSMA, and TTMSSMA (Figure 5), where differences in the activation enthalpy ($\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger}$) and entropy ($\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger}$)

between isotactic and syndiotactic propagations can be obtained according to the following equation:

$$\ln(P_i/P_s) = (\Delta S_i^\ddagger - \Delta S_s^\ddagger)/R - (\Delta H_i^\ddagger - \Delta H_s^\ddagger)/RT \tag{1}$$

where P_i and P_s are the probabilities or contents of the isotactic and syndiotactic diads in the polymers, respectively, R is the gas constant, and T is the polymerization temperature. The obtained $\Delta H_i^\ddagger - \Delta H_s^\ddagger$ and $\Delta S_i^\ddagger - \Delta S_s^\ddagger$ values are summarized in Table 2.
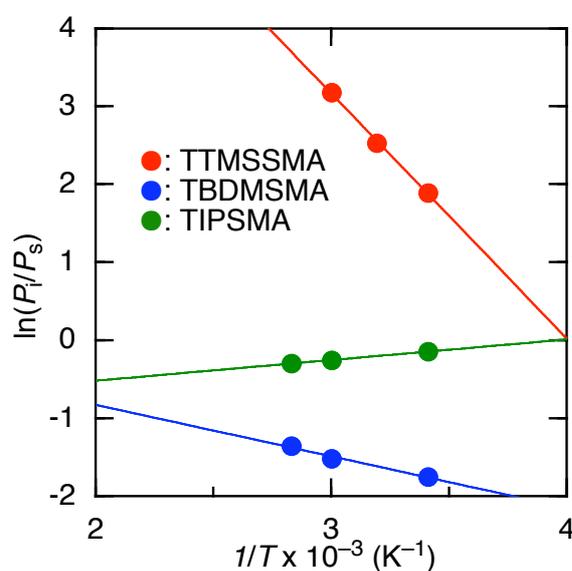
Figure 5. Fordham plots of the tacticity data for the polymerization of silyl methacrylates in various solvents from 20 to 80 °C.

Table 2. Activation Parameters for Radical Polymerization of Various Silyl Methacrylates[a]

silyl group	$\Delta H_i^\ddagger - \Delta H_s^\ddagger$ (kJ/mol)	$\Delta S_i^\ddagger - \Delta S_s^\ddagger$ (J/K·mol)
TBDMS	5.51	4.14
TIPS	–2.20	8.47
TTMSS	26.1	104
MMA[b]	3.47	–1.42

[a] Calculated from eq 1. [b] Reference 27.

The positive values of $\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger}$ and $\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger}$ for TBDMSMA indicate that the syndiospecific propagation is governed not by an entropic factor, but rather, by an enthalpic factor. As for TIPSMA, the fact that almost no difference in $\Delta H_i^{\ddagger}$ and $\Delta H_s^{\ddagger}$ was observed suggests a low stereoselectivity of the reaction, i.e., atactic propagation occurs.

In contrast to these results, TTMSSMA shows relatively large positive $\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger}$ values, which indicates that the high isospecificity is mainly attributable to an entropic factor. As reported previously, an extremely bulky methacrylate such as TrMA can continue its chain growth via helical conformation to result in the isospecific enchainment.[9–11,29] This fact means that the conformational factor plays an important role in determining the tacticity during the chain propagation and would be closely related to the entropic factor.

The thermal properties of the obtained poly(silyl methacrylate)s, PMMAs, and PMAAs were evaluated by differential scanning calorimetry (DSC) under a nitrogen atmosphere (Table 1; see also Figure 6 and 7). Glass-transition temperatures (T_g) were observed for almost all of the poly(silyl methacrylate)s, except for poly(TTMSSMA). Poly(TBDMSMA), poly(TBDPSMA), and poly(TPSMA) exhibited relatively high T_g values ($T_g > 130$ °C) because of the bulky *tert*-butyl or phenyl groups. In contrast, for poly(TTMSSMA), no thermal transition peaks were observed until 242 °C, where the polymers began to decompose. As reported for PMMAs with different tacticities,[31–34] the T_gs of the converted PMMAs similarly decreased with increasing isotacticity, although molecular weight effects were also observed.

As for PMAAs, which do not have a T_g below their decomposition temperatures (~ 200 °C) owing to the formation of anhydride groups by elimination of water between the pendent carboxylic acids,[35–37] their thermal properties were evaluated for PMAAs containing anhydride

forms via preheating up to 300 °C.   The T_g values of the formed andydro-PMAAs apparently decreased with an increase of isotacticity [$T_g = 163$ °C (sample obtained from entry 3 in Table 1), 158 °C (entry 7), 125 °C (entry 13), and Figure 7] as reported,[37] although the content of the anhydride forms for each sample was unknown.

Thus, the radical polymerization of a series of silyl methacrylates easily enables the synthesis of poly(methacrylate)s with different tacticities and thermal properties.
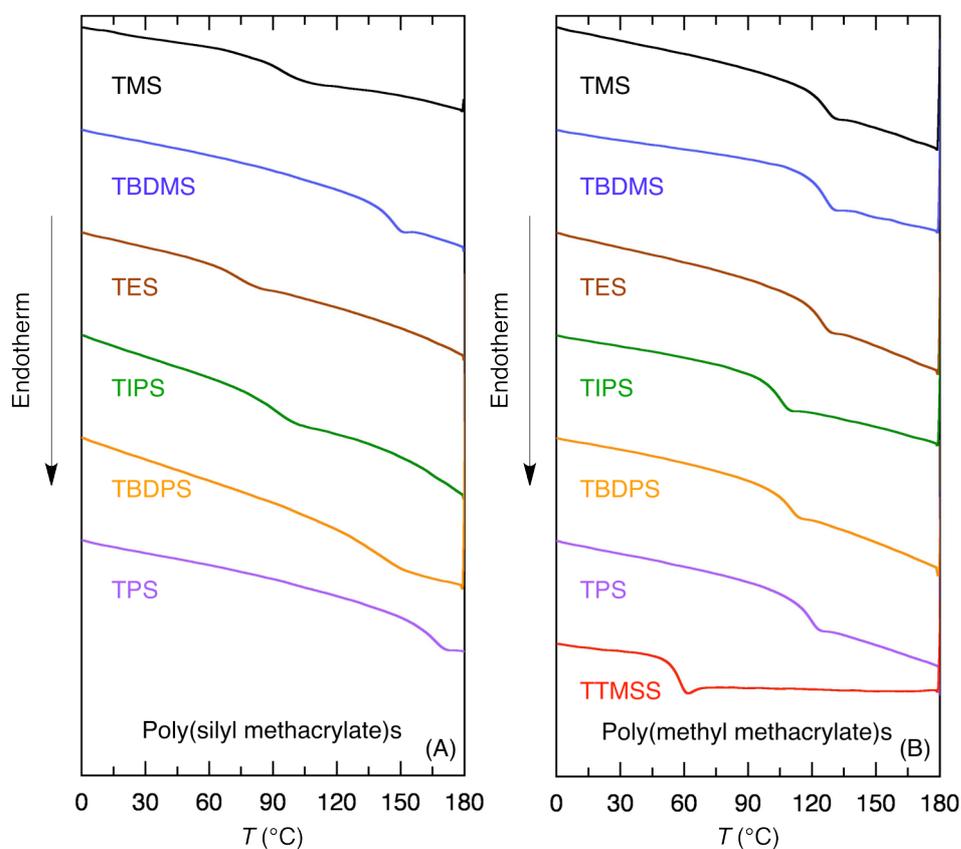

Figure 6.   Differential scanning calorimetry (DSC) curves of various poly(silyl methacrylate)s (A) and poly(methyl methacrylate)s (B) obtained from radical polymerization various silyl methacrylates with AIBN in toluene at 60 °C in the same experiment as for Figure 1.
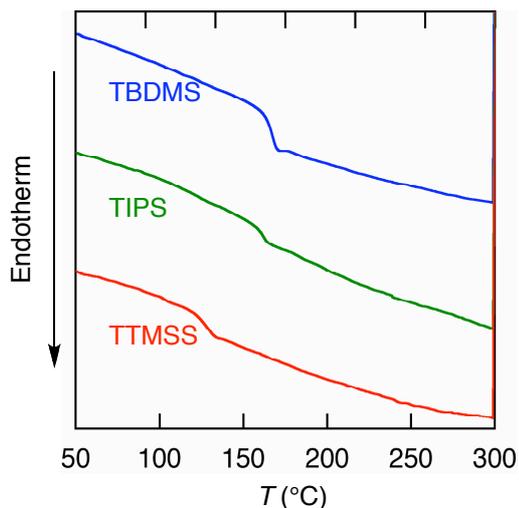
Figure 7. DSC curves of anhydro poly(methacrylic acid)s obtained from radical polymerization various silyl methacrylates with AIBN in toluene at 60 °C.

RAFT Polymerization of Various Silyl Methacrylates

The RAFT polymerization of various silyl methacrylates was investigated for the synthesis of well-defined poly(methacrylic acid)s and poly(methacrylate)s with controlled molecular weights and various tacticities. The author used CDB as a RAFT agent, which is effective in controlling the radical polymerization of various methacrylates,[29,38-42] including TBDMSA,[21] in conjunction with AIBN in toluene at 60 °C (Table 3 and Figure 8). The RAFT polymerizations occurred smoothly and proceeded at almost the same rate as the free radical polymerizations (Figure 8A). The M_n values of the obtained poly(silyl methacrylate)s increased in direct proportion to the monomer conversion, whereas they were generally lower than the calculated values, which were based on the assumption that one CDB molecule generates one living polymer chain, because they were measured using SEC based on PMMA standards (Figure 8B). The RAFT polymerization of TTMSSMA also resulted in insoluble polymers, as was observed during the free radical polymerization.

These poly(silyl methacrylate)s obtained from RAFT polymerizations were converted into PMAAs and subsequently PMMAs, and then analyzed using SEC and ^{13}C NMR. Figure 9 shows M_n, M_w/M_n, and the SEC curves of the resultant PMMAs. The M_ns increased in direct

proportion to the monomer conversion and agreed well with the calculated values, except for that of the PMMA converted from poly(TTMSSMA).   These results indicate that most silyl methacrylates can be polymerized in a controlled fashion via RAFT polymerization with CDB, except for TTMSSMA, where an M_ns higher than the calculated value was obtained due to the slow addition-fragmentation process of the bulky monomer[29] and the low solubility of the resulting polymers.

The tacticities of the polymers obtained in the RAFT polymerization (Table 3) were similar to those obtained in the free radical polymerizations (Table 1), where the isotacticity can be changed from 3.3% to 93.1%.   These similarities indicate that the RAFT agent does not affect the tacticity.   These results show that stereospecific controlled/living radical polymerization of silyl methacrylates can be achieved by the use of CDB as a RAFT agent.

Table 3.   RAFT Polymerization of Various Silyl Methacrylates[a]

entry	silyl group	time (h)	conv[b] (%)	poly(silyl methacrylate) M_n (calcd)	$M_n{}^c$	$M_w/M_n{}^c$	converted PMMA[d] M_n (calcd)[f]	$M_n{}^c$	$M_w/M_n{}^c$	$rr/mr/mm{}^e$
1	TMS	35	94	15100	11300	1.40	9700	10000	1.45	65.3/31.1/3.3
2	TBDMS	32	96	19500	12200	1.39	9900	10800	1.48	65.9/30.5/3.6
3	TES	45	93	18900	11000	1.46	9600	9100	1.57	57.9/36.4/5.7
4	TIPS	120	78	19200	7600	1.54	8100	6400	1.52	30.2/49.8/20.0
5	TBDPS	125	83	27200	8700	1.60	8600	6600	1.61	35.9/49.9/14.2
6	TPS	46	94	32700	9300	1.46	9600	8000	1.29	46.3/44.5/8.9
7	TTMSS	56	66	n.d.[f]	n.d.[f]	n.d.[f]	6900	8600	1.30	2.6/5.1/93.1

[a] [silyl methacrylate]$_0$ = 1.0 M, [CDB]$_0$ = 10.0 mM, [AIBN]$_0$ = 5.0 mM, in toluene at 60 °C.   [b] By ^{1}H NMR.   [c] By SEC using PMMA standard.   [d] For PMMA converted from the poly(silyl methacrylate).   [e] By ^{13}C NMR.   [f] Insoluble polymer.
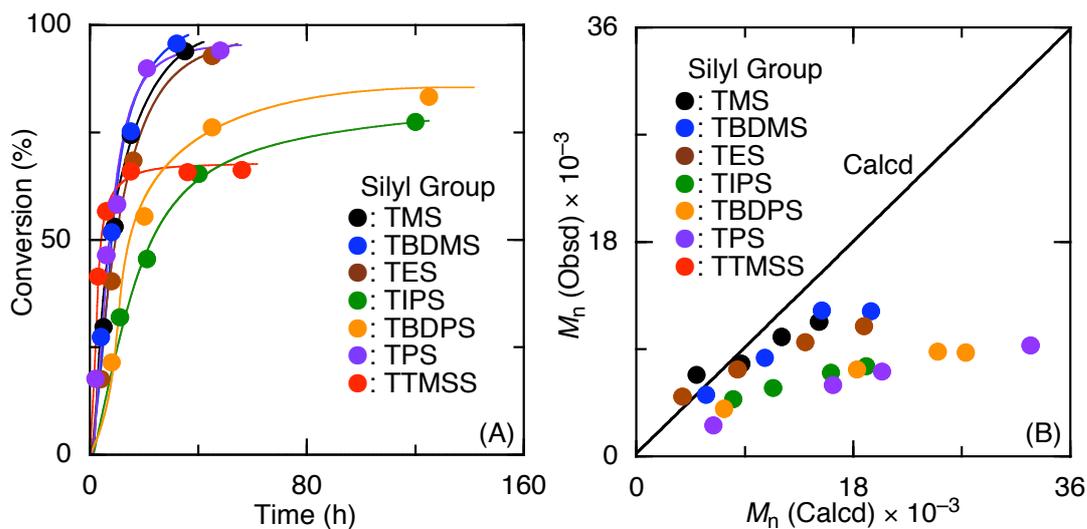
Figure 8. (A) Time-conversion curves and (B) M_n and M_w/M_n curves of poly(silyl methacrylate)s for the RAFT polymerization of various silyl methacrylates with AIBN in toluene at 60 °C: [silyl methacrylate]$_0$ = 1.0 M; [CDB]$_0$ = 10 mM; [AIBN]$_0$ = 5.0 mM.
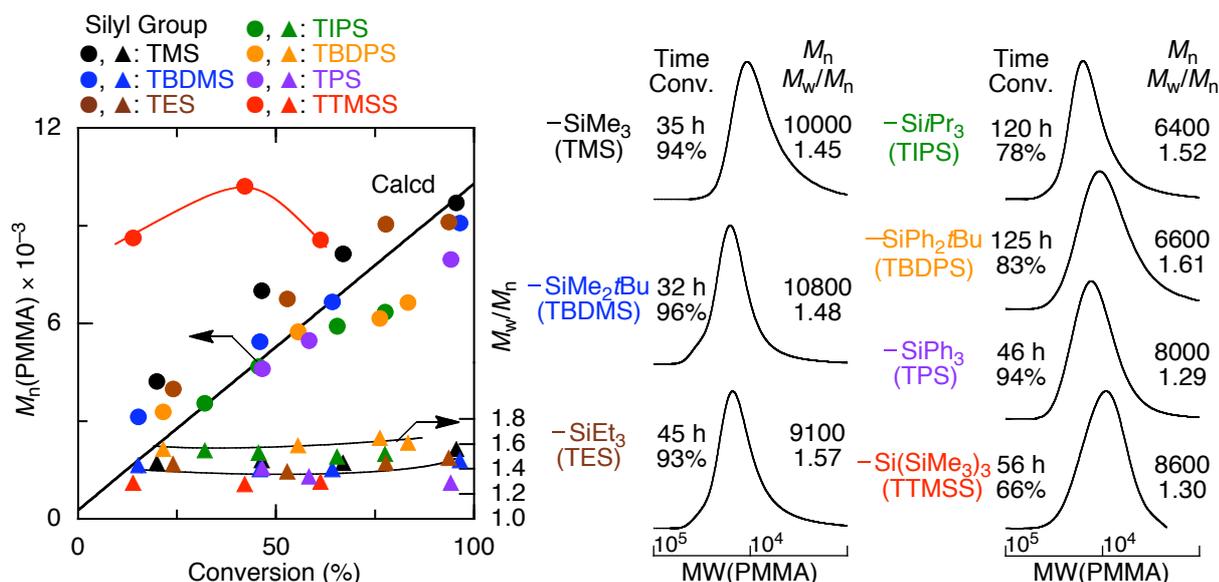

Figure 9. M_n, M_w/M_n, and SEC curves of poly(MMA) obtained from the RAFT polymerization of various silyl methacrylates with CDB/AIBN in toluene at 60 °C followed by the post reactions: [silyl methacrylate]$_0$ = 1.0 M; [CDB]$_0$ = 10 mM; [AIBN]$_0$ = 5.0 mM. The diagonal line indicates the calculated M_n assuming the formation of one polymer chain per CDB molecule.

Synthesis of Stereoblock Polymers

One of the most meaningful applications of stereospecific controlled/living radical polymerization is the synthesis of stereoblock polymers in which the tacticity and other properties can be changed at the blocking point.[29,43–46] For the synthesis of novel stereoblock poly(methacrylate)s and PMAAs, we utilized RAFT polymerizations of silyl methacrylates with different substituents. the author first polymerized TBDMSMA with AIBN in the presence of CDB in toluene at 60 °C to prepare the syndiotactic-rich poly(TBDMSMA) with a controlled molecular weight (M_n = 8200, M_w/M_n = 1.21) and a RAFT moiety at the chain end (Figure 10A and Figure 11A). After recovering the prepolymer by precipitation, we used it as a macroinitiator for the RAFT block copolymerization of TIPSMA to synthesize the atactic block segments (Figure 10C). The SEC curves of the obtained polymers shifted to high molecular weights while retaining narrow MWDs (M_n = 18500, M_w/M_n = 1.20). The unit ratio of TIPSMA and TBDMSMA in the block copolymers was calculated from the peak intensity ratio from the ^{1}H NMR spectra of the characteristic methylsilyl protons in the TBDMSMA unit to all the protons in the TIPSMA and TBDMSMA units, as shown in Figure 11B. The observed value, 41/59 (TBDMSMA/TIPSMA), was in good agreement with the calculated value (41/59) obtained from the monomer feed ratio and monomer conversions. These results indicate that the formation of the block copolymers of TBDMSMA and TIPSMA occurred by RAFT copolymerizations.

The silyl groups in the prepolymer and block copolymers were deprotected and then converted into their methyl esters to allow further analysis of their molecular weights (Figures 10B and 10D) and tacticities (Figures 12B and 12C). The obtained PMMAs also showed narrow SEC curves, which shifted to high molecular weights (M_n = 7700 → 16100) while keeping narrow MWDs (M_w/M_n ~ 1.3) as the polymerization proceeded. The tacticity changed from *rr/mr/mm* = 65.9/30.5/3.6 to *rr/mr/mm* = 44.5/42.5/13.0 for the block copolymerization of TIPSMA, which showed more or less atactic enchainment. The tacticity of the second block segments were calculated from these tacticities, and the unit ratio of the original block copolymer

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(TBDMSMA/TIPSMA = 41/59) was calculated to be 29.8/50.7/19.5, which is almost the same as that obtained for the RAFT homopolymerization of TIPSMA (30.2/49.8/19.8) and indicates the formation of atactic block segments. Thus, the syndiotactic-rich-*b*-atactic stereoblock PMAA or PMMA was obtained by the RAFT block copolymerization of TBDSMA and TIPSMA followed by simple transformation reactions.
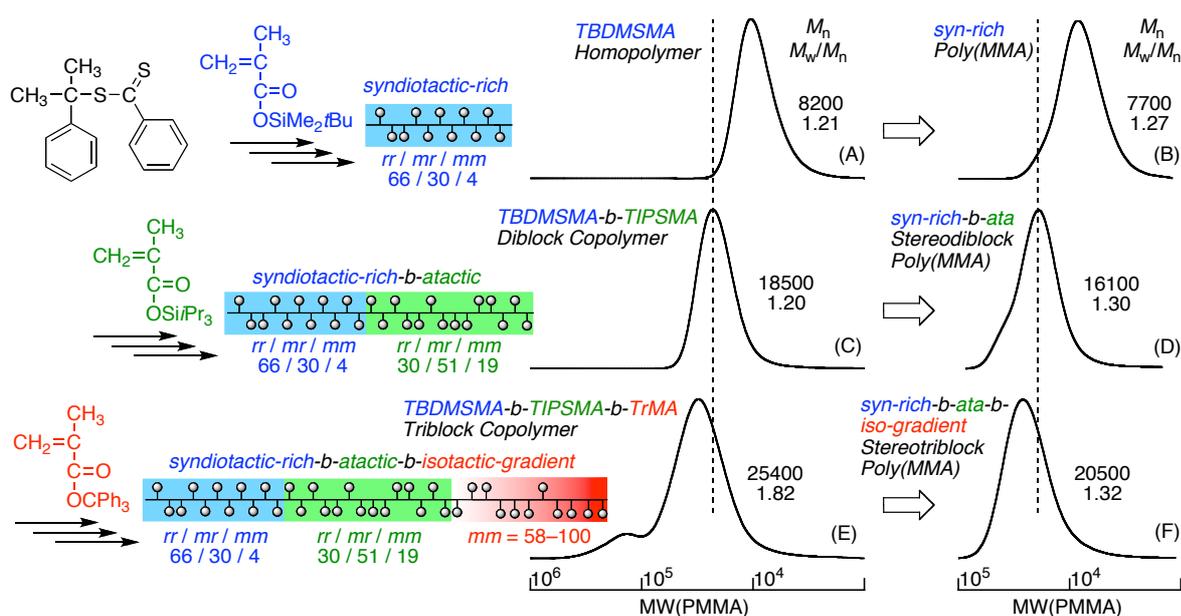

Figure 10. RAFT block copolymerization of TBDMSMA, TIPSMA, and TrMA in toluene at 60 °C for stereoblock polymers. (A): poly(TBDMSMA) obtained in the RAFT polymerization of TBDMSMA; $[TBDMSMA]_0 = 3.0$ M; $[CDB]_0 = 30$ mM; $[AIBN]_0 = 5.0$ mM. (B): syndiotactic-rich PMMA converted from (A). (C): poly(TBDMSMA-*b*-TIPSMA) obtained in the RAFT block polymerization of TIPSMA from the poly(TBDMSMA) macro-RAFT agent; $[TIPSMA]_0 = 2.0$ M; $[poly(TBDMSMA)]_0 = 10$ mM; $[AIBN]_0 = 3.3$ mM. (D): syndiotactic-rich-*b*-atactic PMMA converted from (C). (E): poly(TBDMSMA-*b*-TIPSMA-*b*-TrMA) obtained in the RAFT block polymerization of TrMA from the poly(TBDMSMA-*b*-TIPSMA) macro-RAFT agent; $[TrMA]_0 = 0.50$ M; $[poly(TBDMSMA-$*b*$-TIPSMA)]_0 = 6.0$ mM; $[AIBN]_0 = 3.0$ mM. (F): syndiotactic-rich-*b*-atactic-*b*-isotactic-stereogradient PMMA converted from (E).
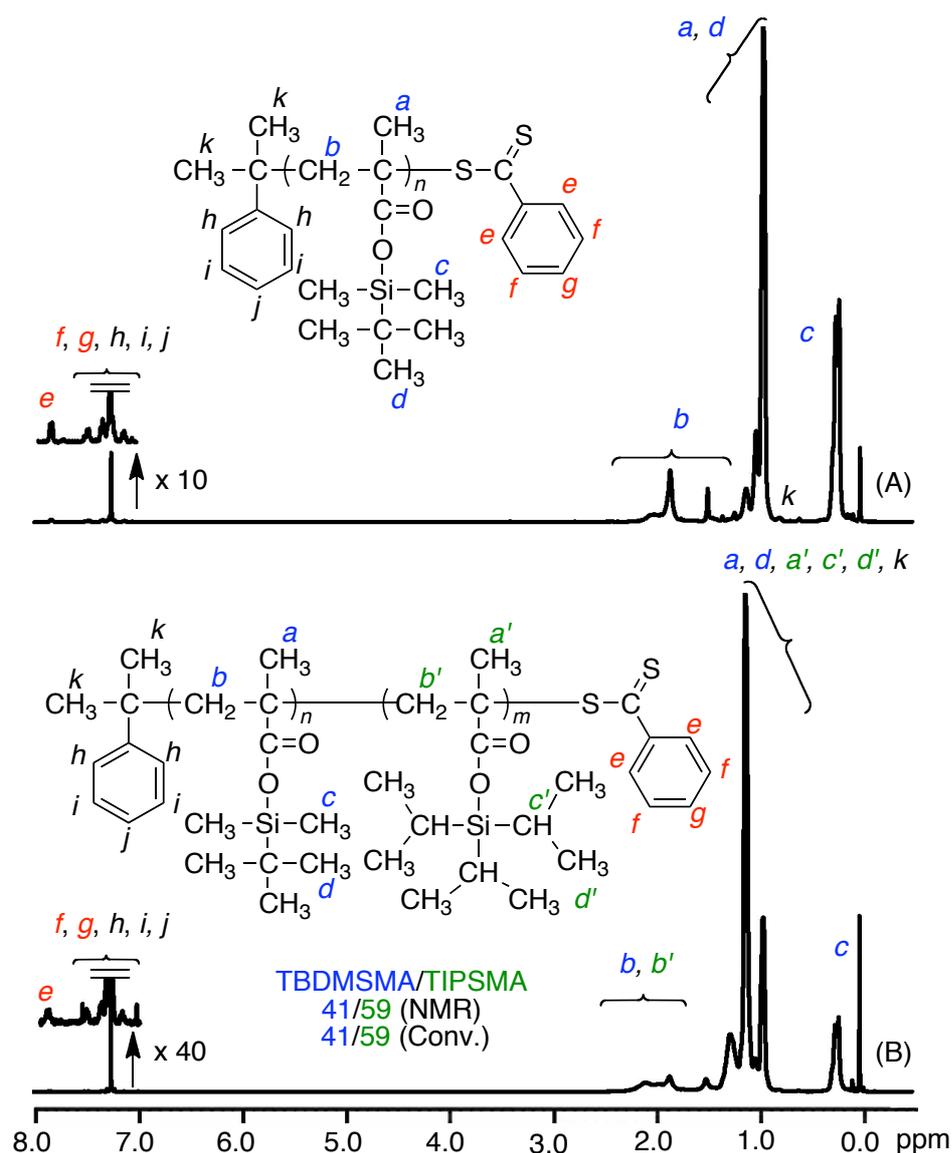
Figure 11. ^{1}H NMR spectra (CDCl$_3$, 55 °C) of poly(TBDSMA) obtained in the RAFT polymerization of TBDMSA in toluene at 60 °C ([TBDMSMA]$_0$ = 3.0 M, [CDB]$_0$ = 30 mM, [AIBN]$_0$ = 5.0 mM) (A) and poly(TBDMSMA-*b*-TIPSMA) obtained in the RAFT block polymerization of TIPSMA from the poly(TBDMSMA) macro-RAFT agent in toluene at 60 °C ([TIPSMA]$_0$ = 2.0 M; [poly(TBDMSMA)]$_0$ = 10 mM; [AIBN]$_0$ = 3.3 mM) (B).
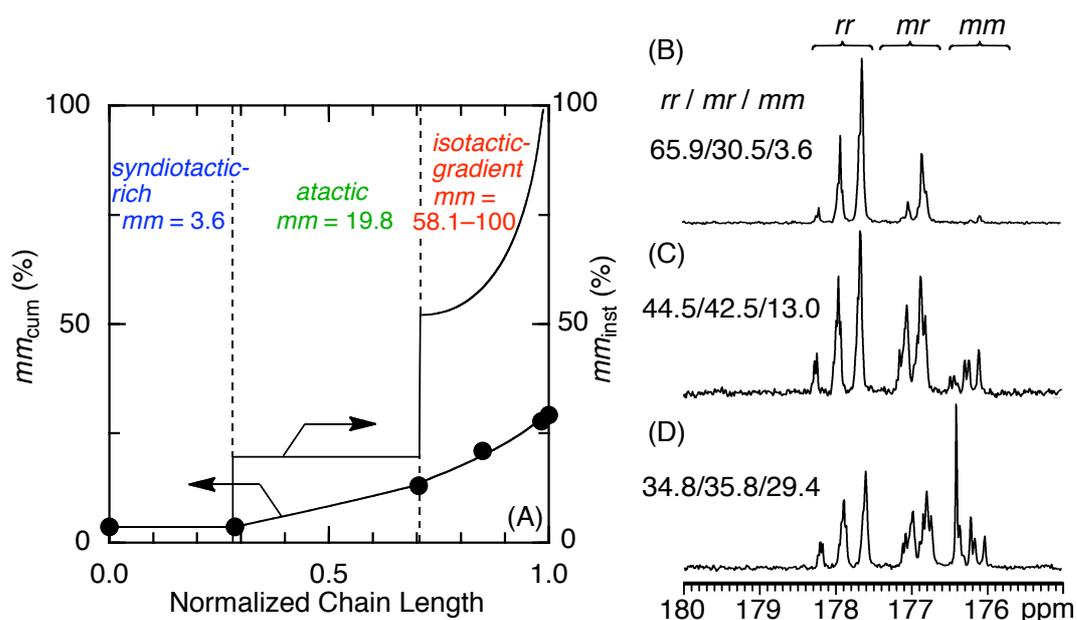
Figure 12. Dependences of cumulative and instantaneous *mm* triad contents on the normalized chain length (A). ^{13}C NMR spectra (CDCl$_3$, 55 °C) of poly(MMA) obtained from poly(TBDSMA) (B), poly(TBDMSMA-*b*-TIPSMA) (C), and poly(TBDMSMA-*b*-TIPSMA-*b*-TrMA) (D).

Furthermore, we employed poly(TBDMSMA-*b*-TIPSMA) as a macroinitiator for the RAFT block copolymerization of TrMA to enchain the isotactic-stereogradient segments.[29] The SEC curves of the obtained polymers were slightly broadened and bimodal due to aggregation of less soluble and rigid poly(TrMA) segments[29,47] (Figures 10E), whereas PMMA obtained after the removal of the silyl and trityl groups followed by methylation showed a similarly narrow MWD ($M_w/M_n \sim 1.3$) and an increase in molecular weight ($M_n = 16100 \rightarrow 20500$) (Figure 10F). In addition, the tacticity of the whole polymers further changed to *rr*/*mr*/*mm* = 34.8/35.8/29.4 (Figure 12D), where the isotactic content apparently increased. The cumulative isotacticity (mm_{cum}),[29] i.e., an isotacticity of the whole chain at a given conversion and the instantaneous isotacticity (mm_{inst}), which was calculated from mm_{cum}, was plotted against the normalized chain length, i.e., the ratio of chain length at a given conversion to the full chain length at the final

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conversion (Figure 12A). The mm_{inst} value in the third block segment of the resulting polymers increased from 58.1% to nearly 100% as TrMA was consumed. These results indicate the formation of stereo-triblock PMMA, which consists of syndiotactic-rich ($rr = 65.9\%$), atactic ($mr = 50.7\%$), and isotactic-stereogradient ($mm = 58.1–100\%$) segments at 28/42/30 unit ratios, by RAFT block copolymerization of these protected methacrylic monomers followed by post-reactions.

Conclusions

In conclusion, a series of silyl methacrylates with varying substituent bulkiness is a novel platform for the easy preparation of poly(methacrylate)s and poly(methacrylic acid)s with various tacticities that range from syndiotactic-rich to atactic and highly isotactic enchainment. Specifically, the novel bulky silyl methacrylate, supersilyl methacrylate, is radically polymerizable and results in a highly isotactic polymer ($mm > 90\%$) that is comparable to those obtained from a series of bulky triarylmethyl methacrylates. Thus, this monomer is another type of bulky methacrylate that can generate rigid helical vinyl polymers and also chiral polymers by further design of the polymerization system.[8,48] In addition to tacticity control, RAFT copolymerization of this series of silyl methacrylates enabled molecular-weight control and was applicable to the synthesis of various stereoblock poly(methacrylate)s and poly(methacrylic acid)s.

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Chapter 4

Asymmetric Polymerization of Bulky Silyl Methacrylate

Abstract

A highly bulky tris(trimethylsilyl)silyl methacrylate (TTMSSMA) was polymerized with asymmetric anionic and radical initiating systems. Asymmetric anionic polymerization of TTMSSMA was carried out with 9-fluoreneyllithium (Fl-Li) in the presence of (–)-sparteine [(–)-Sp], (*R*, *R*)-(–)-2,3-dimethoxy-1,4-bis(dimethylamino)butane [(–)-DDB], and its (*S*, *S*)-(+)-enantiomer [(+)-DDB] as a chiral ligand in toluene at –78 and –40 °C. The Fl-Li/(–)-Sp system induced quantitative consumptions of the monomer at –78 °C to give insoluble products as in the anionic polymerization of a similarly bulky methacrylate, suggesting formation of rigid helical polymers. The tacticity of the polymers was evaluated after converted into poly(methyl methacrylate) and proved highly isotactic (*mm* > 99%). The insoluble poly(TTMSSMA) solid sample obtained with Fl-Li/(–)-Sp showed chirality, which was measured by diffuse reflectance circular dichroism (DRCD) spectroscopy. Furthermore, the polymers obtained with [(–)-DDB] and [(+)-DDB] showed mirror-imaged spectra each other. These results indicated that TTMSSMA undergoes asymmetric anionic polymerization with these chiral initiating systems via formation of prevailing one-handed helical conformation. In contrast, the obtained polymers in radical polymerization in the presence of (+)- and (–)- menthol did not show any circular dichroism.

Introduction

Bulky methacrylates, such as triphenylmethyl methacrylate (TrMA) and 1-phenyldibezosuberyl methacrylate (PDBSMA), give highly isotactic and optically active polymers via asymmetric anionic polymerization with a chiral initiating system.[1,2] The obtained polymers have a stable one-handed helical conformation,[1–4] and some of them are utilized as chiral stationary phases for high-performance liquid chromatography with their high chiral recognition ability.[5] Furthermore, PDBSMA,[6–8] which produce the nearly complete isotatic polymer by radical polymerization, affords the excess single-hnaded helical polymers even by the radical polymerization in the presence of optically active additives.[7] In addition, bulky *N*-(triphenylmethyl)methacrylamide derivatives with similar triarylmethyl substituents also gave prevailing one-handed helical polymers by radical polymerization in the presence of chiral compounds. In these asymmetric polymerizations, the bulky triarylmethyl substituents take important roles in the formation of the helical conformation, as well as the high isotacticity of the resulting polymers.[1e,8] However, all these effective bulky substituents are based on the triarylmethyl skeleton [3,7–11] and there have been no other effective groups for inducing helix-sense-selective polymerizations and/or highly isotactic polymerizations.

Tris(trimethylsilyl)silyl group (TTMSS), called as hypersilyl, sisyl, or super silylgroup,[12] is an extremely bulky silyl group, and has been recently been used for a variety of highly diastereoselective reaction, including [2 + 2] cyclizations, Mukaiyama aldol reactions, and cascade reactions of its silyl enol ether by Yamamoto et al.[13] These bulky silyl ethers are stable under these ionic conditions to induce various stereoselective organic reactions due to its highly bulky nature. Quite recently, as described in chapter 3, the author have found that the novel bulky silyl methacrylate, super silyl methacrylate (TTMSSMA) was synthesized and radically polymerized to give highly isotactic polymers (*mm* > 90%) comparable to those obtained from bulky triarylmethyl methacrylates.[14] These results suggested that TTMSS group would be candidate, which induces aymmetric polymerizations with appropriate chiral initiating systems to

result in novel optically active polymers under chiral conditions.

In this chapter, the author thus investigated asymmetric polymerizations of TTMSSMA using chiral initiating systems, which are effective for anionic and radical polymerizations of triarylmethyl methacrylate, to synthesize novel optically active polymers with one-handed helical structure (Scheme 1). The organolithium-based systems consisting of 9-fluoreneyllithium (Fl-Li) and (–)-sparteine [(–)-Sp] induced the asymmetric anionic polymerization of TTMSSMA quantitatively to result in insoluble but highly isotactic (*mm* > 99%) and optically active polymers, which was confirmed by diffuse reflectance circular dichroism (DRCD) spectroscopy.
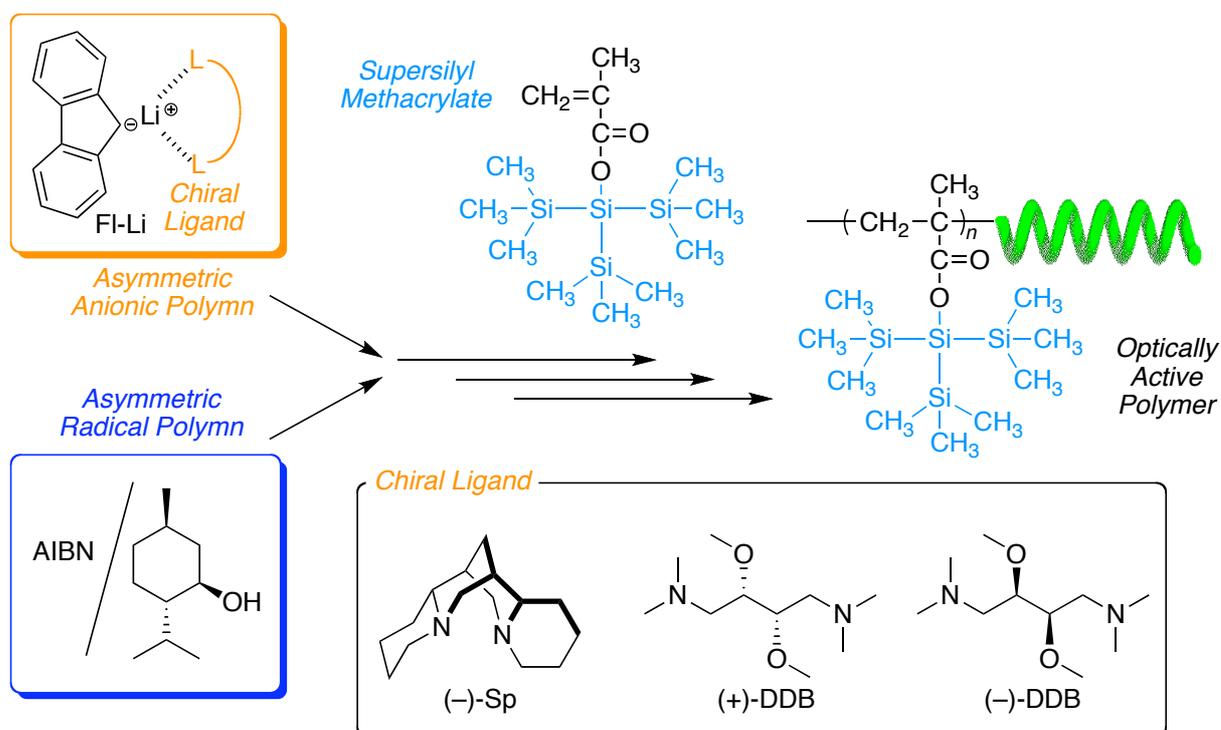
Scheme 1. Asymmetric Polymerization of Bulky Silyl Methacrylate

Experimental Section

Materials

Fluorene (TCI, >95%) was purified by recrystallization from hexane twice. (*S,*
S)-(+)-2,3-Dimethoxy-1,4-bis(dimethylamino)butane [(+)-DDB] (TCI, >97%), (*R,*
R)-(–)-2,3-dimethoxy-1,4-bis(dimethylamino)butane [(–)-DDB] (TCI, >90%), and
1,2,3,4-tetrahydronaphthalene (WAKO, 97%) were distilled from calcium hydride under reduced
pressure before use. (–)-Sparteine [(–)-Sp] was obtained from (–)-sparteine sulfate pentahydrate
(WAKO, 98%) with washing NaOH a.q. and distilled from calcium hydride under reduced
pressure before use. α,α-Azobis(isobutyronitrile) (AIBN) (Kishida, >99%) was purified by
recrystallization from methanol. Toluene (Kanto, >99.5%; H_2O < 10ppm) and THF (Kanto,
>99.5%; H_2O < 10ppm) were dried and deoxygenized by passage through columns of Glass
Contour Solvent Systems before use. Trimethylsilyl diazomethane (Aldrich, 2.0 M in Et_2O),
tetrabutylammonium fluoride (TBAF) (Aldrich, 1.0 M in THF), (–)-menthol (Kishida, 99%),
(+)-menthol (TCI, 99%), and *n*BuLi (Kanto, 1.57 M in *n*-hexane) were used as received.
Tris(trimethylsilyl)silyl methacrylate (TTMSSMA) was synthesized according to chapter 3.[14]

General Procedure for Asymmetric Anionic Polymerization

Polymerization was carried out by the syringe technique under dry argon in sealed glass
tubes. A typical example for polymerization of TTMSSMA with Fl-Li in toluene is given below.
Fl-Li was prepared by adding *n*BuLi (1.00 mL of 1.57 M solution in *n*-hexane) to a solution of
fluorene (0.261 g, 1.57 mmol) in toluene (14.0 mL) at room temperature. The Fl-Li solution was
mixed with (–)-Sp (0.43 mL, 1.87 mmol) and then left for 10 min at room temperature to prepare
the chiral initiator solution. In another glass tube were placed toluene (0.94 mL) and toluene
solution of TTMSSMA (0.86 mL of 1.16 M, 7.00 mmol) containing a small amount of
1,2,3,4-tetrahydronaphthalene (0.05 mL) as an internal standard at room temperature to obtain the
monomer solution. Then, the monomer solution was cooled at −78 °C, into which a prescribed

amount of an initiator solution (0.20 mL) was added. In predetermined intervals, the polymerization was terminated by the addition of a small amount of degassed methanol (ca 1.00 mL) to the reaction mixtures. Monomer conversion was determined from the concentration of residual monomer measured by ^{1}H NMR with 1,2,3,4-tetrahydronaphthalene as an internal standard (e.g., 96% conversion in 48 h). The quenched reaction solutions were washed with *n*-hexane and then dried to give poly(TTMSSMA).

General Procedure for Asymmetric Radical Polymerization

A typical example for polymerization of TTMSSMA with AIBN/(–)-menthol in toluene is given below. In a 50 mL round-bottomed flask were placed (–)-menthol (1.71 g, 10.9 mmol), TTMSSMA (0.63 mL, 1.62 mmol), toluene (0.33 mL) as an internal standard, and toluene solutions of AIBN (0.32 mL of 200 mM solution) at room temperature. The total volume of the reaction mixture was 3.2 mL. Immediately after mixing, aliquots (0.50 mL each) of the solution were distributed via a syringe into baked glass tubes, which were then sealed by flame under nitrogen atmosphere. The tubes were immersed in thermostatic oil bath at 60 °C. In predetermined intervals, the polymerization was terminated by the cooling of the reaction mixtures to −78 °C. Monomer conversion was determined from the concentration of residual monomer measured by ^{1}H NMR with toluene as an internal standard (e.g., 83% conversion in 30 h). The quenched reaction solutions were evaporated to dry to give poly(TTMSSMA).

Transformation of Poly(TTMSSMA) into Poly(methacrylic Acid) and Poly(methyl Methacrylate)

The obtained poly(TTMSSMA)s were converted into poly(methacrylic acid) (PMAA) and poly(methyl methacrylate) (PMMA). The silyl groups in poly(TTMSSMA) were deprotected by TBAF. A typical example for poly(TTMSSMA) by deprotection of the silyl group followed by methylation with trimethylsilyl diazomethane is as follows: a portion of the

poly(TTTMSSMA) (50 mg) obtained with Fl-Li/(–)-Sp was freeze-dried with benzene and a THF solution of TBAF (1.0 M, 5.00 mL) was added dropwise at 0 °C over a period of 10 min under stirring.   The solution was stirred at 40 °C for an additional 24 h.   The deprotection was quenched by adding methanol (5.00 mL). After concentrating it by evaporation, the product was dissolved in 20 mL of a toluene/CH$_3$OH mixture (4/1 vol) and then an Et$_2$O solution of trimethylsilyl diazomethane (2.0 M, 5.00 mL) was added.   After 12 h, the methylation was quenched by adding a small amount of acetic acid.   The mixture was washed with distilled water and evaporated to dryness under reduced pressure, and then vacuum-dried to give PMMA (12 mg, M_n = 37500, M_w/M_n = 2.20) containing a small amount of the residual silyl fluoride.

Polymer samples for NMR analysis were fractionated by preparative size-exclusion chromatography (SEC) (column: Shodex K-2002) to be free from low molecular weight compounds without loss of MMA oligomers if present.

Chiral Absorption

A finely ground polymer (15 mg) was put in a 2-mL screw-capped glass vial.   A solution of a racemic compound in methanol (200 μL, conc. = 0.25 g/mL) was added to the polymer.   The mixture was allowed to stand for 12 h in a tightly capped container.   The e.e. of the analyte in the sample solution was analyzed using the supernatant solution (10 μL) by an HPLC system equipped with a Jasco UV-970 UV detector, a Jasco OR-990 polarimeter, and a Daicel Chiralcel OD column (0.46 cm i.d. × 25 cm)

Measurements

Monomer conversion was determined from the concentration of residual monomer measured by ^{1}H NMR spectroscopy with 1,2,3,4-tetrahydronaphthalene or toluene as an internal standard. ^{1}H NMR spectra for monomer conversion were recorded in CDCl$_3$ at 25 °C on a Varian Mercury 300 spectrometer, operating at 300 MHz. ^{1}H and ^{13}C NMR spectra of the

obtained polymers were recorded in CDCl$_3$ at 55 °C on a JEOL ECS-400 spectrometer, operating at 400 and 100 MHz for ^{1}H and ^{13}C, respectively. The triad tacticity of the polymer was determined by the area of the a-methyl protons at 0.8–1.3 ppm in the ^{1}H NMR spectrum or carbonyl C=O carbons at 175–180 ppm in the ^{13}C NMR spectrum of the side chain. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the product polymers were determined by SEC in CHCl$_3$ at 40 °C on two polystyrene gel columns [Shodex K-805 (pore size: 20–1000 Å; 8.0 mm i.d. × 30 cm) × 2; flow rate 1.0 mL/min] connected to Jasco PU-2080 precision pump and a Jasco RI-2031 detector. The columns were calibrated against 8 standard PMMA samples (Shodex; M_p = 875–1950000; M_w/M_n = 1.02–1.09). Diffuse reflectance circular dichroism (DRCD) spectra were measured on a Jasco J-800 spectropolarimeter with a Jasco PCD-466 apparatus for the poly(TTMSSMA) sample (15 mg) grounded with 130 mg KCl in pressed quartz plate.

Results and Discussion

Anionic Polymerization of TTMSSMA

Anionic polymerization of TTMSSMA in the absence of chiral ligands was first investigated with Fl-Li as an initiator in toluene and THF at −78 °C. (entries 1, 2 in Table 1). The monomer was polymerized faster in THF than in toluene (Figure 1A), which is consistent with the solvent effects on the anionic polymerization of MMA[15] and TrMA,[16] in which propagating anion in THF become more reactive than in toluene due to coordination of THF to Li$^+$. All the obtained polymers were insoluble, similar to those obtained in radical polymerization,[14] most probably due to the rigid helical structure, as observed for other bulky triarylmethyl methacrylates such as TrMA and PDBSMA.[7a]

The obtained poly(TTMSSMA)s were then converted into PMMAs via deprotection of the silyl groups followed by methylation to measure the molecular weight and tacticity. The molecular weights based on PMMA calibration by SEC were higher than the calculated values.

Table 1. Anionic and Radical Polymerization of TTMSSMA[a]

entry	initiator/additive	temp. (°C)	$[M]_0/[I]_0$	time (h)	conv.[b] (%)	M_n[c,d]	M_w/M_n[c,d]	f[e] (%)	$mm/mr/rr$[e]
1	Fl-Li	−78	50	27	17	66700	1.87	1.5	95.8/2.7/1.5
2[f]	Fl-Li	−78	50	24	>99	11400	1.67	45	90.2/7.1/2.7
3	Fl-Li/(+)-DDB	−78	50	21	9	–	–	–	–
4	Fl-Li/(−)-Sp	−78	50	24	96	37500	2.22	13	99.4/0.4/0.2
5	Fl-Li/(−)-Sp	−78	30	24	>99	27700	2.41	3.5	99.1/0.7/0.2
6	Fl-Li/(−)-Sp	−78	10	24	>99	13500	2.25	8.6	99.2/0.6/0.2
7	Fl-Li/(−)-Sp	−40	50	0.5	>99	26300	1.84	19	95.8/2.2/2.0
8	Fl-Li/(+)-DDB	−40	50	5	95	8400	1.48	59	61.7/23.3/15.0
9	Fl-Li/(−)-DDB	−40	50	5	>99	6100	1.74	85	61.3/23.6/15.1
10	AIBN	60	50	85	75	16400	2.16	–	96.3/1.9/1.8
11[g]	AIBN/(−)-menthol	60	50	30	88	28100	3.68	–	96.0/1.9/1.5
12[h]	AIBN/(+)-menthol	60	50	30	85	47800	5.04	–	96.2/1.7/1.8

[a] Polymerization condition: $[TTMSSMA]_0 = 0.50$ M in toluene, $[Fl\text{-}Li]_0/[chiral\ ligand] = 1.0/1.2$ (entries 1–9) or $[AIBN]_0 = 20$ mM (entries 10–12). [b] By ^{1}H NMR. [c] By SEC. [d] After converted to poly(MMA). [e] f (initiator efficiency) $= M_n(calcd)/M_n(SEC)$. [f] In THF. [g] In toluene/(−)-menthol $= 1/3$ (v/v). [h] In toluene/(+)-menthol $= 1/3$ (v/v).
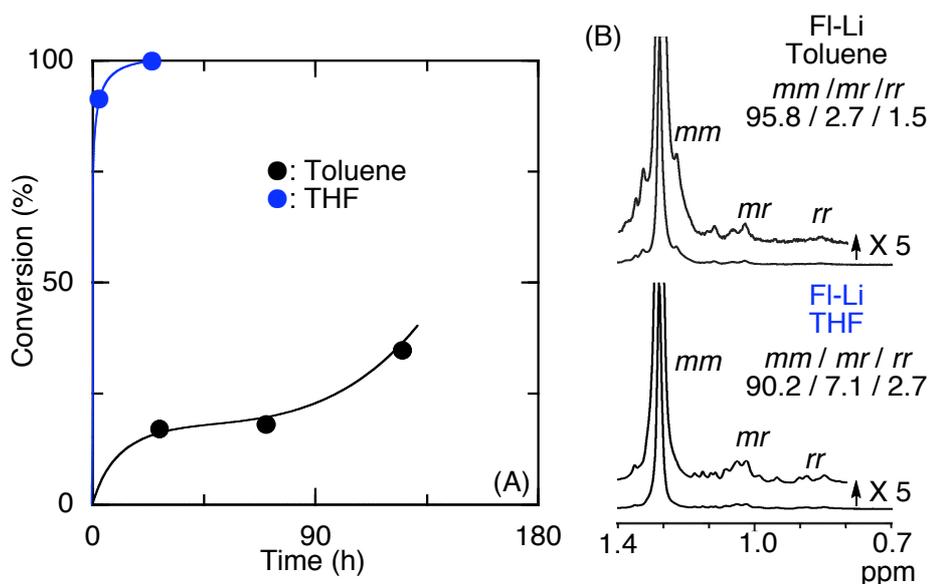
Figure 1. Time-conversion curves for anionic polymerization of TTMSSMA in toluene or THF at −78 °C (A) and ^{1}H NMR spectra (B) of poly(MMA) converted from the obtained poly(TTMSSMA): $[TTMSSMA]_0 = 0.50$ M; $[Fl\text{-}LI]_0 = 10$ mM.

The initiator efficiency thus obtained in toluene (1.5%) was much lower than that in THF (45%) due to the more pronounced aggregation of the initiator in nonpolar solvent, toluene.   As shown in the ^{1}H NMR spectra of α-methyl protons of the obtained PMMAs (Figure 1B), the polymers obtained in anionic polymerization also possessed a high isotacticity, which depended on the solvent; *mm* = 95% in toluene and 90% in THF.   Similar high isotacticities in anionic polymerizations were also reported for triarylmethyl methacrylate, indicating the formation of helical polymers from TTMSSMA.

Asymmetric Anionic Polymerization of TTMSSMA

Asymmetric anionic polymerization of TTMSSMA was then investigated with Fl-Li in the presence of chiral ligands, such as (−)-Sp and (+)-DDB, which are effective in the asymmetric anionic polymerization of bulky triarylmethyl methacrylate,[1–3] in toluene at −78 °C (entries 3 and 4 in Table 1).   The Fl-Li/(−)-Sp system induced quantitative polymerizations to result in insoluble polymers whereas no polymerization occurred with the Fl-Li/(+)-DDB system at −78 °C.

The poly(TTMMSMA) obtained with Fl-Li/(−)-Sp was characterized by diffuse reflectance circular dichroism (DRCD),[17] which can measure the chirality of the solid sate (Figure 2A).   The obtained poly(TTMMSMA) exhibited characteristic CD in the backbone region; *i.e.*, carbonyl group at 220 nm and super silyl group at 255 nm due to σ-conjugation of Si–Si groups.[18] These chiralities arise from the helical conformation of the main chain of poly(TTMMSMA) thus obtained as reported for the other bulky polymers, poly(triarylmethyl methacrylates) obtained under the similar conditions.[3b,]   The obtained polymer was further converted into PMAA and subsequently PMMA to analyze the tacticity and the molecular weights.   The polymer showed almost complete isotacticity (*mm* = 99%)
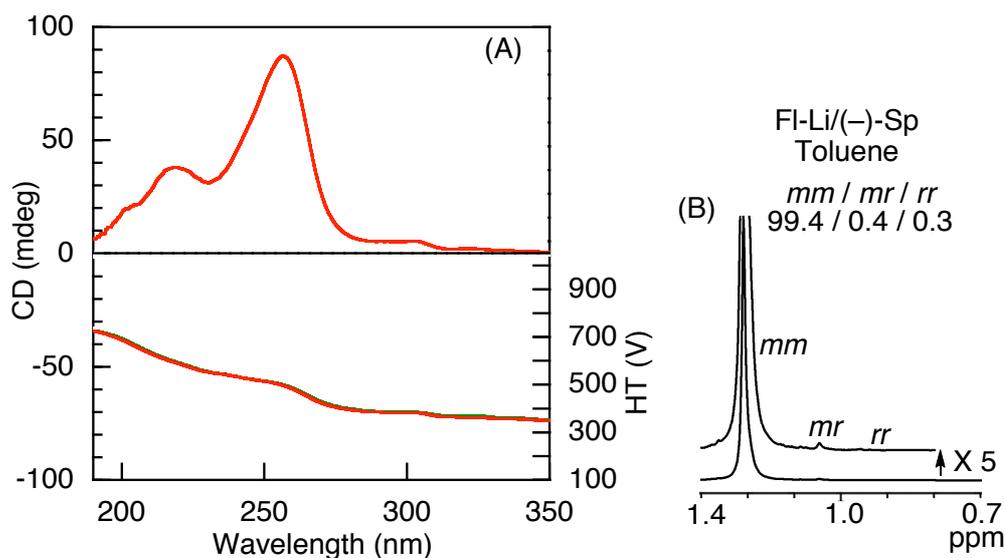
Figure 2. DRCD spectrum of poly(TTMSSMA) (A) and ^{1}H NMR spectrum (B) of PMMA converted from the poly(TTMSSMA) in the asymmetric anionic polymerization of TTMSSMA in toluene at -78 °C: [TTMSSMA]$_0$ = 0.50 M; [Fl-LI]$_0$ = 10 mM; [(−)-Sp]$_0$ = 12 mM.
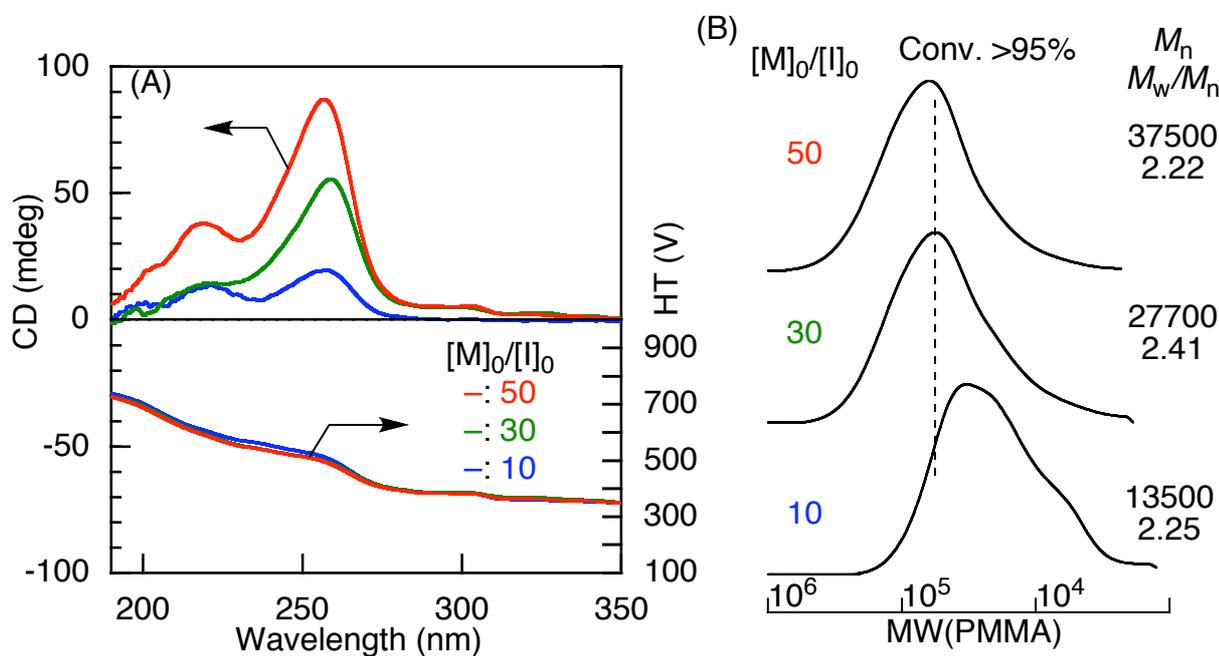

Figure 3. (A) DRCD spectra of poly(TTMSSMA) obtained in the asymmetric anionic polymerization of TTMSSMA at -78 °C: [TTMSSMA]$_0$ = 0.50 M; [Fl-Li]$_0$ = 10−50 mM; [(−)-Sp]$_0$ = 12−60 mM. (B) SEC curves of PMMA converted from the poly(TTMSSMA).

The effects of the initial monomer to initiator ratios on the asymmetric anionic polymerization were also examined ([TTMSSMA]$_0$/[Fl-Li]$_0$ = 50–10, entries 4–6 in Table 1).   In all the case, TTMMSSMA was consumed quantitatively to result in the insoluble polymers.   All the obtained polymers showed similar patterns of the DRCD spectra, the intensity of which decreased with decreasing the feed ratio (Figure 3A).   The molecular weights of PMMA converted from the obtained poly(TTMSSMA) decreased upon decreasing the feed ratio of [TTMSSMA]$_0$/[Fl-Li]$_0$ (Figure 3B) while keeping the high isotacticity.   These results indicate that the Fl-Li works as an initiator to induce the asymmetric anionic polymerization of TTMSSMA in the presence of (–)-Sp and to give the prevailing one-handed helical polymers.

The effects of polymerization temperature and chiral ligand structure were also examined (entries 7–9 in Table 1).   The polymerization with Fl-Li/(–)-Sp at –40 °C also induced quantitative polymerizations to result in optically active and isotactic polymers with similar molecular weights.   Although the obtained polymer showed a similar DRCD
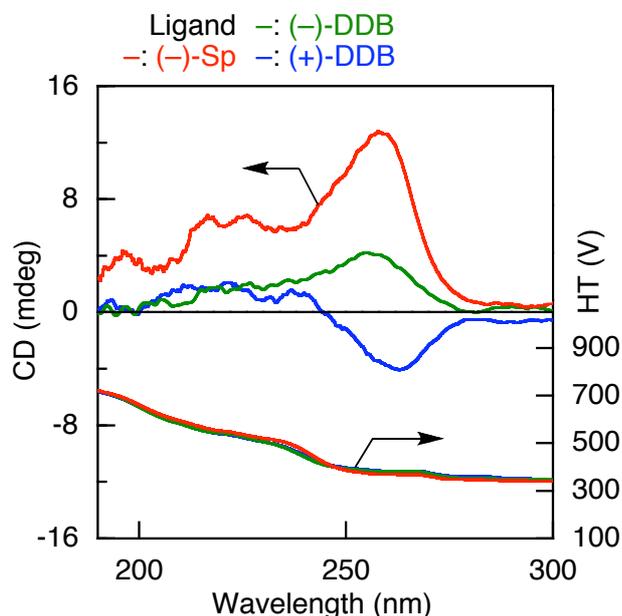
Figure 4.   DRCD spectra of poly(TTMSSMA) obtained in the asymmetric aninoic polymerization of TTMSSMA with Fl-Li/(–)-Sp, (–)-DDB, or (+)-DDB in toluene at –40 °C: [TTMSSMA]$_0$ = 0.50 M; [Fl-Li]$_0$ = 10 mM; [chiral ligand]$_0$ = 12 mM.

spectrum, its intensity was lower than that obtained at –78 °C (Figure 4). In addition, the isotacticity became slightly lower (*mm/mr/rr* = 95.8/2.2/2.0). These results indicate that the isospecificity and helix-sense selectivity decreases at higher temperatures. The Fl-Li/(+)-DDB or (–)-DDB system led to a quantitative polymerization at –40 °C whereas no polymer was obtained with Fl-Li/(+)-DDB at –78 °C as described above. Both the polymers showed similar molecular weights and isotacticities (*mm/mr/rr* = 61/23/15), which were slightly lower than that obtained with Fl-Li/(–)-Sp at –40 °C. The DRCD spectra of the polymers were almost mirror images of each other although their intensities were lower. These results indicate again that TTMSSMA is polymerized by the chiral initiating systems to give the prevailing one-handed helical polymers, in which a helical conformation with a right- or left-handed helicity in excess is induced by the chirality of ligands.

Radical Polymerization of TTMSSMA in the Presence of (–)- or (+)-Menthol

The possibility of asymmetric radical polymerization of TTMSSMA was examined using (–)- or (+)-menthol as an optically additive or chain-transfer agent, which is effective in the asymmetric radical polymerization of PDBSMA[7] and triarylmethyl methacrylamides,[19,20] in conjunction with AIBN in toluene at 60 °C (entries 10–12 in Table 1). Irrespective of the presence and absence of the chiral additives, the radical polymerizations occurred smoothly to produce the insoluble polymers. All the obtained polymers were similarly isotactic (*mm/mr/rr* = 96/2/2) whereas almost no CD was observed for the DRCD spectra. These results suggest the chain-transfer constant of menthol to the growing radical of TTMMSMA is too low to induce the helix-sense-selective radical polymerization.

Chiral Adsorption with Optically Active Poly(TTMSSMA)

The chiral recognition ability of the optically active poly(TTMSSMA) was evaluated by the chiral adsorption method using Tröger base and *trans*-stilbene oxide as the racemates for the

polymers obtained with Fl-Li/(−)-Sp system at −78 °C (Table 2).   Tröger base and *trans*-stilbene oxide was adsorbed by 52% and 19%, respectively, on the optically active poly(TTMSSMA). The e.e.s in solution were very low compared with that of optically active poly(TrMA)[21] probably due to that the almost nonpolar supersilyl group in the side chain of the helix cannot distinguish the chirality of these polar compounds.

Table 2.   Chiral Recognition Ability of the Optically Active Poly(TTMSSMA)[a]

Racemate	Solvent	Adsorbed Analyte (%)	*ee* in solution
	MeOH	52[b]	(+)-0.46[b]
	MeOH	19[b]	(−)-2.4[b]
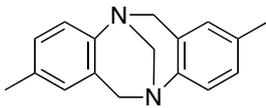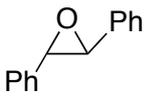
[a] Polymer 15 mg; racemate 0.05 mg (200 μL portion from 0.25 mg/mL in MeOH).

[b] Determined by HPLC analysis of supernatant solution using Chiralcel OD column; hexane/IPA (95/5); flow rate = 0.5 mL/min.

Conclusions

The novel bulky silyl methacrylate, TTMSSMA, undergoes asymmetric anionic polymerization in the presence of appropriate chiral ligands such as (−)-Sp to result in optically active polymers with prevailing one-handed helical conformation as in a series of the bulky triarylmethyl methacrylates.   This finding will contribute to developments in asymmetric polymerizations as well as helical polymeric materials based on designed bulky monomers.

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List of Publications

Papers

Chapter 1

"Stereogradient Polymers Formed by Controlled/Living Radical Polymerization of Bulky Methacrylate Monomer"

Kenji Ishitake, Kotaro Satoh, Masami Kamigaito, and Yoshio Okamoto

Angew. Chem. Int. Ed. **2009**, *48*, 1991–1994.

Chapter 2

"From-Syndiotactic-to-Isotactic Stereogradient Methacrylic Polymers by RAFT Copolymerization of Methacrylic Acid and Its Bulky Esters"

Kenji Ishitake, Kotaro Satoh, Masami Kamigaito, and Yoshio Okamoto

Polym. Chem. **2012**, *in press.* (DOI: 10.1039/C1PY00401H)

Chapter 3

"Stereospecific Free Radical and RAFT Polymerization of Bulky Silyl Methacrylates for Stereo- and Molecular Weight-Controlled Poly(methacrylic Acid)"

Kenji Ishitake, Kotaro Satoh, Masami Kamigaito, and Yoshio Okamoto

Macromolecules **2011**, *44*, 9108–9117. (Cover)

Chapter 4

"Asymmetric Anionic Polymerization of Bulky Silyl Methacrylates"

Kenji Ishitake, Kotaro Satoh, Masami Kamigaito, and Yoshio Okamoto

in preparation.

Other Related Papers

"Syndiotactic PMMA Brush Polynorbornene via Living Radical and Ring-Opening Metathesis Polymerization and Their Stereocomplex Formation"

Kenji Ishitake, Kotaro Satoh, Masami Kamigaito, Jing M. Ren, Anton Blencowe,

and Greg G. Qiao

in preparation.

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