Macromolecules

ARTICLE

pubs.acs.org/Macromolecules

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

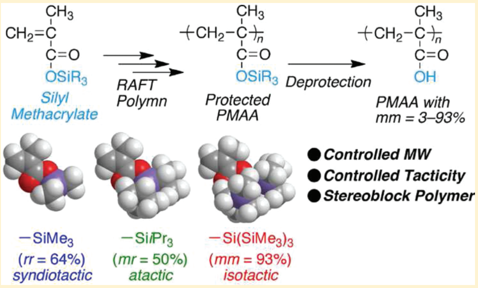
Kenji Ishitake,[†] Kotaro Satoh,[†] Masami Kamigaito,[*,†] and Yoshio Okamoto[‡,§]

[†]Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

[‡]Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

[§]College of Material Science and Chemical Engineering, Harbin Engineering University, Nantong St. Harbin, P. R. China

S *Supporting Information*



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 $(Me_3Si)_3Si$] were 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 trimethylsilyldiazomethane 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 and PMMAs 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 silyl methacrylates followed by simple postreactions. 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 and PMMA that consisted of syndiotactic-rich, atactic, and isotactic stereogradient segments.

■ INTRODUCTION

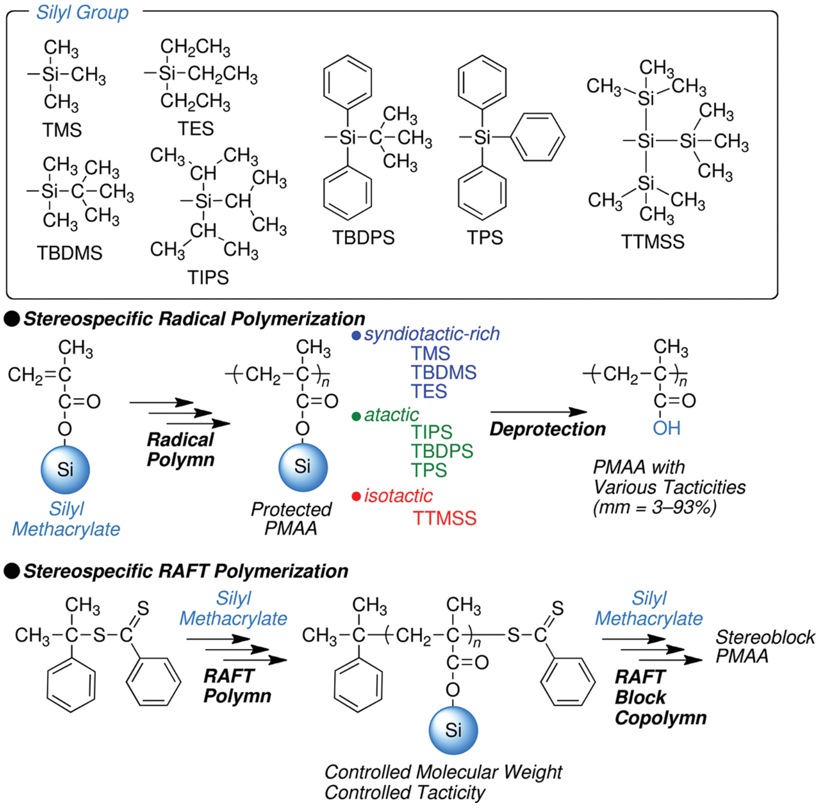
Silyl groups are among the most frequently used protective groups for alcoholic protons and can similarly be used for protecting carboxylic acidic protons in their silyl ester forms.[1] Various silyl groups have been prepared and adapted for the realization of selective deprotection reactions of silyl 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]

Received: September 23, 2011
Revised: October 29, 2011
Published: November 16, 2011

Scheme 1. Stereospecific RAFT Polymerization of Various Silyl Methacrylates for Stereocontrolled and Molecular Weight Controlled Poly(methacrylic acid) and Its Ester



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* = 64−98%) 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 copolymerized radically or anionically, which were particularly directed to photoresist 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$_3$Si, Ph_2tBuSi, Ph_3Si, and $(Me_3Si)_3Si$] and examined the effect of stereospecificity on the radical polymerization (Scheme 1). We focused our 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, we 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 postreactions was also investigated.

■ 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 min just before use. Cumyl dithiobenzoate (CDB) was synthesized according to the literature.[20] Trimethylsilyldiazomethane (Aldrich, 2.0 M in Et_2O), 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%) were 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). Into the suspension, 2.78 M TBDMS-Cl solution (51.0 mL, 0.142 mol) was added dropwise at 0 °C over a period of 30 min under stirring. After stirring at ambient temperature for an 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%, bp 52 °C/533 Pa). ^{1}H NMR ($\mathrm{CDCl_3}$, rt): δ 0.30 (s, 6H, $\mathrm{Si(C\mathit{H}_3)_2C(CH_3)_3}$), 0.96 (s, 9H, $\mathrm{Si(CH_3)_2C(C\mathit{H}_3)_3}$), 1.92 (dd, 3H, $\mathrm{CH_2{=}C{-}C\mathit{H}_3}$), 5.56 (m, 1H, cis $\mathrm{C\mathit{H}_2{=}C{-}CH_3}$), 6.09 (m, 1H, trans $\mathrm{C\mathit{H}_2{=}C{-}CH_3}$). ^{13}C NMR ($\mathrm{CDCl_3}$, rt): δ −4.8 ($\mathrm{Si(\mathit{C}H_3)_2C(CH_3)_3}$), 17.8 ($\mathrm{Si(CH_3)_2\mathit{C}(CH_3)_3}$), 18.5 ($\mathrm{CH_2{=}C{-}\mathit{C}H_3}$), 25.7 ($\mathrm{Si(CH_3)_2C(\mathit{C}H_3)_3}$), 126.1 ($\mathrm{\mathit{C}H_2{=}C{-}CH_3}$), 137.9 ($\mathrm{CH_2{=}\mathit{C}{-}CH_3}$), 167.7 ($\mathrm{\mathit{C}O_2Si(CH_3)_2C(CH_3)_3}$).

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). Into the suspension, 2.70 M TES-Cl solution (25.3 mL, 0.149 mol) was added dropwise at 0 °C over a period of 30 min under stirring. After stirring at ambient temperature for an 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%, bp 77 °C/666 Pa). ^{1}H NMR ($\mathrm{CDCl_3}$, rt): δ 0.76−0.84 (q, 6H, $\mathrm{Si(C\mathit{H}_2CH_3)_3}$), 0.93−1.03 (t, 9H, $\mathrm{Si(CH_2C\mathit{H}_3)_3}$), 1.93 (dd, 3H, $\mathrm{CH_2{=}C{-}C\mathit{H}_3}$), 5.58 (m, 1H, cis $\mathrm{C\mathit{H}_2{=}C{-}CH_3}$), 6.11 (m, 1H, trans $\mathrm{C\mathit{H}_2{=}C{-}CH_3}$). ^{13}C NMR ($\mathrm{CDCl_3}$, rt): δ 4.7 ($\mathrm{Si(\mathit{C}H_2CH_3)_3}$), 6.7 ($\mathrm{Si(CH_2\mathit{C}H_3)_3}$), 18.5 ($\mathrm{CH_2{=}C{-}\mathit{C}H_3}$), 126.1 ($\mathrm{\mathit{C}H_2{=}C{-}CH_3}$), 137.7 ($\mathrm{CH_2{=}\mathit{C}{-}CH_3}$), 167.7 ($\mathrm{\mathit{C}O_2Si(CH_2CH_3)_3}$).

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). Into the suspension, 2.87 M TIPS-Cl solution (36.3 mL, 0.104 mol) was added dropwise at 0 °C over a period of 30 min under stirring. After stirring at ambient temperature for an 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%, bp 78 °C/533 Pa). ^{1}H NMR ($\mathrm{CDCl_3}$, rt): δ 1.04−1.09 (s, 18H, $\mathrm{Si(CH(C\mathit{H}_3)_2)_3}$), 1.21−1.39 (m, 3H, $\mathrm{Si(C\mathit{H}(CH_3)_2)_3}$), 1.95 (dd, 3H, $\mathrm{CH_2{=}C{-}C\mathit{H}_3}$), 5.59 (m, 1H, cis $\mathrm{C\mathit{H}_2{=}C{-}CH_3}$), 6.14 (m, 1H, trans $\mathrm{C\mathit{H}_2{=}C{-}CH_3}$). ^{13}C NMR ($\mathrm{CDCl_3}$, rt): δ 12.1 ($\mathrm{Si(\mathit{C}H(CH_3)_2)_3}$), 17.9 ($\mathrm{Si(CH(\mathit{C}H_3)_2)_3}$), 18.6 ($\mathrm{CH_2{=}C{-}\mathit{C}H_3}$), 126.1 ($\mathrm{\mathit{C}H_2{=}C{-}CH_3}$), 137.8 ($\mathrm{CH_2{=}\mathit{C}{-}CH_3}$), 167.4 ($\mathrm{\mathit{C}O_2Si(CH(CH_3)_2)_3}$).

***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 added dropwise at 0 °C over a period of 30 min under stirring. After stirring at ambient temperature for an 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%, bp 120 °C/40 Pa). ^{1}H NMR ($\mathrm{CDCl_3}$, rt): δ 1.10 (s, 9H, $\mathrm{SiPh_2C(C\mathit{H}_3)_3}$), 1.96 (dd, 3H, $\mathrm{CH_2{=}C{-}C\mathit{H}_3}$), 5.64 (m, 1H, cis $\mathrm{C\mathit{H}_2{=}C{-}CH_3}$), 6.25 (m, 1H, trans $\mathrm{C\mathit{H}_2{=}C{-}CH_3}$), 7.32−7.42 (m, 6H, *m*, *p*-Ar*H*), 7.62−7.68 (d, 4H, *o*-Ar*H*). ^{13}C NMR ($\mathrm{CDCl_3}$, rt): δ 18.7 ($\mathrm{CH_2{=}C{-}\mathit{C}H_3}$), 19.4 ($\mathrm{SiPh_2\mathit{C}(CH_3)_3}$), 27.1 ($\mathrm{SiPh_2C(\mathit{C}H_3)_3}$), 126.7 ($\mathrm{\mathit{C}H_2{=}C{-}CH_3}$), 127.9, 130.1, 132.0, and 135.5 (phenyl), 137.7 ($\mathrm{CH_2{=}\mathit{C}{-}CH_3}$), 166.6 ($\mathrm{\mathit{C}O_2SiPh_2C(CH_3)_3}$).

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). Into the suspension, 0.832 M triphenylsilyl chloride solution (102 mL, 0.849 mol) was added dropwise at 0 °C over a period of 30 min under stirring. After stirring at ambient temperature for an 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 $\mathrm{CHCl_3}$ as an eluent. TPSMA was obtained as white solid (7.71 g, 64%). ^{1}H NMR ($\mathrm{CDCl_3}$, rt): δ 2.00 (m, 3H, $\mathrm{CH_2{=}C{-}C\mathit{H}_3}$), 5.67 (m, 1H, cis $\mathrm{C\mathit{H}_2{=}C{-}CH_3}$), 6.31 (m, 1H, trans $\mathrm{C\mathit{H}_2{=}C{-}CH_3}$), 7.32−7.42 (m, 9H, *m*, *p*-Ar*H*), 7.63−7.69 (d, 6H, *o*-Ar*H*). ^{13}C NMR ($\mathrm{CDCl_3}$, rt): δ 18.5 ($\mathrm{CH_2{=}C{-}\mathit{C}H_3}$), 127.2 ($\mathrm{\mathit{C}H_2{=}C{-}CH_3}$), 128.1, 130.7, 132.4, and 135.8 (phenyl), 137.4 ($\mathrm{CH_2{=}\mathit{C}{-}CH_3}$), 167.0 ($\mathrm{\mathit{C}O_2SiPh_3}$).

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). Into the suspension, 0.834 M tris(trimethylsilyl)silyl chloride solution (67.8 mL, 56.4 mmol) was added dropwise at 0 °C over a period of 30 min under stirring. After stirring at ambient temperature for an 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%, bp 106 °C/133 Pa). ^{1}H NMR ($\mathrm{CDCl_3}$, rt): δ 0.22 (s, 27H, $\mathrm{Si(Si(C\mathit{H}_3)_3)_3}$), 1.91 (m, 3H, $\mathrm{CH_2{=}C{-}C\mathit{H}_3}$), 5.55 (m, 1H, cis $\mathrm{C\mathit{H}_2{=}C{-}CH_3}$), 6.00 (m, 1H, trans $\mathrm{C\mathit{H}_2{=}C{-}CH_3}$). ^{13}C NMR ($\mathrm{CDCl_3}$, rt): δ 0.01 ($\mathrm{Si(Si(\mathit{C}H_3)_3)_3}$), 18.9 ($\mathrm{CH_2{=}C{-}\mathit{C}H_3}$), 125.5 ($\mathrm{\mathit{C}H_2{=}C{-}CH_3}$), 137.6 ($\mathrm{CH_2{=}\mathit{C}{-}CH_3}$), 169.3 ($\mathrm{\mathit{C}O_2Si(Si(CH_3)_3)_3}$).

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), and 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) 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 a 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

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

					poly(silyl methacrylate)			converted PMMA[f]			
entry	silyl group	temp (°C)	time (h)	conv[c] (%)	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	28 200	2.42	90	26 700	2.41	63.7/31.6/4.7	124
2[b]	TBDMS	20	72	92	46 100	2.47	140	38 800	2.82	73.5/23.5/3.0	126
3	TBDMS	60	30	93	30 600	2.77	146	23 500	3.13	67.4/29.3/3.3	122
4	TBDMS	80	24	89	17 000	2.39	137	13 600	2.53	63.7/31.7/4.6	118
5	TES	60	30	88	30 900	2.42	74	26 700	2.41	59.5/36.2/4.3	120
6[b]	TIPS	20	580	88	28 000	2.00	115	20 600	2.08	29.1/49.0/21.9	100
7	TIPS	60	80	68	18 000	2.08	87	11 300	2.21	31.4/50.6/18.3	102
8	TIPS	80	14	34	8 300	1.99	91	6 500	1.91	32.5/49.7/17.8	95
9	TBDPS	60	145	80	23 400	2.99	131	16 200	2.37	35.9/49.9/14.2	107
10	TPS	60	30	93	32 800	4.17	161	40 400	2.41	46.6/44.9/8.5	116
11[b]	TTMSS	20	280	93	n.d.[h]	n.d.[h]		50 700	2.96	8.4/9.5/82.1	56
12	TTMSS	40	80	90	n.d.[h]	n.d.[h]		92 000	2.94	4.3/6.2/89.5	58
13	TTMSS	60	56	66	n.d.[h]	n.d.[h]		34 900	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.

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 six glass tubes, and the tubes were sealed by flame under a 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 = 30 600, 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 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 (84.8 mg, 85% yield, M_n = 23 500, 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 trimethylsilyldiazomethane 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 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_3OH mixture (4/1 vol), and then an Et_2O solution of trimethylsilyldiazomethane (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, 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 = 34 900, 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 α-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 = 875−1 950 000; 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 first heated to 180 at 10 °C/min, equilibrated at this temperature for 5 min, and cooled to −50 at 10 °C/min. After being held at this temperature for 5 min, the sample was then

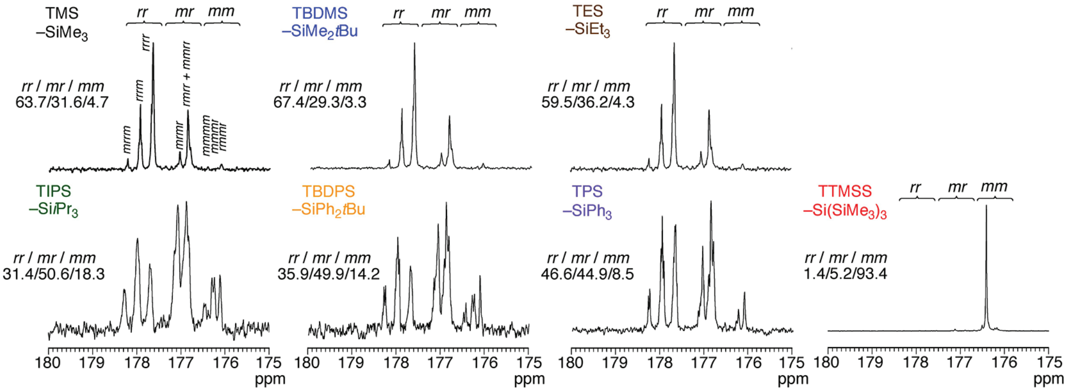


Figure 1. ^{13}C NMR spectra ($CDCl_3$, 55 °C) of poly(MMA)s converted from the poly(silyl methacrylate)s obtained in the free radical polymerization of various silyl methacrylates in toluene at 60 °C: [silyl methacrylate]$_0$ = 1.0 M; [AIBN]$_0$ = 5.0 mM.

reheated to 180 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 at 10 °C/min for mainly removing moisture, equilibrated at this temperature for 5 min, and cooled to −50 at 10 °C/min. After being held at this temperature for 5 min, the sample was then reheated to 300 at 5 °C/min to form the anhydride structure of PMAA and cooled to −50 at 10 °C/min. After being held at this temperature for 5 min, the sample was reheated again to 300 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 were 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 S1 in Supporting Information). 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]

The resulting poly(silyl methacrylate)s were analyzed by ^{1}H NMR spectroscopy (Figure S2 in Supporting Information) 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 trimethylsilyldiazomethane. 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 1 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, where the isotactic index, *mm*, varied from 3.5% 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_3C—) resulted in a nearly atactic polymer (*rr*/*mr*/*mm* = 33/53/14), and triphenylmethyl (R—:Ph_3C—) gave an isotactic-rich (*rr*/*mr*/*mm* = 12/24/64) structure under similar conditions,[10,11b] whereas their silyl versions, i.e., triethylsilyl (Et_3Si—) and triphenylsilyl (Ph_3Si—), 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 2 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

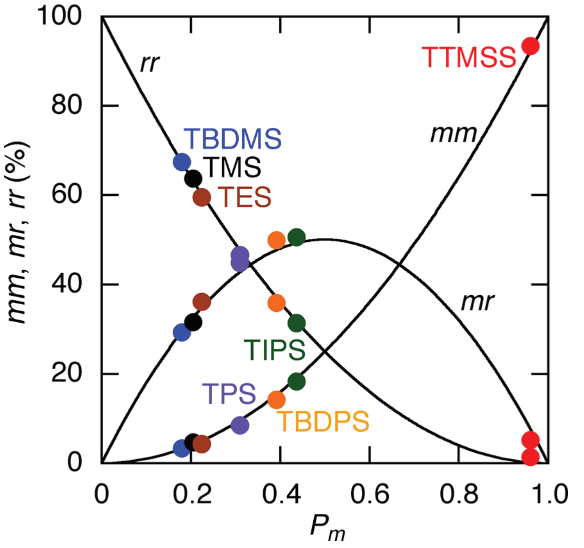


Figure 2. Probabilities or contents of isotactic (*mm*), heterotactic (*mr*), and syndiotactic (*rr*) triads as a function of P_m, the probabilities or contents of the meso diads in the radical polymerization of various silyl methacrylates in toluene at 60 °C. P_m was calculated according to the following equation, $P_m = mm + mr/2$, by using the observed *mm* and *mr* values. The solid lines indicate the theoretical lines for Bernoullian statistics.

figure, and the plots are within the bounds, except for TPS and TTMSS. 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]

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 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 S3 in Supporting Information), 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:

$$\ln(P_i/P_s) = (S_i^\ddagger - S_s^\ddagger)/R - (H_i^\ddagger - H_s^\ddagger)/RT \qquad (1)$$

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.

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 Figures S4 and S5 in Supporting Information). 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)] as reported,[37] although the content of the anhydride forms for each sample was unknown.

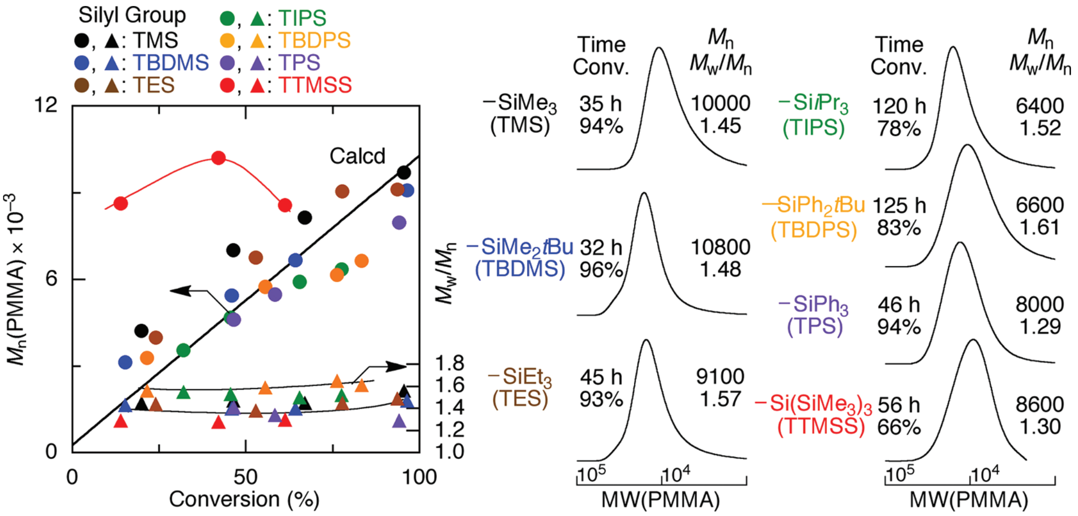


Figure 3. M_n, M_w/M_n, and SEC curves of poly(MMA) obtained from the RAFT polymerization of various silyl methacrylates with CDB/AIBN in toluene at 60 °C followed by the postreactions: [silyl methacrylate]$_0$ = 1.0 M; [CDB]$_0$ = 10 mM; [AIBN]$_0$ = 5.0 mM. The diagonal line indicates the calculated M_n assuming the formation of one polymer chain per CDB molecule.

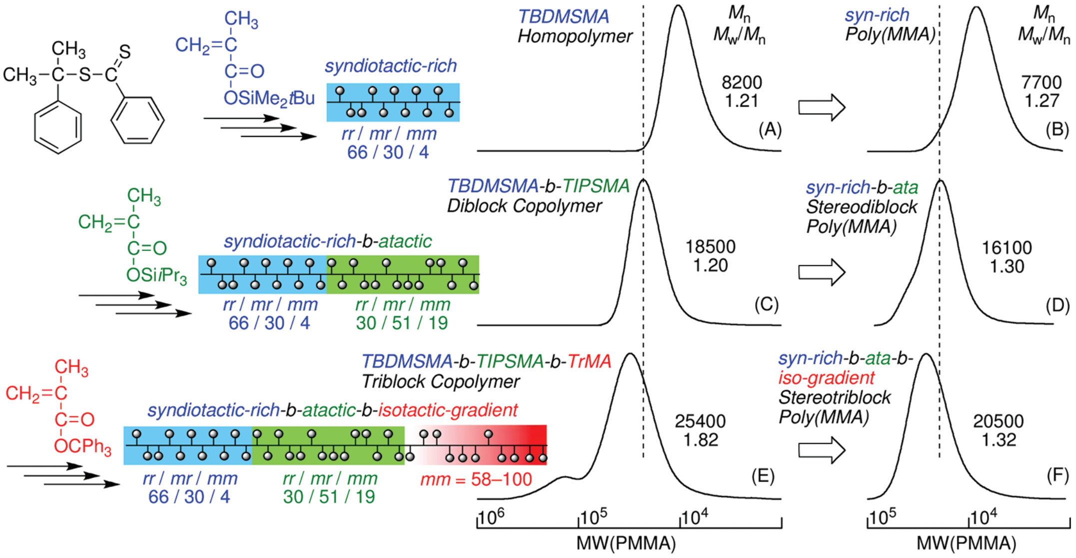


Figure 4. RAFT block copolymerization of TBDMSMA, TIPSMA, and TrMA in toluene at 60 °C for stereoblock polymers. (A) Poly(TBDMSMA) obtained in the RAFT polymerization of TBDMSMA; [TBDMSMA]$_0$ = 3.0 M; [CDB]$_0$ = 30 mM; [AIBN]$_0$ = 5.0 mM. (B) Syndiotactic-rich PMMA converted from (A). (C) Poly(TBDMSMA-*b*-TIPSMA) 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).

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

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. We used CDB as a RAFT agent, which is effective in controlling the radical polymerization of various methacrylates,[29,38−42] including TBDMSMA,[21] in conjunction with AIBN in toluene at 60 °C (Table S1 and Figure S6 in Supporting Information). The RAFT polymerizations occurred smoothly and proceeded at almost the same rate as the free radical polymerizations (Figure S6A). 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 S6B). The RAFT polymerization of TTMSSMA also resulted in insoluble polymers, as was observed during the free radical polymerization.

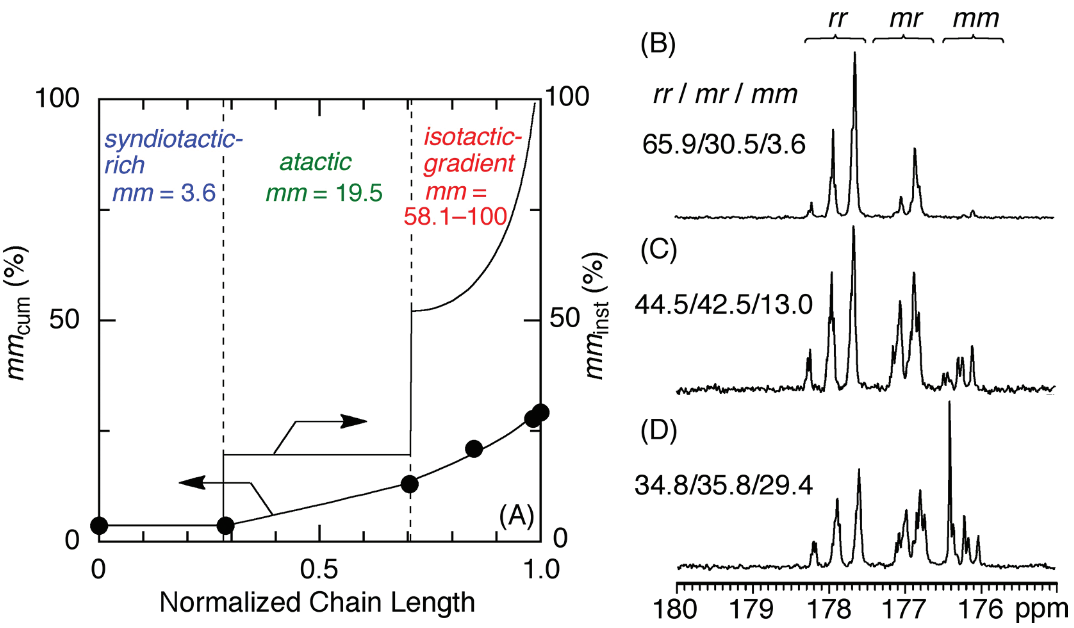


Figure 5. Dependences of cumulative and instantaneous *mm* triad contents on the normalized chain length (A). ^{13}C NMR spectra ($CDCl_3$, 55 °C) of poly(MMA) obtained from poly(TBDSMA) (B), poly(TBDMSMA-*b*-TIPSMA) (C), and poly(TBDMSMA-*b*-TIPSMA-*b*-TrMA) (D).

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 3 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 S1) 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.

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. We 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 4A and Figure S7A in Supporting Information). 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 4C). The SEC curves of the obtained polymers shifted to high molecular weights while retaining narrow MWDs (M_n = 18 500, 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 S7B. 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 (Figure 4B,D) and tacticities (Figure 5B,C). The obtained PMMAs also showed narrow SEC curves, which shifted to high molecular weights (M_n = 7700 → 16 100) while keeping narrow MWDs ($M_w/M_n \sim 1.3$) 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 (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.

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] (Figure 4E), 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 ($M_n = 16\,100 \rightarrow 20\,500$) (Figure 4F). In addition, the tacticity of the whole polymers further changed to $rr/mr/mm$ = 34.8/35.8/29.4 (Figure 5D), 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 conversion (Figure 5A). 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 stereotriblock 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 postreactions.

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.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Polymerization results, ^{1}H NMR spectra, and DSC curves of the obtained polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

ACKNOWLEDGMENT

This work was supported in part by JSPS Research Fellowships for Young Scientists for K.I. (No. 22-8509), a Grant-in-Aid for Young Scientists (S) for M.K. (No. 19675003) by the Japan Society for the Promotion of Science, and the Global COE Program "Elucidation and Design of Materials and Molecular Functions".

REFERENCES

(1) Greene, T. A.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 3rd ed.; Wiley-Interscience: New York, 1999.

(2) Bock, H.; Meuret, J.; Ruppert, K. *Angew. Chem., Int. Ed.* **1993**, *32*, 414–416.

(3) (a) Boxer, M. B.; Albert, B. J.; Yamamoto, H. *Aldrichim. Acta* **2009**, *42*, 1–15. (b) Boxer, M. B.; Yamamoto, H. *Org. Lett.* **2005**, *7*, 3127–3129. (c) Boxer, M. B.; Yamamoto, H. *J. Am. Chem. Soc.* **2006**, *128*, 48–49.

(4) (a) Hirao, A.; Nakahama, S. *Prog. Polym. Sci.* **1992**, *17*, 283–317. (b) Hirao, A.; Loykulnant, S.; Ishizone, T. *Prog. Polym. Sci.* **2002**, *27*, 1399–1471.

(5) Sawamoto, M. *Prog. Polym. Sci.* **1991**, *16*, 111–172.

(6) Webster, O. W. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2855–2860.

(7) (a) Takenaka, K.; Hirao, A.; Nakahama, S. *Makromol. Chem.* **1992**, *193*, 1943–1953. (b) Takenaka, K.; Kawamoto, S.; Miya, M.; Takeshita, H.; Shiomi, T. *Polym. Int.* **2010**, *59*, 891–895.

(8) (a) Okamoto, Y.; Yashima, E. *Prog. Polym. Sci.* **1990**, *15*, 263–298. (b) Okamoto, Y.; Nakano, T. *Chem. Rev.* **1994**, *94*, 349–372.

(9) Satoh, K.; Kamigaito, M. *Chem. Rev.* **2009**, *109*, 5120–5156.

(10) (a) Yuki, H.; Hatada, K.; Kikuchi, Y.; Niinomi, T. *J. Polym. Sci., Part B* **1968**, *6*, 753–761. (b) Yuki, H.; Hatada, K.; Niinomi, T.; Kikuchi, Y. *Polym. J.* **1970**, *1*, 36–45.

(11) (a) Nakano, T.; Mori, M.; Okamoto, Y. *Macromolecules* **1993**, *26*, 867–868. (b) Nakano, T.; Matsuda, A.; Okamoto, Y. *Polym. J.* **1996**, *28*, 556–558.

(12) Kitayama, T.; He, S.; Hironaka, Y.; Iijima, T.; Hatada, K. *Polym. J.* **1995**, *27*, 314–318.

(13) Tsuruta, T.; Furukawa, J. *Bull. Inst. Chem. Res. Kyoto Univ.* **1962**, *40*, 151–170.

(14) Aylward, N. N. *J. Polym. Sci., Part A-1* **1970**, *8*, 319–328.

(15) Chapman, A.; Jenkins, A. D. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 3075–3078.

(16) Durand, P.; Margaillan, A.; Camail, M.; Vernet, J. L. *Polymer* **1994**, *35*, 4392–4396.

(17) Affrossman, S.; Angadji, H.; Bakhshaee, M.; Coffey, K.; Chow, F. L.; Hayward, D.; McLeod, G. D.; Pethrick, R. A.; Whittaker, P. *Polymer* **1989**, *30*, 1022–1026.

(18) (a) Mormann, W.; Ferbitz, J. *Macromol. Chem. Phys.* **2002**, *203*, 2616–2623. (b) Ferbitz, J.; Mormann, W. *Macromol. Chem. Phys.* **2003**, *204*, 577–583.

(19) (a) *Handbook of RAFT Polymerization*; Barner-Kowollik, C., Ed.; Wiley-VCH: Weinheim, Germany, 2008. (b) Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2005**, *58*, 379–410. (c) Moad, G.; Rizzardo, E.; Thang, S. H. *Polymer* **2008**, *49*, 1079–1131. (d) Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2009**, *62*, 1402–1472.

(20) (a) Chiefari, J.; Mayadunne, R. T. A.; Moad, G.; Rizzardo, E.; Thang, S. H. PCT Int. Appl. WO 99/31144. (b) Moad, G.; Chiefari, J.; Chong, Y. K.; Krstina, J.; Mayadunne, R. T. A.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polym. Int.* **2000**, *49*, 993–1001.

(21) (a) Nguyen, M. N.; Bressy, C.; Margaillan, A. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 5680–5689. (b) Nguyen, M. N.; Bressy, C.; Margaillan, A. *Polymer* **2009**, *50*, 3086–3094. (c) Bressy, C.; Nguyen, M. N.; Tanguy, B.; Ngo, V. G.; Margaillan, A. *Polym. Degrad. Stab.* **2010**, *95*, 1260–1268.

(22) Okamoto, Y.; Suzuki, K.; Yuki, H. *J. Polym. Sci., Polym. Chem.* **1980**, *18*, 3043–3051.

(23) Chûjô, R.; Hatada, K.; Kitamaru, R.; Kitayama, T.; Sato, H.; Tanaka, Y. *Polym. J.* **1987**, *19*, 413–424.

(24) Okamoto, Y.; Ishikura, M.; Hatada, K.; Yuki, H. *Polym. J.* **1983**, *15*, 851–853.

(25) Frisch, H. L.; Mallows, C. L.; Heatley, F.; Bovey, F. A. *Macromolecules* **1968**, *1*, 533–537.

(26) Moad, G.; Solomon, D. H.; Spurling, T. H.; Johns, S. R.; Willing, R. I. *Aust. J. Chem.* **1986**, *39*, 43–50.

(27) (a) Bovey, F. A. *J. Polym. Sci.* **1960**, *46*, 59–64. (b) Bovey, F. A.; Tiers, G. V. D. *J. Polym. Sci.* **1960**, *44*, 173–182.

(28) (a) Isobe, Y.; Yamada, K.; Nakano, T.; Okamoto, Y. *Macromolecules* **1999**, *32*, 5979–5981. (b) Isobe, Y.; Yamada, K.; Nakano, T.; Okamoto, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4693–4703.

(29) (a) Ishitake, K.; Satoh, K.; Kamigaito, M.; Okamoto, Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 1991–1995.(b) Ishitake, K.; Satoh, K.; Kamigaito, M.; Okamoto, Y. *Polym. Chem.* DOI: 10.1039/C1PY00401H.

(30) Fordham, J. W. L. *J. Polym. Sci.* **1959**, *39*, 321–334.

(31) Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1968**, *1*, 537–540.

(32) (a) Yuki, H.; Hatada, K. *Adv. Polym. Sci.* **1979**, *31*, 1–45. (b) Kitayama, T.; Masuda, E.; Yamaguchi, M.; Nishiura, T.; Hatada, K. *Polym. J.* **1992**, *24*, 817–827.

(33) Thompson, E. V. *J. Polym. Sci., Part A-2* **1966**, *4*, 199–208.

(34) Allen, P. E. M.; Host, D. M.; Truong, V. T.; Williams, D. R. G. *Eur. Polym. J.* **1985**, *21*, 603–610.

(35) Geuskens, G.; Hellinckx, E.; David, C. *Eur. Polym. J.* **1971**, *7*, 561–568.

(36) Lohmeyer, J. H. G. M.; Tan, Y. Y.; Challa, G. *Polymer* **1978**, *19*, 1171–1175.

(37) Massimo, L.; Kitayama, T.; He, S.; Hatada, K.; Chinatore, O. *Polym. Bull.* **1997**, *39*, 85–91.

(38) (a) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559–5562. (b) Chong, Y. K.; Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1999**, *32*, 2071–2074. (c) Rizzardo, E.; Chiefari, J.; Mayadunne, R. T. A.; Moad, G.; Thang, S. H. *ACS Symp. Ser.* **2000**, *768*, 278–296.

(39) Saricilar, S.; Knott, R.; Barner-Kowollik, C.; Davis, T. P.; Heuts, J. P. A. *Polymer* **2003**, *44*, 5169–5176.

(40) Hotchkiss, J. W.; Lowe, A. B.; Boyes, S. G. *Chem. Mater.* **2007**, *19*, 6–13.

(41) Suzuki, S.; Whittaker, M. R.; Wentrup-Byrne, E.; Monteiro, M. J.; Grondahl, L. *Langmuir* **2008**, *24*, 13075–13083.

(42) He, L.; Read, E. S.; Armes, S. P.; Adams, D. J. *Macromolecules* **2007**, *40*, 4429–4438.

(43) (a) Ray, B.; Isobe, Y.; Matsumoto, K.; Habaue, S.; Okamoto, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2004**, *37*, 1702–1710. (b) Sugiyama, Y.; Satoh, K.; Kamigaito, M.; Okamoto, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 2086–2098. (c) Shibata, T.; Satoh, K.; Kamigaito, M.; Okamoto, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 3609–3615. (d) Tao, Y.; Satoh, K.; Kamigaito, M. *Macromol. Rapid Commun.* **2011**, *32*, 226–232.

(44) Lutz, J.-F.; Neugebauer, D.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2003**, *125*, 6986–6996.

(45) (a) Nuopponedn, M.; Kalliomki, K.; Laukkanen, A.; Hietala, S.; Tenhu, H. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 38–46. (b) Hietala, S.; Nuopponedn, M.; Kalliomki, K.; Tenhu, H. *Macromolecules* **2008**, *41*, 2627–2631. (c) Nuopponedn, M.; Kalliomki, K.; Aseyev, V.; Tenhu, H. *Macromolecules* **2008**, *41*, 4881–4886.

(46) Chong, Y. K.; Moad, G.; Rizzardo, E.; Skidmore, M. A.; Thang, S. H. *Macromolecules* **2007**, *40*, 9262–9271.

(47) Nakano, T.; Okamoto, Y.; Hatada, K. *J. Am. Chem. Soc.* **1992**, *114*, 1318–1329.

(48) (a) Nakano, T.; Okamoto, Y. *Chem. Rev.* **2001**, *101*, 4013–4038. (b) Okamoto, Y.; Nakano, T.; Habaue, S.; Shiohara, K.; Maeda, K. *J. Macromol. Sci., Pure Appl. Chem.* **1997**, *A34*, 1771–1783. (c) Nakano, T.; Okamoto, Y. *Macromol. Rapid Commun.* **2000**, *21*, 603–612. (d) Okamoto, Y.; Nakano, T. *Catalytic Asymmetric Synthesis*, 2nd ed.; Wiley-Interscience: New York, 2000; pp 757−796.