

Helix-Sense-Selective Free Radical Polymerization of 1-Phenyldibenzosuberyl Methacrylate

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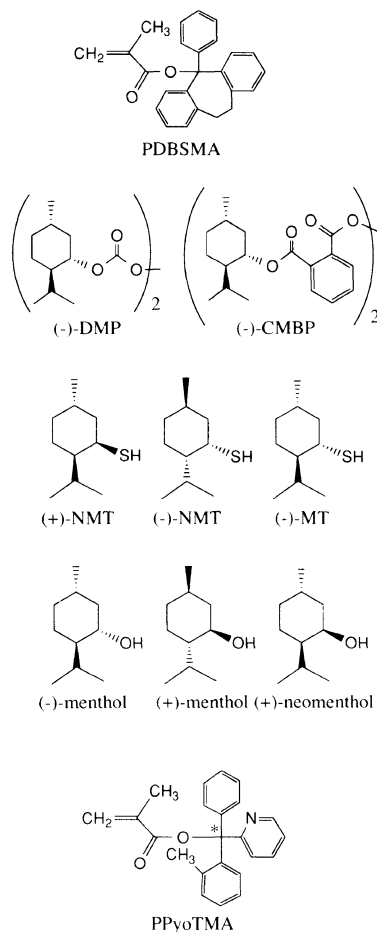
ABSTRACT: The helix-sense-selective free radical polymerization of 1-phenyldibenzosuberyl methacrylate was carried out in toluene at 40 or 50°C under chiral reaction conditions which involve (1) (–)-dimenthyl peroxydicarbonate and (–)-*o*-carbomenthoxybenzoyl peroxide as an initiator, (2) (–)- and (+)-menthol, (+)-neomenthol, and (+)-1-phenyl-1-butanol as a reaction solvent (additive), (3) (+)- and (–)-neomenthanethiol and (–)-menthanethiol as a chain transfer agent, and (4) (–)-phenyl-2-pyridyl-*o*-tolylmethyl methacrylate as a comonomer for copolymerization. Highly isotactic, optically active polymers having a helical conformation with excess right- or left-handed helicity were obtained. In the polymerization using an optically active initiator, helix-sense-selection appeared to take place through primary radical termination. The helix-sense-selection in the polymerization in the presence of the optically active alcohols and thiols was found to involve chain transfer process. In polymerization using thiols, both hydrogen transfer reaction from a thiol to a growing radical and initiation by thio radical were suggested to be responsible for the selectivity. In the case of the copolymerization, the optically active monomeric unit incorporated into the polymer chain was found to induce excessive single handed helicity where the selected helicity reversed depending on the amount of the incorporated optically active monomeric units.

KEY WORDS Free Radical Polymerization / Helix / Optically Active Polymer / Copolymerization / Chain Transfer / Tacticity / 1-Phenyldibenzosuberyl Methacrylate / Phenyl-2-pyridyl-*o*-tolylmethyl Methacrylate /

Highly isotactic, optically active polymers having a one-handed helical conformation are obtained by asymmetric (helix-sense-selective) polymerization of bulky methacrylates¹ including triphenylmethyl methacrylate² (TrMA) and its analogues. Some helical polymethacrylates are important because they exhibit excellent chiral recognition ability toward racemates when used as a chiral packing material for high-performance liquid chromatography (HPLC).^{3,4} One-handed helical polymers have been synthesized also from other types of achiral monomers including acrylates,⁵ acrylamides,⁶ chloral,⁷ isocyanides,^{8,9} and isocyanates.¹⁰ However, helix-sense-selective polymerization is possible only by anionic and transition metal-mediated mechanisms so far and therefore, monomers suitable for this type of polymerization have been limited to those having no functional groups which would inhibit polymerization reaction.

Here we present full details of the helix-sense-selective polymerization of 1-phenyldibenzosuberyl methacrylate¹¹ (PDBSMA) through free radical mechanism; this is the first example of the synthesis of an optically active, helical polymer having an excessive single-handed helicity from a achiral monomer by radical polymerization and preliminary results have been briefly reported.¹² PDBSMA was designed after TrMA¹³ and we recently found that this monomer gives a highly isotactic polymer (*mm* > 99%) by conventional free radical polymerization.¹⁴ Since PDBSMA gives an almost perfectly isotactic, one-handed helical polymer under anionic polymerization conditions similar to those for poly(TrMA) synthesis,^{12a,14} the poly(PDBSMA) prepared by radical polymerization should be an equimolar mixture of right- and left-handed helices. On the basis of this stereochemistry of PDBSMA polymerization, we have investigated the synthesis of single-handed helical poly(PDBSMA) by radical polymerization under chiral con-

ditions.¹² Chiral reaction conditions were introduced by the use of (1) (–)-dimenthyl peroxydicarbonate ((–)-DMP) and (–)-*o*-carbomenthoxybenzoyl peroxide ((–)-CMBP) as an initiator, (2) (+)- and (–)-neomenth-



anethiol (NMT) and (–)-menthanethiol ((–)-MT) as a chain transfer agent, (3) (–)- and (+)-menthol, (+)-neomenthol, and (+)-1-phenyl-1-butanol as a reaction solvent (additive), and (4) (–)-phenyl-2-pyridyl-*o*-tolyl-methyl methacrylate (PPyoTMA) as a comonomer for copolymerization.

EXPERIMENTAL

Materials

Toluene was purified by the usual method, dried by being mixed with *n*-BuLi, and distilled under high vacuum immediately before use. Diisopropyl peroxydicarbonate ((iso-PrOCOO)₂) was kindly provided by NOF Co. (*Taketoyo-cho, Chita-gun, Aichi 470-23, Japan*) and used as a toluene solution (0.309 M). The synthesis of PDBSMA has been reported elsewhere.^{12a,13} PPyoTMA was available from our recent work.^{15,16} (+)-Menthol (Janssen Chimica), (–)-menthol (Kishida), (+)-neomenthol (Aldrich), (+)-1-phenyl-1-butanol (Aldrich), and thiophenol (TCI) were used as obtained.

(–)-Dimenthyl Peroxydicarbonate ((–)-DMP)

Sodium peroxide (1.41 g, 18.1 mmol) was dissolved in 11 ml of ice water in a 200-ml flask equipped with a dropping funnel. (–)-Menthyl chloroformate (Aldrich) (1.97 g, 9.01 mmol) dissolved in 2.8 ml of benzene was added dropwise with stirring at 0°C. Reaction was continued for 7 h at 0°C and for 11 h at ambient temperature (*ca.* 25°C). The product was extracted by two portions of 10 ml of ether and the ethereal solution was washed with water. The organic layer was dried on Na₂SO₄ and then the solvent was removed to give an oily product. Yield 1.49 g (40%). IR (NaCl plate) 1798 cm⁻¹ (C=O). [α]₃₆₅²⁵ –240°; [α]_D²⁵ –79° (CHCl₃, conc. 1.0). ¹H NMR (CDCl₃) δ 4.67 (m, 1H, 1-H of menthyl moiety (–CH–O–)), d 2.15 (m, 1H, methine of isopropyl), 1.95 (m, 1H, 6-H of menthyl moiety), 1.70 (m, 2H, 3-H and 4-H of menthyl moiety), 1.50 (m, 2H, 2-H and 5-H of menthyl moiety), 0.75–1.15 (m, 3H, 3-H, 4-H, and 6-H of menthyl moiety), 0.95 (d, 3H, methyl of isopropyl), 0.92 (d, 3H, methyl of isopropyl), 0.82 (d, 3H, 5-methyl of menthyl moiety). (–)-DMP was used as a toluene solution (0.171 M) for polymerization.

(–)-*o*-Carbomethoxybenzoyl Peroxide¹⁷ ((–)-CMBP)

Phthalic anhydride (1.0 g, 6.8 mmol) and (–)-menthol (1.2 g, 7.7 mmol) were reacted at 120°C for 17 h in a 25-ml flask equipped with a condenser. The reaction mixture was added to 20% aq Na₂CO₃ (50 ml); the unreacted menthol and the diester of phthalic acid were removed by extraction with three portions of 30 ml of ether. The aqueous layer was acidified (pH 3) by adding 2 N aq HCl and then extracted by 90 ml of CHCl₃. Removal of CHCl₃ gave a crystalline product which was recrystallized from a mixture of acetic acid (19 ml) and H₂O (11 ml) to give phthalic acid monomethyl ester. Yield 1.1 g (54%). mp 111–113°C. IR (KBr) 1725 cm⁻¹ (C=O of ester), 1690 cm⁻¹ (C=O of acid).

Acid chloride was prepared by the reaction of the monoester (2.3 g, 7.6 mmol) with thionyl chloride (2.5 ml) in the presence of a small amount of pyridine followed by removal of thionyl chloride in excess. A benzene

(2.5 ml) solution of the crude acid chloride was added dropwise to a water solution of sodium peroxide (1.3 g, 16.6 mmol) at 0°C in a 25-ml flask and the reaction mixture was stirred for 5 h. The product was extracted with ether (50 ml) and the ethereal layer was dried on Na₂SO₄. An oily product was obtained upon removal of solvent. Yield 0.43 g (0.64 mmol). [α]₃₆₅²⁵ –310°; [α]_D²⁵ –81° (dioxane, conc. 1.0) (lit.¹⁷ [α]_D²⁵ –91°). ¹H NMR (CDCl₃) δ 7.60–8.05 (m, 4H, aromatic) 4.95 (m, 1H, 1-H of menthyl moiety (–CH–O–)), δ 2.15 (m, 1H, methine of isopropyl), 1.95 (m, 1H, 6-H of menthyl moiety), 1.70 (m, 2H, 3-H and 4-H of menthyl moiety), 1.53 (m, 2H, 2-H and 5-H of menthyl moiety), 0.85–1.10 (m, 3H, 3-H, 4-H, and 6-H of menthyl moiety), 0.93 (d, 3H, methyl of isopropyl), 0.90 (d, 3H, methyl of isopropyl), 0.79 (d, 3H, 5-methyl of menthyl moiety). (–)-CMBP was used as a toluene solution (0.181 M) for polymerization.

(+)-Neomenthanethiol¹⁸ ((+)-NMT)

In a 50-ml flask, (–)-menthol (3.12 g, 20.0 mmol) was dissolved in 30 ml of dry pyridine. *p*-Toluenesulfonyl chloride (7.22 g, 40.5 mmol) was added to the solution. The reaction mixture was stirred at 0°C for 5 h, poured into 50 ml of ice water, and white precipitates appeared. The precipitates were collected by filtration and dried under high vacuum. Yield 5.19 g (83.7%).

(–)-Menthyl *p*-toluenesulfonyl (5.19 g, 16.7 mmol) obtained above was added to a dimethyl sulfoxide (15 ml) solution of potassium thioacetate in a 50-ml flask. The reaction was performed at 45°C for 24 h with stirring. The reaction mixture was extracted by water/CHCl₃. Removal of solvent from the organic layer gave a dark liquid which was distilled to give (+)-neomenthyl thioacetate (bp 73–75°C/0.3 mmHg) Yield 2.75 g (76.6%).

In a 50-ml flask equipped with a condenser and dropping funnel, LiAlH₄ (0.60 g, 158 mmol) was suspended in dry ether (20 ml) under Ar atmosphere. (+)-Neomenthyl thioacetate (2.75 g, 12.8 mmol) dissolved in dry ether (7 ml) was added to the suspension dropwise from the funnel and the mixture was refluxed for 2 h. The reaction was quenched by adding a small amount of water and then 10% aq H₂SO₄ was added until the white gel which appeared on quenching the reaction was completely dissolved. The product was extracted with ether. Yield 0.89 g (40%, total yield 26%). [α]₃₆₅²⁵ +142°; [α]_D²⁵ +47.8° (CHCl₃, conc. 1.52) (lit.¹⁸ [α]_D²⁵ +53.9°). ¹H NMR (CDCl₃) δ 3.48 (m, 1H, 1-H of menthyl moiety (–CH–SH)), d 1.25–1.88 (m, 6H, methine of isopropyl, 2-H, 3-H, 4-H, 5-H, 6-H of menthyl moiety), 1.22 (d, 1H, –SH), 0.80–1.16 (m, 3H, 3-H, 4-H, and 6-H of menthyl moiety), 0.92 (d, 3H, methyl of isopropyl), 0.90 (d, 3H, methyl of isopropyl), 0.80 (d, 3H, 5-methyl of menthyl moiety). (+)-NMT was used as a toluene solution (0.423 M) for polymerization.

In the original report¹⁸ on (+)-NMT synthesis, the products were found to be a mixture of (+)-NMT and (–)-MT, a diastereomer of (+)-NMT, at a ratio of 95/5 by ³¹P NMR analysis of a phosphorous-containing derivative of the product. However, we determined the content of (–)-MT in our products to be less than 1% by direct ¹H NMR analysis where the peaks areas of –CH₃ doublet signals at 0.8 ppm and 0.75 ppm for

(+)-NMT and (-)-MT, respectively, were compared.

(-)-Neomenthanethiol ((-)-NMT)

(-)-NMT was obtained from (+)-menthol (7.28 g, 46.6 mmol) in the same manner as for (+)-NMT synthesis. Yield 2.84 g (16.5 mmol). $[\alpha]_{365}^{25} - 141^\circ$; $[\alpha]_{\text{D}}^{25} - 46.4^\circ$ (CHCl_3 , conc. 1.65). (-)-NMT was used as a toluene solution (0.508 M) for polymerization.

(-)-Menthanethiol ((-)-MT)

(-)-MT was obtained from (+)-neomenthol (10.4 g, 66.5 mmol) in the same manner as for (-)-NMT synthesis. $[\alpha]_{365}^{25} - 88^\circ$; $[\alpha]_{\text{D}}^{25} - 33^\circ$ (CHCl_3 , conc. 0.78). $^1\text{H NMR}$ (CDCl_3) δ 3.50 (m, 1H, 1-H of menthyl moiety (-CH-SH) 0.75–2.7 (m, 9H, methine of isopropyl, 2-H, 3-H, 4-H, 5-H, 6-H of menthyl moiety), 1.30 (d, 1H, -SH), 0.92 (d, 3H, methyl of isopropyl), 0.85 (d, 3H, methyl of isopropyl), 0.75 (d, 3H, 5-methyl of menthyl moiety). (-)-MT was used as a toluene solution (0.051 M) for polymerization.

Polymerization

Polymerization was carried out in a glass ampoule sealed with a three-way stopcock under dry N_2 atmosphere. Liquid materials were transferred to the ampoule using a syringe and the solid monomers using a funnel having a N_2 gas inlet tube. The reaction mixture was precipitated in hexane to remove unreacted monomer. The polymeric products was collected with a centrifuge and fractionated into tetrahydrofuran (THF)-insoluble, THF-soluble and benzene-hexane (1:1, v/v) (B/H)-insoluble, and B/H-soluble parts. The molecular weight of the fractions decreased in this order. B/H-soluble part of polymerization products of a bulky methacrylate is generally oligomers whose main chain is too short to take a stable helical conformation.^{2b,13} The second fraction is termed simply "the B/H-insoluble part" in the followings. Stereochemical analysis was performed mainly for this fraction having degree of polymerization (*DP*) of 40–50.

Poly(PDBSMA) was converted to poly(MMA) by methanolysis in the presence of a small amount of HCl followed by methylation using CH_2N_2 . The procedure was the same as reported for poly(TrMA).^{2b}

DP of the products was determined by GPC analysis of poly(MMA) derived from the original polymer using polystyrene standard samples.

Compositions of the two monomeric units in copolymer of PDBSMA and PPyOTMA were determined by $^1\text{H NMR}$ analysis of methanolysis product of the copolymer. The copolymer was decomposed by methanolysis in HCl-methanol and the resulting methanol solution was neutralized by adding a methanol solution of NaOH. The solvent was then removed and the residue was extracted with CHCl_3 . The CHCl_3 -soluble part containing methyl 1-phenyldibenzosuberil and methyl phenyl-2-pyridyl-*o*-tolylmethyl ethers was subjected to the NMR analysis.

Measurement

Optical activity measurement was performed using a JASCO DIP-181 polarimeter. Circular dichroism (CD) spectra were taken on a JASCO J-720L spectropolar-

imeter. Absorption spectra were obtained with a JASCO Ubest 55 spectrometer. IR spectra were measured using a JASCO FT/IR-7000 spectrometer. NMR spectra were taken with a Varian VXR-500 (500 MHz). HPLC resolution of poly(PDBSMA) was carried out using a JASCO PU-980 chromatographic pump, a 181C polarimeter (α_{Hg}) equipped with a flow cell (50 mm), and a 875-UV detector (254 nm, cell length 1 mm). GPC analysis of poly(PDBSMA) was performed using TSK-G3000H8 and Shodex KF-80M columns connected in series attached to a JASCO 880-PU chromatographic pump with a 875-UV UV detector (254 nm, cell length 5 mm) and DIP-182 polarimetric detector ($\alpha_{780\text{nm}}$, cell length 50 mm). GPC analysis of poly(MMA) was conducted using TSK-G4000H8 and Shodex AC802.5 columns connected in series attached to a JASCO PU-980 chromatographic pump with a 830-RI refractive index detector.

RESULTS AND DISCUSSION

Structure of Highly Isotactic Poly(PDBSMA) Prepared by Free Radical Polymerization under Achiral Conditions

PDBSMA gives a highly isotactic polymer by radical polymerization as reported recently. The isotactic specificity has been ascribed to the helical structure of the growing radical.¹⁴ The helical structure of poly(PDBSMA) synthesized under achiral conditions was evident in this study by HPLC analysis of the polymer using a chiral stationary phase consisting of optically active poly(TrMA). The chiral stationary phase is known to resolve right- and left-handed helices of highly isotactic poly(TrMA).¹⁹ Figure 1 shows the chromatograms of HPLC separation of poly(PDBSMA) (*DP* = 50) prepared using (iso-PrOCOO)₂ in toluene at 40°C using the (+)-poly(TrMA) stationary phase chemically bonded to silica gel.^{19b} A clear separation into (+)- and (-)-fractions can be seen from the chromatogram of polarimetric detector, strongly suggesting that the sample polymer is an equimolar amount mixture of right- and left-handed helices, *i.e.*, a racemic mixture of helices. This implies that one-handed helical poly(PDBSMA) is obtainable if chiral factors are introduced in the reaction

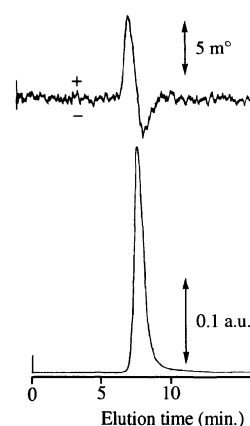


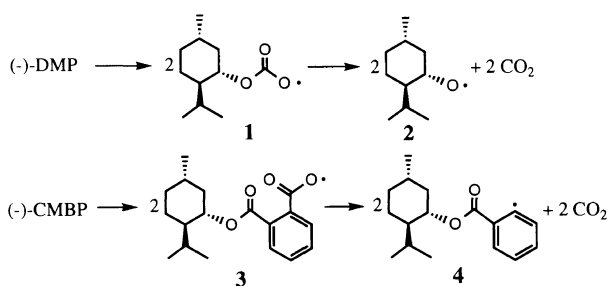
Figure 1. HPLC resolution of highly isotactic poly(PDBSMA) prepared by free radical polymerization under achiral conditions. The top chromatogram was obtained by polarimetric detection (α_{365}) and the bottom one by UV detection (254 nm). HPLC conditions: column (+)-poly(TrMA)-bonded silica gel (25 \times 0.46 (i.d.) cm); eluent, THF; flow rate, 0.5 ml min^{-1} ; temp, 5°C.

conditions.

It is notable that the elution order of the (+)- and (-)-fractions are opposite to that in the resolution of poly(TrMA) using the same chiral HPLC column; (+)-poly(TrMA) is more strongly adsorbed onto the (+)-poly(TrMA) stationary phase.¹⁹ This suggests that the mechanism of chiral adsorption of (+)- and (-)-poly(PDBSMA) onto the one-handed helical poly(TrMA) on the stationary phase is different from that in the resolution of poly(TrMA).

Polymerization Using Optically Active Radical Initiators

To achieve chiral induction in the radical polymerization of PDBSMA, polymerization was carried out using optically active (-)-DMP and (-)-CMBP which were prepared from (-)-menthol. In this experiment, we expected that one of the right- and left-handed helices is predominantly formed through initiation by **1** or **2** derived from (-)-DMP and by **3** or **4** derived from (-)-CMBP (Scheme 1) or in the following early stages of polymerization. Table I shows the conditions and results of the polymerization. The polymers obtained with (-)-DMP and (-)-CMBP had highly isotactic configuration as well as those obtained by the polymerization with (iso-PrOCOO)₂.¹⁴ When (-)-DMP was used as the initiator, the B/H-insoluble polymer obtained at [monomer]/[initiator]=50 did not show significant optical activity (run 1). However, the B/H-insoluble polymer obtained at [monomer]/[initiator]=1 showed dextrorotation (run 2) in spite of the higher reaction temperature for this run. The optically active polymer showed CD absorption whose spectral pattern was similar to that of one-handed helical, dextrorotatory poly(PDBSMA) obtained by asymmetric anionic polymerization,^{12a,13} indicating that the dextro-



Scheme 1. Generation of optically active radicals from (-)-DMP and from (-)-CMBP.

rotation of the polymer of run 2 is based on the helical structure of the main chain with single-handed helicity in excess (Figure 2). Production of the optically inactive polymer at the higher [monomer]/[initiator] ratio suggests that the helix-sense-selection took place more effectively through reactions of a growing radical with the initiator or its primary radical (primary radical termination) than through the initiation reaction or following stages of polymerization; that is, one of the right- and left-handed helical growing radicals reacts predominantly. This conclusion is supported by GPC analysis of the B/H-insoluble polymer of run 2 (Figure 3). As shown in the figure, the dextrorotatory polymer of run 2 consists of (+)-fraction with higher molecular weight and (-)-fraction with lower molecular weight, possibly due to unequal rates of primary radical termination of (+)- and (-)-helical growing radicals having opposite sense of helicity.

Polymerization with (-)-CMBP gave a dextrorotatory

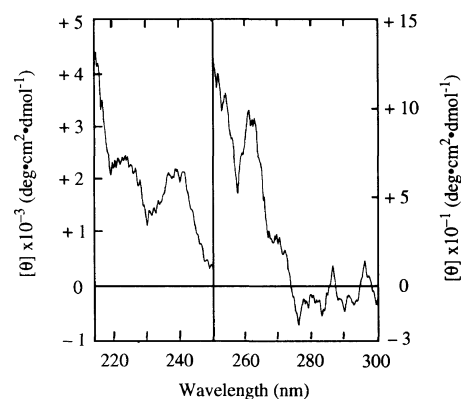


Figure 2. CD spectrum of poly(PDBSMA) of run 2 in Table I [THF, ambient temperature].

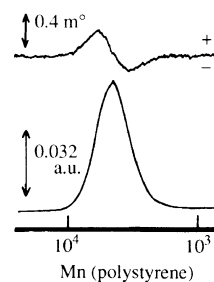


Figure 3. GPC curves of the B/H-insoluble poly(PDBSMA) of run 2 in Table I. The top chromatogram was obtained by polarimetric detection ($\alpha_{780\text{nm}}$) and the bottom by UV detection (254 nm).

Table I. Polymerization using optically active initiators^a

Run	Initiator	[M]/[I] ^c %	Yield ^d %	THF-sol. part				
				THF-insol. part		B/H ^b -sol. part		
				Yield %	Yield %	Yield %	Yield %	
1	(-)-DMP	50	75	69	1	~0°	40	5
2	(-)-DMP	1	48	30	3	+40°	44	15
3	(-)-CMBP	1	59	41	12	+20°	40	6

^a Conditions: monomer, 0.3 g (run 1), 0.5 g (run 2), 0.2 g (run 3); toluene, 5 ml (run 1), 8 ml (run 2), 3.5 ml (run 3); temp, 40°C (run 1), 50°C (runs 2 and 3); time 24 h. ^b A mixture of benzene and hexane (1:1). ^c Ratio of monomer to initiator in the feed. ^d Hexane-insoluble products. ^e Measured in THF. ^f Determined by GPC of poly(MMA) derived from the original polymer using polystyrene standard samples.

polymer; however, the CD spectral pattern of the polymer was different from that of the polymer obtained using (–)-DMP and was rather similar to that of (–)-CMBP (Figure 4). This suggests that the CD absorption of this polymer is based mainly on the chiral group attached to the chain terminals originating from the initiator. Excess one-handed helicity may not be induced in this case.

Polymerization Using Chiral Chain Transfer Agents

Polymerization in the presence of a chiral thiol may be helix-sense-selective through elemental reactions of the chain transfer process illustrated in Scheme 2, which are hydrogen transfer from a thiol to a helical radical (A), initiation of polymerization by the thio radical formed in (A) (B), and termination by the thio radical

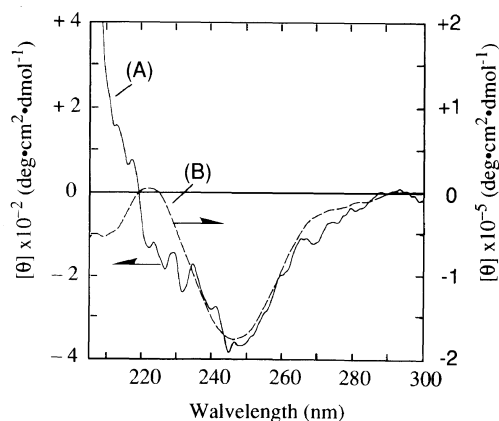
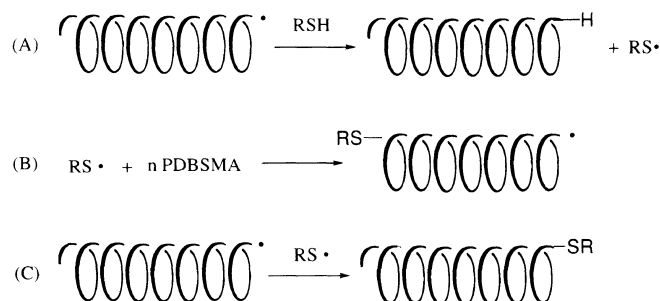


Figure 4. CD spectra of poly(PDBSMA) of run 3 in Table I (A) and (–)-CMBP (B) [THF, ambient temperature].



Scheme 2. Reactions involved in chain transfer process mediated by a thiol.

(C). In reactions (A) and (C), the reaction rates may be different for right- and left-handed helical radicals and in reaction (C), the initiation and following early stages of polymerization may lead to excess single-handed helicity of the main chain.

We employed (+)- and (–)-NMT and (–)-MT as chiral transfer agents; both NMT and MT were effective in obtaining optically active, highly isotactic polymers (Table II). The CD spectrum of the B/H-insoluble, levorotatory polymer of run 3 had a symmetrical pattern to that of the one-handed helical (+)-polymer obtained by anionic polymerization,^{12a,13} suggesting that the chiroptical properties of this polymer are due to a helical conformation (Figure 5 (A)). Polymerizations using (+)-NMT gave levorotatory polymers (runs 1–4) and that using (–)-NMT gave a dextrorotatory polymer (run 5); this confirms that helix-sense-selection took place on the basis of the chirality of NMT. Also, (–)-MT, a diastereomer of NMT, led to a dextrorotatory polymer.

GPC curves of the B/H-insoluble polymer obtained in run 3 are shown in Figure 6 (A). The levorotatory polymer consists of (–)-fraction with higher molecular weight and (+)-fraction with lower molecular weight. The (+)- and (–)-fractions were collected by GPC separation. The CD spectral pattern of the (+)-fraction was symmetrical to that of the (–)-fraction (Figure 5 (B) and (C)), meaning that the specific rotation in opposite sign is based on opposite excess helicity of the main chain. These results indicate that chiral induction

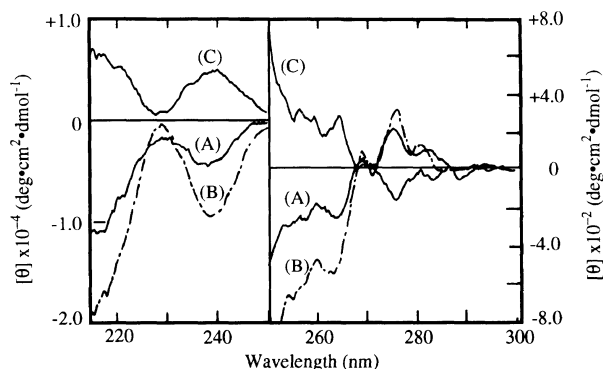


Figure 5. CD spectra of the poly(PDBSMA) of run 3 in Table II. B/H-insoluble part (A), (–)-fraction separated from A (B), and (+)-fraction separated from A (C) [THF, ambient temperature].

Table II. Polymerization using (iso-PrOCOO)₂ in the presence of optically active thiols^a

Run	Thiol	[Thiol]/[Monomer]	Yield ^c %	THF-insol. part		THF-sol. part			
				Yield %	DP ^d	B/H ^b -insol. part		B/H ^b -sol. part	
						Yield %	[α] ₃₆₅ ^e	DP ^d	Yield %
1	(+)-NMT	0.05	82	73	120	2	–80°	42	7
2	(+)-NMT	0.1	80	70	110	3	–130°	41	7
3	(+)-NMT	0.2	71	54	84	5	–140°	42	12
4	(+)-NMT	0.4	18	~0		11	–140°	40	7
5	(–)-NMT	0.4	19	~0		10	+110°	51	9
6	(–)-MT	0.05	86	82	150	2	+60°	50	2

^a Conditions: monomer, 0.5 g; toluene, 8 ml; [monomer]/[(iso-PrOCOO)₂] = 50; temp, 40°C; time, 24 h. ^b A mixture of benzene and hexane (1:1). ^c Hexane-insoluble products. ^d Determined by GPC of poly(MMA) derived from the original polymer using polystyrene standard samples. ^e Measured in THF.

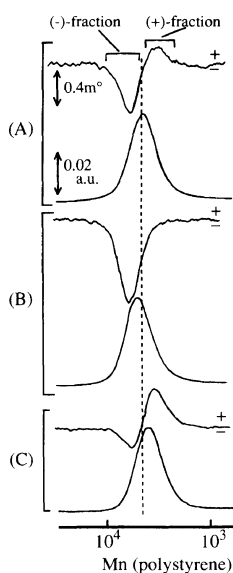


Figure 6. GPC curves of the poly(PDBSMA) of run 3 in Table II: The curves (A)—(C) correspond to the CD analysis samples (A)—(C) in Figure 5. The top chromatogram of each of (A)—(C) was obtained by polarimetric detection ($\alpha_{780\text{nm}}$) and the bottom of each by UV detection (254 nm).

at least in part took place in the termination process (reactions (A) and (C) in Scheme 2). The helical radical leading to the (+)-polymer more readily reacts with the thiol than its counterpart. The specific rotation of the (–)-fraction was estimated to be $[\alpha]_{365} - 750^\circ$ from the GPC curves shown as Figure 6 (B) using a one-handed helical (+)-poly(PDBSMA) ($[\alpha]_{365} + 1788^\circ$) as the standard sample. The value of levorotation corresponds to an enantiometric excess (e.e.) of ca. 40%, i.e., a mixture of (+)- and (–)-helices in a ratio of 3 to 7.

For a deeper insight into the polymerization mechanism and stereochemistry, ^1H NMR analysis was performed for PMMAs derived from the polymerization products of run 3 (Figures 7 and 8). Highly isotactic configuration was evident from the spectra and in addition, the polymers appeared to bear neomenthyl moiety originating from (+)-NMT. The ratios of the peak area of $\alpha\text{-CH}_3$ signals (1.1–1.3 ppm) to that of the $\omega\text{-end-CH}_3$ signals, which are doublet because of the coupling with the $\omega\text{-end}$ methine proton, were 85/1 and 40/1, respectively, for the THF-insoluble polymer (Figure 7(A)) and B/H-insoluble polymer (Figure 8). These values well correspond to the DP of the polymers determined by GPC, indicating that the polymers have one hydrogen at the $\omega\text{-end}$. The number of neomenthyl groups per chain was determined to be ca. 1 and 0.2 for the THF-insoluble and B/H-insoluble parts, respectively, by comparing the peak area of the $\omega\text{-end-CH}_3$ signals with that of the peaks around 0.9 ppm which should be due to three methyl groups of the neomenthyl moiety. These results suggest that the structure of the THF-insoluble polymer corresponds to **I** and that of the B/H-insoluble polymer to a mixture of **I** and **II** existing in a ratio of 2/8. The isopropoxy group of **II** originates from the initiator ((*iso*-PrOCOO) $_2$). The structure of the B/H-insoluble polymer having a hydrogen at the $\omega\text{-end}$ suggests that the helix-sense-selection took place mainly through hydrogen transfer when this fraction is produced (Scheme 2 (A)).

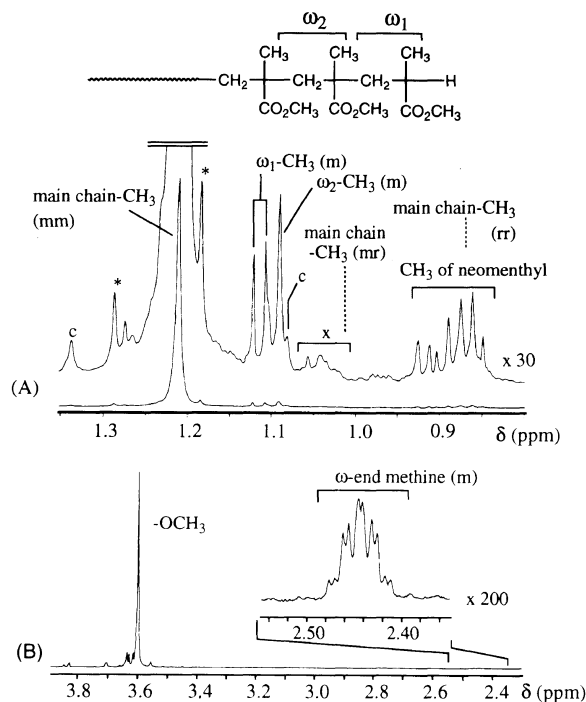


Figure 7. ^1H NMR spectra of poly(MMA) derived from the THF-insoluble poly(PDBSMA) of run 3 in Table II: α -methyl (A) and methoxy and $\omega\text{-end}$ methine (B) regions [500 MHz, CDCl_3 , 60°C]. c, *, and x denote ^{13}C satellite bands, peaks probably due to the $\alpha\text{-CH}_3$ groups in the vicinity of chain terminals, and impurity peaks, respectively.

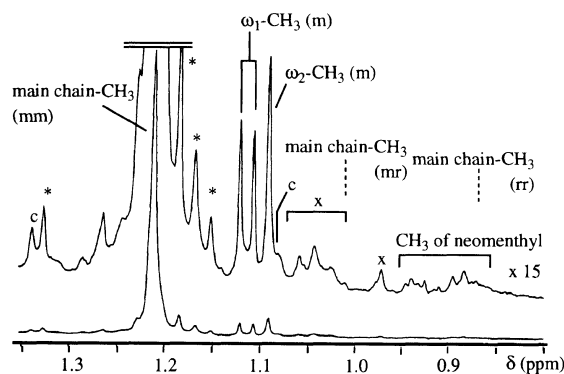
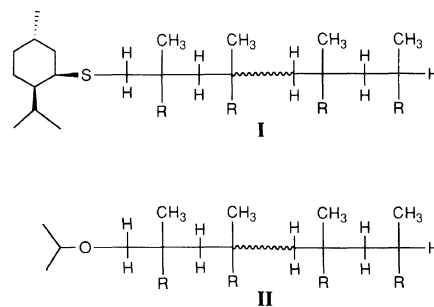


Figure 8. ^1H NMR spectra of poly(MMA) derived from the B/H-insoluble poly(PDBSMA) of run 3 in Table II [500 MHz, CDCl_3 , 60°C]. c, *, and x denote ^{13}C satellite bands, peaks probably due to the $\alpha\text{-CH}_3$ groups in the vicinity of chain terminals, and impurity peaks, respectively.



Structures **I** and **II** rule out the possibility of termination through recombination which would not be plausible because of the steric bulkiness of the growing radical. Hydrogen transfer from $\alpha\text{-CH}_3$ group to the radical which is known for the MMA polymerization²⁰

Table III. Polymerization using (iso-PrOCOO)₂ in mixtures of toluene and optically active alcohols^a

Run	Alcohol (amount, g)	Toluene ml	Monomer g	Temp. C	Yield ^c %	THF-sol. part					
						THF-insol. part		B/H ^b -insol. part			B/H ^b -sol. part
						Yield		Yield	[α] ₃₆₅ ^d	DP	Yield
						%		%	%		%
1	(+)-Menthol (4)	1.5	0.1	50	43	41	1	-200°	50 ^e	0.3	
2	(-)-Menthol (4)	1.5	0.1	50	45	43	1	+180°	50 ^e	0.4	
3	(-)-Menthol (20)	7.5	0.5	40	88	87	0.2	+80°	50 ^f	0.5	
4	(+)-Neomenthol (8)	4	0.2	40	71	69	2	+90°	50 ^f	~0	
5	(+)-1-Phenyl- 1-butanol (4.4)	4	0.5	50	57	49	0.2	~0°	50 ^f	8	
6 ^g	(-)-Menthol (3.4)	4	0.5	50	49	43	0.5	~0°	40 ^h	5	

^a Conditions: [monomer]/[initiator]=30 (runs 1–4), 20 (runs 5 and 6). ^b A mixture of benzene and hexane (1:1). ^c Hexane-insoluble products. ^d Measured in THF. ^e Determined by GPC of poly(MMA) derived from the original polymer using polystyrene standard samples. ^f Estimated from the peak-top molecular weight of GPC curves of the original polymer. The peak-top molecular weights of these polymers were the same as that on the GPC curve of the poly(PDBSMA) of run 2. ^g Polymerization in the presence of thiophenol at [monomer]/[thiophenol]=15.

seems not to take place because no clear vinylidene signals were seen in the ¹H NMR spectra of PMMAs derived from the three fractions of the products.

From the NMR spectra shown in Figures 7 and 8, not only the propagation but also the termination reaction (hydrogen transfer to the growing radical) were almost perfectly isotactic specific. ω-End-CH₃ doublet signals due to meso and racemo ω-end dyad structures are distinguishable by ¹H NMR analysis.^{2b} In Figures 7(A) and 8, no clear peaks of ω-end-CH₃ group based on racemo dyad are seen. The exclusive ω-end meso configuration is further evident by the ω-end methine signals (Figure 7(B)). The ω-end methine proton shows different chemical shifts depending on the dyad tacticity at the ω-end.^{21,22} These results are surprising because even in the asymmetric anionic polymerization of TrMA in toluene at -78°C using fluorenyllithium(-)-sparteine, the stereoselectivity of the termination (protonation of the anion) is *m/r*=8/2.^{2b} The unusually high selectivity of the radical reaction may be ascribable to the steric crowdedness around the growing end of the rigid, helical polymer chain. The stereoselectivity of the hydrogen transfer observed in this study is comparable to the highest values reported for similar types of radical reactions involving low-molecular-weight substrates.²³

Polymerization Using Optically Active Solvents

Polymerization in an optically active medium may be helix-sense-selective because the propagation rates of right- and left-handed helical radicals might be different due to the existence of a chiral substance. Chain transfer involving the chiral medium, if any, may also be responsible for the helix-sense-selection as shown in the preceding section.

Polymerization with (iso-PrOCOO)₂ in a mixture of toluene and optically active alcohols gave highly isotactic, optically active polymers whose specific rotations depended on the structure of the alcohol and reaction conditions (Table III). The polymers obtained using (+)- and (-)-menthol under the same reaction conditions showed specific rotations of similar magnitude and in opposite sign (runs 1 and 2). The CD spectral pattern of the polymer obtained with (+)-menthol was

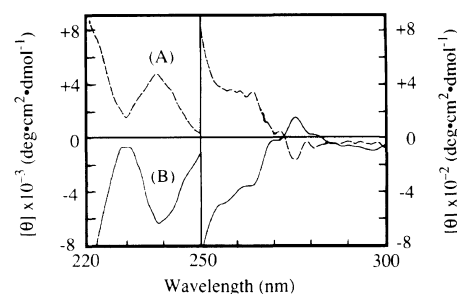


Figure 9. CD spectra of poly(PDBSMA) of run 1 in Table III (A) and that of run 2 in Table III (B) [THF, ambient temperature]. The spectral data are cited from ref 12a.

nearly symmetrical to that of the polymer obtained with (-)-menthol (Figure 9) and it was similar to that of the one-handed helical polymer obtained by asymmetric anionic polymerization. These results indicate that a helical conformation with a right- or left-handed helicity in excess was induced for the polymer main chain on the basis of the chirality of menthol. The formation of optically active polymers in runs 3 and 4 is due to the same reason.

The mechanism of the chiral induction was based on the termination in the chain transfer process involving menthol as follows. The polymerization using (-)-menthol in the presence of thiophenol gave a polymer showing no significant optical activity (run 6). Thiols have much higher chain transfer rate constants than alcohols. Probably, the chain transfer with achiral thiophenol was much more influential than that with chiral (-)-menthol. The B/H-insoluble part of run 3 was found to be a mixture of (+)-fraction with higher molecular weight and (-)-fraction with lower molecular weight by GPC analysis (Figure 10). This suggests that termination of polymer radicals occurred in a helix-sense-selective manner similarly to reactions (A) and (C) in Scheme 2 proposed for the polymerization using chiral thiols.

The polymerization at 40°C using (-)-menthol (run 3) may be under less influence of chain transfer than the polymerization at 50°C. This would explain the lower optical activity of the polymer obtained in run 3 than

that of the polymer in run 2. The butanol derivative may not have a suitable structure for chiral induction (run 5).

Copolymerization with Optically Active PPyoTMA

The helix-sense-selectivity was studied for the copolymerization of PDBSMA with a small amount of optically active PPyoTMA. PPyoTMA is known to give a helical polymer by radical polymerization¹⁶ as well as by anionic polymerization.¹⁵ In both polymerizations, the helicity of the main chain is controlled by the side chain chirality through polymerization. Free radical polymerization of (+)-PPyoTMA (*e.e.* 100%, $[\alpha]_{365} + 190^\circ$) in toluene at 40°C gives a levorotatory polymer ($[\alpha]_{365} - 617^\circ$) having a triad isotacticity (*mm*) of 75%.¹⁶ On the basis of the radical homopolymerization of (+)-PPyoTMA, chiral PPyoTMA monomeric units incorporated into highly isotactic poly(PDBSMA) chain may induce a single-handed helicity of PDBSMA sequence.

The conditions and results of the polymerization are shown in Table IV. The copolymerization was carried out using (iso-PrOCOO)₂ as an initiator in the presence of thiophenol since the polymerization in the absence of thiophenol gave only THF-insoluble polymers whose analysis of chiroptical properties is difficult. In all the experiments, optically active polymers were obtained. The THF-insoluble part having higher molecular weight consisted mainly of PDBSMA monomeric units and was highly isotactic. The B/H-insoluble part with lower molecular weight had a higher content of PPyoTMA

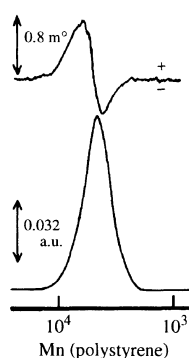


Figure 10. GPC curves of the B/H-insoluble poly(PDBSMA) of run 3 in Table III. The top chromatogram was obtained by polarimetric detection ($\alpha_{780\text{nm}}$) and the bottom by UV detection (254 nm).

monomeric units and was less isotactic. In GPC analysis of the B/H-insoluble polymers using a polarimetric and a UV detectors, the chromatogram measured by the polarimetric detector well corresponded to that by the UV detector, suggesting that the B/H-insoluble polymers are not a mixture of homopolymers but uniform copolymers. The PPyoTMA contents of the B/H-insoluble polymer were higher than the ratio of PPyoTMA to PDBSMA in the feed mixture. This means that there are at least two kinds of growing species with different activities toward the two monomers in the polymerization system: one reacts exclusively with PDBSMA monomer to form the THF-insoluble polymer and the other leads to the B/H-insoluble copolymer. The *mm* triad content of the B/H-insoluble copolymer was lower than expected from the weighted average of the isotacticities of the homopolymers of PPyoTMA (*mm* 75%¹⁶) and PDBSMA (*mm* >99%¹⁴) considering the composition of the two monomeric units. This eliminates the possibility of block-like structures of the copolymers.

The specific rotation of the B/H-insoluble part depended greatly on the content of PPyoTMA monomeric unit; the polymer of run 1 was levorotatory while those of runs 2 and 3 having less amount of PPyoTMA monomer units were dextrorotatory. In order to study the chiral structure of the polymers, CD spectra were measured (Figure 11). The CD spectral pattern of

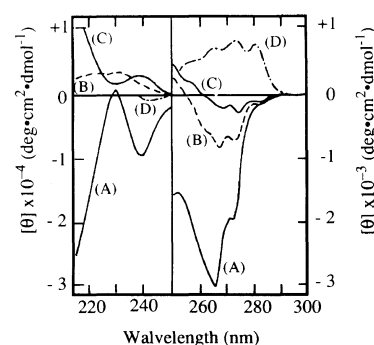


Figure 11. CD spectra of poly(PDBSMA)s of run 1 (A), run 2 (B), and run 3 (C) in Table IV and the spectrum corresponding to the (+)-poly[(-)-PPyoTMA]²⁴ (D). (A)–(C) were taken in THF. The spectrum (D) was synthesized as a mirror image from the spectrum taken in CHCl₃ of (-)-poly[(+)-PPyoTMA] obtained by radical polymerization; the band intensity has been reduced to 20% of the original spectrum. Some spectral data are indicated in ref 12a.

Table IV. Copolymerization of PDBSMA with PPyoTMA in the presence of thiophenol using (iso-PrOCOO)₂^a

Run	PPyoTMA in feed mol%	Yield ^c %	THF-insol. part				THF-sol. part					
			Yield %	Tacticity, <i>mm</i> %	PPyoTMA unit in polymer mol%	B/H ^b -insol. part		B/H ^b -sol. part				
						Yield %	Tacticity, <i>mm</i> %	Yield %	Tacticity, <i>mm</i> %			
1	20 [(-)-isomer] ^f	59	44	138	95.3	1.1	9	-352°	44	87.4	22	5.8
2	10 [(-)-isomer] ^f	58	52	142	95.9	1.0	5	+53°	39	83.7	18	1.4
3	5 [(-)-isomer]	74	66	176	97.3	0.4	7	+183°	31	81.9	13	1.3
4	5 [(+)-isomer] ^g	65	60	160	96.1	0.4	5	-11°	29	82.7	15	0.3

^a Conditions: monomer, 0.5 g; toluene, 4 ml; [monomer]/[(iso-PrOCOO)₂] = 100; [thiophenol]/[(iso-PrOCOO)₂] = 4.7; temp, 40°C; time, 24 h.

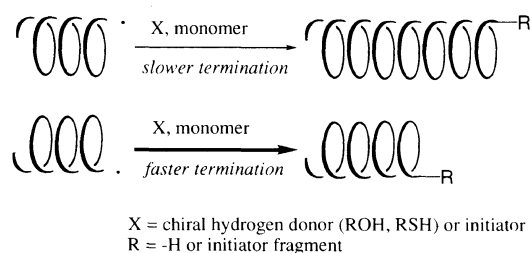
^b A mixture of benzene and hexane (1:1). ^c Hexane-insoluble products. ^d Determined by GPC of poly(MMA) derived from the original polymer using polystyrene standard samples. ^e Measured in THF. ^f (-)-PPyoTMA, 98.7% *e.e.* ^g (+)-PPyoTMA, 79.6% *e.e.*

the polymers changed greatly with the content of PPyoTMA monomeric units. The spectrum of the dextrorotatory polymer of run 3 (Figure 11(C)) has a very similar pattern to that of the one-handed helical (+)-poly(PDBSMA) obtained by anionic polymerization^{12a,13} and different from that of the homopolymer of (-)-PPyoTMA^{16,24} (Figure 11(D)), suggesting that the chiroptical properties of this polymer are due to the excess right- or left-handed helical sequences consisting mainly of PDBSMA monomeric units. This means that a single-handed helix was successfully induced by the incorporated PPyoTMA monomeric units. However, the spectra of the polymers of runs 1 and 2 had different patterns to that of the polymer of run 3. Because the polymer of run 1 is levorotatory, the chiroptical properties can't be ascribed only to the successive (-)-PPyoTMA monomeric units. The homopolymerization of (-)-PPyoTMA should give a dextrorotatory polymer ($[\alpha]_{365} + 617^\circ$). The CD bands of the polymer of run 1 may be based on the helical conformation consisting both of PPyoTMA units and PDBSMA units. It is notable that the CD bands of the polymers of runs 1 and 3 are reversed in the wavelength range of 200 to 250 nm. This means that the predominant helicity of these two polymers may be opposite. If this is the case, the helicity of the copolymer induced by the incorporated PPyoTMA units should be sensitive to the content of the PPyoTMA unit. One may assume that more sporadically incorporated PPyoTMA units are likely to induce (+)-helical PDBSMA sequences and more successively incorporated PPyoTMA units (-)-helical PDBSMA sequences.

There was a dramatic effect of *e.e.* of PPyoTMA on the optical activity of the obtained polymer (runs 3 and 4). A decrease of 19% in *e.e.* of PPyoTMA, which corresponds to the change in the content of minor isomer from *ca.* 1% to 10%, resulted in a remarkable decrease in specific rotation of the B/H-insoluble polymer. This indicates that a succession of the PPyoTMA monomeric units of the same chirality is important in inducing single-handed helicity.

SUMMARY

This paper presents the first example of helix-sense-selective polymerization of an achiral monomer by free radical mechanism. The free radical polymerization of PDBSMA using optically active initiators, transfer agents, solvents, and a comonomer gave polymers showing optical activity and CD adsorption based on an excess right- or left-handed helical conformation. The helix-sense-selection in the homopolymerizations appeared to be based mainly on differences in the rates of the termination (primary radical termination and radical quenching processes through chain transfer) for right- and left-handed helical growing radicals. This can be interpreted as helix-sense-selective inhibition of propagation (Scheme 3). A similar concept has been proposed for helical polyisocyanide synthesis mediated by transition metal catalysis.^{8b} On the basis of this mechanism, the THF-insoluble polymer having higher molecular weight might have greater excess of single-handed helicity than the B/H-insoluble part having lower



Scheme 3. Helix-sense-selective termination (inhibition) of helical radicals.

molecular weight though the chiroptical properties of the THF-insoluble polymer is currently unknown. The sense of helix in the copolymer was sensitive to the content of the optically active monomeric unit: more sporadically and more successively incorporated optically active monomeric units induced the opposite sense of helix.

The methods of helix-sense-selective free radical polymerization introduced in this work are considered to be applicable to the wide range of PDBSMA derivatives and related bulky monomers having the functional groups which kill anionic species. *E.e.* of the polymer helices was up to *ca.* 40% even after GPC separation in the present study. However, higher helix-sense-selectivity should be possible using more properly designed structures of chiral additives.

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