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ARTICLE

A Reactive Helix: Synthesis, Chemical Modification, and Polymerization of an Optically Active Polymethacrylate

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ABSTRACT: 1-(*p*-Vinylphenyl)dibenzosuberyl methacrylate (**VDBSMA**) having two reactive vinyl groups in a molecule was synthesized and polymerized using α,α′-azobis(isobutyronitrile) as a radical initiator and using the complexes of 9-fluorenyllithium with (*S*)-(+)-1-(2-pyrrolidinylmethyl)pyrrolidine, (−)-sparteine, and (*S*,*S*)-(+)-2,3-dimethoxy-1,4-bis(dimethylamino)butane as optically active anionic initiators. The free radical polymerization led to an insoluble material, indicating that both methacrylic and styrenic moieties participated in the polymerization and a cross-linked gel was produced. In contrast, the anionic polymerization proceeded exclusively through the addition reaction of methacrylic moiety leaving the styrenic vinyl group intact leading to soluble polymers. The resulting poly(**VDBSMA**)s having a polymethacrylate-type main-chain structure were highly isotactic and showed high optical activity and intense circular dichroism (CD) spectra, indicating that the polymers have a single-handed helical conformation. Thus, a single-handed helical polymer having side-chain vinyl groups, which can be chemically modified, was successfully synthesized. The side-chain vinyl group was converted to 2-hydroxyethyl group, 1,2-dihydroxyethyl group, and carboxylic acid group by polymer reaction without seriously deteriorating the single-handed helical conformation of the polymer. In this way, single-handed helical polymers with side-chain protonic groups which would be difficult to be prepared by direct asymmetric anionic polymerization of the corresponding monomers were conveniently synthesized. In addition, radical polymerization of poly(**VDBSMA**) as a macromonomer afforded an optically active adduct consisting of single-handed helical chains.

Introduction

Optically active polymers whose chirality is based on a single-handed helical conformation is drawing attention because such polymers have high potentialities in practical applications such as chiral separation, nonlinear optical devices, and chiral catalysts.[1] In this context, various helical polymers have been synthesized, and their structure−property relation has been investigated. Optically active, helical polymers can be prepared by polymerization of an optically active monomer or by asymmetric polymerization of a properly designed achiral monomer (helix-sense-selective polymerization),[1a−f] or through supramolecular interaction between an achiral polymer and added chiral molecules.[1j−m] Among various examples of asymmetric polymerization, anionic polymerization of designed bulky methacrylates and acrylates using the complexes of organolithiums with chiral ligands as initiators has been studied systematically and demonstrated to conveniently afford single-handed helical polymers. The first monomer used for such polymerization was triphenylmethyl methacrylate (TrMA),[2−4] and thereafter, many derivatives and analogues of TrMA were designed and subjected to asymmetric anionic polymerization.[1a−f] However, monomer design was limited to those without protonic functional groups because the growing species in anionic polymerization is readily quenched by a protonic group, and hence, it has been difficult to synthesize a helical polymethacrylate with protonic side chain groups whose interaction or reaction with added polar molecules might be effective in performing chiral molecular recognition and in creating novel chiral polymeric materials with a helical chain in their core part.

Here, we present the synthesis of optically active, single-handed helical polymethacrylates having protonic side-chain groups without using monomers protonic groups. Such polymers (poly-**1**, poly-**2**, and poly-**3**) were synthesized by polymer reactions of single-handed helical poly(1-(*p*-vinylphenyl)dibenzosuberyl methacrylate) (poly(**VDBSMA**)) which was prepared by the asymmetric polymerization of 1-(*p*-vinylphenyl)dibenzosuberyl methacrylate (**VDBSMA**) (Scheme 1). 1-Phenyldibezosuberyl methacrylate (**PDBSMA**), the parent monomer of **VDBSMA** without styrenic vinyl group, has been synthesized and polymerized using chiral complexes to afford a single-handed helical polymer.[5,6]

Poly(**VDBSMA**), the intermediate polymer, was prepared by asymmetric anionic polymerization of **VDBSMA** using the complexes of 9-fluorenyllithium (FlLi) with (−)-sparteine (Sp), (*S*,*S*)-(+)-2,3-dimethoxy-1,4-bis(dimethylamino)butane ((+)-DDB), and (*S*)-(+)-1-(2-pyrrolidinylmethyl)pyrrolidine (PMP). Each monomeric unit of poly(**VDBSMA**) has a reactive side-chain vinyl group. The vinyl group could be converted to protonic 2-hydroxyethyl group, 1,2-dihydroxyethyl group, and carboxylic group by polymer reaction without seriously deteriorating the single-handed helix, leading to optically active, single-handed helical polymers with protonic side chain groups (poly-**1**, poly-**2**, and poly-**3** in Scheme 1). Direct synthesis of these polymers from corresponding monomers by asymmetric anionic polymerization would be impossible unless the protonic groups of such monomers are

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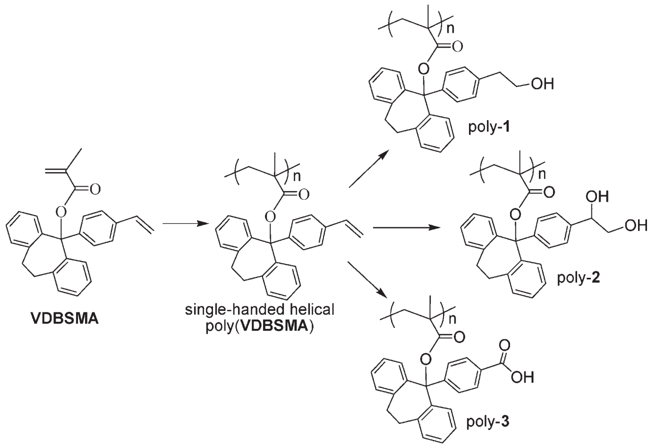
Scheme 1. Polymerization of VDBSMA and Synthesis of Single-Handed Helical Polymethacrylates Bearing Protonic Side-Chain Groups via Chemical Modification of Poly(VDBSMA)



protected prior to polymerization. In addition, even if the corresponding protected monomers were used, the protected polar groups may possibly prevent chiral ligands used for asymmetric polymerization from effectively coordinating with lithium countercation at the growing chain end. Evidentially, addition of achiral coordinating molecules has been reported to reduce helix-sense selectivity in asymmetric polymerization of a bulky methacrylate.[7] The synthetic concept presented in this work involving asymmetric anionic polymerization of a monomer with a reactive side-chain group and polymer reactions modifying the side-chain group may open a way to produce single-handed helical polymers with a variety of polar functional groups which are difficult to synthesize by direct polymerization of corresponding, designed monomers. Furthermore, poly(**VDBSMA**) was effective as a macromonomer leading to a polymeric adduct consisting of single-handed helical chains.

Polymer reactions have been widely used to modify material properties[8] and have been applied also for some synthetic helical polymers. However, examples involving reactive helical polymers whose conformation is intact through side-chain reactions are limited.[9−13] In addition, almost quantitative side-chain modification of a synthetic helical polymer having pendent vinyl group has not been reported.

Experimental Section

Materials. 4-Chlorostyrene (TCI), Mg turnings (Nacalai Tesque), I_2 (Wako Chemical), dibenzosuberone (TCI), NaH (suspension in paraffin, assay 60%, Wako Chemical), BH_3−tetrahydrofuran (THF) complex (Aldrich, 1.0 M, a THF solution), $K_3Fe(CN)_6$ (Wako), $MeSO_2NH_2$ (Aldrich), and OsO_4 (Wako) were used as received. $KMnO_4$ (Aldrich) was ground to a fine powder with a mortar. Methacryloyl chloride (Wako Chemical) was purified by distillation under N_2 atmosphere. Fluorene (Nacalai Tesque) was first recrystallized from ethanol and then from hexane; mp 104.5−105.0 °C. Chiral ligands, (−)-sparteine (Sp) (Aldrich), (*S*,*S*)-(+)-2,3-dimethoxy-1,4-bis(dimethylamino)butane ((+)-DDB), and (*S*)-(+)-1-(2-pyrrolidinylmethyl)pyrrolidine (PMP) (Aldrich) were dried over CaH_2 and distilled under reduced pressure. α,α′-Azobis(isobutyronitrile) (AIBN) (Wako) was recrystallized from an ethanol solution at room temperature. *n*-BuLi (Nacalai Tesque, 1.6 M, a hexane solution) was used after titration. Tetrahydrofuran (THF) (Wako) was refluxed over sodium benzophenone ketyl and distilled under N_2 atmosphere. Toluene used for polymerization was purified in the usual manner, mixed with a small amount of *n*-BuLi, and distilled under high vacuum immediately before use.

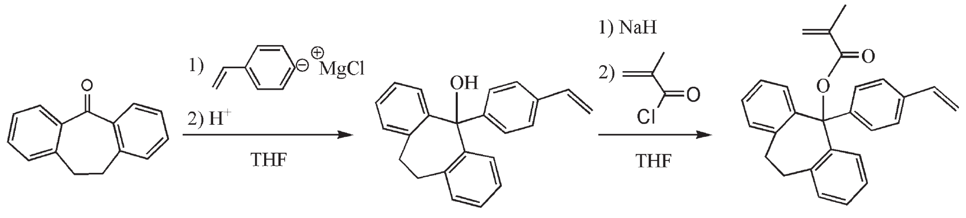
Synthesis of 1-(*p*-Vinylphenyl)dibenzosuberol. Mg turnings (11.4 g, 471 mmol) were placed in a 500 mL flask equipped with a dropping funnel and a reflux condenser, and the flask was evacuated and flame-dried with stirring. Stirring was continued for 4 h to activate the Mg surface under vacuum. After flushing the flask with N_2 gas, dry THF (160 mL) and a small amount of I_2 were introduced. A solution of 4-chlorostyrene (54.0 g, 390 mmol) in dry THF (100 mL) were added dropwise to the mixture in the flask from the dropping funnel with stirring. The color of the reaction mixture slowly changed to dark green. The reaction mixture was stirred under reflux for 3 h to afford a THF solution of 4-vinylmagnesium chloride (1.22 M).

Dibenzosuberone (48.5 g, 232 mmol) was dissolved in dry THF (160 mL) in a flame-dried 1-L flask. To this solution was slowly added the Grignard reagent solution prepared above (280 mL, 342 mmol) with stirring at 0 °C. After stirring for 16 h at room temperature, the reaction mixture was quenched by adding saturated aqueous NH_4Cl (50 mL). The product was extracted with diethyl ether−water, and the organic layer was dried on $MgSO_4$. Concentration of the dried organic layer afforded a crude oily material. The crude material was recrystallized from a diethyl ether solution to give colorless crystalline product (51.3 g, 70.5%). Mp: 87.5−88.2 °C. ^1H NMR (500 MHz, $CDCl_3$, Me_4Si) δ 2.29 (s, 1H, −OH), 2.72−2.87 (m, 4H, $-CH_2$-CH_2-), 5.22 (d, 1H, vinyl H), 5.77 (d, 1H, vinyl H), 6.61−6.67 (m, 1H, vinyl H), 6.62−8.05 (m, 12H, aromatic H). Anal. Calcd for $C_{23}H_{20}O$: C, 88.43; H, 6.54. Found: C, 88.48; H, 6.49.

Synthesis of VDBSMA. In a 1-L flask equipped with a dropping funnel and a reflux condenser flushed with N_2 gas was placed NaH (suspension in paraffin) (3.48 g, 145 mmol). THF (200 mL) was introduced with a syringe to remove paraffin from NaH, and supernatant THF wash was removed after stirring. THF (240 mL) was added to the washed NaH, and 1-(*p*-vinylphenyl)dibenzosuberol (30.2 g, 96.7 mmol) dissolved in THF (200 mL) was added dropwise with stirring. The reaction mixture was refluxed for 20 h with stirring to form sodium alkoxide. Methacryloyl chloride (11.5 mL, 118 mmol) was slowly added to the reaction mixture cooled to 0 °C, and the mixture was stirred for 10 min at 0 °C. The mixture was then warmed to room temperature and further stirred for 4 h. The reaction mixture was decomposed by adding water. The product was extracted with $CHCl_3$−water. The organic layer was washed with saturated aqueous Na_2CO_3 and with brine in this order and was then dried on $MgSO_4$. Removal of solvent gave a crude material. This material was recrystallized from diethyl ether and then from a benzene−hexane (1/1, v/v) mixture to afford a colorless crystalline product (19.27 g, 52.4%). Mp: 98.2−98.9 °C. ^1H NMR (500 MHz, $CDCl_3$, Me_4Si): δ 1.99 (s, 3H, $-CH_3$), 3.19 (s, 4H, $-CH_2CH_2-$), 5.20 (d, 1H, styrenic vinyl H), 5.65 (d, 1H, styrenic vinyl H), 5.67 (d, 1H, methacrylic vinyl H), 6.28 (d, 1H, methacrylic vinyl H), 6.62−6.66 (m, 1H, styrenic vinyl H), 7.08−7.40 (m, 12H, aromatic H). Anal. Calcd for $C_{27}H_{24}O$: C, 85.23; H, 6.36. Found: C, 88.02; H, 6.39.

Polymerization. Preparation of initiator solution and asymmetric anionic polymerization were carried out in dry toluene under dry N_2 atmosphere. Polymerization procedure is described for run 1 in Table 3 as an example. Fluorene (0.0771 g, 0.464 mmol) was placed in a flame-dried glass ampule sealed with a three-way stopcock, which was then evacuated on a vacuum line and was flushed with dry N_2 gas. After this procedure was repeated three times, a three-way stopcock was attached to the ampule and dry toluene (1.10 mL) was introduced with a syringe to dissolve fluorene. *n*-BuLi in hexane (0.290 mL, 0.464 mmol) and (+)-PMP (0.0900 mL, 0.0851 g, 0.552 mmol) were added to the resultant solution with a syringe in this order, and the mixture was stood at room temperature for 10 min to obtain orange-colored PMP-FlLi complex solution (0.300 M). In a similar manner to the preparation of the fluorene solution, **VDBSMA** (1.0 g, 2.63 mmol) was dried and dissolved in dry toluene (20 mL) in a flame-dried glass ampule sealed with

Scheme 2. Synthesis of VDBSMA



VDBSMA

a three-way stopcock. The monomer solution was cooled to −78 °C, and the PMP-FlLi solution (0.438 mL, 0.131 mmoL) was added with a syringe to initiate the polymerization. After 3 h of initiation, the reaction was terminated by adding MeOH (0.05 mL). The reaction mixture was poured into a large excess of MeOH, and the MeOH-insoluble part was collected with a centrifuge and was dried under high vacuum at 60 °C for 2 h. The MeOH-insoluble product was obtained as colorless powder (0.990 g, yield 97%). The MeOH-insoluble polymer was dissolved in $CHCl_3$ (10 mL), and the solution was poured into a mixture of benzene and hexane (1/1, v/v) (150 mL) to remove oligomeric products. The MeOH-insoluble, benzene−hexane-insoluble part was collected with a centrifuge and was dried under high vacuum at 60 °C for 2 h to afford a colorless product (0.946 g, 93%). The conversion of poly(**VDBSMA**) to PMMA was performed in the same manner as applied for poly(**TrMA**) according to the literature.[4]

Conversion of the Side-Chain Vinyl Group of Poly(VDBSMA) to the 2-Hydroxyethyl Group (Synthesis of Poly-1). The reaction was carried out under N_2 atmosphere. Poly(**VDBSMA**) (DP = 22, $M_w/M_n = 1.05$, $[\alpha]_{365}$ +2038° (THF)) (1.00 g, 2.63 mmol (monomeric unit)) was dissolved in dry THF (48 mL) in a flame-dried 200 mL flask. To the polymer solution cooled at 0 °C was slowly added BH_3−THF complex in a THF solution (3.20 mL, 3.20 mmol). The reaction mixture became gradually viscous within 5 min of completion of the addition. The reaction mixture was stirred for 1 h at 0 °C and then for 15 h at room temperature. The mixture was cooled to 0 °C again, and 3 N aqueous NaOH (8.80 mL) and 30% aqueous solution of H_2O_2 (8.80 mL) were slowly added in this order. The reaction mixture became yellow. After stirring for 3 h at 0 °C, brine was added to the mixture. The product was extracted with THF, and the organic layer was concentrated to give a crude polymer. The crude product was washed first with diethyl ether and then with *n*-hexane to give a colorless polymer (1.04 g, 99.2%).

Conversion of the Side-Chain Vinyl Group of Poly(VDBSMA) to the 1,2-Dihydroxyethyl Group (Synthesis of Poly-2). The reaction was carried out in the dark. $K_3Fe(CN)_6$ (2.60 g, 7.89 mmol), $MeSO_2NH_2$ (250 mg, 2.63 mmol), and K_2CO_3 (1.09 g, 7.89 mmol) were dissolved in a mixture of THF (28 mL) and water (14 mL) in a 200 mL flask. The solution was cooled to 0 °C to afford a yellowish orange half-solid mixture. To this mixture was added OsO_4 (66.8 mg, 0.263 mmol), and the mixture was stirred for 30 min. Poly(**VDBSMA**) (DP = 22, $M_w/M_n = 1.05$, $[\alpha]_{365}$ +2038° (THF)) (1.00 g, 2.63 mmol (monomeric unit)) dissolved in THF (20 mL) was added dropwise to the mixture with stirring. The reaction mixture was warmed to room temperature after completion of the addition and was further stirred for 24 h to give a reddish brown suspension. The reaction was then decomposed by adding saturated aqueous $NaHSO_3$ and brine in this order. The product was extracted with THF, and the organic layer was concentrated to give a crude polymer. The crude product washed with a mixture of acetone and hexane (2/1, v/v) to give a colorless polymer (0.987 g, 89.8%).

Conversion of the Side-Chain Vinyl Group of Poly(VDBSMA) to the Carboxylic Group (Synthesis of Poly-3). In a 200 mL flask were placed poly(**VDBSMA**) (DP = 22, $M_w/M_n = 1.05$, $[\alpha]_{365}$ +2038° (THF)) (950 mg, 2.50 mmol (monomeric unit)), Na_2CO_3 (225 mg, 2.12 mmol), and *tert*-butyl alcohol (0.57 mL). To this mixture was added THF (95 mL) to dissolve the polymer. The solution containing suspended Na_2CO_3 was cooled at 0 °C, and $KMnO_4$ (1.19 g, 7.51 mmol) dissolved in water (17.8 mL) was slowly added with a syringe to give a dark purple mixture. The mixture was warmed to room temperature and was stirred for 4 h to give a dark brown suspension. The mixture was filtrated, and the filtrate was concentrated to give a pale yellow material which is considered to be a potassium salt form of the product. This material was suspended in a MeOH−THF mixture (2/1, v/v) (150 mL) with an acidic ion-exchange resin, and the mixture was stirred for 30 min. The mixture was filtrated, and the filtrate was concentrated to afford a crude polymer. The crude polymer was washed with an acetone-*n*-hexane (1/1, v/v) mixture to give a pale orange product (750 mg, 75.5%).

Measurements. The ^1H NMR spectra were recorded on a JEOL JNM-ECP500 spectrometer (500 MHz for ^1H measurement). SEC was carried out using a chromatographic system consisting of a Hitachi L-7100 pump, an L-7420 UV detector (254 nm), and an L-7490 RI detector equipped with TOSOH TSK gel G3000H_{HR} and G6000H_{HR} columns connected in series (eluent, THF; flow rate, 1.0 mL/min). SEC experiments were also performed using a chromatographic system with a JASCO PU2080Plus chromatographic pump with a Viscotek TDA300 detector system consisting of viscometric, right-angle laser-light scattering (RALS), and RI detectors and a Wyatt Technology Dawn E multiangle laser-light scattering (MALLS) detector system equipped with TOSOH TSKgel G3000H_{HR}, and G6000H_{HR} columns connected in series (eluent, THF; flow rate, 1.0 mL/min). IR spectra were measured with a JASCO FT/IR-420 spectrophotometer using KBr pellet samples. Absorption spectra were measured with JASCO V-550 and V-570 spectrophotometers. Circular dichroism (CD) spectra were taken on a JASCO J-820 spectrometer. Specific rotation was measured using a JASCO P-1030 digital polarimeter.

Results and Discussion

Synthesis and Stability of VDBSMA Monomer. VDBSMA was synthesized by a two-step reaction according to Scheme 2 starting from dibenzosuberone (cf. Experimental Section) and was purified by recrystallization to give a material pure enough to be used for anionic polymerization.

Triarylmethyl methacrylates are known to be prone to hydrolysis of the ester bonding by protonic solvents or moisture in the air. This often leads to degradation of helical structure of poly(triarylmethyl methacrylate)s. Hence, it is important to test the stability of ester bonding of a newly made monomer. The stability of **VDBSMA** was examined by monitoring its methanolysis reaction carried out in a mixture of $CDCl_3$ and CD_3OD (1/1, v/v) at 35 °C in an NMR sample tube by ^1H NMR spectroscopy by the reported method.[6] The first-order methanolysis rate constant and half-life period of **VDBSMA** are indicated in Table 1 together with those of other methacrylate monomers with a similar backbone. **VDBSMA** was slightly less stable compared with **PDBSMA**, its parent compound without a vinyl group, but was more stable than **TrMA**.[14] This result combined with the fact that optically active poly(**TrMA**) has been commercialized as a chiral selector material for HPLC[15−17] indicates that poly(**VDBSMA**) would have sufficient stability as a polymeric material. The lower stability of **VDBSMA** in comparison to **PDBSMA** may arise from higher stability of 1-(*p*-vinylphenyl)dibenzosuberyl cation than 1-(*p*-vinylphenyl)-dibenzosuberyl cation, which are considered to be an intermediate species of solvolysis, because of the larger π-conjugation system in **VDBSMA** delocalizing and stabilizing the positive charge involving a vinyl group than that of **PDBSMA**.

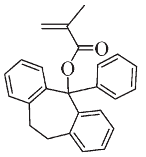
Polymerization of VDBSMA. The conditions and results of free-radical polymerization using AIBN and asymmetric aninoic polymerization using Sp-FlLi, DDB-FlLi, and PMP-FlLi at [M]/[I] = 20 are summarized in Table 2. The free-radical polymerization with AIBN in THF afforded a mostly insoluble material, suggesting that both methacrylic and styrenic vinyl groups of **VDBSMA** monomer reacted during the polymerization leading to a cross-linked gel. In contrast, the anionic polymerizations using the three optically active complexes in toluene gave soluble polymers. With DDB and PMP as chiral ligands, the polymer yield was nearly quantitative in the reaction time of 3 h. The relatively low polymer yield in the system with Sp may mean that the reaction was slower when this ligand was used. The same tendency has been reported for **TrMA** polymerization using the same initiators.[4] The anionic polymerization products contained a small amount of oligomers which were removed from the polymers by washing with a mixture benzene and hexane (1/1, v/v). The polymers obtained using PMP and DDB had rather narrow molecular weight distributions, implying that the reaction systems with PMP and DDB may have a living nature.

In the anionic polymerizations, only the methacrylic vinyl group reacted leaving the styrenic vinyl group intact (Scheme 1). This was evidenced by ^{1}H NMR spectral analyses. Figure 1 shows the ^{1}H NMR spectra of **VDBSMA** monomer and the poly(**VDBSMA**) obtained by anionic polymerization using DDB-FlLi (run 2 in Table 1). In the spectrum of the polymer, the signals based on methacrylic-type vinyl group completely disappeared and those based on styrene-type vinyl group were quantitatively observed. These results clearly indicate that the polymer has a polymethacrylate structure having the unreacted styrenic vinyl group in the side chain. In addition, the upfield-shifted α-methyl signal in the range of 0−0.5 ppm suggests a helical conformation of the poly(**VDBSMA**).[18]

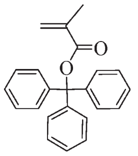
Table 1. First-Order Rate Constants and Half-Life Periods in Methanolysis Reaction of Methacrylates[a]

run	monomer	k/h^{-1}	half-life period/min
1	**VDBSMA**	0.61	69.3
2	**PDBSMA**[b]	0.46	89.0
3	**TrMA**[c]	2.86	14.5

[a] Solvolysis reactions were carried out in a mixture of $CDCl_3$ and CD_3OD (1/1, v/v) at 35 °C. [b] Cited from ref 6. [c] Cited from ref 14.



PDBSMA



TrMA

The polymethacrylate structure of poly(**VDBSMA**) was further supported by the fact that the poly(**VDBSMA**) was converted to PMMA by hydrolysis of ester bonding using MeOH containing a small amount of HCl and methylation of the hydrolysis products using CH_2N_2. ^{1}H NMR analyses of the products confirmed the chemical and stereostructure of the PMMA (Figure 2). The polymers obtained by asymmetric anionic polymerization were nearly completely isotactic as found by ^{1}H NMR spectra of PMMAs derived from the poly(**VDBSMA**)s. As an example, the spectrum of PMMA derived from the polymer obtained using DDB-FlLi (run 2 in Table 1) is shown in Figure 2. The spectrum shows a typical AB quartet splitting of the methylene protons based on the *mmm* tetrad and the α-methyl signal based exclusively on *mm* triad.

In addition, the polymers obtained by asymmetric anionic polymerization showed large dextrorotation. The degree of optical rotation was greater than those of single-handed helical poly(**TrMA**) and poly(**PDBSMA**),[6] the parent polymer of poly(**VDBSMA**) without vinyl group. These results strongly suggests that the poly(**VDBSMA**) obtained in this work has a single-handed helical structure.

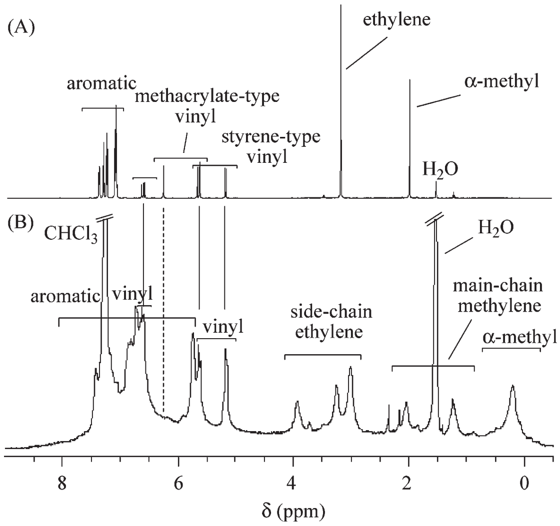


Figure 1. ^{1}H NMR spectra of **VDBSMA** (A) and poly(**VDBSMA**) prepared using DDB-FlLi (run 2 in Table 2) (B) [500 MHz, $CDCl_3$].

Table 2. Polymerization of VDBSMA Using Various Initiators[a]

							benzene−hexane(1/1)-insoluble part				
run	initiator	solvent	[M]/[I]	temp (°C)	time (h)	yield[b] (%)	content (%)	$[\alpha]^{25}_{365}$[c] (deg)	DP[d]	M_w/M_n[d]	*mm*[e] (%)
1	AIBN	THF	50	60	24	95[f]					
2	DDB-FlLi	toluene	20	−78	24	>99	82	+1900	30	1.07	>99
3	Sp-FlLi	toluene	20	−78	24	61	82[g]	−1920[h]	38	1.33	>99
4	PMP-FlLi	toluene	20	−78	3	97	93	+1975[i]	23	1.07	>99

[a] Conditions: **VDBSMA,** 300 mg (runs 1−3), 1.0 g (run 4), [VDBSMA]$_o$ = 0.15 M. [b] MeOH-insoluble part. [c] Measured in THF (concentration 0.5 g/dL, cell length 0.1 dm). [d] Determined by SEC of PMMA derived from poly(VDBSMA). [e] Determined by ^{1}H NMR of PMMA derived from poly(VDBSMA). [f] Not precipitated in methanol. Yield was estimated by ^{1}H NMR analysis of THF-soluble part (32%) of the product (unreacted monomer content 84%) assuming that THF-insoluble product (68%) contains no monomer. [g] Consisted of THF-soluble (18%) and -insoluble (82%). [h] THF-soluble part. [i] $[\alpha]^{25}_{435}$ +892°, $[\alpha]^{25}_{546}$ +485°, $[\alpha]^{25}_{577}$ +422°, $[\alpha]^{25}_{589}$ +411° (in THF, concentration 0.3 g/dL, cell length 0.1 dm).

Among the three optically active anionic initiator complexes, PMP-FlLi gave the polymer with the largest optical activity and the DP closest to the [M]/[I] ratio in feed. This means that PMP-FlLi among the three initiators best controls the polymerization of **VDBSMA** from the views of stereochemistry and livingness. Using PMP-FlLi, polymerizations were further conducted at different [M]/[I] ratios (Table 3). In the polymerizations for 3 h, polymer yield decreased with an increase in [M]/[I] ratio (Table 3, runs 1−4). This suggests that the reaction time of 3 h is not long enough to achieve complete monomer consumption at [M]/[I] = 40 and larger. When the polymerization time was extended to 48 h, the polymer yield at [M]/[I] = 40 was nearly quantitative and that at [M]/[I] = 80 reached 84%. These two systems gelled during the polymerization due to low solubility of the products: most part of the isolated products in these two systems were insoluble in THF or $CHCl_3$. The observed gelation and insolubility of the products are due not to reactions of the side-chain vinyl groups but to molecular aggregations as discussed below.

In the polymerizations at [M]/[I] = 20−60 for 3 h, mostly soluble products with relatively narrow molecular weight distributions were obtained. DP of the obtained polymer was higher at a higher [M]/[I] ratio, suggesting again that these reaction systems may have a living nature. The specific rotation of the polymers with DP of 40 and 57 were larger than +2000°. These may be the highest specific rotations ever observed for single-handed helical (meth)acrylic polymers. Also, these polymers indicated intense circular dichroism (CD) spectra, supporting their single-handed helical structure (Figure 3). The CD spectral patterns of the polymers slightly differed depending on DP. This might reflect molecular aggregation of the polymer chain as discussed below.[7]

Although the polymers obtained in runs 1−3 of Table 3 had relatively narrow molecular weight distributions as determined as PMMA derived from the original form, the SEC curve of the original poly(**VDBSMA**)s obtained at [M]/[I] = 40 and 60 indicated broader or multi modal distributions (Figure 4). This indicate that poly(**VDBSMA**) forms aggregates when its DP is 40 or greater.

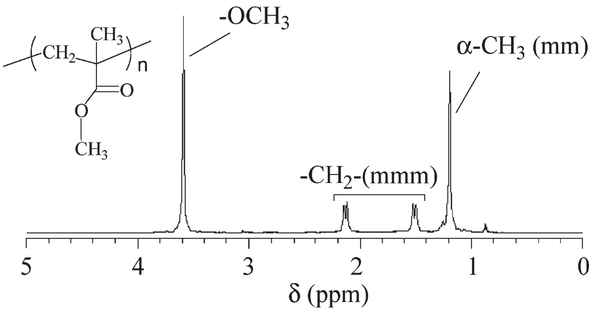


Figure 2. ^{1}H NMR spectra of PMMA derived from the poly(**VDBSMA**) prepared using DDB-FlLi (run 2 in Table 2) [500 MHz, $CDCl_3$].

Side-Chain Modification of Poly(VDBSMA). In order to obtain single-handed helical, optically active polymethacrylates bearing protonic side-chain groups, the side-chain vinyl group of the single-handed helical poly(**VDBSMA**) prepared using PMP-FlLi at [M]/[I] = 20 (DP = 22, $M_w/M_n = 1.05$, $[\alpha]_{365}$ +2038° (THF)) was converted to 2-hydroxyethyl, 1,2-dihydroxyethyl, and carboxylic acid groups (poly-**1**, poly-**2**, and poly-**3**, respectively, in Scheme 1). The conversion of vinyl to 2-hydroxyethyl was conducted by hydroboration followed by hydrolysis, that of vinyl to 1,2-dihydoxyethyl by oxidation with OsO_4 followed by decomposition using aqueous $NaHCO_3$, and that of vinyl to carboxylic acid by oxidation with $KMnO_4$ followed by treatment with an acidic ion-exchange resin. These reactions were confirmed by FT-IR and ^{1}H NMR spectra of the products (Figures 5 and 6, respectively).

In the FT-IR spectra (Figure 5), the relatively weak but clearly observed bands based on the vinyl C═C around 1650 cm^{-1} for poly(**VDBSMA**) was not observed for poly-**1**, poly-**2**, and poly-**3**. In addition, the IR bands due to O−H stretching around 3500 cm^{-1} which were absent in the spectrum of poly(**VDBSMA**) emerged for poly-**1**, poly-**2**, and poly-**3**. Further, all polymers indicated C═O bands of ester group around 1730 and 1150 cm^{-1}. Also, poly-**3** indicated a C═O band around 1690 cm^{-1} based on carboxylic acid group. These results support the conversion of the

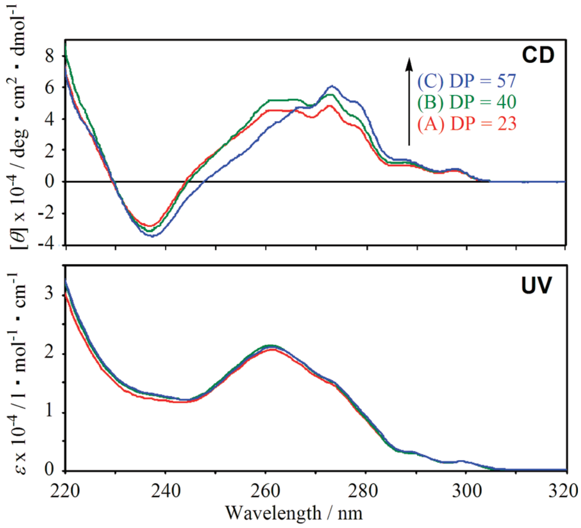


Figure 3. CD (top panel) and UV (bottom panel) spectra of poly(**VDBSMA**) having different degrees of polymerization: run 1 in Table 3 (A), run 2 in Table 3 (B), and run 3 in Table 3 (C) [in THF, at room temperature].

Table 3. Asymmetric Anionic Polymerization of VDBSMA with PMP-FlLi in Toluene at −78 °C[a]

					THF-sol., benzene−hexane(1/1)-insol. part				
run	[M]/[I]	time (h)	yield[b] (%)	THF-insol. part content	content (%)	$[\alpha]^{25}_{365}$[c] (deg)	DP[d]	M_w/M_n[d]	*mm*[e] (%)
1	20	3	97	∼0	96	+1975[f]	23	1.07	>99
2	40	3	76	2	89	+2170	40	1.10	>99
3	60	3	63	3	90	+2140	57	1.19	>99
4	80	3	53	28					
5	40	48	96	89	DP = 99, M_w/M_n = 1.53, *mm* > 99%[g]				
6	80	48	84	>99	DP = 149, M_w/M_n = 1.59, *mm* > 99%[g]				

[a] Conditions: **VDBSMA**, 1.0 g (run 1), 500 mg (runs 2−6); [VDBSMA] = 0.15 M. [b] MeOH-insoluble part. [c] Measured in THF (concentration 0.5 g/dL, cell length 0.1 dm). [d] Determined by SEC of poly(MMA) derived from poly(VDBSMA). [e] Determined by ^{1}H NMR of poly(MMA) derived from poly(VDBSMA). [f] $[\alpha]^{25}_{435}$ +892°, $[\alpha]^{25}_{546}$ +485°, $[\alpha]^{25}_{577}$ +422°, $[\alpha]^{25}_{589}$ +411° (in THF, concentration 0.3 g/dL, cell length 0.1 dm). [g] Values corresponding to the MeOH-insoluble part without fractionation using THF.

vinyl group of poly(**VDBSMA**) to the corresponding protonic groups of poly-**1**, poly-**2**, and poly-**3** and clearly indicate that the reagents used for the side chain vinyl group conversion did not affect (hydrolyze) the ester linkage in the side chain.

The ^{1}H NMR spectra (Figure 6) of poly-**1**, poly-**2**, and poly-**3** indicated no signal of the styrenic vinyl group of poly(**VDBSMA**). For poly-**1** and poly-**2**, proton signals arising from the 2-hydroxyethyl and 1,2-dihydroxyethyl groups were clearly observed. Furthermore, it is important to note that α-methyl signals appeared in the range 0−0.5 ppm, indicating that the helical structure of poly(**VDBSMA**) was not deteriorated by the side-chain modification reactions. Helical polymethacrylates with bulky side groups have been reported to indicate the α-methyl signals around 0.5 ppm.[18] In the spectrum of poly-**3**, several minor signals marked by an asterisk were observed in the range 4.5−5.5 ppm. These signals might arise from 1,2-dihydroxyethyl groups that may exist to a minor extent.

Chirality of poly-**1**, poly-**2**, and poly-**3** was assessed by CD spectra and optical activity measurements. Figure 7 shows the CD and UV spectra of the three polymers along with that of poly(**VDBSMA**). The UV spectra of poly-**1**, poly-**2**, and poly-**3** lacked the absorption band around 260 nm, confirming that π-conjugation systems of the three polymers are smaller than that of poly(**VDBSMA**) because of the consumption of the vinyl group of poly(**VDBSMA**) by the polymer reactions. The three polymers indicated intense CD and exhibited large dextrorotation: $[\alpha]^{25}_{365}$ +1276°, $[\alpha]^{25}_{435}$ +735°, $[\alpha]^{25}_{546}$ +403°, $[\alpha]^{25}_{577}$ +350°, $[\alpha]^{25}_{589}$ +333° for poly-**1** (in THF, concentration 0.5 g/dL, cell length 0.1 dm), $[\alpha]^{25}_{365}$ +1463°, $[\alpha]^{25}_{435}$ +844°, $[\alpha]^{25}_{546}$ +469°, $[\alpha]^{25}_{577}$ +407°, $[\alpha]^{25}_{589}$ +394° for poly-**2** (in THF-MeOH (1/1, v/v), concentration 0.5 g/dL, cell length 0.1 dm), and $[\alpha]^{25}_{365}$ +1221°, $[\alpha]^{25}_{435}$ +697°, $[\alpha]^{25}_{546}$ +384°, $[\alpha]^{25}_{577}$ +336°, $[\alpha]^{25}_{589}$ +321° for poly-**3** (in THF-MeOH (1/1, v/v), concentration 1.0 g/dL, cell length 0.1 dm), suggesting that single handedness of the polymer helix was maintained during the polymer reaction of poly(**VDBSMA**) leading to poly-**1**, poly-**2**, and poly-**3**. Hence, the helical polymethacrylates having protonic side-chain groups with single-handedness

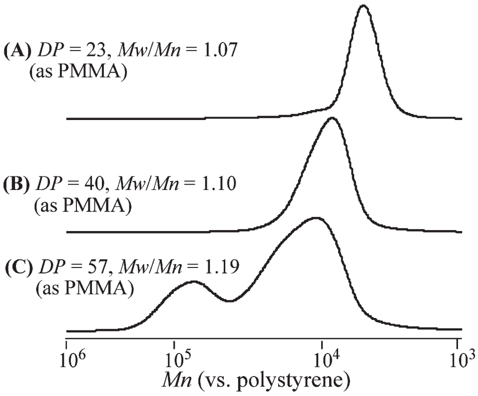


Figure 4. SEC curves of poly(**VDBSMA**)s having different degrees of polymerization: run 1 in Table 3 (A), run 2 in Table 2 (B), and run 3 in Table 3.

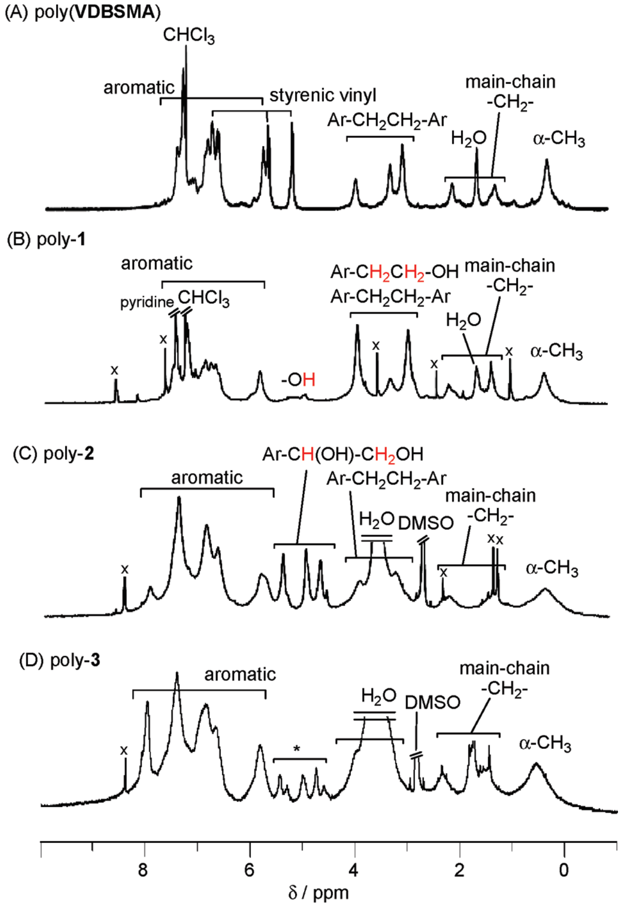


Figure 6. 500 MHz ^{1}H NMR spectra of poly(**VDBSMA**) (run 1 in Table 3) in $CDCl_3$, (A), poly-**1** in $CDCl_3$−pyridine-d_5 (5/1, v/v), (B), poly-**2** in DMSO-d_6 (C), and poly-**3** in DMSO-d_6 (D). Key (×) impurity signals; (∗) see text.

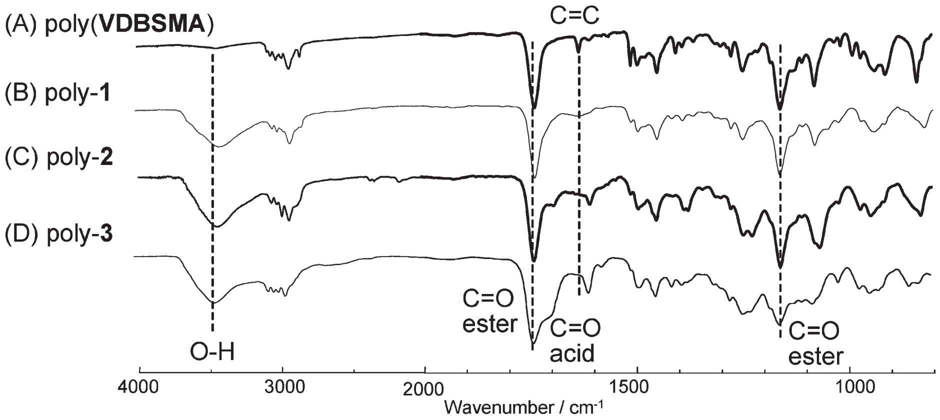


Figure 5. FT-IR spectra of poly(**VDBSMA**) (run 1 in Table 3) (A), poly-**1** (B), poly-**2** (C), and poly-**3** (D) (KBr pellet).

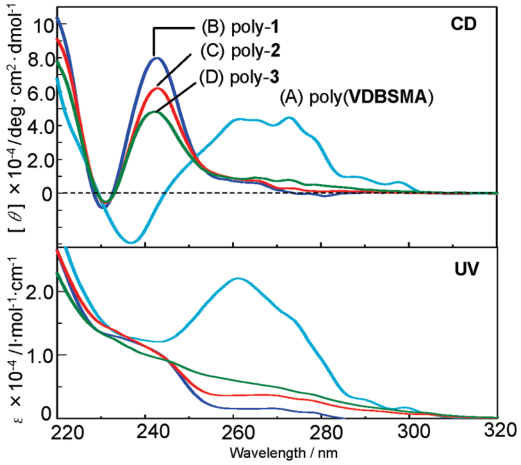


Figure 7. CD (top panel) and UV (bottom panel) spectra of poly(**VDBSMA**) (run 1 in Table 3) in THF (A), poly-**1** in THF−MeOH (1/1, v/v) (B), poly-**2** in THF−MeOH (1/1, v/v) (C), and poly-**3** in THF−MeOH (1/1, v/v) (D).

Table 4. Solubilities of Poly(VDBSMA), Poly-1, Poly-2, and Poly-3[a]

	polymer			
solvent	poly(**VDBSMA**)	poly-**1**	poly-**2**	poly-**3**
$CHCl_3$	*S*	*I*	*I*	*I*
THF	*S*	*S*	*I*	*I*
$CHCl_3$−pyridine[b]	*I*	*S*	*I*	*I*
THF-MeOH[c]	*I*	*S*	*S*	*S*
pyridine	*I*	*S*	*S*	*S*
DMF	*I*	*S*	*S*	*S*
DMSO	*I*	*S*	*S*	*S*
MeOH	*I*	*I*	*S*	*S*
H_2O	*I*	*I*	*I*	*I*

[a] Polymer 1 mg, solvent 0.1 mL. *S* = soluble, *I* = insoluble. [b] 5/1, v/v. [c] 1/1, v/v.

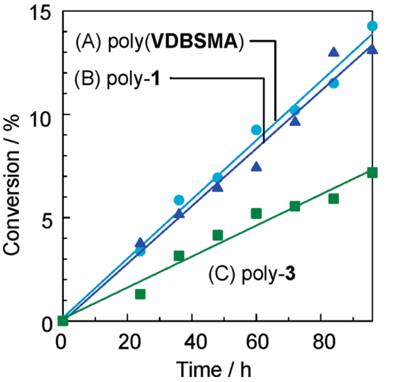


Figure 8. First-order plots for methanolysis reactions of poly(**VDBSMA**) (run 1 in Table 3) (A), poly-**1** (B), and poly-**3** (C) in a mixture of $CDCl_3$, CD_3OD, and C_5D_5N (2/1/1, v/v/v) at 60 °C.

Table 5. First-Order Rate Constants and Half-Life Periods in Methanolysis Reaction of Polymethacrylates[a]

run	polymer[b]	k/h^{-1}	half-life period/min
1	poly(**VDBSMA**)[c]	0.15	20 700
2	poly-**1**	0.14	21 540
3	poly-**3**	0.077	39 120

[a] Solvolysis reactions were carried out in a mixture of $CDCl_3$, CD_3OD, and C_5D_5N (1/1/2, v/v/v) at 60 °C. [b] [Monomeric unit]$_o$ = 0.0195 M. [c] Run 1 in Table 3.

were successfully prepared by polymer reaction of poly(**VDBSMA**). It is difficult to discuss at this point whether or not the differences in CD intensity and optical activity of the three polymers may mean differences in the degree of single handedness because their chemical structures are different.

Solubilities of Poly(VDBSMA), Poly-1, Poly-2, and Poly-3. Solubilities of the four polymers in various solvents are summarized in Table 4. Although poly(**VDBSMA**) (run 1 from Table 3) was soluble only in $CHCl_3$ and in THF among the tested solvents, poly-**1**, poly-**2**, and poly-**3** derived from poly(**VDBSMA**) were soluble in more polar solvents. This suggests that the three polymers effectively interact with solvent molecules through hydrogen bonding. Thus, introduction of protonic groups to the side chain of helical polymethacrylate was demonstrated to expand the applicability of polymer for polar solvent systems.

Stabilities of Poly(VDBSMA), Poly-1, and Poly-3. The introduced protonic groups of the side-chain might possibly induce decomposition of the ester linkage of the polymers. In order to address this point, stabilities of poly(**VDBSMA**) (run 1 in Table 3), poly-**1**, and poly-**3** were tested by monitoring methanolysis reactions of these polymers carried out in a mixture of $CDCl_3$, CD_3OD, and C_5D_5N (2/1/1, v/v/v) at 60 °C in an NMR sample tube by ^{1}H NMR spectra (Figure 8, Table 5). From the plots shown in Figure 8, the first-order decomposition rate constants and half-life periods for the three polymers were estimated and summarized in Table 5. The first-order decomposition rate constants and half-life periods of poly(**VDBSMA**) and poly-**1** were close, indicating that these two polymers have similar stabilities. The side-chain −OH groups of poly-**1** do not seem to accelerate decomposition under the reaction conditions employed in this work. The rate constant of decomposition of poly-**3** was approximately half that of poly(**VDBSMA**), meaning that poly-**3** is twice more stable than poly(**VDBSMA**). This is probably because the triarylmethyl cation originating from the side-chain group of poly-**3**, which may be an intermediate species of decomposition, is destabilized by the electron-withdrawing effect of the −COOH group. This effect is considered to predominate over acidic catalysis effects of the −COOH group. These results clearly indicate that the polymethacrylates having protonic side-chain groups have sufficient stability for applications.

Radical Polymerization of Poly(VDBSMA). Reactivity of poly(**VDBSMA**) was investigated from the view of an intermolecular (interhelix) reaction. Poly(**VDBSMA**) (run 1 in Table 3) was subjected to free-radical polymerization reaction with AIBN (Table 6). Here, the polymer may be recognized as a polyfunctional, helical macromonomer. At [AIBN]$_o$ = 0.004 M (run 2 in Table 6), consumption of the side-chain vinyl group was incomplete and the product was mostly insoluble in THF, indicating that a gel was formed. However, at [AIBN]$_o$ = 0.02 (run 1 in Table 6), the side-chain vinyl group was almost quantitatively consumed and the product was mostly soluble in THF. From the comparison of absolute molecular weights (M_w's determined by MALLS) of the source poly(**VDBSMA**) (10 580) and the poly[poly(**VDBSMA**)] (325 200), the poly[poly(**VDBSMA**)] is considered to consist of approximately 30 helical chains. In addition, the much smaller Mark−Houwink−Sakurada constant (0.19) of the poly[poly(**VDBSMA**)] than that of the source poly(**VDBSMA**) (0.76) suggests that the constituent poly(**VDBSMA**) chains in the poly[poly(**VDBSMA**)] have a relatively random arrangement and the poly[poly(**VDBSMA**)] has a rather globule-like shape.[19,20] The poly[poly(**VDBSMA**)] indicated intense CD ($[\theta]_{245}$ +32000 deg cm^2 dmol^{-1} in THF). This indicates that single-handed helicity of poly(**VDBSMA**) is maintained in the course of radical polymerization in the formation an optically active macromolecular adduct.

Table 6. Radical Polymerization of Poly(VDBSMA) Using AIBN in THF at 60 °C for 39 h[a]

				THF-insol. part	THF-soluble part			
run	[poly(**VDBSMA**)]$_o$ (M)	[AIBN]$_o$ (M)	convn[b] (%)	yield(%)	yield (%)	M_w[c]	M_w/M_n[c]	Mark−Houwink−Sakurada constant (a)[d]
1	0.01[e]	0.02	> 99	13	87	325 200	1.49	0.19
2	0.01[e]	0.004	49	78	22	n.d.	n.d.	n.d.

[a] Poly(**VDBSMA**) (run 1 in Table 3) 50 mg. M_w = 10 580, M_w/M_n = 1.05 as determined by SEC with multiangle light-scattering (MALLS) detection. Mark−Houwink−Sakurada constant (*a*) 0.76 as determined by SEC equipped with online viscometer and RI and right-angle light-scattering detectors. [b] Conversion ratio of the side-chain vinyl group estimated by FT-IR. [c] Determined by SEC with MALLS detection. [d] Determined by SEC equipped with online viscometer and RI and right-angle light-scattering detectors. [e] Monomeric unit.

Conclusions

Single-handed helical, optically active poly(**VDBSMA**) bearing reactive vinyl side groups was obtained by asymmetric anionic polymerization of the corresponding monomer. Simple chemical modifications of the side-chain vinyl group of this polymer afforded poly-**1**, poly-**2**, and poly-**3** having protonic side-chain groups without seriously deteriorating the helical structure. In this way, without laborious monomer syntheses and protection/deprotection chemistry, single-handed helical polymethacrylates with protonic side-chain groups were readily obtained. In addition, radical polymerization of poly(**VDBSMA**) as a macromonomer afforded a novel optically active material consisting of helical chains whose helicity was maintained through the reaction.

The synthetic concept introduced in this work is not limited to the three protonic groups described here as representative examples but can be extended to a wide range of functional, protonic groups. Also, the concept is applicable for a wide variety of helical (meth)acrylic and related polymers, and facile introduction of protonic side-chain groups will greatly widen the scope of application of helical polymers.

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