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ORIGINAL PAPER

Asymmetric anionic polymerization of 7-cyano-7-phenyl-1,4-benzoquinone methide

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Abstract Asymmetric anionic polymerizations of a prochiral monomer, 7-cyano-7-phenyl-1,4-benzoquinone methide (**3**), using chiral initiators were performed under various conditions, and optically active polymers having configurational chirality in the main chain were obtained though their specific rotation values are quite small. The optically active polymer with a negative specific rotation value of −4.4° was obtained by polymerization of **3** with a lithium isopropylphenoxide (^{i}PrPhOLi)/(−)-sparteine ((−)-Sp) in a mixture solution of dichloromethane/toluene ratio of 30/70 (in vol%) at −40 °C. Stereostructures of 1-mer, 2-mer, and oligomers obtained by asymmetric anionic oligomerization of **3** with ^{i}PrPhOLi/(−)-Sp were examined in detail. It was found that the stereoselectivity turned out to be the opposite between the initiation reaction and the propagation one.

Keywords Asymmetric anionic polymerization · Optically active polymer · Chiral initiator · Stereocontrol · Quinone methide · Optical resolution

Introduction

Asymmetric polymerization, classified in asymmetric synthesis polymerization (asymmetric chirogenic polymerization), helix-sense-selective polymerization, and enantiomer-selective polymerization, is one of promising methods to introduce the chirality into the polymer chain and to synthesize optically active polymers. There

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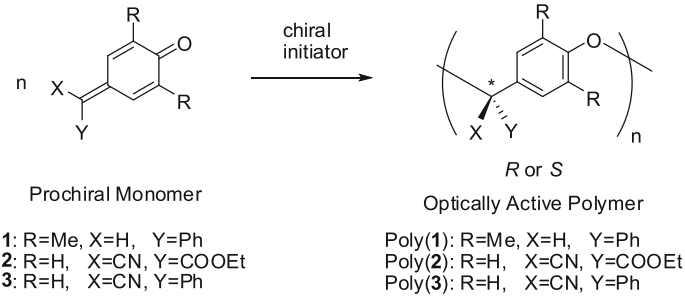
are a large number of reports about the asymmetric polymerizations based on vinyl monomers, diene monomers, cyclic olefin monomers, aldehyde monomers, isocyanate monomers and so on [1–7].

Unsubstituted 1,4-benzoquinone methide (QM) is unstable and it reacts spontaneously to afford a carbon–carbon bonded dimer or carbon–oxygen bonded oligomers at room temperature [8, 9]. However, introduction of electron-accepting and/or electron-donating substituents on the exomethylene carbon of the QM reduces its reactivity, leading to isolable monomers as crystals at room temperature: e.g., 7,7-dicyano-1,4-benzoquinone methide [10], 7-(alkoxycarbonyl)-7-cyano-1,4-benzoquinone methides [11], 7,7-bis(alkoxycarbonyl)-1,4-benzoquinone methides [12], 7,7-diphenyl-1,4-benzoquinone methide [13], 4-(1′,3′-dithiolan-2′-ylidene)-2,5-cyclohexanedien-1-one [14], and 2,6-dimethyl-7-phenyl-1,4-benzoquinone methide [15]. The polymerization behaviors of these isolable QMs have been investigated, and it was found that the radical and anionic polymerizations of QMs take place between the substituted exomethylene carbon atom and exocarbonyl oxygen with formation of stable aromatic structure to afford the polymers, poly(oxy-1,4-phenylene-substituted methylene)s [11, 12, 15, 16]. As QMs having two different substituents on the exomethylene carbon are regarded as prochiral monomers, many asymmetric carbons might be generated in the main chain of the polymers through the polymerization process. Here, if the configuration of the newly created chiral center is controlled to either *R* or *S* through the polymerization process, it is expected that novel optically active polymers would be obtained. Previously, we carried out the asymmetric anionic polymerizations of 7-phenyl-2,6-dimethyl-1,4-benzoquinone methide (**1**) [17] and 7-cyano-7-ethoxycarbonyl-1,4-benzoquinone methide (**2**) [18, 19] using various chiral anionic initiators and obtained optically active polymers having configurational chirality in the main chain (Scheme 1).

When the chiral initiator with (−)-2,2′-isopropylidenebis(4-phenyl-2-oxazoline) ((−)-PhBox) as a chiral ligand was used for the asymmetric anionic polymerizations of **1** and **2**, **2** yielded its polymer with a large positive specific optical rotation value, but **1** did its polymer with a very small specific rotation value. The (−)-PhBox was a less effective chiral ligand for the asymmetric polymerization of **1** in comparison with (−)-sparteine ((−)-Sp). The relationships of specific rotation values of



Scheme 1 Preparation of optically active polymers by polymerizations of prochiral monomers (**1–3**) with chiral initiators

polymers with the substituents on the exomethylene carbon of the monomers and with chiral ligands of initiators are still unclear.

In this study, we investigated asymmetric anionic polymerizations of 7-cyano-7-phenyl-1,4-benzoquinone methide (**3**) using chiral initiators, specific optical rotation values of the obtained polymers, and stereoselectivity of oligomers to obtain the information related to molecular structures of monomers and ligands leading to high stereocontrol in the polymer derived from a prochiral monomer.

Experimental

Measurements

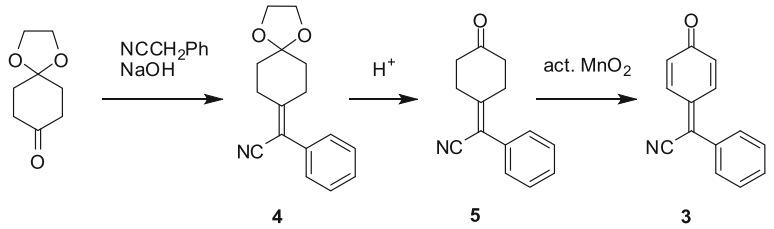
Melting points were measured with a Yanaco MP-S3 micro melting point apparatus. Infrared (IR) spectra were recorded on a JASCO IR-700 spectrometer. ^{1}H and ^{13}C NMR spectra were measured with a JEOL JNM-EX270 (270 MHz for ^{1}H) spectrometer in chloroform-*d* ($CDCl_3$) with tetramethylsilane as an internal standard. The specific rotation was obtained with a JASCO P-1030 polarimeter. The molecular weights of polymers were determined by gel permeation chromatography (GPC) on a JASCO PU-1580 chromatograph equipped with a JASCO RI-930 refractive index detector and two TOSOH TSKgel MultiporeH_{XL}-M columns using tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 mL/min and polystyrene standards for calibration at room temperature. The relationship of molecular weight with specific rotation of polymer was examined by GPC on a Shodex System-21 equipped with a Shodex UV-41 detector and a JASCO OR-990 polarimetric detector using two columns, Shodex KF-803 and KF-806L, connected in series (eluent: THF, temperature: 40 °C). Optical resolution of oligomers was performed on a JASCO PU-1580 chromatograph equipped with a UV (JASCO MD-910) and circular dichroism (JASCO CD-1595) detector using chiral column, Daicel Chiralpak AD, at room temperature. A mixture solution of hexane/ethanol (90/10 in vol%) was used as an eluent at a flow rate of 0.5 mL/min.

Materials

Toluene was purified in the usual manner and distilled over sodium metal. THF and dichloromethane were distilled over sodium metal and calcium hydride, respectively. 4-Isopropylphenol (Tokyo Kasei Kogyo) was recrystallized from hexane. (−)-Sp (Tokyo Kasei Kogyo) was dried over calcium hydride overnight, and then distilled under reduced pressure. Other chiral ligands, (*S*)-(−)-2,2′-isopropylidenebis(4-phenyl-2-oxazoline) ((−)-PhBox) (Aldrich), (*S,S*)-(+)-2,3-dimethoxy-1,4-bis(dimethylamino) butane ((+)-DDB) (Tokyo Kasei Kogyo), and (*R*)-(+)-2-(methoxymethyl)pyrrolidine ((+)-MMP) (Merk), were used without further purification.

Monomer synthesis

7-Cyano-7-phenyl-1,4-benzoquinone methide (**3**) was synthesized according to the method reported previously (Scheme 2) [20].



Scheme 2 Preparation route of **3**

*4-[1′-Cyano-1′-(phenyl)methylene]-1,4-dioxaspiro[4.5]decane (**4**)*

1,4-Cyclohexanedione monoethylene ketal (10 g, 64 mmol) and benzyl cyanide (7.5 g, 64 mmol) were dissolved in 120 mL of ethanol. To the resulting solution was added 7.78 g (76 mmol) of 40% sodium hydroxide aqueous solution. After stirring for 3 days at room temperature, 200 mL of water was added to the reaction mixture, and then extracted three times with 200 mL of diethyl ether. The extracts were combined and then dried over anhydrous magnesium sulfate. It was placed under reduced pressure to remove diethyl ether to give viscous oil, which was dissolved in a small amount of chloroform. The resulting solution was passed through a silica gel column by using chloroform as an eluent. The second elution band was collected and placed under reduced pressure to remove solvent to obtain colorless viscous oil, which was recrystallized from a mixture solution of hexane and dichloromethane to give **4** as white needles. Yield: 9.0 g (55.0%). mp: 64 °C; IR (KBr, cm^{-1}): ν_{CH} 3018–2990, ν_{CH} 2960–2860, ν_{CN} 2202, $\nu_{C=C}$ 1624, $\nu_{C=C}$ 1446. ^{1}H NMR ($CDCl_3$, ppm): δ 7.43–7.26 (m, 5H), 3.99 (s, 4H), 2.87 (t, $J = 6.6$ Hz, 2H), 2.50 (t, $J = 6.6$ Hz, 2H), 1.89 (t, $J = 6.6$ Hz, 2H), 1.70 (t, $J = 6.6$ Hz, 2H). ^{13}C NMR ($CDCl_3$, ppm): δ 158.7 (>C=), 133.6 (>C<), 129.2 (CH), 128.7 (CH), 128.4 (CH), 118.0 (>C=), 109.0 (CN), 107.1 (>C<), 64.6 (CH_2), 35.1 (CH_2), 27.9 (CH_2). Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27%; H, 6.72%; N, 5.48%; O, 12.53%. Found: C, 75.33%; H, 6.84%; N, 5.27%, O, 12.56%.

*4-[1′-Cyano-1′-(phenyl)methylene]cyclohexanone (**5**)*

4 (5.02 g, 19.6 mmol) was placed in a 300 mL of flask, to which was added 126 mL of a 2% aqueous sulfuric acid solution, and refluxed for 1.5 h. After cooling, the reaction mixture was extracted three times with 400 mL of chloroform. The combined organic fractions were washed twice with 100 mL of water, dried over anhydrous magnesium sulfate, filtered, and the solvent of the filtrate was evaporated under reduced pressure. The crude product was purified by silica-gel column chromatography using chloroform as an eluent to give **5** as colorless oil. Yield 3.43 g (82.8%). IR (KBr, cm^{-1}): ν_{CH} 3064, 2970, 2908, ν_{CN} 2210, $\nu_{C=C}$ 1717, $\nu_{C=C}$ 1443. ^{1}H NMR ($CDCl_3$, ppm): δ 7.26–7.43 (m, 5H), 3.11 (t, $J = 6.92$ Hz, 2H), 2.77 (t, $J = 6.92$ Hz, 2H), 2.63 (t, $J = 6.92$ Hz, 2H), 2.43 (t, $J = 6.92$ Hz, 2H). ^{13}C NMR ($CDCl_3$, ppm): δ 208.6 (C=O), 155.1 (>C=), 133.0 (>C<), 128.9 (CH), 128.9 (CH), 117.7 (CN), 111.5 (>C=), 38.6 (CH_2), 38.5 (CH_2), 31.1 (CH_2), 27.8 (CH_2).

Anal. Calcd for $C_{14}H_{13}NO$: C, 79.59%; H, 6.21%; N, 6.63%; O, 7.59%. Found: C, 79.36%; H, 6.34%; N, 6.64%; O, 7.66%.

*7-Cyano-7-phenyl-1,4-benzoquinone methide (**3**)*

5 (0.5 g, 2.37 mmol) was dissolved in 250 mL of chloroform, and then into the resulting solution were added 10 g of activated manganese dioxide. The mixture was refluxed with stirring for 1 h, cooled, and then filtered. The orange filtrate was placed under reduced pressure to remove chloroform to give an orange solid residue, which was dissolved in a small amount of chloroform. The resulting solution was passed through a silica gel column by using chloroform as an eluent. The orange elution band was collected and placed under reduced pressure to remove solvent to obtain an orange solid, which was recrystallized from a mixture solution of hexane and dichloromethane to give **3** as orange needles. Yield: 0.28 g (57.0%). mp: 113 °C; IR (KBr, cm^{-1}): ν_{CH} 3064, ν_{CN} 2204, $\nu_{C=O}$ 1631, $\nu_{C=C}$ 1515. ^{1}H NMR ($CDCl_3$, ppm): δ 7.85 (d, $J = 2.64$ Hz, 1H), 7.51–7.57 (m, 5H), 7.47 (d, $J = 2.64$ Hz, 1H), 6.62 (d, $J = 1.65$ Hz, 1H), 6.49 (d, $J = 1.65$ Hz, 1H). ^{13}C NMR ($CDCl_3$, ppm): δ 186.4 (C=O), 139.6 (>C=), 136.9 (CH), 134.4 (CH), 131.8 (CH), 131.3 (CH), 131.2 (CH), 131.1 (CH), 130.4 (CH), 129.3 (CH), 123.8 (>C=), 117.1 (CN). Anal. Calcd for $C_{14}H_9NO$: C, 81.14%; H, 4.39%; N, 6.76%; O, 7.71%. Found: C, 80.83%; H, 4.52%; N, 6.72%; O, 7.93%.

Polymerization procedure

Asymmetric anionic polymerization

Asymmetric anionic polymerization was carried out in a glass ampoule equipped with a three-way stopcock. A given amount of **3** was placed in the ampoule, dried under reduced pressure, and then filled with nitrogen. Into it was added toluene, dichloromethane, or a mixture solution of dichloromethane/toluene (30/70 in vol%) by a syringe, and the resulting solution was cooled to −40 °C. The polymerization was initiated by adding the initiator solution, which was prepared by mixing lithium 4-isopropylphenoxide (^{i}PrPhOLi) (1.0 equiv.) and a chiral ligand (1.1 equiv.) such as (−)-Sp, (−)-PhBox, (+)-DDB, and (+)-MMP in dry toluene at room temperature just before use, and the reaction mixture was stirred at −40 °C for a given time. The polymerization was terminated by adding an excess amount of dry acetic anhydride. The resulting solution was poured into a large excess amount of hexane, and the deposited polymer was collected by centrifugation, and dried in vacuo.

Oligomerization and isolation of 1-mer and 2-mer

Asymmetric anionic oligomerizations of **3** (0.23 mol/L) with a ^{i}PrPhOLi/(−)-Sp initiator were carried out at [monomer]/[initiator] ratio of 2 in a mixture solution of dichloromethane/toluene (30/70 in vol%) at −40 °C for 12 h. The oligomerization was terminated by adding an excess amount of dry acetic anhydride. The reaction mixture was poured into 10 mL of chloroform, and the resulting solution was

washed with water, 1 N hydrochloric acid, saturated sodium bicarbonate aqueous solution, and saturated sodium chloride aqueous solution, and then dried over anhydrous magnesium sulfate. The filtrate was added to a large excess amount of hexane, and the product was separated in two parts, hexane-soluble part and hexane-insoluble one. The 1-mer and 2-mer were obtained from hexane-soluble part and hexane-insoluble one, respectively, by column chromatography treatment [SiO_2, hexane/diethyl ether (3/1 v/v)].

1-Mer

41.6 mg (14.8% yield). IR (NaCl, cm^{-1}): ν_{CH} 3026, $\nu_{C=O}$ 1763, $\nu_{C=C}$ 1505. ^{1}H NMR ($CDCl_3$, ppm): δ 7.57 (d, $J = 8.58$ Hz, 2H), 7.37–7.58 (m, 5H), 7.13 (d, $J = 8.91$ Hz, 2H), 7.05 (d, $J = 8.91$ Hz, 2H), 6.83 (d, $J = 8.91$ Hz, 2H), 2.81 (sept, $J = 6.93$ Hz, 1H), 2.29 (s, 3H), 1.18 (d, $J = 6.93$ Hz, 6H). ^{13}C NMR ($CDCl_3$, ppm): δ 169.0 (C=O), 152.4 (Ar, quaternary), 151.1 (Ar, quaternary), 144.2 (Ar, quaternary), 138.5 (Ar, quaternary), 136.5 (Ar, quaternary), 129.3 (Ar, CH), 128.9 (Ar, CH), 127.9 (Ar, CH), 127.1 (Ar, CH), 126.6 (Ar, CH), 121.9 (Ar, CH), 119.6 (CN), 118.2 (Ar, CH), 81.3 (>C<, quatrenary), 33.3 (CH), 23.9 (CH_3), 21.1 (CH_3).

2-Mer

43.6 mg (15.5% yield). IR (NaCl, cm^{-1}):ν_{C-H} 3024, 2966, $\nu_{C=O}$ 1712, $\nu_{C=C}$ 1503. ^{1}H NMR ($CDCl_3$, ppm): δ 7.48 (d, $J = 8.58$ Hz, 2H), 7.41–7.49 (m, 10H), 7.31 (d, $J = 8.58$ Hz, 2H), 7.07 (d, $J = 8.90$ Hz, 2H), 6.95 (d, $J = 8.58$ Hz, 2H), 6.88 (d, $J = 8.58$ Hz, 2H), 6.70 (d, $J = 8.58$ Hz, 2H), 2.73 (sept, $J = 6.93$ Hz, 1H), 2.23 (s, 3H), 1.10 (d, $J = 6.93$ Hz, 6H). ^{13}C NMR ($CDCl_3$, ppm): δ 169.0 (C=O), 155.0 (Ar, quaternary), 152.4 (Ar, quaternary), 151.3 (Ar, quaternary), 144.2 (Ar, quaternary), 138.5 (Ar, quaternary), 137.8 (Ar, quaternary), 135.9 (Ar, quaternary), 129.6 (Ar, CH), 129.1 (Ar, CH), 128.8 (Ar, CH), 128.0 (Ar, CH), 127.8 (Ar, CH), 126.5 (Ar, CH), 122.1 (Ar, CH), 119.5 (CN), 118.2 (Ar, CH), 117.8 (Ar, CH), 81.4 (>C<, quatrenary), 33.3 (CH), 24.0 (CH_3), 21.1 (CH_3).

Results and discussion

Asymmetric anionic polymerization of **3** with a ^{i}PrPhOLi/(−)-Sp initiator

Previously, we carried out asymmetric anionic polymerization of **1** with the ^{i}PrPhOLi/(−)-Sp initiator in a mixture solution of dichloromethane/toluene (30/70 in vol%), and we obtained optically active polymer with a negative specific rotation value ($[\alpha]_{435} = -5.9°$) though it was small [16, 18]. This indicates that an optically active polymer can be obtained from a prochiral quinone methide monomer by asymmetric anionic polymerization, that is, that the configuration of stereocenters created in the main chain is biased to either *R* or *S* through the asymmetric anionic polymerization process. Therefore, we carried out the asymmetric anionic polymerization of **3** with the ^{i}PrPhOLi/(−)-Sp initiator in three solvents such as

toluene, dichloromethane, and a mixture solution of dichloromethane/toluene (30/70 in vol%) at −40 °C at a [**3**]/[initiator] ratio of 10 to investigate the effect of solvent polarity on the specific optical rotation of the resulting polymers. The results are summarized in Table 1.

Hexane-insoluble polymers were obtained in a moderate yield in a polar solvent such as dichloromethane and in high yields in less polar solvents such as toluene and a mixture solution of dichloromethane/toluene. The molecular weights of resulting polymers were in the range 2200–2500. These polymerizations afforded optically active polymers (poly(**3**)) with a specific rotation value ($[\alpha]_{435}$) of −3.8° in toluene, −4.4° in a mixture solution of dichloromethane/toluene (30/70 in vol%), and −0.4° in dichloromethane, respectively, indicating that stereocontrol of newly created chiral center is not performed well in a more polar solvent.

To investigate the relationship of the specific rotation of poly(**3**) with molecular weights, asymmetric anionic polymerizations with the ^{i}PrPhOLi/(−)-Sp initiator were carried out at various [monomer]/[initiator] ratios. The results are summarized in Table 2.

Table 1 Asymmetric anionic polymerizations of **3** with ^{i}PrPhOLi/(−)-Sp in various solvents at −40 °C

Run	[**3**]/[initiator]	Solvent (mL)	Time (h)	Yield[a] (%)	M_n^b	M_w/M_n^b	$[\alpha]_{435}^c$
1	10	Toluene 2.15	96	88.3	2200	1.4	−3.8°
2	10	CH_2Cl_2/toluene (30/70 in vol%) 2.15	96	83.5	2200	1.3	−4.4°
3	10	CH_2Cl_2 2.15	96	66.6	2500	1.4	−0.4°

Conditions: [**3**] = 0.23 mol/L

[a] Hexane-insoluble part

[b] Determined by GPC as polystyrene standard

[c] In $CHCl_3$

Table 2 Asymmetric anionic polymerizations of **3** with ^{i}PrPhOLi/(−)-Sp at various feed ratios at −40 °C

Run	[**3**]/[initiator]	Solvent (mL)	Time (h)	Yield[a] (%)	M_n^b	M_w/M_n^b	$[\alpha]_{435}^c$
1	5	CH_2Cl_2/toluene (30/70 in vol%), 2.15	96	64.0	1900	1.2	−3.9°
2	10	CH_2Cl_2/toluene (30/70 in vol%), 2.15	96	83.5	2200	1.3	−4.4°
3	20	CH_2Cl_2/toluene (30/70 in vol%), 2.15	96	86.4	3500	1.4	−4.2°
4	30	CH_2Cl_2/toluene (30/70 in vol%), 2.15	96	87.3	3700	1.5	−3.6°

Conditions: [**3**] = 0.23 mol/L

[a] Hexane-insoluble part

[b] Determined by GPC as polystyrene standard

[c] In $CHCl_3$

Polymers were obtained as molecular weights in the range 1900–3700 at different [**3**]/[initiator] ratios. On the polymerization at a constant monomer concentration of 0.23 mol/L, polymers obtained with the ^{i}PrPhOLi/(−)-Sp initiator have almost constant specific rotation values ($[\alpha]_{435}$) of around −4° regardless of their molecular weights, suggesting that the stereocontrol is conducted in the same extent through whole polymer. Figure 1 shows the GPC curve of poly(**3**) obtained by asymmetric anionic polymerization with the ^{i}PrPhOLi/(−)-Sp initiator (Table 2, run 2) monitored with ultraviolet (UV) (bottom chromatogram) and polarimetric (PM) detectors (top chromatogram). The PM detector demonstrated a negative peak, whose peak pattern is quite similar to corresponding UV chromatogram. This result indicates that the optical rotation of poly(**3**) obtained by asymmetric anionic polymerization do not depend upon the molecular weights, and the configurations of all asymmetric carbons in the polymer chain are controlled in almost same degree. In other words, this means that addition reactions of a propagating anion to the monomer must take place with the same stereoselectivity in every propagating step.

Unfortunately, polymers with the large specific rotation values were not obtained with the ^{i}PrPhOLi/(−)-Sp initiator. Therefore, we attempted to perform the polymerizations of **3** using other chiral initiators, ^{i}PrPhOLi/chiral ligand complex initiators, with (−)-PhBox, (+)-DDB, and (+)-MMP as chiral ligands in dichloromethane/toluene ratio of 30/70 (in vol%) at −40 °C. The results are summarized in Table 3. Polymerization proceeded homogeneously in all of three systems, and polymers were obtained as hexane-insoluble parts. Polymer yields and specific rotation values were dependent upon chiral ligands, and obtained polymers had positive or negative specific rotation values.

When (+)-MMP was used as a chiral ligand, polymer with a negative specific rotation of a relatively large value ($[\alpha]_{435} = -4.9°$) was obtained. However, the peaks assigned to (+)-MMP were observed even after repeating the dissolution–precipitation process, suggesting the presence of the (+)-MMP at the end of the polymer chain. In the case of (+)-DDB, the polymer obtained was a very low yield, and also specific rotation value of the polymer is smaller than that of the case of (−)-Sp. When the (−)-PhBox was used, the obtained polymer was a positive

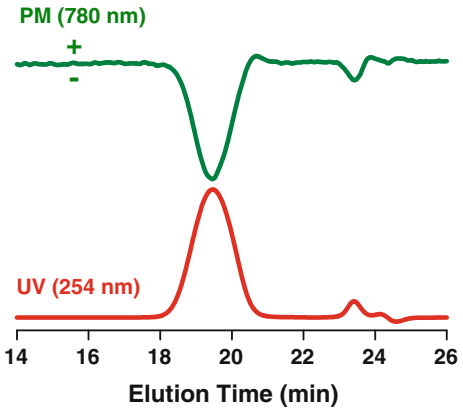


Fig. 1 GPC chart of poly(**3**) obtained with ^{i}PrPhOLi/(−)-Sp initiator (Table 2, run 2)

Table 3 Asymmetric anionic polymerization of **3** with ^{i}PrPhOLi and various chiral ligands at −40 °C

Run	[**3**]/[initiator]	Chiral ligand	Time (h)	Yield[a] (%)	M_n^b	M_w/M_n^b	$[\alpha]_{435}^c$
1	10	(−)-Sp	96	83.5	2200	1.3	−4.4°
2	10	(−)-PhBox	96	52.4	2200	1.5	+2.8°
3	10	(+)-DDB	96	7.4	2700	1.9	−0.1°
4	10	(+)-MMP	96	23.6	1700	1.1	−4.9°

Conditions: [**3**] = 0.23 mol/L. Solvent: dichloromethane/toluene (30/70 in vol%)

[a] Hexane-insoluble part

[b] Determined by GPC as polystyrene standard

[c] In $CHCl_3$

specific rotation value of +2.8°, which is contrast to the result of the asymmetric anionic polymerization of monomer **2** under the same condition, where the polymer with a positive specific optical rotation value of +90.4° was formed [17]. At present, (−)-Sp is a most effective chiral ligand to control the configurations of chiral carbons in the polymer chain on the asymmetric anionic polymerization of **3**. The relationship of the specific optical rotation of **3** with the chiral initiators is similar to that of **1** rather than **2**. It is, therefore, considered that formation of optically active polymer with a large specific rotation value by the polymerization of **2** using ^{i}PrPhOLi/(−)-PhBox initiator would originate in the ethoxycarbonyl group present in the monomer **2**.

Stereoselectivity in the initiation and propagation steps

Okamoto and co-workers [21] reported the asymmetric oligomerization and chromatographic analyses of oligomers to obtain information on the stereochemical mechanism of asymmetric polymerization of triphenylmethyl methacrylate. To investigate the extent of stereocontrol in the formation of an optically active poly(**3**), we carried out the asymmetric anionic oligomerization of **3** with the ^{i}PrPhOLi/(−)-Sp initiator at [**3**]/[initiator] ratio of 2 for 12 h, and 1-mer and 2-mer, which correspond to the products formed at the initial stage of the polymerization, were isolated and characterized. The results are summarized in Table 4.

The 1-mer showed a small positive specific rotation value and the 2-mer did a small negative one, suggesting that stereoselectivity is the opposite between the initiation reaction and the propagation one. To obtain further information on

Table 4 Asymmetric anionic oligomerization of **3** with ^{i}PrPhOLi/(−)-Sp at −40 °C

Run	[**3**]/[initiator]	Time (h)	Yield (g) (%)	$[\alpha]_{435}^a$
1	2	12	1-Mer, 41.6 (14.8)	+0.8°
			2-Mer, 43.6 (15.5)	−1.2°

Conditions: [**3**] = 0.23 mol/L. Solvent: dichloromethane/toluene (30/70 in vol%). Terminator: acetic anhydride

[a] In $CHCl_3$

stereoselectivity for the 1-mer and 2-mer, their optical resolutions were conducted with high pressure liquid chromatography (HPLC) analysis on the chiral column using hexane/ethanol (90/10 in vol%) as an eluent. The chromatograms of the optical resolution for the 1-mer obtained with the ^{i}PrPhOLi/(−)-Sp initiator are shown in Fig. 2, where top and bottom chromatograms are monitored by CD and UV detectors, respectively. In Fig. 2, the 1-mer with a positive CD sign is first eluted and followed by the 1-mer with a negative CD one, indicating that both components are enantiomers. From the peak area obtained on the UV chromatogram in Fig. 2, a ratio of the first-eluted component (1-mer with a positive CD sign)/the second-eluted one (1-mer with a negative CD sign) in the enantiomers is determined to be 51/49 in mol%. The absolute configuration of the chiral carbon in the 1-mer has not been determined yet.

Here, assuming that the first-eluted component (1-mer with a positive CD sign) has a chiral carbon of a *R*-configuration and the second-eluted one (1-mer with a negative CD sign) does a chiral carbon of a *S*-configuration, 1-mer with the *R*-configurational chirality is formed in a slight excess amount compared to 1-mer with the *S*-configurational chirality, and the enantiomeric excess (ee) is calculated to be 2% ee(*R*). This indicates that addition of a lithium 4-isopropylphenoxide anion coordinated with a (−)-Sp ligand to the monomer takes place in *Re*-face (front side) attack/*Si*-face (back side) attack ratio of 51/49%, leading to enantiomer in a *R*-configurational 1-mer/*S*-configurational 1-mer ratio of 51/49 in mol% (Scheme 3). Very small ee value indicates that stereoselectivity in the initiation reaction is quite low.

Next, as to the 2-mer, its optical resolution was conducted with HPLC analysis as well as the case of the 1-mer. The chromatograms of the optical resolution for the 2-mer obtained with the ^{i}PrPhOLi/(−)-Sp initiator are shown in Fig. 3, where four diastereomers are separated completely.

From the peak area obtained on the UV chromatogram in Fig. 3, the ratio of the first-eluted component with a positive CD sign/the second-eluted one with a negative CD sign/the third-eluted one with a positive CD sign/the fourth-eluted one

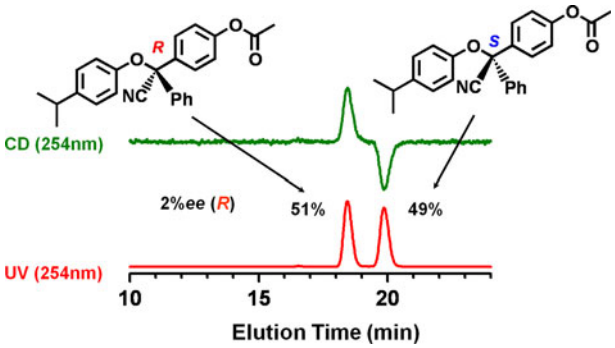
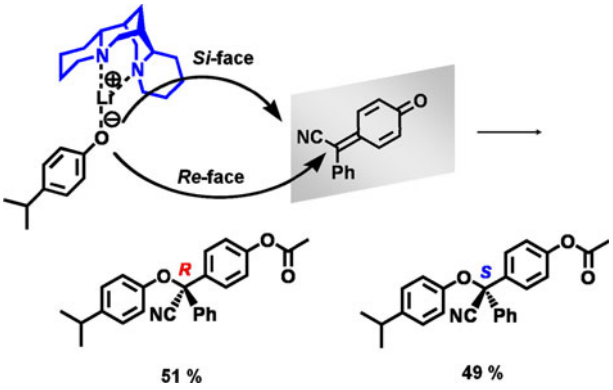


Fig. 2 HPLC chromatograms of optical resolution of the 1-mer obtained with the ^{i}PrPhOLi/(−)-Sp initiator (column: Daicel Chiralpak AD-H, eluent: hexane/ethanol = 90/10 (in vol%), flow rate: 0.5 mL/min). The *top* chromatogram was measured by CD detector (254 nm) and *bottom* by UV detector (254 nm)



Scheme 3 Stereoselectivity in the addition reaction of the ^{i}PrPhOLi/(−)-Sp initiator to monomer **3** in the initiation step

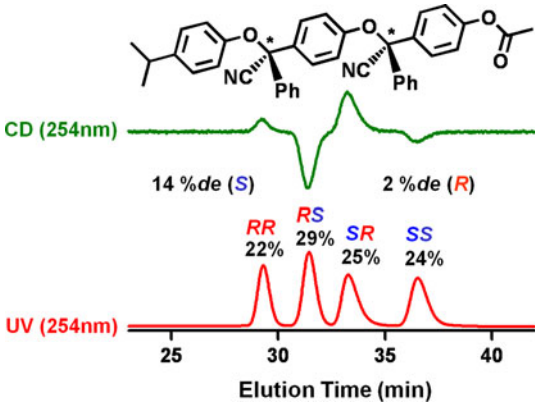


Fig. 3 HPLC chromatograms of optical resolution of the 2-mer obtained with the ^{i}PrPhOLi/(−)-Sp initiator (column: Daicel Chiralpak AD, eluent: hexane/ethanol = 90/10 (in vol%), flow rate: 0.5 mL/min). The *top* chromatogram was measured by CD detector (254 nm) and *bottom* by UV detector (254 nm)

with a negative CD sign is determined to be 22/29/25/24 in mol%. Each peak in Fig. 3 is assigned as follows. Addition of enantiomers in the 1-mer to monomer **3** might form four diastereomers in the 2-mer as shown in Chart 1.

On the basis of the result of the optical resolution of the 1-mer, total amount of the 2-mer with *(R,R)*- and *(R,S)*-configurations derived from the *R*-configurational 1-mer should be 51 mol%, and total amount of the 2-mer with *(S,R)*- and *(S,S)*-configurations derived from the *S*-configurational 1-mer should be 49 mol%, respectively. In the UV chromatogram of the 2-mer in Fig. 3, total amount of the first-eluted (22 mol%) and the second-eluted (29 mol%) components is 51 mol% and also total amount of the third-eluted (25 mol%) and the fourth-eluted (24 mol%) components is 49 mol%, respectively. Therefore, a combination of the first-eluted and second-eluted components might be assigned to the 2-mer with *(R,R)*- and *(R,S)*-configurations, respectively, and also the third-eluted and the fourth-eluted components might be assigned to the *(S,R)*- and *(S,S)*-configurations, respectively. The CD spectra of each peak for the 2-mer are shown in Fig. 4, where the first-eluted component and the fourth-eluted one are mirror images of each other

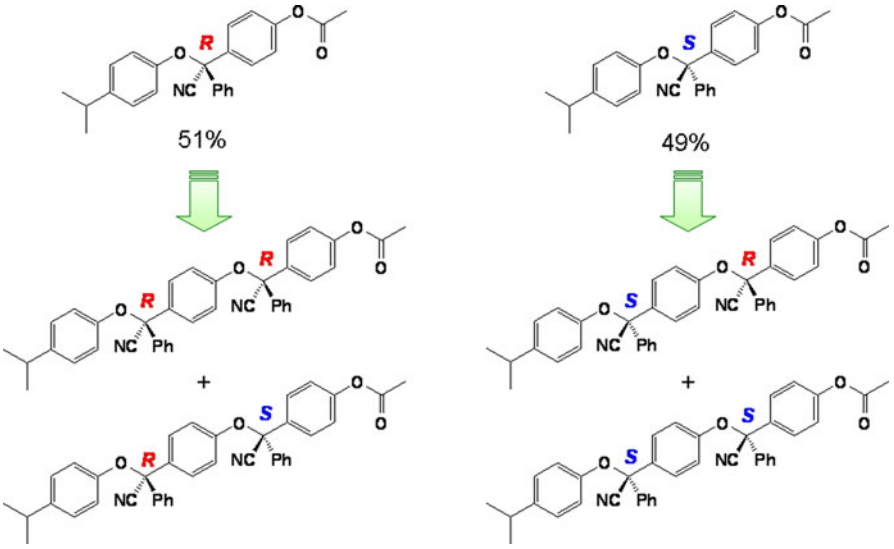


Chart 1 Diastereomers of the 2-mer

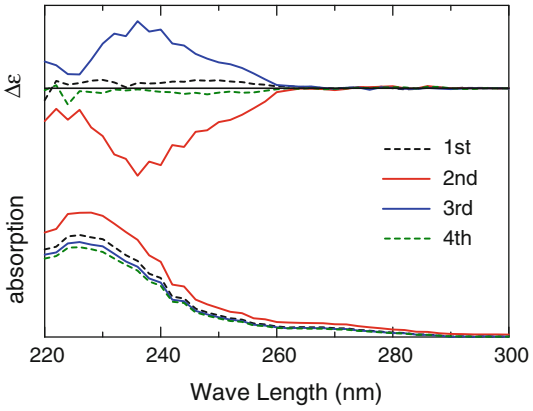


Fig. 4 CD spectra and absorption patterns of the 2-mers obtained with the ^{i}PrPhOLi/(−)-Sp initiator

and also the second-eluted component and the third-eluted one are, indicating that each combination is enantiomers.

On the assumption in optical resolution of the 1-mer that the 1-mer with a *R*-configuration is first eluted and followed by the 1-mer with a *S*-configuration, the 2-mer with a *(R,R)*-configuration might be eluted faster than that with a *(R,S)*-configuration. From these findings, the first-eluted, the second-eluted, the third-eluted, and the fourth-eluted components in the chromatograms in Fig. 3 could be assigned reasonably in turn to the 2-mers with a *(R,R)*-configuration, a *(R,S)*-one, a *(S,R)*-one, and a *(S,S)*-one, respectively. On the basis of this assignment, the 2-mer with a *(R,S)*-configuration (29 mol%) is formed in a slight excess amount than that with a *(R,R)*-configuration (22 mol%) from a 1-mer with a *R*-configuration, and the

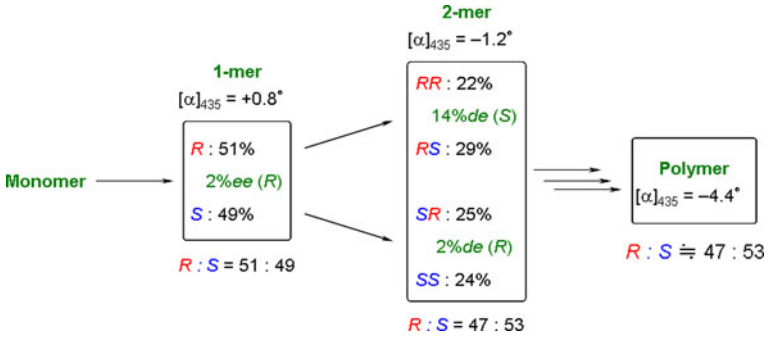


Chart 2 Stereoselectivity on initiation and propagation reactions with the ^{i}PrPhOLi/(−)-Sp initiator

diastereomeric excess (de) is calculated to be 14% de(*RS/RR*), and also 2-mer with a *(S,R)*-configuration (25 mol%) is formed in a slight excess amount than that with a *(S,S)*-configuration (24 mol%) from the 1-mer with a *S*-configuration, and the de is calculated to be 2% de(*SR/SS*), respectively. This indicates that stereoselectivity on the propagation reaction to 2-mer by addition reaction of a 1-mer anion to a monomer is low. Addition reaction of a 1-mer anion to a monomer might take place to form a 2-mer with an excessive *S*-configurational chiral carbon (29 + 24 mol% = 53 mol%) compared with the *R*-configurational one (22 + 25 mol% = 47 mol%). Here, the propagation reaction to 3-mer, 4-mer, 5-mer, and oligomer, and polymer might proceed in same extent of stereoselectivity like as the propagation reaction to the 2-mer, absolute configuration of chiral carbon in the polymer chain is calculated to be *R*:*S* = 47:53. Stereoselectivity on the initiation and propagation reactions in the polymerization of **3** with the ^{i}PrPhOLi/(−)-Sp initiator is summarized in Chart 2. In the case of the ^{i}PrPhOLi/(−)-Sp initiator, the stereoselectivity is low on both initiation reaction and propagation reaction, that is, stereocenters generated in the resulting polymer are not highly stereocontrolled.

Conclusions

Asymmetric anionic polymerizations of **3** using chiral anionic initiator were examined under various conditions. Asymmetric anionic polymerization of **3** using chiral initiator with (−)-Sp among chiral initiators to be investigated showed the best results although the specific rotation value of the polymer obtained was quite small. Stereostructures of 1-mer, 2-mer, and oligomers obtained by asymmetric anionic oligomerization of **3** with ^{i}PrPhOLi/(−)-Sp were examined in detail, and it was found that the stereoselectivity turned out to be the opposite between the initiation reaction and the propagation one. Asymmetric anionic polymerization behavior of **3** was very similar to that of **1** rather than **2**. It is concluded that the presence of the ethoxycarbonyl group in the monomer **2** would lead to the formation of optically active polymer with a large specific rotation value.

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