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ARTICLE

Stereocontrol of Optically Active Polymer by Asymmetric Anionic Polymerization of 7-Cyano-7-ethoxycarbonyl-1,4-benzoquinone Methide

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ABSTRACT: Asymmetric anionic polymerization of a prochiral quinone methide monomer, 7-cyano-7-ethoxycarbonyl-1,4-benzoquinone methide (**1**), was examined using two chiral anionic initiators, lithium 4-isopropylphenoxide (^{i}PrPhOLi)/(−)-sparteine((−)-Sp) and ^{i}PrPhOLi/(S)-(−)-2,2′-isopropylidenebis(4-phenyl-2-oxazoline) ((−)-PhBox) initiators, in a mixture solution of dichloromethane/toluene (30/70 in vol %), and optical activities of the resulting polymers and oligomers (1-mer and 2-mer) were investigated in detail. On asymmetric anionic polymerization of **1** with ^{i}PrPhOLi/(−)-Sp initiator, stereoselectivity was quite low on both initiation and propagation reactions, while in the case of ^{i}PrPhOLi/(−)-PhBox initiator, stereoselectivity was quite low on the initiation reaction, but the propagation reaction proceeded stereoselectively, resulting in an optically active polymer of **1** (poly(**1**)) with a large positive specific rotation.

Introduction

Naturally occurring polymers such as proteins, polysaccharides, nucleic acids, and so on have many optically active centers and functional groups, and some of them show the characteristic functionalities such as molecular recognition ability and catalytic activity because of controlled higher-order structure. Until now, an enormous number of functional polymers have been synthesized and have contributed to the development of our society. However, synthetic polymers with the same functionalities as naturally occurring polymers have not been reported yet. To construct the functional polymers that will be as effective as naturally occurring polymers, for example, synthesis of optically active polymers, is one of the most interest topics and of importance. Asymmetric polymerization, classified in asymmetric synthesis polymerization (asymmetric chirogenic polymerization), helix-sense-selective polymerization, and enantiomer-selective polymerization, is one of the promising methods to introduce the chirality into the polymer chain and to synthesize optically active polymers. There 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]

Unsubstituted 1,4-benzoquinone methide (QM) is an unstable compound at room temperature, and it reacted spontaneously to produce a dimer and/or oligomers.[2] However, substitution of hydrogen atoms on an exomethylene carbon of the QM with electron-accepting substituents and/or electron-donating ones reduces their reactivities, leading to isolable monomers as crystals at room temperature: for example, 7,7-dicyano-1,4-benzoquinone methide,[3] 7-(alkoxycarbonyl)-7-cyano-1,4-benzoquinone methides,[4] 7,7-bis-(alkoxycarbonyl)-1,4-benzoquinone methides,[5] 7,7-diphenyl-1,4-benzoquinone methide,[6] 7-cyano-7-phenyl-1,4-benzoquinone methide,[7] 4-(1′,3′-dithiolan-2′-ylidene)-2,5-cyclohexanedien-1-one,[8] and 2,6-dimethyl-7-phenyl-1,4-benzoquinone methide.[9] We have investigated their solution and solid-state polymerization behaviors.[4,5,7−14] In the polymerizations of many QMs, carbon−oxygen bond formation between the substituted exomethylene carbon atom and exocabonyl oxygen and stable aromatic ring formation might take place to yield polymers with characteristic main-chain structures, poly(oxy-1,4-phenylene-substituted methylene)s. Here, when the polymerizations of prochiral monomers, QMs with two different substituents on the exomethylene carbon, take place, stereocenters could be generated in main chains through the polymerization process. If the stereocenters generated by the stereospecific addition of the growing species to the exomethylene carbon of QM would have either *R* or *S* configuration in excess by the asymmetric synthesis polymerization, a novel optically active polyether, composed of an asymmetric carbon having two different substituents with a *p*-phenylene unit, should be formed (Scheme 1).

In the previous communication, to obtain an optically active polymer having configurational chirality in the main chain, we carried out asymmetric anionic polymerization of 7-cyano-7-ethoxycarbonyl-1,4-benzoquinone methide (**1**) with various chiral anionic initiators and also investigated the effects of the chiral ligand and solvent polarity on the specific rotations of the resulting polymers.[15]

In this work, we investigated asymmetric anionic polymerizations of **1** with two chiral anionic initiators, lithium 4-isopropylphenoxide (^{i}PrPhOLi)/(−)-sparteine((−)-Sp) and ^{i}PrPhOLi/(S)-(−)-2,2′-isopropylidenebis(4-phenyl-2-oxazoline) ((−)-PhBox) initiators, and the stereostructures of oligomers such as 1-mer and 2-mer obtained by oligomerizations with both initiators in detail, and then the stereocontrol in the formation of the optically active polymer of **1** (poly(**1**)) was discussed.

Experimental Section

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 TOSOH CCPE 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

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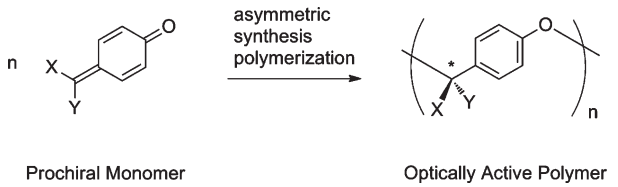
Scheme 1. Preparation of Optically Active Polymer by Polymerization of Prochiral Monomer



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-806 L, connected in series (eluent: THF; temperature: 40 °C). Optical resolution of oligomers were 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. 7-Cyano-7-ethoxycarbonyl-1,4-benzoquinone methide (**1**) was synthesized according to the method reported previously.[15] 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. (−)-Sparteine ((−)-Sp) (Tokyo Kasei Kogyo) was dried over calcium hydride overnight and then distilled under reduced pressure. (*S*)-(−)-2,2′-Isopropylidenebis(4-phenyl-2-oxazoline) ((−)-PhBox) (Aldrich) was used without further purification.

Asymmetric Anionic Polymerization. Asymmetric anionic polymerization was carried out in a glass ampule equipped with a three-way stopcock. A given amount of **1** was placed in the ampule, dried under reduced pressure, and then filled with nitrogen. Into it was added a mixture solution of dry dichloromethane/toluene (30/70 in vol %) by a syringe, and the resulting solution was cooled to −78 °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 and (−)-PhBox in dry toluene at room temperature just before use, and the reaction mixture was stirred at −78 °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 **1** with ^{i}PrPhOLi/(−)-Sp and ^{i}PrPhOLi/(−)-PhBox initiators were carried out at the monomer/initiator ratio of 2 in a mixture solution of dichloromethane/toluene (30/70 in vol %) at −78 °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 concentrated and passed through a silica gel column by using hexane/diethyl ether (2/1) as an eluent. The first elution band and the second one were collected and placed under reduced pressure to give 1-mer and 2-mer as white solids, respectively.

With ^{i}PrPhOLi/(−)-Sp Initiator. 1-mer: 114.8 mg (19.7% yield); mp 61.5−62.5 °C. IR (KBr, cm^{-1}): ν_{CH} 2970, ν_{CN} 2310, $\nu_{C=O}$ 1766, ν_{C-O} 1200. ^{1}H NMR ($CDCl_3$, ppm): δ 7.82 (d, J = 8.58 Hz, 2H), 7.21 (d, J = 8.91 Hz, 2H), 7.16 (d, J = 8.91 Hz, 2H), 7.00 (d, J = 8.58 Hz, 2H), 4.26 (q, J = 7.26 Hz, 2H), 2.87 (sept, J = 6.93 Hz, 1H), 2.32 (s, 3H), 1.22 (d, J = 6.93 Hz, 6H), 1.21 (t, J = 7.26 Hz, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ 168.9 (C═O), 164.7 (C═O), 152.3 (Ar, quaternary), 152.0 (Ar, quaternary), 144.5 (Ar, quaternary), 130.9 (Ar, CH), 127.4 (Ar, quatrenary), 127.4 (Ar, CH), 122.2 (Ar, CH), 118.0 (Ar, CH), 115.5 (CN), 79.0 (⟩C⟨, quatrenary), 63.9 (CH_2), 33.3 (CH), 23.9 (CH_3), 21.0 (CH_3), 13.6 (CH_3). Anal. Calcd for $C_{22}H_{23}NO_5$: C, 69.28%; H, 6.08%; N, 3.67%; O, 20.97%. Found: C, 68.98%; H, 6.18%; N, 3.63%.

2-mer: 100.3 mg (17.2% yield); mp 90.5−92.0 °C. IR (NaCl, cm^{-1}): ν_{C-H} 2970, ν_{CN} 2324, $\nu_{C=O}$ 1770, ν_{C-O} 1200. ^{1}H NMR ($CDCl_3$, ppm): δ 7.81 (d, J = 8.91 Hz, 2H), 7.76 (d, J = 8.58 Hz, 2H), 7.23 (d, J = 8.90 Hz, 2H), 7.23 (d, J = 8.90 Hz, 2H), 7.15 (d, J = 8.91 Hz, 2H), 6.99 (d, J = 8.58 Hz, 2H), 4.25 (q, J = 7.26 Hz, 4H), 2.87 (sept, J = 6.93 Hz, 1H), 2.33 (s, 3H), 1.29−1.17 (t, J = 7.26 Hz, 6H), 1.21 (d, J = 6.60 Hz, 6H). ^{13}C NMR ($CDCl_3$, ppm): δ 168.9 (C═O), 164.7 (C═O), 164.0 (C═O), 155.6 (Ar, quaternary), 152.3 (Ar, quaternary), 144.5 (Ar, quaternary), 130.0 (Ar, quaternary), 128.8 (Ar, quaternary), 127.7 (Ar, CH), 127.5 (Ar, CH), 127.4 (Ar, CH), 122.4 (Ar, CH), 122.3 (Ar, CH), 117.9 (Ar, CH), 115.5 (CN), 115.0 (CN), 78.9 (⟩C⟨, quaternary), 78.8 (⟩C⟨, quaternary), 64.3 (CH_2), 63.9 (CH_2), 33.3 (CH), 24.0 (CH_3), 21.1 (CH_3), 13.7 (CH_3). Anal. Calcd for $C_{33}H_{32}N_2O_8$: C, 67.80%; H, 5.52%; N, 4.79%; O, 21.89%. Found: C, 67.16%; H, 5.51%; N, 4.74%.

With ^{i}PrPhOLi/(−)-PhBox Initiator. 1-mer: 55.6 mg (9.5% yield). 2-mer: 48.5 mg (8.3% yield). Spectral data were the same as those for the case with ^{i}PrPhOLi/(−)-Sp initiator.

Table 1. Asymmetric Anionic Polymerizations[a] of 1 with the ^{i}PrPhOLi/(−)-Sp and ^{i}PrPhOLi/(−)-PhBox Initiators at Various [1]/[Initiator] Feed Ratios

run	ligand	[1]/[initiator]	time/h	yield[b]/%	M_n[c]	M_w/M_n[c]	$[\alpha]_{435}$[d] (deg)
1	(−)-Sp	10	24	76	2400	1.12	−5.9
2		20	48	77	1700	1.77	−2.3
3		30	48	80	5700	2.15	−4.4
4		50	48	54	6500	2.20	−3.4
5	(−)-PhBox	10	48	59	2100	1.28	+90.4
6		20	48	30	1600	1.26	+91.8
7		30	96	38	2600	1.31	+58.4
8		50	120	11	1800	1.25	+55.8

[a] Conditions: [**1**] = 0.23 mol/L; solvent: dichloromethane/toluene = 30/70 (in vol %); temperature: −78 °C. [b] Hexane-insoluble part. [c] Determined by GPC as polystyrene standard. [d] In chloroform.

Results and Discussion

Asymmetric Anionic Polymerization with ^{i}PrPhOLi/(−)-Sp and ^{i}PrPhOLi/(−)-PhBox Initiators. In the previous communication, we carried out the asymmetric anionic polymerization of **1** with various chiral anionic initiators and investigated the effects of the chiral ligand and solvent polarity on the specific rotations of the resulting polymers. The polymerization of **1** using the ^{i}PrPhOLi/(−)-Sp initiator in a mixture solution of dichloromethane/toluene (30/70 in vol %) at −78 °C afforded an optically active polymer of **1** (poly(**1**)) with a maximum negative specific rotation ($[\alpha]_{435}$ = −5.9°), and the polymerization of **1** using the ^{i}PrPhOLi/(−)-PhBox initiator under the same condition afforded an optically active poly(**1**) with a large positive specific rotation ($[\alpha]_{435}$ = +90.4°).[15]

To investigate the relationship of the molecular weight with the specific rotation of poly(**1**), asymmetric anionic polymerizations with the ^{i}PrPhOLi/(−)-Sp and ^{i}PrPhOLi/(−)-PhBox initiators were carried out at various [monomer]/[initiator] feed ratios. The results are summarized in Table 1.

Polymers were obtained as molecular weights in the range 1700−6500 at various [**1**]/[initiator] feed ratios for the case of the ^{i}PrPhOLi/(−)-Sp initiator and in the range 1600−2600 for the case of the ^{i}PrPhOLi/(−)-PhBox initiator, respectively. In the polymerization at a constant monomer concentration of 0.23 mol/L, specific rotation of the polymer obtained with ^{i}PrPhOLi/(−)-Sp initiator has a almost constant value of around $[\alpha]_{435}$ = −4° regardless of the molecular weights, suggesting that the stereocontrol is conducted in the same degree through whole polymer. On the other hand, the specific rotations of polymers obtained with the ^{i}PrPhOLi/(−)-PhBox initiator increased with

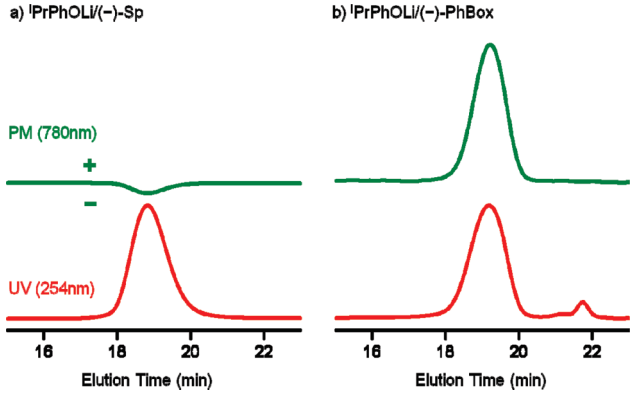


Figure 1. GPC charts of (a) poly(**1**) obtained with the ^{i}PrPhOLi/(−)-Sp initiator (Table 1, run 2) and (b) poly(**1**) obtained with the ^{i}PrPhOLi/(−)-PhBox initiator (Table 1, run 6).

an increase in the [**1**]/[^{i}PrPhOLi/(−)-PhBox] feed ratios, reached a maximum value at the [**1**]/[^{i}PrPhOLi/(−)-PhBox] ratio of 20 (Table 1, run no. 6), and then decreased. Similar behavior was observed in an asymmetric anionic polymerization of 2,6-dimethyl-7-phenyl-1,4-benzoquinone methide with fluorenyllithium (FlLi)/(−)-Sp initiator.[16] In the previous work, we proposed that the aggregation state composed of the several propagating anions were changed by the initiator concentration, and the optical rotation of obtained polymers may be mainly governed by the aggregation state. It is, therefore, considered that this behavior observed in the case of the ^{i}PrPhOLi/(−)-PhBox initiator is ascribed to the initiator concentration.

Figures 1a,b show the GPC curves of poly(**1**)s obtained by asymmetric anionic polymerization with the ^{i}PrPhOLi/(−)-Sp initiator (Table 1, run 2) and with the ^{i}PrPhOLi/(−)-PhBox initiator (run 6), respectively, monitored with ultraviolet (UV) (bottom chromatogram) and polarimetric (PM) detectors (top chromatogram).

The PM detector demonstrated a negative peak for the poly(**1**) obtained with ^{i}PrPhOLi/(−)-Sp initiator and a positive peak for the ^{i}PrPhOLi/(−)-PhBox initiator, and also both peak patterns are quite similar to corresponding UV chromatograms, which show unimodal GPC curves. These results indicate that the optical rotations of poly(**1**) obtained with both initiator systems do not depend upon the molecular weights, and the configurations of all asymmetric carbons in the polymer chain are controlled in almost the 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.

Stereoselectivity in the Initiation and Propagation Steps. Okamoto and co-workers reported the asymmetric oligomerization and chromatographic analyses of oligomers to obtain information on the stereochemical mechanism of asymmetric polymerization of triphenylmethyl methacrylate.[17] To investigate a degree of stereocontrol in the formation of an optically active poly(**1**), we also carried out the asymmetric anionic oligomerization of **1** with the ^{i}PrPhOLi/(−)-Sp initiator and with the ^{i}PrPhOLi/(−)-PhBox initiator at the [**1**]/[initiator] ratio of 2 for 12 h, and isolated 1-mer and 2-mer, which correspond to the products formed at the initial stage in the polymerization, were characterized. The results are summarized in Table 2.

The 1-mer and 2-mer obtained with the ^{i}PrPhOLi/(−)-Sp initiator showed a small negative specific rotation similar to that of corresponding polymer. On the other hand, the products obtained with the ^{i}PrPhOLi/(−)-PhBox initiator showed a very small negative specific rotation for the 1-mer and a large positive one for 2-mer, indicating that, in the asymmetric anionic

Table 2. Asymmetric Anionic Oligomerizations[a] of 1 with ^{i}PrPhOLi/(−)-Sp and ^{i}PrPhOLi/(−)-PhBox Initiators

run	ligand	[**1**]/[initiator]	time/h	yield/%	$[\alpha]_{435}$[b] (deg)
1	(−)-Sp	2	12	1-mer: 19.7	−2.5
				2-mer: 17.2	−3.1
2	(−)-PhBox	2	12	1-mer: 9.5	−1.5
				2-mer: 8.2	+20.2

[a] Conditions: [**1**] = 0.23 mol/L, solvent: dichloromethane/toluene = 30/70 (in vol %); temperature: −78 °C. [b] In chloroform.

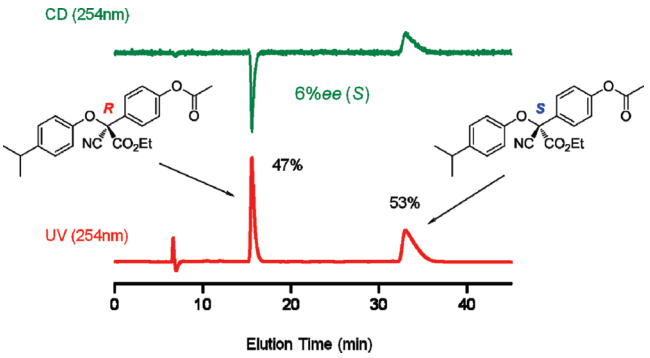


Figure 2. HPLC chromatograms of optical resolution of the 1-mer obtained with the ^{i}PrPhOLi/(−)-Sp initiator (column: Daicel Chiralpak AD, eluent: hexane/ethanol = 90/10 (in vol %), flow rate: 0.5 mL/min). The top chromatogram was measured by CD detector (254 nm) and bottom by UV detector (254 nm).

polymerization, stereoselectivity in an initiation reaction is definitely different from that in a propagation reaction. To obtain further information on stereoselectivity in the 1-mer and 2-mer, optical resolutions of them were conducted with high-pressure liquid chromatography (HPLC) analysis on the chiral column using hexane/ethanol (90/10 in vol %) as an eluent. The chromatogram of the optical resolution of the 1-mer obtained with the ^{i}PrPhOLi/(−)-Sp initiator is shown in Figure 2, where top and bottom chromatograms were monitored by CD and UV detectors, respectively.

In Figure 2, the 1-mer with a negative CD sign was first eluted and followed by the 1-mer with a positive CD one, indicating that both components are enantiomers. From the peak area obtained on the UV chromatogram in Figure 2, a ratio of the first-eluted component (1-mer with a negative CD sign)/the second-eluted one (1-mer with a positive CD sign) in the enantiomers is determined to be 47/53 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 negative CD sign) has a chiral carbon of a *R*-configuration and the second-eluted one (1-mer with a positive CD sign) does a chiral carbon of a *S*-configuration, 1-mer with the *S*-configurational chirality is formed in a slight excess amount than 1-mer with the *R*-configurational chirality, and the enantiomeric excess (*ee*) is calculated to be 6.0% *ee*(*S*). This indicates that, as shown in Scheme 2, addition of a lithium 4-isopropylphenoxide anion coordinated with a (−)-Sp ligand to the monomer **1** takes place in *Re*-face (front side) attack/*Si*-face (back side) attack ratio of 47%/53%, leading to enantiomer in a *R*-configurational 1-mer/*S*-configurational 1-mer ratio of 47/53 in mol %. However, as shown in a low *ee* value, stereoselectivity in the initiation reaction is quite low.

Next, to obtain information about the stereoselectivity in the 2-mer, optical resolution of the 2-mer was conducted with HPLC analysis like the 1-mer. The chromatograms of the optical resolution of the 2-mer obtained with the ^{i}PrPhOLi/(−)-Sp initiator are shown in Figure 3, where four diastereomers are separated completely.

From the peak area obtained on the UV chromatogram in Figure 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 with a negative CD sign is determined to be 25/22/25/28 in mol %. Each peak in Figure 3 was assigned as follows. Addition of enantiomers in the 1-mer to monomer **1** might form four diastereomers in the 2-mer as shown in Chart 1.

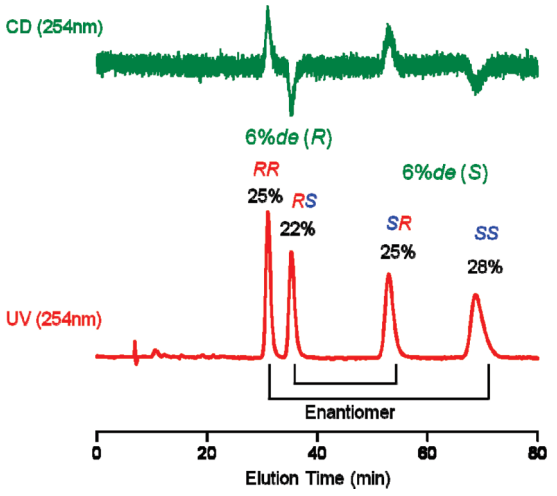
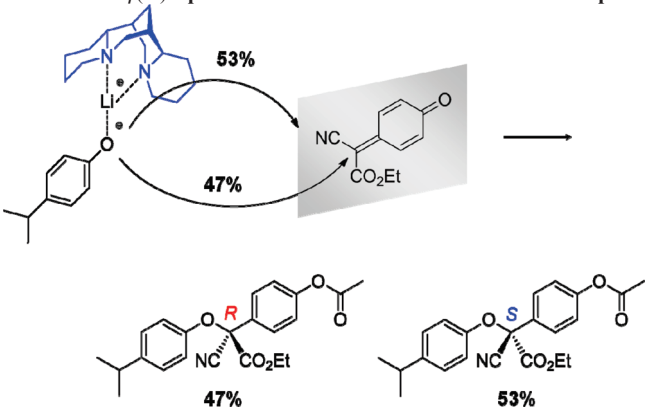


Figure 3. HPLC chromatograms of optical resolution of the 2-mer obtained with the ^{i}PrPhOLi/(−)-Sp initiator (column: Daicel Chiralpak AD, eluent: hexane/ethanol = 90/10 (in vol %), flow rate: 0.5 mL/min). The top chromatogram was measured by CD detector (254 nm) and bottom by UV detector (254 nm).

Scheme 2. Stereoselectivity in the Addition Reaction of the ^{i}PrPhOLi/(−)-Sp Initiator to Monomer 1 in the Initiation Step



On the basis of the result of the optical resolution of the 1-mer, the total amount of the 2-mer with (*R*,*R*)- and (*R*,*S*)-configurations derived from the *R*-configurational 1-mer should be 47 mol %, and the total amount of the 2-mer with (*S*,*R*)- and (*S*,*S*)-configurations derived from the *S*-configurational 1-mer should be 53 mol %. In the UV chromatogram of the 2-mer in Figure 3, the total amount of the first-eluted (25 mol %) and the second-eluted (22 mol %) components is 47 mol % and also the total amount of the second-eluted (22 mol %) and the third-eluted (25 mol %) components is 47 mol %. Therefore, either a combination of the first-eluted and the second-eluted components or a combination of the second-eluted and the third-eluted components might be assigned to the 2-mer with (*R*,*R*)- and (*R*,*S*)-configurations. The CD spectra of each peak for the 2-mer are shown in Figure 4, where the first-eluted component and the fourth-eluted one are mirror images of each other and also the second-eluted component and the third-eluted one are, indicating that each combination is enantiomers.

Therefore, a combination of the first-eluted and the second-eluted components might be assigned to the 2-mer with (*R*,*R*)- and (*R*,*S*)-configurations. 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

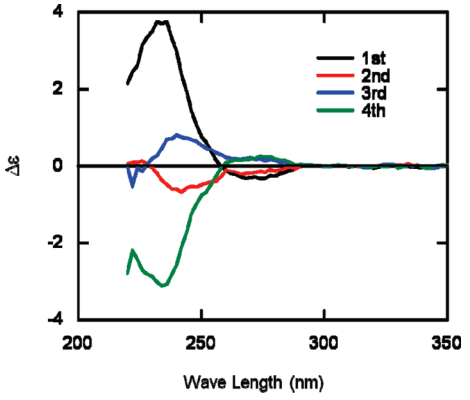
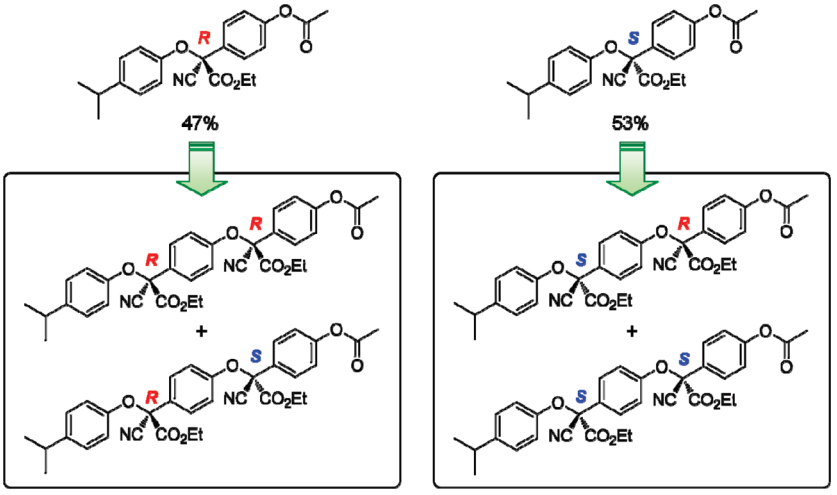


Figure 4. CD spectra of the 2-mer obtained with the ^{i}PrPhOLi/(−)-Sp initiator.

Chart 1. Diastereomers of the 2-mer



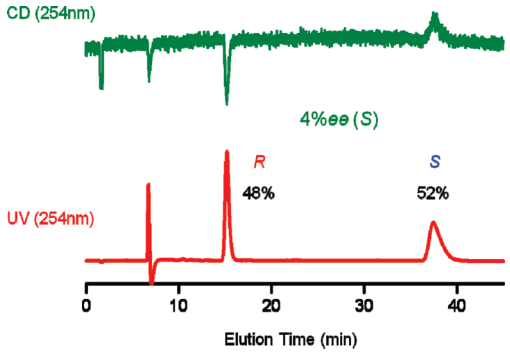
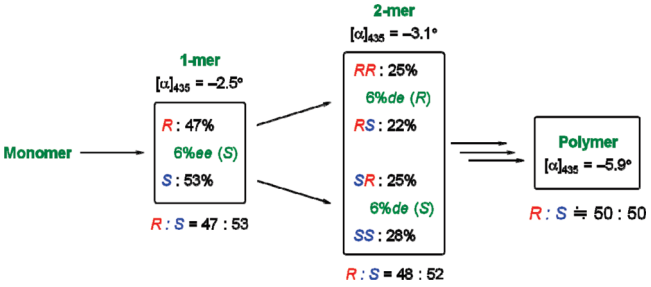


Figure 5. HPLC chromatograms of optical resolution of the 1-mer obtained with the ^{i}PrPhOLi/(−)-PhBox initiator (column: Daicel Chiralpak AD, eluent: hexane/ethanol = 90/10 (in vol %), flow rate: 0.5 mL/min). The top chromatogram was measured by CD detector (254 nm) and bottom by UV detector (254 nm).

Chart 2. Stereoselectivity on Initiation Reaction and Propagation Reaction with the ^{i}PrPhOLi/(−)-Sp Initiator



first-eluted, the second-eluted, the third-eluted, and the fourth-eluted components in the chromatograms in Figure 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,R*)-configuration (25 mol %) is formed in a slight excess amount than that with a (*R,S*)-configuration (22 mol %) from a 1-mer with a *R*-configuration, and the diastereomeric excess (*de*) is calculated to be 6% *de*(*R*), and also 2-mer with a (*S,S*)-configuration (28 mol %) is formed in a slight excess amount than that with a (*S,R*)-configuration (25 mol %) from the 1-mer with a *S*-configuration, and the *de* is calculated to be 6% *de*(*S*), respectively. This indicates that setereoselectivity on the propagation reaction from 1-mer to 2-mer by addition reaction of a 1-mer anion to a monomer is quite low. It is assumed that the propagation reaction to 3-mer, 4-mer, 5-mer, and oligomer, and polymer might proceed in same degree of stereoselectivity like as the propagation reaction to the 2-mer. Stereoselectivity on the initiation and propagation reactions in the polymerization of **1** with the ^{i}PrPhOLi/(−)-Sp initiator is summarized in Chart 2.

In the case of the ^{i}PrPhOLi/(−)-Sp initiator, the stereoselectivity is quite low on both initiation reaction and propagation reaction; that is, stereocenters generated in the resulting polymer are not highly stereocontrolled.

In the case with the ^{i}PrPhOLi/(−)-PhBox initiator, optical resolution of isolated 1-mer was conducted with HPLC analysis as the case with the ^{i}PrPhOLi/(−)-Sp initiator. The chromatograms of the optical resolution are shown in Figure 5, where the 1-mer with a *R*-configuration/the 1-mer with a *S*-configuration ratio is determined to be 48/52 in mol %.

The 1-mer with the *S*-configurational chirality is formed in a slight excess amount than that with the *R*-configurational chirality, and the enantiomeric excess (*ee*) is calculated to be 4% *ee*(*S*). Low *ee* value indicates that the stereoselectivity on the initiation reaction is quite low as the case with the ^{i}PrPhOLi/(−)-Sp initiator. Next, optical resolution of the 2-mer was conducted with HPLC analysis, and the chromatograms are shown in Figure 6.

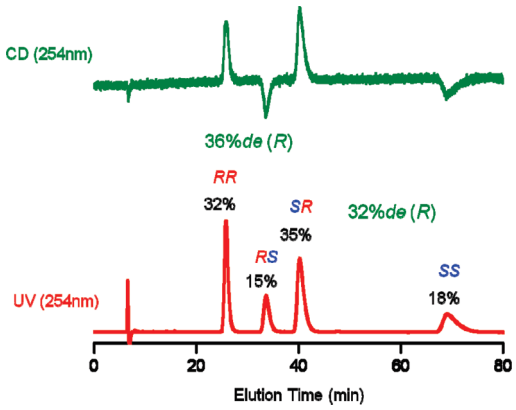
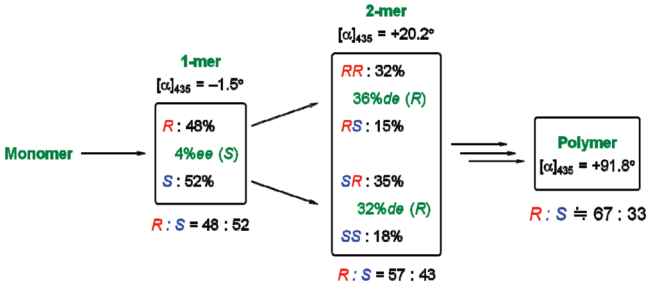


Figure 6. HPLC chromatograms of optical resolution of the 2-mer obtained with the ^{i}PrPhOLi/(−)-PhBox initiator (column: Daicel Chiralpak AD, eluent: hexane/ethanol = 90/10 (in vol %), flow rate: 0.5 mL/min). The top chromatogram was measured by CD detector (254 nm) and bottom by UV detector (254 nm).

Chart 3. Stereoselectivity on Initiation and Propagation Reaction with the ^{i}PrPhOLi/(−)-PhBox Initiator



Each component is assigned reasonably in turn to the 2-mer with a (*R,R*)-configuration, a (*R,S*)-one, a (*S,R*)-one, and a (*S,S*)-one as shown in Chart 1, and the ratio of the first-eluted component/the second-eluted component/the third-eluted component/the fourth-eluted component is determined to be 32/15/35/18 in mol %. The 2-mers with a (*R,R*)-configuration (32 mol %) and with a (*S,R*)-configuration (35 mol %) are produced in almost twice amount higher than the corresponding ones with a (*R,S*)-configuration (15 mol %) and with a (*S,S*)-configuration (18 mol %), respectively, and also the diastereomeric excess (*de*) is calculated to be 36% *de*(*R*) for the 1-mer with a *R*-configuration and 32% *de*(*R*) is for the 1-mer with a *S*-configuration, respectively. In the case with the ^{i}PrPhOLi/(−)-PhBox initiator, addition reaction of the 1-mer anion to a monomer might take place stereoselectively regardless of the configurational chirality in a 1-mer anion to form a 2-mer with an excessive *R*-configurational chiral carbon (32 mol % + 35 mol % = 67 mol %) in comparison with the *S*-configurational chiral carbon (15 mol % + 18 mol % = 33 mol %). Probably, the propagation reaction to 3-mer, 4-mer, 5-mer, and oligomer, and polymer is considered to proceed in same degree (*R*-configuration/*S*-configuration = 67/33 in mol %) of stereoselectivity. Stereoselectivity on the initiation and propagation reactions in the polymerization of **1** with the ^{i}PrPhOLi/(−)-PhBox initiator is summarized in Chart 3.

In the case of the ^{i}PrPhOLi/(−)-PhBox initiator, stereoselectivity is quite low on the initiation reaction, but high stereoselectivity is observed in the propagation reaction. Such high stereoselectivity on the propagation reaction results in the poly(**1**) with a large positive specific rotation value (+91.8°).

Conclusions

Asymmetric anionic polymerization of a prochiral quinone methide monomer, 7-cyano-7-ethoxycarbonyl-1,4-benzoquinone methide (**1**), was examined using two chiral anionic initiators, ^{i}PrPhOLi/(−)-Sp and ^{i}PrPhOLi/(−)-PhBox initiators, in a mixture solution of dichloromethane/toluene (30/70 in vol %), and optical activity of the polymers obtained and oligomers (1-mer and 2-mer) were investigated in detail. The ^{i}PrPhOLi/(−)-Sp initiator produced the poly(**1**) with a small negative specific rotation value, and the ^{i}PrPhOLi/(−)-PhBox initiator produced the poly(**1**) with a large positive specific rotation value. From the stereostructures of the 1-mer and 2-mer obtained by the oligomerization of **1** with both initiators, stereoselectivities in asymmetric anionic polymerization with ^{i}PrPhOLi/(−)-Sp initiator are quite low on both initiation and propagation reactions, while in the case of ^{i}PrPhOLi/(−)-PhBox initiator, stereoselectivity on the initiation reaction is quite low, but the propagation reaction proceeded stereoselectively to form a poly(**1**) with a large positive specific rotation; that is, a large positive specific rotation value observed in the poly(**1**) is ascribed to the bias in the absolute configuration of the chiral carbon in the polymer main chain.

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