Asymmetric Anionic Polymerizations of 7-Cyano-7-Alkoxycarbonyl-1,4-Benzoquinone Methides

Takeshi Nagai,[1] Takahiro Uno,[1] Masataka Kubo,[2] Takahito Itoh[1]

[1]Division of Chemistry for Materials, Graduate School of Engineering, Mie University, 1577 Kurima Machiya-cho, Tsu, Mie 514-8507, Japan
[2]Graduate School of Regional Innovation Studies, Mie University, 1577 Kurima Machiya-cho, Tsu, Mie 514-8507, Japan
Correspondence to: T. Itoh (E-mail: itoh@chem.mie-u.ac.jp)

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ABSTRACT: Asymmetric anionic polymerizations of 7-cyano-7-alkoxycarbonyl-1,4-benzoquinone methides (**1**) with various alkoxy groups were performed using chiral initiators such as lithium isopropylphenoxide (^{i}PrPhOLi)/(*S*)-(–)-2,2′-isopropylidene-bis(4-phenyl-2-oxazoline) ((–)-PhBox) and lithium isopropylphenoxide (^{i}PrPhOLi)/(–)-sparteine ((–)-Sp) to investigate the effect of the alkoxy groups of alkoxycarbonyl substituent in the monomers **1** and chiral ligands of chiral initiators on the control of chiral center in the formation of polymers. Molar optical rotation values of the polymers were significantly dependent upon alkoxy groups, and the polymers with higher molar optical rotation were obtained in monomers with primary alkoxy groups. The asymmetric anionic oligomerizations of the quinone methides having methoxy(**1a**), ethoxy(**1b**), and *n*-propoxy(**1c**) groups with chiral initiators were carried out. Both 1-mers and 2-mers were isolated and their optical resolutions were performed to determine the extent of stereocontrol. High stereoselectivity was observed at the propagation reaction, but not at the initiation reaction. The effect of the counterion on the control of chiral center in the formation of the polymer was investigated in the asymmetric anionic polymerizations of **1b** with ^{i}PrPhOM(M = Li, Na, K)/(–)-Sp and ^{i}PrPhOM(M = Li, Na, K)/(–)-PhBox initiators and discussed. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 466–479, 2012

KEYWORDS: anionic polymerization; chiral; initiators; synthesis

INTRODUCTION Asymmetric polymerization, classified in asymmetric synthesis polymerization (IUPAC nomenclature: 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 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] Optically active polymers are applied to chiral stationary phases for high performance liquid chromatography, polymeric reagents, and catalysts because of their excellent chiral recognition abilities toward a wide range of racemic compounds.[2]

We recently reported the asymmetric anionic polymerization of a prochiral monomer, 7-cyano-7-ethoxycarbonyl-1,4-benzoquinone methide (**1b**), using various chiral anionic initiators, and the synthesis of an optically active polymer (poly(**1b**)) having configurational chirality in the main chain (Scheme 1).[3,4]

The asymmetric anionic polymerization of **1b** with a complex of lithium 4-isopropylphenoxide and (–)-2,2′-isopropylidenebis(4-phenyl-2-oxazoline) as the chiral ligand (^{i}PrPhOLi/(–)-PhBox) yielded an optically active polymer with a large positive specific rotation ($[\alpha]_{435} = +90.4^{\circ}$).[4] Moreover, to understand the stereocontrol process in asymmetric polymerization of **1b**, we carried out the asymmetric anionic oligomerization of **1b** and investigated the stereostructures of oligomers such as 1-mer and 2-mer formed in the early stage of the polymerization. It was found that the extent of stereoselectivity in the formation of 1-mer as the initiation step is quite low, but the formation of 2-mer corresponding to the propagation step proceeds stereoselectively in the diastereomeric excess (*de*) of 36%.[4] However, the value of 36% *de* for stereocontrol of polymer main chain was still not so high. Here, investigation of substituent effect on the stereocontrol by asymmetric anionic polymerizations of 7-cyano-7-alkoxycarbonyl-1,4-benzoquinone methides with various alkoxy groups other than the ethoxy group is expected to provide a clue to achieve the greater extent of stereocontrol of chiral center for the polymer derived from a prochiral monomer.

In this work, the asymmetric anionic polymerizations of 7-cyano-7-alkoxycarbonyl-1,4-benzoquinone methides bearing various alkoxy groups such as methoxy(**1a**), ethoxy(**1b**),

SCHEME 1 Preparation of optically active polymer by polymerization of prochiral monomer **1b**.

n-propoxy(**1c**), isopropoxy(**1d**), butoxy(**1e**), isobutoxy(**1f**), *sec*-butoxy(**1g**), *tert*-butoxy(**1h**), benzyloxy(**1i**), and benzhydryloxy(**1j**) using chiral initiators will be reported.

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* with tetramethylsilane as an internal standard. The specific optical rotation at 435 nm ($[\alpha]_{435}$) was obtained with a JASCO P-1030 polarimeter. The molar optical rotations of polymers ($[\phi]_{435}$) were calculated from the specific optical rotation of polymers and the molecular weights of those monomer unit (M) according to the following equation: $[\phi]_{435} = M[\alpha]_{435}/100$. 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. 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

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 and distilled under reduced pressure. (*S*)-(–)-2,2′-Isopropylidenebis(4-phenyl-2-oxazoline) ((–)-PhBox) (Aldrich) was used without further purification.

Monomer Synthesis

4-[(Alkoxycarbonyl)cyanomethylene]cyclohexanones (**2a-j**) and 7-alkoxycarbonyl-7-cyano-1,4-benzoquinone methides (**1a-j**) were synthesized by the same procedure reported previously (Scheme 2).[5,6]

4-[(Alkoxycarbonyl)cyanomethylene]cyclohexanones (2a-j)

1,4-Cyclohexanedione monoethylene ketal (10 g, 64 mmol) and alkyl cyanoacetate (70 mmol) were refluxed in the presence of 0.4 g of ammonium acetate and 2 mL of acetic acid in 150 mL of toluene using Dean-Stark water separator to isolate water formed for 48 h. The reaction mixture was washed twice with 100 mL of water and dried over anhydrous magnesium sulfate. It was placed under reduced pressure to remove toluene to give a pale yellow solid, to which was added 200 mL of a 2% aqueous sulfuric acid solution, and refluxed for 1 h. After cooling, the reaction mixture was extracted with chloroform (400 mL × 3). 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 eluent followed by recrystallization from a mixture solution of hexane and dichloromethane.

4-[1′-Cyano-1′-(methoxycarbonyl)methylene] cyclohexanone (2a)

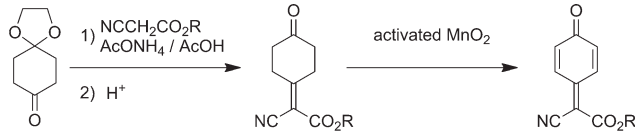
From methyl cyanoacetate, **2a** was obtained as pale yellow needles (58.4% yield): mp: 67.0–69.0 °C; IR (KBr, cm^{-1}): ν_{CH} 2970, ν_{CN} 2224, $\nu_{C=O}$ 1728, $\nu_{C=C}$ 1599, ν_{C-O} 1254, 1109.

^{1}H NMR ($CDCl_3$, ppm): δ 3.86 (s, 3H), 3.41 (t, J = 6.93 Hz, 2H), 3.14 (t, J = 6.93 Hz, 2H), 2.58 (t, J = 6.93 Hz, 2H), 2.55 (t, J = 6.60 Hz, 2H). ^{13}C NMR ($CDCl_3$, ppm): δ 208.3 (C=O), 175.0 (C=O), 161.6 (>C=), 114.6 (CN), 104.2 (>C=), 52.6 (CH_3), 36.8 (CH_2), 36.7 (CH_2), 31.8 (CH_2), 27.9 (CH_2). Anal. Calcd for $C_{10}H_{11}NO_3$: C, 62.16%; H, 5.74%; N, 7.25%. Found: C, 61.85%; H, 5.73%; N, 7.32%.

4-[1′-Cyano-1′-(ethoxycarbonyl)methylene] cyclohexanone (2b)

From ethyl cyanoacetate, **2b** was obtained as white needles (74.0% yield): mp: 80-80.5 °C; IR (KBr, cm^{-1}): ν_{CH} 2996, ν_{CN} 2226, $\nu_{C=O}$ 1725, $\nu_{C=C}$ 1596, ν_{C-O} 1253, 1105.

^{1}H NMR ($CDCl_3$, ppm): δ 4.31 (q, J = 7.30 Hz, 2H), 3.41 (t, J = 6.90 Hz, 2H), 3.13 (t, J = 6.60 Hz, 2H), 2.57 (t, J = 6.90 Hz, 2H), 2.55 (t, J = 6.60 Hz, 2H), 1.37 (t, J = 7.30 Hz, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ 208.2 (C=O), 174.2 (C=O), 161.3 (>C=), 114.7 (CN), 104.9 (>C=), 62.1 (CH_2), 37.0 (CH_2), 36.9 (CH_2), 31.9 (CH_2), 28.0 (CH_2), 14.0 (CH_3). Anal. Calcd



2a: Me
2b: Et
2c: ^{n}Pr
2d: ^{i}Pr
2e: ^{n}Bu
2f : ^{i}Bu
2g: ^{s}Bu
2h: ^{t}Bu
2i : CH_2Ph
2j : $CHPh_2$

1a: Me
1b: Et
1c: ^{n}Pr
1d: ^{i}Pr
1e: ^{n}Bu
1f : ^{i}Bu
1g: ^{s}Bu
1h: ^{t}Bu
1i : CH_2Ph
1j : $CHPh_2$

SCHEME 2 Preparation route of 7-alkoxycarbonyl-7-cyano-1,4-benzoquinone methides.

for $C_{11}H_{13}NO_3$: C, 63.75%; H, 6.32%; N, 6.76%. Found: C, 63.90%; H, 6.58%; N, 6.67%.

4-[1′-Cyano-1′-(propoxycarbonyl)methylene] cyclohexanone (2c)

From propyl cyanoacetate, **2c** was obtained as white needles (31.7% yield): mp: 87.5-88.0 °C; IR (KBr, cm^{-1}): ν_{CH} 2976, ν_{CN} 2220, $\nu_{C=O}$ 1722, $\nu_{C=C}$ 1594, ν_{C-O} 1285, 1116.

^{1}H NMR ($CDCl_3$, ppm): δ 4.20 (t, J = 6.60 Hz, 2H), 3.41 (t, J = 6.93 Hz, 2H), 3.13 (t, J = 6.77 Hz, 2H), 2.57 (t, J = 6.93 Hz, 2H), 2.55 (t, J = 6.77 Hz 2H), 1.82-1.69 (m, 2H), 1.10 (t, J = 7.42 Hz, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ 208.2 (C=O), 174.2 (C=O), 161.3 (>C=), 114.6 (CN), 104.7 (>C=), 67.4 (CH_2), 36.9 (CH_2), 36.8 (CH_2), 31.8 (CH_2), 27.9 (CH_2), 21.7 (CH_2), 10.2 (CH_3). Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14%; H, 6.83%; N, 6.33%. Found: C, 64.98%; H, 6.89%; N, 6.35%.

4-[1′-Cyano-1′-(isopropoxycarbonel)methylene] cyclohexanone (2d)

From isopropyl cyanoacetate, **2d** was obtained as white needles (64.8% yield): mp: 52.0-54.0 °C; IR (KBr cm^{-1}): ν_{CH} 2984, ν_{CN} 2220, $\nu_{C=O}$ 1721, $\nu_{C=C}$ 1597, ν_{C-O} 1286, 1099.

^{1}H NMR ($CDCl_3$, ppm): δ 5.19-5.08 (m, 1H), 3.40 (t, J = 6.76 Hz, 2H), 3.12 (t, J = 6.60 Hz, 2H), 2.57 (t, J = 6.76 Hz, 2H), 2.55 (t, J = 6.60 Hz, 2H), 1.34 (d, J = 5.94 Hz, 6H). ^{13}C NMR ($CDCl_3$, ppm): δ 208.3 (C=O), 173.7 (C=O), 160.8 (>C=), 114.7 (CN), 105.2 (>C=), 70.0 (CH), 37.0 (CH_2), 36.9 (CH_2), 31.8 (CH_2), 27.9 (CH_2), 21.5 (CH_3). Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14%; H, 6.83%; N, 6.33%. Found: C, 65.14%; H, 6.91%; N, 6.32%.

4-[1′-Cyano-1′-(butoxycarbonyl) methylene]cyclohexanone (2e)

From butyl cyanoacetate, **2e** was obtained as white needles (85% yield): mp: 65-66 °C; IR (KBr, cm^{-1}): ν_{CN} 2202, $\nu_{C=O}$ 1687, $\nu_{C=C}$ 1565, ν_{C-O} 1233, 1085.

^{1}H NMR ($CDCl_3$, ppm): δ 4.24 (t, J = 6.6 Hz, 2H), 3.41 (t, J = 6.6 Hz, 2H), 3.13 (t, J = 6.6 Hz, 2H), 2.55 (t, J = 6.6 Hz, 4H), 1.69 (q, J = 6.6 Hz, 2H), 1.44 (q, J = 7.3 Hz, 2H), 0.96 (t, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ 208.2 (C=O), 174.1 (C=O), 161.3 (>C=), 114.6 (CN), 104.8 (>C=), 65.8 (CH_2), 36.95 (CH_2), 36.86 (CH_2), 31.8 (CH_2), 30.3 (CH_2), 27.9 (CH_2), 18.9 (CH_2), 13.5 (CH_3). Anal. Calcd. for $C_{13}H_{17}NO_3$: C, 66.36%; H, 7.29%; N, 5.95%. Found: C, 66.21%; H, 7.37%; N, 5.99%.

4-[1′-Cyano-1′-(isobutoxycarbonyl)methylene] cyclohexanone (2f)

From isobutyl cyanoacetate, **2f** was obtained as a white needles (82.3% yield): mp: 53.0-54.0 °C; IR (KBr, cm^{-1}): ν_{CH} 2966, ν_{CN} 2222, $\nu_{C=O}$ 1724, $\nu_{C=C}$ 1595, ν_{C-O} 1246, 1106.

^{1}H NMR ($CDCl_3$, ppm): δ 4.02 (d, J = 6.59 Hz, 2H), 3.41 (t, J = 6.93 Hz, 2H), 3.14 (t, J = 6.93 Hz, 2H), 2.58 (t, J = 6.93 Hz, 2H), 2.55 (t, J = 6.93 Hz, 2H), 2.02-1.99 (m, 1H), 1.05 (d, J = 6.92 Hz, 6H). ^{13}C NMR ($CDCl_3$, ppm): δ 208.5 (C=O), 174.5 (C=O), 161.6 (>C=), 115.0 (CN), 105.2 (>C=), 72.2 (CH_2), 37.3 (CH_2), 37.3 (CH_2), 32.2 (CH), 28.3 (CH_2), 27.9 (CH_2), 19.2 (CH_3). Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36%; H, 7.28%; N, 5.95%. Found: C, 66.31%; H, 7.03%; N, 6.12%.

4-[1′-Cyano-1′-(sec-butoxycarbonyl) methylene]cyclohexanone (2g)

From *sec*-butyl cyanoacetate, **2g** was obtained as a yellow oil (82.0% yield): IR (neat, cm^{-1}): ν_{CH} 2978, ν_{CN} 2224, $\nu_{C=O}$ 1723, $\nu_{C=C}$ 1602, ν_{C-O} 1288, 1098.

^{1}H NMR ($CDCl_3$, ppm): δ 4.99 (m, 1H), 3.41 (t, J = 6.93 Hz, 2H), 3.13 (t, J = 6.93 Hz, 2H), 2.53-2.60 (m, 4H), 1.77-1.58 (m, 2H), 1.31 (d, J = 6.27 Hz, 3H), 0.96 (t, J = 7.43 Hz, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ 208.3 (C=O), 173.7 (C=O), 160.9 (>C=), 114.7 (CN), 105.2 (>C=), 74.5 (CH), 37.0 (CH_2), 36.9 (CH_2), 31.8 (CH_2), 28.5 (CH_2), 27.9 (CH_2), 19.2 (CH_3), 9.44 (CH_3). Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36%; H, 7.29%; N, 5.95%. Found: C, 66.39%; H, 7.35%; N, 5.92%.

4-[1′-Cyano-1′-(tert-butoxycarbonyl) methylene]cyclohexanone (2h)

From *tert*-butyl cyanoacetate, **2h** was obtained as a white needles (50.2% yield): mp: 94.0-95.0 °C; IR (KBr, cm^{-1}): ν_{CH} 2978, ν_{CN} 2218, $\nu_{C=O}$ 1715, $\nu_{C=C}$ 1604, ν_{C-O} 1260, 1160.

^{1}H NMR ($CDCl_3$, ppm): δ 3.37 (t, J = 7.26 Hz, 2H), 3.10 (t, J = 7.26 Hz, 2H), 2.58-2.58 (m, 4H), 1.54 (s, 9H). ^{13}C NMR ($CDCl_3$, ppm): δ 208.4 (C=O), 172.5 (C=O), 160.4 (>C=), 115.0 (CN), 106.3 (>C=), 83.6 (>C<), 37.1 (CH_2), 37.1 (CH_2), 31.8 (CH_2), 27.9 (CH_2), 27.7 (CH_3). Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36%; H, 7.29%; N, 5.95%. Found: C, 66.39%; H, 7.35%; N, 5.92%.

4-[1′-Cyano-1′-(benzyloxycarbonyl) methylene]cyclohexanone (2i)

From benzyl cyanoacetate, **2i** was obtained as a white needles (14.4% yield): mp: 115-117 °C; IR (KBr, cm^{-1}): ν_{CH} 2866, ν_{CN} 2198, $\nu_{C=O}$ 1691, $\nu_{C=C}$ 1569, ν_{C-O} 1242, 1196.

^{1}H NMR ($CDCl_3$, ppm): δ 7.41 (s, 5H), 5.29 (s, 2H), 3.40 (t, J = 13.9 Hz, 2H), 3.13 (t, J = 13.5 Hz, 2H), 2.54 (m, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ 208.2 (C=O), 175.2 (C=O), 161.1 (>C=), 134.9 (Ar, CH), 128.7 (Ar, CH), 128.6 (Ar, CH), 128.1 (Ar, CH), 114.6 (CN), 104.6 (>C=), 67.4 (CH_2), 36.9 (CH_2), 36.8 (CH_2), 32.0 (CH_2), 28.1 (CH_2). Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.35%; H, 5.63%; N, 5.20%. Found: C, 71.39%; H, 5.56%; N, 5.21%.

4-[1′-Cyano-1′-(benzhydryloxycarbonyl) methylene]cyclohexanone (2j)

From benzhydryl cyanoacetate, **2h** was obtained as a pale yellow needles (51.1% yield): mp: 97.0-98.0 °C; IR (KBr, cm^{-1}): ν_{CH} 3038, ν_{CN} 2298, $\nu_{C=O}$ 1724, $\nu_{C=C}$ 1592, ν_{C-O} 1243, 1103.

^{1}H NMR ($CDCl_3$, ppm): δ 7.27-7.45 (m, 10H), 6.93 (s, 1H), 3.37 (t, J = 6.93 Hz, 2H), 3.13 (t, J = 6.60 Hz, 2H), 2.46-2.55(m, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ 208.2 (C=O), 175.2 (C=O), 161.1 (>C=), 134.9 (Ar, CH), 128.7 (Ar, CH), 128.6 (Ar, CH), 128.1 (Ar, CH), 114.6 (CN), 104.6 (>C=), 67.4 (CH), 36.9 (CH_2), 36.8 (CH_2), 32.0 (CH_2), 28.1 (CH_2). Anal. Calcd for $C_{22}H_{19}NO_3$: C, 76.50%; H, 5.54%; N, 4.06%. Found: C, 76.57%; H, 5.55%; N, 4.05%.

7-Alkoxycarbonyl-7-cyano-1,4-benzoquinone methides (1a-j)

About 2 g of compounds **2a-j** was dissolved in 800 mL of chloroform, and then into the resulting solution were added

10 g of activated manganese dioxide and 10 g of 4Å molecular sieves. The mixture was refluxed with stirring for 15-40 min, 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 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 hexane or a mixture solution of hexane and dichloromethane to give orange needles.

7-Cyano-7-(methoxycarbonyl)-1,4-benzoquinone methide (1a)

Yield: 23%; mp: 104-105 °C; IR (KBr, cm^{-1}): ν_{CH} 2960, ν_{CN} 2216, $\nu_{C=O}$ 1726, $\nu_{C=C}$ 1639, ν_{C-O} 1240, 1081.

^{1}H NMR ($CDCl_3$, ppm): δ 8.58 (dd, J = 2.64, 10.56 Hz, 1H), 7.72 (dd, J = 1.98, 10.22 Hz, 1H), 6.62 (dd, J = 2.48, 10.07 Hz, 1H), 6.54 (dd, J = 1.98, 10.23 Hz, 1H), 3.97 (s, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ 186.0 (C=O), 160.9 (C=O), 148.8 (>C=), 136.1 (CH), 133.5 (CH), 132.7 (CH), 132.4 (CH), 114.4 (CN), 110.8 (=C<), 53.8 (CH_3). Anal. Calcd for $C_{10}H_7NO_3$: C, 63.49%; H, 3.73%; N, 7.40%. Found: C, 62.38%; H, 3.56%; N, 7.73%.

7-Cyano-7-(ethoxycarbonyl)-1,4-benzoquinone methide (1b)

Yield: 41.2%; mp. 56.5-57.5 °C; IR (KBr, cm^{-1}): ν_{CH} 2982, ν_{CN} 2218, $\nu_{C=O}$ 1738, $\nu_{C=C}$ 1642, ν_{C-O} 1236, 1083.

^{1}H NMR ($CDCl_3$, ppm): δ 8.57 (dd, J = 2.64, 10.23 Hz, 1H), 7.72 (dd, J = 1.98, 9.98 Hz, 1H), 6.62 (dd, J = 2.64, 9.90 Hz, 1H), 6.54 (dd, J = 1.98, 10.23 Hz, 1H), 4.43 (q, J = 6.93 Hz, 2H), 1.42 (t, J = 6.93 Hz, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ 186.1 (C=O), 160.5 (C=O), 148.5 (>C=), 136.2 (CH), 133.5 (CH), 132.8 (CH), 132.4 (CH), 114.5 (CN), 111.5 (=C<), 63.5 (CH_2), 14.0 (CH_3). Anal. Calcd for $C_{11}H_9NO_3$: C, 65.02%; H, 4.46%; N, 6.89%. Found: C, 64.81%; H, 4.43%; N, 6.95%.

7-Cyano-7-(propoxycarbonyl)-1,4-benzoquinone methide (1c)

Yield: 15.2%; mp: 68-69.5 °C; IR (KBr, cm^{-1}): ν_{CH} 2970, ν_{CN} 2216, $\nu_{C=O}$ 1716, $\nu_{C=C}$ 1642, ν_{C-O} 1266, 1083.

^{1}H NMR ($CDCl_3$, ppm): δ 8.58 (dd, J = 2.47. 10.39 Hz, 1H), 7.72 (dd, J = 1.82, 10.06 Hz, 1H), 6.62 (dd, J = 2.64, 9.90 Hz, 1H), 6.54 (dd, J = 1.82, 10.40 Hz, 1H), 4.31 (t, J = 6.60 Hz, 2H), 1.87-1.74 (m, 2H), 1.04 (t, J = 7.43 Hz, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ 186.1 (C=O), 160.5 (C=O), 148.5 (>C=), 136.2 (CH), 133.4 (CH), 132.8 (CH), 132.4 (CH), 114.5 (CN), 111.4 (=C<), 68.8 (CH_2), 21.7 (CH_2), 10.2 (CH_3). Anal. Calcd for $C_{12}H_{11}NO_3$: C, 66.35%; H, 5.10%; N, 6.45%. Found: C, 65.54%; H, 4.97%; N, 6.37%.

7-Cyano-7-(isoproxycarbonyl)-1,4-benzoquinone methide (1d)

Yield: 44.0%; mp: 91.0-92.0 °C; IR (KBr, cm^{-1}): ν_{CH} 2990, ν_{CN} 2218, $\nu_{C=O}$ 1721, $\nu_{C=C}$ 1643, ν_{C-O} 1250, 1100.

^{1}H NMR ($CDCl_3$, ppm): δ 8.54 (dd, J = 2.64, 10.23 Hz, 1H), 7.71 (dd, J = 1.82, 10.06 Hz, 1H), 6.61 (dd, J = 2.64, 10.23 Hz, 1H), 6.53 (dd, J = 1.98, 10.23 Hz, 1H), 5.17-5.26 (m, 1H), 1.40 (d, J = 6.27 Hz, 6H). ^{13}C NMR ($CDCl_3$, ppm): δ 186.1 (C=O), 159.9 (C=O), 148.1 (>C=), 136.2 (CH), 133.3 (CH), 132.8 (CH), 132.3 (CH), 114.4 (CN), 112.0 (=C<), 71.9 (CH), 21.5 (CH_3). Anal. Calcd for $C_{12}H_{11}NO_3$: C, 66.35%; H, 5.10%; N, 6.45%. Found: C, 66.35%; H, 5.01%; N, 6.47%.

7-Cyano-7-(butoxycarbonyl)-1,4-benzoquinone methide (1e)

Yield: 22.3%; mp: 61.0-62.0 °C; IR (KBr): ν_{CH} 2958, ν_{CN} 2318, $\nu_{C=O}$ 1716, $\nu_{C=C}$ 1642, ν_{C-O} 1265, 1082.

^{1}H NMR ($CDCl_3$, ppm): δ 8.58 (dd, J = 2.47, 10.39 Hz, 1H), 7.72 (dd, J = 1.98, 10.22 Hz, 1H), 6.62 (dd, J = 2.64, 10.22 Hz, 1H), 6.53 (dd, J = 1.82, 10.44 Hz, 1H), 4.35 (t, J = 6.60 Hz, 2H), 1.82-1.71 (m, 2H), 1.54-1.41 (m, 2H), 0.98 (t, J = 7.42 Hz, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ 186.0 (C=O), 160.5 (C=O), 148.4 (>C=), 136.2 (CH), 133.4 (CH), 132.8 (CH), 132.3 (CH), 114.4 (CN), 111.4 (=C<), 67.1 (CH_2), 30.2 (CH_2), 18.9 (CH_2), 13.5 (CH_3). Anal. Calcd for $C_{13}H_{13}NO_3$: C, 67.52%; H, 5.67%; N, 6.06%. Found: C, 67.40%; H, 5.61%; N, 6.10%.

7-Cyano-7-(isobutoxycarbonyl)-1,4-benzoquinone methide (1f)

Yield: 18.0%; mp: 74.0-75.0 °C; IR (KBr): ν_{CH} 2968, ν_{CN} 2216, $\nu_{C=O}$ 1714, $\nu_{C=C}$ 1642, ν_{C-O} 1263, 1082.

^{1}H NMR ($CDCl_3$, ppm): δ 8.56 (dd, J = 2.64, 10.23 Hz, 1H), 7.72 (dd, J = 1.82, 10.06 Hz, 1H), 6.62 (dd, J = 2.64, 9.90 Hz, 1H), 6.54 (dd, J = 1.98, 10.23 Hz, 1H), 4.13 (d, J = 6.60 Hz, 2H), 2.04-2.14 (m, 1H), 1.03 (d, J = 6.60 Hz, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ 186.1 (C=O), 160.4 (C=O), 148.4 (>C=), 136.2 (CH), 133.4 (CH), 132.8 (CH), 132.4 (CH), 114.4 (CN), 111.4 (=C<), 73.1 (CH_2), 27.6 (CH), 18.9 (CH_3). Anal. Calcd for $C_{13}H_{13}NO_3$: C, 67.52%; H, 5.67%; N, 6.06%. Found: C, 67.40%; H, 5.61%; N, 6.10%.

7-Cyano-7-(sec-butoxycarbonyl)-1,4-benzoquinone methide (1g)

Yield: 12.0%; mp: 57.5-58 °C; IR (KBr, cm^{-1}): ν_{CH} 2980, ν_{CN} 2216, $\nu_{C=O}$ 1717, $\nu_{C=C}$ 1643, ν_{C-O} 1233, 1097.

^{1}H NMR ($CDCl_3$, ppm): δ 8.57 (dd, J = 2.64, 10.23 Hz, 1H), 7.72 (dd, J = 1.98, 9.89 Hz, 1H), 6.61 (dd, J = 2.64, 10.23 Hz, 1H), 6.53 (dd, J = 1.98, 10.23 Hz, 1H), 5.04-5.09 (m, 1H), 1.67-1.80 (m, 2H), 1.37 (d, J = 6.27 Hz, 3H), 0.99 (t, J = 7.43 Hz, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ 186.1 (C=O), 160.1 (C=O), 148.2 (>C=), 136.2 (CH), 133.3 (CH), 132.9 (CH), 132.3 (CH), 114.4 (CN), 112.1 (=C<), 76.4 (CH), 28.5 (CH_2), 19.2 (CH_3), 9.5 (CH_3). Anal. Calcd for $C_{13}H_{13}NO_3$: C, 67.52%; H, 5.67%; N, 6.06%. Found: C, 67.37%; H, 5.65%; N, 6.09%.

7-Cyano-7-(tert-butoxycarbonyl)-1,4-benzoquinone methide (1h)

Yield: 47.3%; mp: 120-121 °C; IR (KBr, cm^{-1}): ν_{CH} 2992, ν_{CN} 2214, $\nu_{C=O}$ 1722, $\nu_{C=C}$ 1642, ν_{C-O} 1251, 1083.

^{1}H NMR ($CDCl_3$, ppm): δ 8.54 (dd, J = 2.64, 10.23 Hz, 1H), 7.69 (dd, J = 1.98, 10.23 Hz, 1H), 6.59 (dd, J = 2.64, 10.22 Hz, 1H), 6.51 (dd, J = 1.98, 10.23 Hz, 1H), 1.60 (s, 9H). ^{13}C NMR ($CDCl_3$, ppm): δ 186.6 (C=O), 159.8 (C=O), 148.0 (>C=), 136.8 (CH), 133.6 (CH), 133.3 (CH), 132.6 (CH),

115.1 (CN), 113.8 (=C<), 86.2 (>C<), 28.3 (CH_3). Anal. Calcd for $C_{13}H_{13}NO_3$: C, 67.52%; H, 5.67%; N, 6.06%. Found: C, 67.37%; H, 5.65%; N, 6.09%.

7-Cyano-7-(benzyloxycarbonyl)-1,4-benzoquinone methide (1i)

Yield: 42.7%; mp: 145-146 °C; IR (KBr, cm^{-1}): ν_{CH} 2920, ν_{CN} 2198, $\nu_{C=O}$ 1694, $\nu_{C=C}$ 1583, ν_{C-O} 1231, 1084.

^1H NMR ($CDCl_3$, ppm): δ 8.54 (dd, J = 2.64, 10.23 Hz, 1H), 7.72 (dd, J = 1.98, 9.89 Hz, 1H), 7.43 (m, 5H), 6.62 (dd, J = 2.64, 10.23 Hz, 1H), 6.54 (dd, J = 1.98, 9.89 Hz, 1H), 5.37 (s, 2H). ^{13}C NMR ($CDCl_3$, ppm): δ 186.0 (C=O), 160.3 (C=O), 148.8 (>C=), 136.1 (CH), 134.1 (Ar, CH), 133.4 (CH), 132.7 (Ar, CH), 128.8 (Ar, CH), 128.3 (Ar, CH), 114.3 (CN), 111.1 (=C<), 68.7 (CH_2). Anal. Calcd for $C_{16}H_{11}NO_3$: C, 72.44%; H, 4.19%; N, 5.28%. Found: C, 72.37%; H, 4.21%; N, 5.22%.

7-Cyano-7-(benzhydryloxycarbonyl)-1,4-benzoquinone methide (1j)

Yield: 19.9%; mp: 125-126.5 °C; IR (KBr, cm^{-1}): ν_{CH} 3042, ν_{CN} 2218, $\nu_{C=O}$ 1726, $\nu_{C=C}$ 1639, ν_{C-O} 1235, 1081.

^1H NMR ($CDCl_3$, ppm): δ 8.57 (dd, J = 2.31, 10.23 Hz, 1H), 7.75 (dd, J = 1.98, 9.89 Hz, 1H), 7.32-7.46 (m, 10H), 7.01 (s, 1H), 6.61 (dd, J = 2.64, 10.23 Hz, 1H), 6.50 (dd, J = 1.98, 9.89 Hz, 1H). ^{13}C NMR ($CDCl_3$, ppm): δ 186.1 (C=O), 159.5 (C=O), 149.2 (>C=), 138.7 (Ar, CH), 136.1 (CH), 133.5 (CH), 132.7 (CH), 132.5 (CH), 128.8 (Ar, CH), 128.5 (Ar, CH), 126.9 (Ar, CH), 114.5 (CN), 111.1 (=C<), 80.0 (CH). Anal. Calcd for $C_{22}H_{15}NO_3$: C, 77.41%; H, 4.43%; N, 4.10%. Found: C, 77.04%; H, 4.32%; N, 4.30%.

Asymmetric Anionic Polymerization

Asymmetric anionic polymerization was carried out in a glass ampoule equipped with a three-way stopcock. A given amount of **1a-j** was placed in the ampoule, dried under reduced pressure, and then filled with nitrogen. Into it was added dry dichloromethane or 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.) (–)-Sp or (–)-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*. Same polymerization was carried out in a mixture solution of dry dichloromethane/toluene (40/60 in vol %) at –40 °C. The rest procedure is similar to the aforementioned method.

Oligomerization with ^{i}PrPhOLi/(–)-PhBox Initiator and Isolation of 1-mer and 2-mer

Asymmetric anionic oligomerization of **1a, 1b,** or **1c** with ^{i}PrPhOLi/(–)-PhBox initiators was carried out at [monomer]/[initiator] ratio of 2 in dichloromethane at –78 °C for 12hr. 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, 1N 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 v/v) 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.

1a: 1-mer: 28.9 mg (10.4% yield). IR (KBr, cm^{-1}): ν_{CH} 2962, ν_{CN} 2312, $\nu_{C=O}$ 1768, ν_{C-O} 1201, 1088. ^1H NMR ($CDCl_3$, ppm): δ 7.82 (d, J = 6.90 Hz, 2H), 7.21-7.24 (m, 4H), 6.99 (d, J = 6.58 Hz, 2H), 3.82 (s, 3H), 2.87 (sept, J = 6.93 Hz, 1H), 2.32 (s, 3H), 1.22 (d, J = 6.93 Hz, 6H). ^{13}C NMR ($CDCl_3$, ppm): δ 169.0 (C=O), 165.3 (C=O), 152.2 (Ar, quaternary), 152.1 (Ar, quaternary), 144.7 (Ar, quaternary), 130.8 (Ar, CH), 127.7 (Ar, quatrenary), 127.5 (Ar, CH), 122.3 (Ar, CH), 118.0 (Ar, CH), 115.4 (CN), 79.0 (>C<, quatrenary), 54.4 (CH_3), 33.4 (CH), 24.0 (CH_3), 21.1 (CH_3).

2-mer: 49.0 mg (17.6% yield). IR (NaCl, cm^{-1}):ν_{C-O} 2964, ν_{CN} 2254, $\nu_{C=O}$ 1761, ν_{C-O} 1215, 1092. ^1H NMR ($CDCl_3$, ppm): δ 7.81 (d, J = 8.91 Hz, 2H), 7.76 (d, J = 8.58 Hz, 2H), 7.26 (d, J = 8.90 Hz, 2H), 7.19 (d, J = 8.58 Hz, 2H), 7.15 (d, J = 8.91 Hz, 2H), 7.06 (d, J = 8.91 Hz, 2H), 3.84 (s, 3H), 3.85 (s, 3H), 2.87 (sept, J = 6.93 Hz, 1H), 2.33 (s, 3H), 1.22 (d, J = 6.93 Hz, 6H). ^{13}C NMR ($CDCl_3$, ppm): δ 169.3 (C=O), 165.7 (C=O), 164.9 (C=O), 155.9 (Ar, quaternary), 152.7 (Ar, quaternary), 145.0 (Ar, quaternary), 130.2 (Ar, quaternary), 129.0 (Ar, quaternary), 128.2 (Ar, CH), 127.8 (Ar, CH), 122.9 (Ar, CH), 122.9 (Ar, CH), 118.4 (Ar, CH), 118.3 (Ar, CH), 116.7 (CN), 115.7 (CN), 79.2 (>C<, quaternary), 78.6 (>C<, quaternary), 55.1 (CH_3), 54.8 (CH_3), 33.7 (CH), 24.3 (CH_3), 21.4 (CH_3).

1b: 1-mer: 15.8 mg (8.3% yield). IR (KBr, cm^{-1}): ν_{CH} 2970, ν_{CN} 2310, $\nu_{C=O}$ 1766, ν_{C-O} 1200. ^1H NMR ($CDCl_3$, ppm): δ 7.82 (d, J = 8.91 Hz, 2H), 7.21 (d, J = 8.91 Hz, 2H), 7.16 (d, J = 8.58 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).

2-mer: 34.3 mg (11.4% yield). IR (NaCl, cm^{-1}):ν_{C-O} 2970, ν_{CN} 2324, $\nu_{C=O}$ 1770, ν_{C-O} 1200. ^1H 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 = 8.58 Hz, 2H), 7.15 (d, J = 8.91 Hz, 2H), 6.99 (d, J = 8.91 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).

1c: 1-mer: 43.3 mg (14.1% yield). IR (KBr, cm^{-1}): ν_{CH} 2966, ν_{CN} 2348, $\nu_{C=O}$ 1765, ν_{C-O} 1200, 1088. ^1H NMR ($CDCl_3$, ppm): δ 7.83 (d, J = 8.91 Hz, 2H), 7.24 (d, J = 8.91 Hz, 2H), 7.21 (d, J = 8.58 Hz, 2H), 7.02 (d, J = 8.58 Hz, 2H), 4.11-4.19 (m, 2H), 2.87 (sept, J = 6.93 Hz, 1H), 2.32 (s, 3H), 1.54-1.64 (m, 2H), 1.22 (d, J = 6.93 Hz, 6H), 0.80 (t, J = 7.43 Hz, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ 169.0 (C=O), 164.8 (C=O), 152.4 (Ar, quaternary), 152.1 (Ar, quaternary), 144.5 (Ar, quaternary), 131.0 (Ar, CH), 127.4 (Ar, quatrenary), 127.4 (Ar, CH), 122.2 (Ar, CH), 117.8 (Ar, CH), 115.6 (CN), 79.0 (>C<, quatrenary), 63.4 (CH_2), 33.4 (CH), 24.0 (CH_3), 21.6 (CH_2), 21.1 (CH_2), 9.96 (CH_3).

2-mer: 67.5 mg (22.0% yield). IR (NaCl, cm^{-1}):ν_{C-O} 2970, ν_{CN} 2350, $\nu_{C=O}$ 1769, ν_{C-O} 1203, 1089. ^1H NMR ($CDCl_3$, ppm): δ 7.84-7.74 (m, 4H), 7.26-7.14 (m, 4H), 7.03-6.97 (m, 4H), 4.22-4.11 (m, 4H), 2.87 (sept, J = 6.93 Hz, 1H), 2.33 (s, 3H), 1.66-1.55 (m, 4H), 1.21 (d, J = 6.93 Hz, 6H), 0.90-0.76 (m, 6H). ^{13}C NMR ($CDCl_3$, ppm): δ 168.9 (C=O), 164.8 (C=O), 164.1 (C=O), 155.6 (Ar, quaternary), 152.3 (Ar, quaternary), 152.2 (Ar, quaternary), 144.5 (Ar, quaternary), 130.1 (Ar, quaternary), 128.9 (Ar, quaternary), 127.7 (Ar, CH), 127.4 (Ar, CH), 127.3 (Ar, CH), 122.4 (Ar, CH), 122.4 (Ar, CH), 118.0 (Ar, CH), 115.5 (CN), 115.0 (CN), 78.9 (>C<, quaternary), 78.4 (>C<, quaternary), 69.7 (CH_2), 69.3 (CH_2), 33.3 (CH), 24.0 (CH_2), 21.6 (CH_2), 21.0 (CH_3), 9.90 (CH_3).

RESULTS AND DISCUSSION

Asymmetric Anionic Polymerizations

We carried out the asymmetric anionic polymerizations of **1a-d**, **1h**, and **1j** with the ^{i}PrPhOLi/(–)-Sp initiator at [monomer]/[^{i}PrPhOLi/(–)-Sp] ratio of 20 in a mixture solution of dichloromethane/toluene (30/70 in vol %) at –78 °C. To perform asymmetric anionic polymerization in the homogeneous state for all of six monomers in a mixture solution of dichloromethane/toluene (30/70 in vol %) at –78 °C, the polymerizations were carried out at a monomer concentration of 0.12 mol/L instead of 0.23 mol/L used in previous work[4] for the asymmetric anionic polymerization of **1b**. Polymerizations proceeded homogenously for all monomers except for **1j**, but **1j** became gradually heterogeneous, due to low solubility of resulting polymer toward a mixture solution of dichloromethane/toluene (30/70 in vol %). The results are summarized in Table 1.

Asymmetric anionic polymerizations afforded optically active polymers in moderate yields, which have the number-average molecular weights in the range 1800 to 3500, and the molecular weight distributions in the range 1.3 to 1.4. The molar optical rotation values of the obtained polymers depend upon the alkoxy groups of the monomers, where the tendency of the values increases with an increase in the bulkiness of the alkoxy groups. **1h** with *tert*-butoxy group provided an optically active polymer with a maximum negative molar optical rotation value ($[\phi]_{435}$ = –12.9°). Here, although **1j** has a more bulky benzhydryloxy group in comparison with **1h**, a polymer with a smaller molar optical rotation value ($[\phi]_{435}$ = –10.6°) is formed, probably due to the change of the system from homogeneous state to heterogeneous state in the progress of polymerization. Anyway, on the basis of the molar optical rotation values, stereoselectivity in the asymmetric anionic polymerizations of **1a-d**, **1h**, and **1j** using the ^{i}PrPhOLi/(–)-Sp initiator might be improved with an increase in the bulkiness of the alkoxy groups of the monomers. However, very low molar optical rotation values of the resulting polymers indicate low stereocontrol in the polymerization reaction.

TABLE 1 Asymmetric Anionic Polymerizations of **1a-d**, **1h**, and **1j** with ^{i}PrPhOLi/(–)-Sp Initiator in Dichloromethane/Toluene (30/70 in vol %) at −78 °C[a]

Monomer	Alkoxy Group	Yield/%[b]	M_n (DP)[c]	$[\alpha]_{435}$[d]	$[\phi]_{435}$[d]
1a	Me	81	2,000 (11)	−1.7°	−3.2°
1b	Et	70	1,900 (9)	−3.5°	−7.1°
1c	^{n}Pr	63	1,900 (9)	−4.5°	−9.8°
1d	^{i}Pr	52	1,800 (8)	−4.0°	−8.7°
1h	^{t}Bu	58	3,500 (15)	−5.6°	−12.9
1j	$CHPh_2$	65	2,100 (9)	−3.1°	−10.6°

[a] Conditions: [Monomer] = 0.12 mol/L, [Monomer]/[Initiator] = 20, Time: 48 h.
[b] Hexane-insoluble part.
[c] Determined by GPC as polystyrene standard. Degree of polymerization (DP) was determined by ^1H NMR.
[d] In chloroform.

Next, we investigated the asymmetric anionic polymerizations of **1a-j** using the ^{i}PrPhOLi/(–)-PhBox initiator at [monomer]/[^{i}PrPhOLi/(–)-PhBox] ratio of 20. To keep a system homogeneous state during the polymerizations at a monomer concentration of 0.23 mol/L for all monomers, polymerizations were performed in two conditions, one is in dichloromethane at –78 °C for **1a-e**, **1g** and **1h**, and another is in a mixture solution of dichloromethane/toluene (40/60 in vol %) at –40 °C for **1a-j**. All polymerization reactions proceeded homogenously. The results in dichloromethane at –78 °C for **1a-e**, **1g** and **1h**, and in a mixture solution of dichloromethane/toluene (40/60 in vol %) at –40 °C for **1a-j** are summarized in Tables 2 and 3, respectively.

In the Table 2, asymmetric anionic polymerizations afforded optically active polymers having the number-average molecular weights in the range 2000 to 3800, and the molecular weight distributions in the range 1.3 to 1.4. In the polymerizations of **1a-d** and **1h** except for **1e** and **1g**, both polymer yields and molecular weights have a tendency to decrease with increasing the bulkiness of alkoxy groups in the monomers. It seems that an attack of the propagating phenoxide anion upon the exomethylene carbon of the monomers is suppressed gradually with an increase in bulkiness of the alkoxy groups. And also, the molar optical rotation values of the polymers showed a tendency of decrease with increasing the bulkiness of the alkoxy groups, and **1b** provided an

TABLE 2 Asymmetric Anionic Polymerizations of **1a-e**, **1g**, and **1h** with ^{i}PrPhOLi/(–)-PhBox Initiator in Dichloromethane at −78 °C[a]

Monomer	Alkoxy Group	Yield/%[b]	M_n (DP)[c]	$[\alpha]_{435}$[d] (°)	$[\phi]_{435}$[d](°)
1a	Me	97	2,400 (16)	+22.1	+41.8
1b	Et	96	2,700 (20)	+53.6	+108.9
1c	^{n}Pr	88	2,600 (17)	+42.0	+91.2
1d	^{i}Pr	52	2,000 (12)	+23.1	+50.2
1e	^{n}Bu	21	3,400 (15)	+45.2	+104.5
1g	^{s}Bu	16	3,800 (16)	−0.74	−1.7
1h	^{t}Bu	45	2,100 (11)	+1.0	+2.3

[a] Conditions: [Monomer] = 0.23 mol/L, [Monomer]/[Initiator] = 20, time: 48 h.
[b] Hexane-insoluble part.
[c] Determined by GPC as polystyrene standard. Degree of polymerization (DP) is determined by ^{1}H NMR.
[d] In chloroform.

optically active polymer with the maximum positive molar optical rotation value ($[\phi]_{435} = +108.9°$).

In the Table 3, all monomers afforded optically active polymers in quantitative yields for **1a-h** and in moderate yields for **1i** and **1j**, which have the number-average molecular weights in the range 2500 to 7000, and the molecular weight distributions in the range 1.3 to 1.4. The lower yield and the lower molecular weights for **1i** and **1j** in comparison with for **1a-h** are due to a lower concentration, arising from a slight heterogeneous state of the systems observed even in this condition. The **1b** afforded an optically active polymer with the maximum positive molar optical rotation value ($[\phi]_{435} = +100.2°$) as well as the case of the asymmetric anionic polymerizations in dichloromethane ($[\phi]_{435} = +108.9°$). This indicates that ethoxy group is a suitable substituent for the stereocontrol among the substituents investigated in the asymmetric anionic polymerizations with a (–)-PhBox ligand. The molar optical rotation of the optically active polymers takes a maximum value at ethoxy group, and decreases in a following order: primary alkoxy > secondary alkoxy > tertiary alkoxy > aromatic ring. This indicates that higher stereocontrol in the polymers was achieved at a monomer with relatively small primary alkoxy group in contrast to the results of the polymerization with a (–)-Sp ligand, where a maximum molar optical rotation value was obtained for **1g** having the bulky *tert*-butoxy group. It is speculated that a specific conformation might be formed between chiral ligand and alkoxy group of alkoxycarbonyl substituents in the monomer **1**, and then a certain specified polymerization, where the size of the monomer could determine the stereoselectivity, might take place.

Stereoselectivity in the Initiation and Propagation Steps

In previous paper,[4] we carried out an asymmetric anionic oligomerization of **1b** with the ^{i}PrPhOLi/(–)-PhBox and ^{i}PrPhOLi/(–)-Sp initiators at [**1b**]/[initiator] ratio of 2 to investigate the degree of stereocontrol in the formation of an optically active polymer and the effect of the initiator systems on the control of chiral center. Here, we carried out the asymmetric anionic oligomerizations of **1a-c** with the ^{i}PrPhOLi/(–)-PhBox initiator in dichloromethane at –78 °C to investigate the effect of alkoxy groups on the control of chiral center in the formation of an optically active polymer. The results are summarized in Table 4, together with the previous result of the oligomerization of **1b** in a mixture solution of dichloromethane/toluene (30/70 in vol %) at –78 °C. In the oligomerization of **1b** in a mixture solution, higher oligomers such as 3-mer and 4-mer were scarcely produced even in 24h. On the other hand, the higher oligomers were slightly produced at the oligomerizations of **1a-c** in dichloromethane.

The 1-mers and 2-mers obtained by oligomerizations (run 1 and 2) of **1a** and **1b** showed a positive specific optical rotation similar to the corresponding polymers. On the other hand, the products obtained by oligomerization (run 3) of **1c** had a very small negative specific optical rotation values for the 1-mer and a large positive one for 2-mer, indicating that, in the asymmetric anionic polymerization of **1c**, stereoselectivity in an initiation reaction is different from that in a propagation reaction. Moreover, opposite sign in the specific optical rotation between 1-mers (positive sign) of **1a,b** and 1-mer (negative sign) of **1c** suggests the different stereoselectivity at the initiation step, and also small values in 1-mers for **1a-c** mean very low control of chiral center. 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 chromatograms of the optical resolution of the 1-mer obtained by oligomerizations are shown in Figure 1(a)

TABLE 3 Asymmetric Anionic Polymerizations of **1a-j** with ^{i}PrPhOLi/(–)-PhBox Initiator in Dichloromethane/Toluene (40/60 in vol %) at −40 °C[a]

Monomer	Alkoxy Group	Yield/%[b]	M_n (DP)[c]	$[\alpha]_{435}$ (°)[d]	$[\phi]_{435}$ (°)[d]
1a	Me	100	5,200 (27)	+44.3	+83.8
1b	Et	99	5,200 (25)	+49.3	+100.2
1c	^{n}Pr	97	6,300 (28)	+42.2	+91.7
1d	^{i}Pr	100	6,300 (28)	+26.9	+58.4
1e	^{n}Bu	100	3,800 (16)	+27.9	+64.5
1f	^{i}Bu	99	7,000 (29)	+39.0	+90.2
1g	^{s}Bu	99	7,000 (29)	+13.8	+31.9
1h	^{t}Bu	97	4,700 (20)	+8.5	+19.7
1i	CH_2Ph	51	2,500 (9)	+4.9	+13.0
1j	$CHPh_2$	59	3,000 (20)	−1.3	−4.4

[a] Conditions: [Monomer] = 0.23 mol/L, [Monomer]/[Initiator] = 20, time: 48 h.
[b] Hexane-insoluble part.
[c] Determined by GPC as polystyrene standard. Degree of polymerization (DP) is determined by ^{1}H NMR.
[d] In chloroform.

TABLE 4 Asymmetric Anionic Oligomerizations of **1a-c** with ^{i}PrPhOLi/(–)-PhBox Initiator at –78 °C[a]

Run	Monomer	Solvent	Time/h	Yield/%	$[\alpha]_{435}$ (°)[b]
1	**1a** (Me)	CH_2Cl_2	12	1-mer: 10.4	+3.7
				2-mer: 17.6	+21.8
2	**1b** (Et)	CH_2Cl_2	12	1-mer: 8.3	+3.0
				2-mer: 11.4	+31.0
3	**1c** (^{n}Pr)	CH_2Cl_2	12	1-mer: 14.1	−6.0
				2-mer: 22.0	+26.2
4[c]	**1b** (Et)	CH_2Cl_2/toluene	12	1-mer: 9.5	−1.5
		(30/70 in vol %)		2-mer: 8.2	+20.2

[a] Conditions: [monomer] = 0.23 mol/L, [Monomer]/[Initiator] = 2.
[b] In chloroform.
[c] Ref. 4.

for **1a**, Figure 1(b) for **1b**, and Figure 1(c) for **1c**, respectively, where top and bottom chromatograms were monitored by CD and UV detectors, respectively.

In Figure 1, the 1-mer with a positive CD sign was first eluted and followed by the 1-mer with a negative CD one, indicating that both components are enantiomers. On the basis of the peak area obtained from the UV chromatograms in Figure 1, 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 52/48 in mol % for **1a**, 52/48 in mol % for **1b**, and 49/51 in mol % for **1c**, respectively. 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 in comparison to 1-mer with the *S*-configurational one for **1a** and **1b**, but in a slight less amount for **1c**, respectively, and the enantiomeric excess (*ee*) is calculated to be 4% *ee*(*R*) for **1a**, 4% *ee*(*R*) for **1b**, and 2% *ee*(*S*) for **1c**, respectively. This indicates that, as shown in Scheme 3, addition of a lithium 4-isopropylphenoxide anion coordinated with a (–)-PhBox ligand to the monomer takes place in *Re*-face (front side) attack/*Si*-face (back side) attack ratio of 52%/48% for **1a**, 52%/48% for **1b**, and 49%/51% for **1c**, respectively, leading to enantiomer in a *R*-configurational 1-mer/*S*-configurational 1-mer ratio of 52/48 in mol % for **1a**, 52/48 in mol % for **1b**, and 49/51 in mol % for **1c**. However, these very low *ee* values for all of 1-mers indicate quite low stereoselectivity in the initiation step.

Next, to examine 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 by oligomerizations are shown in Figure 2(a) for **1a**, Figure 2(b) for **1b**, and Figure 2(c) for **1c**, respectively, where four diastereomers are separated completely for **1a** and **1b**, but not for **1c** though we attempted to separate them in various conditions.

From the peak area obtained on the UV chromatograms in Figure 2, the ratios 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 were determined to be 32/21/29/18 in mol % for **1a** and 37/20/29/14 in mol % for **1b**, respectively. For **1c**, as the peaks of the first-eluted and second-eluted components overlap, the ratio of the first-eluted component/second-eluted one was determined by nonlinear peak separation using Gaussian function, and the ratios of the first-eluted component with a negative CD sign/

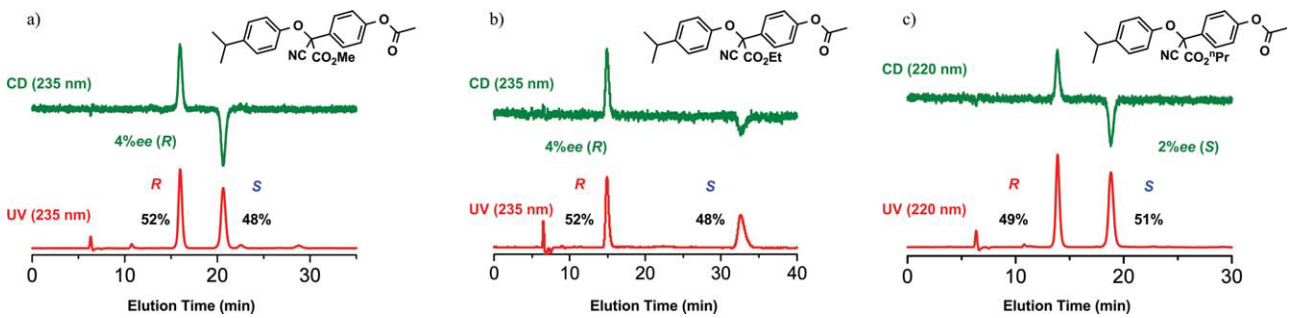
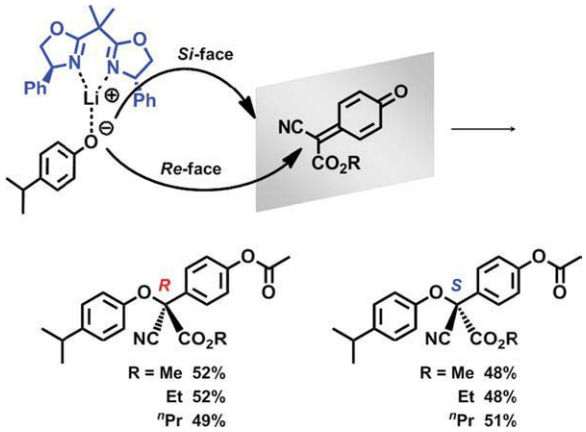


FIGURE 1 HPLC chromatograms of optical resolution of the 1-mers obtained by oligomerizations of (a) **1a**, (b) **1b**, and (c) **1c** with the iPrPhOLi/(–)-PhBox initiator (column: Daicel Chiralpak AD, eluent: hexane/ethanol = 90/10 (in vol %), flow rate: 0.5 mL/min). The top chromatogram was measured by CD detector (235 or 220 nm) and bottom by UV detector (235 or 220 nm).



SCHEME 3 Stereoselectivity in the addition reaction of the iPr-PhOLi/(–)-PhBox initiator to monomer in the initiation step.

the second-eluted one with a positive CD sign/the third-eluted one with a negative CD sign/the fourth-eluted one with a positive CD sign were estimated to be 20/35/14/31 in mol % for **1c**.

Here, addition of enantiomers in the 1-mer to monomer 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 for **1a**, we considered that total amount of the 2-mer with (*R,R)*- and (*R,S*)-configurations derived from the *R*-configurational 1-mer is 52 mol %, and total amount of the 2-mer with (*S,R)*- and (*S,S*)-configurations derived from the *S*-configurational 1-mer is 48 mol %, respectively. In the UV chromatogram of the 2-mer in Figure 2(a), total amount of the first-eluted (32 mol %) and the second-eluted (21 mol %) components is 53 mol % and also total amount of the second-eluted (21 mol %) and the third-eluted (29 mol %) components is 50 mol %, respectively. 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. The first-eluted, the second-eluted, the third-eluted, and the fourth-eluted components in the chromatograms for 2-mers of **1a** [Fig. 2(a)] and **1b** [Fig. 2(b)] 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 other hand, for **1c** [Fig. 2(c)] the first-eluted, the second-eluted, the third-eluted, and the fourth-eluted components could be assigned to the 2-mer with a (*S,R*)-configuration, a (*R,R*)-one, a (*S,S*)-one, and a (*S,R)*-one, respectively, on the basis of their CD signs, which are opposite to those for **1a** and **1b** (a positive CD sign for first-eluted component, a negative CD sign for second-eluted one, a positive CD sign for third-eluted component and a negative CD sign for fourth-eluted one). On the basis of this assignment, for **1a**, the 2-mers with a (*R,R)*-configuration (32 mol %) and with a (*S,R)*-configuration (29 mol %) are produced in larger amount by a factor of 1.6 than those with a (*R,S)*-configuration (21 mol %) and with a (*S,S)*-configuration (18 mol %), respectively, and also the diastereomeric excess (*de*) is calculated to be 21% *de*(*RR/RS*) for the 1-mer with a *R*-configuration and 23% *de*(*SR/SS*) for the 1-mer with a *S*-configuration, respectively. Addition reaction of the 1-mer anion to a monomer **1a** might take place stereoselectively regardless of the configurational chirality in a 1-mer anion to produce a 2-mer with an excessive *R*-configurational chiral carbon (32 mol % + 29 mol % = 61 mol %) in comparison with the *S*-configurational chiral carbon (21 mol % + 18 mol % = 39 mol %). Probably, the propagation reaction to 3-mer, 4-mer, 5-mer, and oligomer, and polymer is considered to proceed in same stereoselectivity (*R*-configuration/*S*-configuration = 61/39 in mol %). Stereoselectivity on the initiation and propagation reactions for the polymerization of **1a** with the ^{i}PrPhOLi/(–)-PhBox initiator is summarized in Chart 2.

For **1b**, the 2-mers with a (*R,R)*-configuration (37 mol %) and with a (*S,R)*-configuration (29 mol %) are produced in

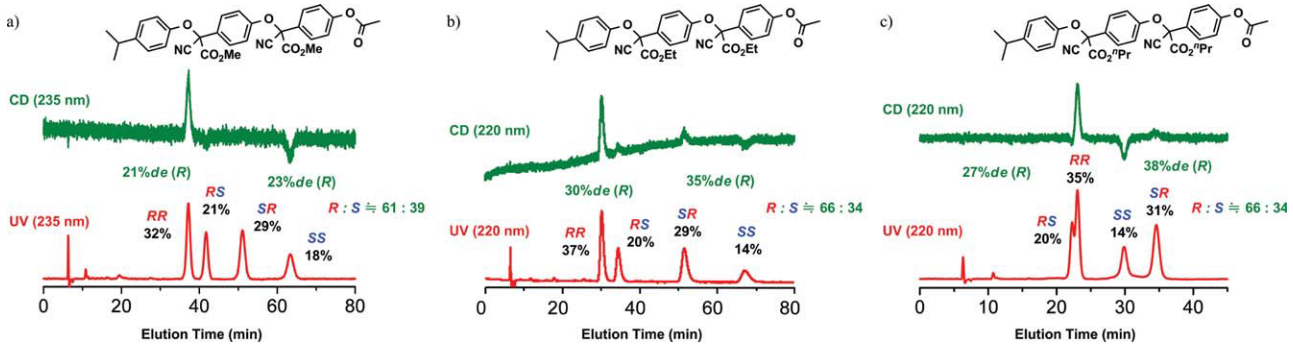


FIGURE 2 HPLC chromatograms of optical resolution of the 2-mers obtained by oligomerizations of (a) **1a** (b) **1b**, and (c) **1c** with the iPrPhOLi/(–)-PhBox initiator (column: Daicel Chiralpak AD, eluent: hexane/ethanol = 90/10 (in vol %), flow rate: 0.5 mL/min). The top chromatogram was measured by CD detector (235 or 220 nm) and bottom by UV detector (235 or 220 nm).

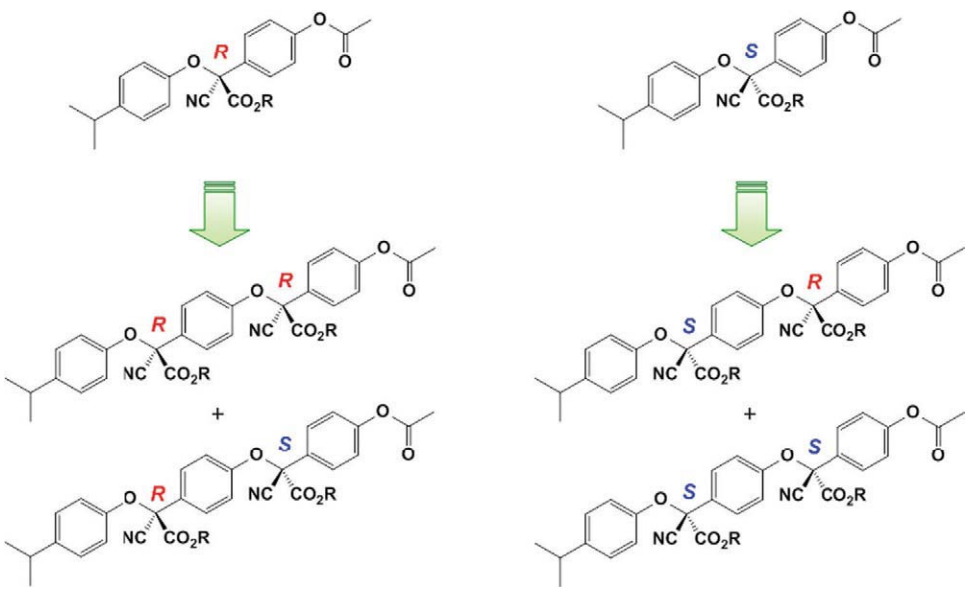


CHART 1 Diastereomers of the 2-mer.

larger amount by a factor of 1.9 than those with a (*R,S)*-configuration (20 mol %) and with a (*S,S)*-configuration (14 mol %), respectively, and also the diastereomeric excess (*de*) is calculated to be 30% *de*(*RR/RS*) for the 1-mer with a *R*-configuration and 35% *de*(*SR/SS*) for the 1-mer with a *S*-configuration, respectively. Addition reaction of the 1-mer anion to a monomer **1b** might take place stereoselectively to produce a 2-mer with a *R*-configurational chiral carbon (37 mol % + 29 mol % = 66 mol %) in excess with respect to a 2-mer with a *S*-configurational chiral carbon (20 mol % + 14 mol % = 34 mol %). Probably, the propagation reaction to 3-mer, 4-mer, 5-mer, and oligomer, and polymer is considered to proceed in same stereoselectivity (*R*-configuration/*S*-configuration = 66/34 in mol %) as well as the case of **1a**. Stereoselectivity on the initiation and propagation reactions for the polymerization of **1b** with the ^{i}PrPhOLi/(–)-PhBox initiator is summarized in Chart 3.

For **1c**, the 2-mers with a (*R,R)*-configuration (35 mol %) and with a (*S,R)*-configuration (31 mol %) are produced in larger amount by a factor of 1.9 than those with a (*R,S)*-configuration (20 mol %) and with a (*S,S)*-configuration (14 mol %), respectively, and also the diastereomeric excess (*de*) is calculated to be 27% *de*(*RR/RS*) for the 1-mer with a *R*-configuration and 38% *de*(*SR/SS*) for the 1-mer with a *S*-configuration, respectively. Addition reaction of the 1-mer anion to a monomer **1c** might take place stereoselectively to produce a 2-mer with a *R*-configurational chiral carbon (35 mol % +

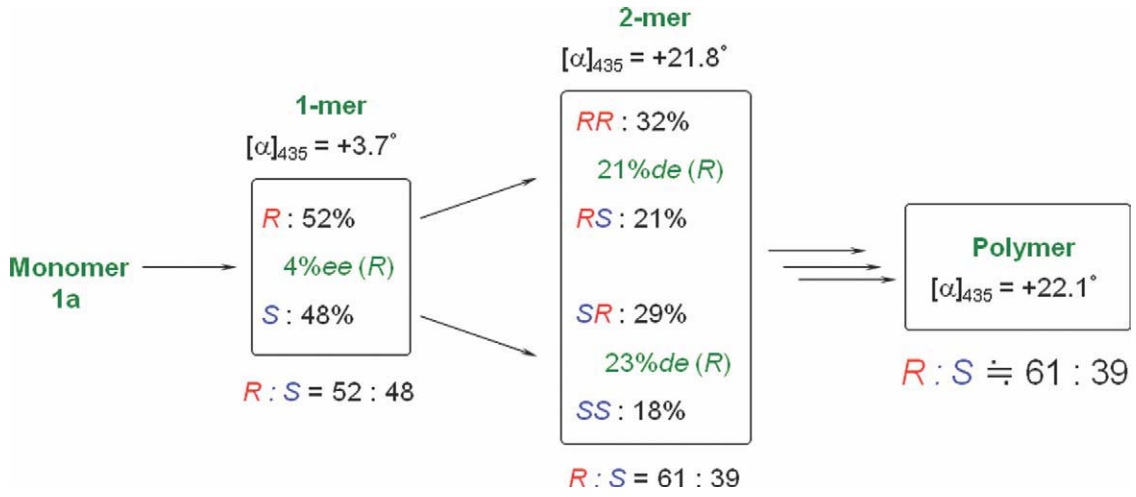


CHART 2 Stereoselectivity on the initiation and propagation reactions for the polymerization of **1a** with the iPrPhOLi/(–)-PhBox initiator.

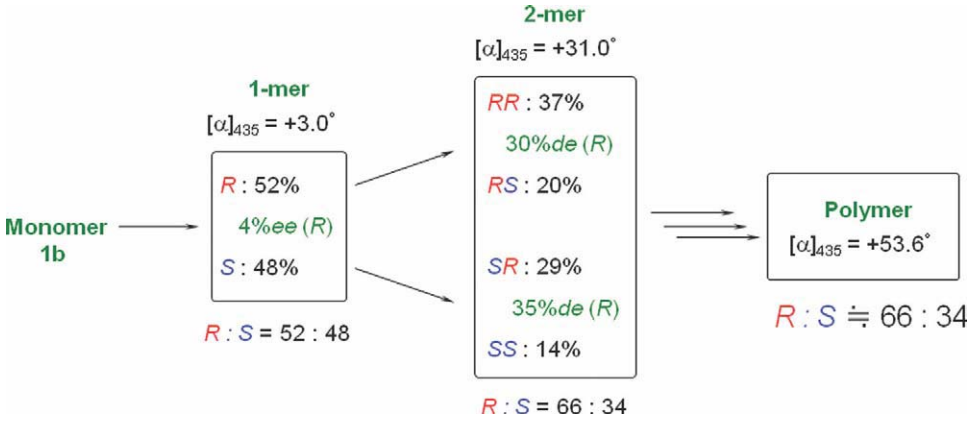


CHART 3 Stereoselectivity on the initiation and propagation reactions for the polymerization of **1b** with the iPrPhOLi/(–)-PhBox initiator.

31 mol % = 66 mol %) in excess with respect to a 2-mer with a *S*-configurational chiral carbon (20 mol % + 14 mol % = 34 mol %). Probably, the propagation reaction to 3-mer, 4-mer, 5-mer, and oligomer, and polymer is considered to proceed in same stereoselectivity (*R*-configuration/*S*-configuration = 66/34 in mol %) as well as the case of **1a** and **1b**. Stereoselectivity on the initiation and propagation reactions for the polymerization of **1c** with the ^{i}PrPhOLi/(–)-PhBox initiator is summarized in Chart 4.

Stereoselectivities of 1-mer and 2-mer in the oligomerizations of **1a-c** with the ^{i}PrPhOLi/(–)-PhBox initiator in dichloromethane at –78 °C are summarized in Table 5, together with the previous result of **1b** in a mixture solution of dichloromethane/toluene (30/70 in vol%) at –78 °C.[4]

These results indicate that, in the initiation reaction step, stereoselective addition reactions of the initiator to monomers hardly take place, and the effect of alkoxy groups such as methoxy, ethoxy, and *n*-propoxy groups was scarcely observed in the stereoselectivity of 1-mers. While, in the propagation reaction step, relatively high stereoselectivity is observed. This indicates that, in the formation of dimer, the alkoxycarbonyl group of the monomers exerts the improvement of the stereoselectivity on the addition reaction of the 1-mer anion to the monomer. Furthermore, the extent of stereoselectivity of 2-mers for **1b** and **1c** were clearly higher than that of 2-mer for **1a**. As the results, the polymers with higher molar optical rotation around 100° were obtained by asymmetric anionic polymerization of **1b** and **1c**. When the oligomerization of **1b** was carried out in a mixture solution of dichloromethane/toluene (30/70 in vol %), 1-mer with *S*-configurational chirality was formed in a slight excess amount compared to 1-mer with *R*-configurational one, which is the reverse of the result in the dichloromethane. It is considered, therefore, that, in a mixture solution of dichloromethane/toluene (30/70 in vol %) containing toluene as a less polar solvent, some change of the distance between the initiator anion and the counterion might take place, and the change might exert a influence on the coordination structure involving a chiral ligand.

Effect of Counterion and Solvent on the Stereocontrol

We investigated the effects of a counterion such as lithium, sodium, and potassium in the initiator, solvent, and a chiral ligand such as (–)-Sp and (–)-PhBox on the specific optical rotation of the polymers. Asymmetric anionic polymerizations

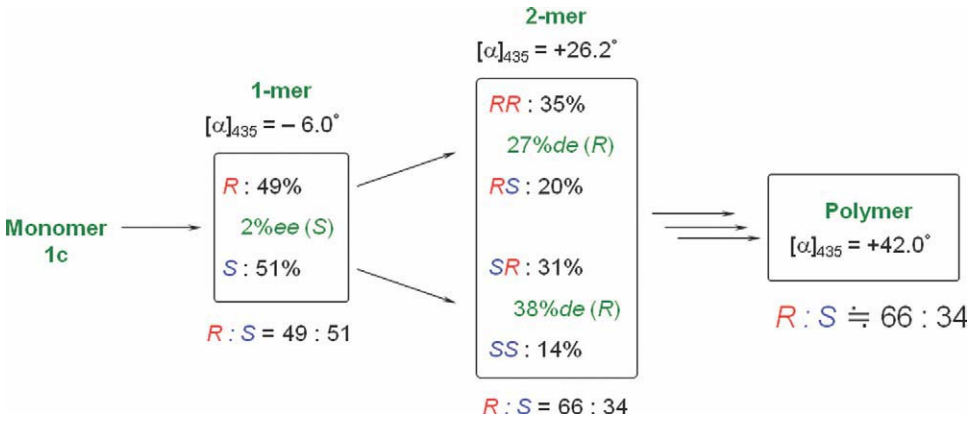


CHART 4 Stereoselectivity on the initiation and propagation reactions for the polymerization of **1c** with the iPrPhOLi/(–)-PhBox initiator.

TABLE 5 Stereoselectivity on the Initiation and Propagation Reactions in Asymmetric Anionic Polymerizations of **1a-c** with the ^{i}PrPhOLi/(–)-PhBox Initiator

Run	Monomer	Solvent	Initiation Reaction 1-mer (*R*:*S*)	Propagation Reaction 2-mer (*R*:*S*)
1	**1a** (Me)	CH_2Cl_2	4% *ee* (*R*) (52:48)	21% *de* (*RR*/*RS*)
				23% *de* (*SR*/*SS*)
				(*R*:*S* = 61:39)
2	**1b** (Et)	CH_2Cl_2	4% *ee* (*R*) (52:48)	30% *de* (*RR*/*RS*)
				35% *de* (*SR*/*SS*)
				(*R*:*S* = 66:34)
3	**1c** (^{n}Pr)	CH_2Cl_2	2% *ee* (*S*) (49:51)	27% *de* (*RR*/*RS*)
				38% *de* (*SR*/*SS*)
				(*R*:*S* = 66:34)
4[a]	**1b** (Et)	CH_2Cl_2/toluene (30/70 in vol %)	4% *ee* (*S*) (48:52)	36% *de* (*RR*/*RS*)
				32% *de* (*SR*/*SS*)
				(*R*:*S* = 57:43)

[a] Ref. 4.

of **1b** were carried out in dichloromethane and in a mixture solution of dichloromethane/toluene (30/70 in vol %) at –78 °C, and the results are summarized in Table 6 for the ^{i}PrPhOM (M = Li, Na, K)/(–)-Sp initiator and Table 7 for the ^{i}PrPhOM (M = Li, Na, K)/(–)-PhBox initiator, respectively.

Polymerizations of **1b** with ^{i}PrPhONa/(–)-Sp and ^{i}PrPhOK/(–)-Sp initiators afford the corresponding polymers with high molecular weights of 12,500–54,800 in high yields of 83–89% in both solvents, dichloromethane and a mixture solution of dichloromethane/toluene (30/70 in vol %). The polymers obtained with ^{i}PrPhONa/(–)-Sp and ^{i}PrPhOK/(–)-Sp initiators in both solvents have much higher molecular weights than those obtained with ^{i}PrPhOLi/(–)-Sp initiator, indicating that the polymerizations with ^{i}PrPhONa/(–)-Sp and ^{i}PrPhOK/(–)-Sp initiators would take place in much faster propagation reaction than initiation one, that is, suggesting that in the cases of Na^+ and K^+ as a counterion the polymerization would proceed in much higher degree of dissociation state between the carbanion center and the counterion relative to the case of Li^+ as a counterion. The specific optical rotation values of polymers obtained with all of three initiators increase in changing from a polar solvent such as dichloromethane to a less polar solvent such as a mixture solution of dichloromethane/toluene (30/70 in vol %), although their values are relatively small. Generally, it is well-known that in anionic polymerizations in less or non polar solvents the dissociation of carbanion center and counterion is suppressed and favors to ion pair formation.[7] It is, therefore, considered that dissociation between the carbanion and the counterion is in a small degree in a mixture solution of dichloromethane/toluene (30/70 in vol %) containing toluene as a less polar solvent and favors ion pair formation to free ion, leading to improvement of stereoselectivity in the addition reaction.

Polymerizations of **1b** with ^{i}PrPhOLi/(–)-PhBox initiator affords corresponding polymers with the molecular weights of 2700 in dichloromethane and 1600 in a mixture solution of dichloromethane/toluene (30/70 in vol %). The specific optical rotation values of polymers obtained in dichloromethane and in a mixture solution of dichloromethane/toluene (30/70 in vol %) are +53.6° and +91.8°, respectively. While, polymerizations of **1b** with ^{i}PrPhONa/(–)-PhBox initiator

TABLE 6 Asymmetric Anionic Polymerization of **1b** with ^{i}PrPhOM/(–)-Sp Initiators[a]

Counter Cation	Solvent	Time/h	Yield/%[b]	M_n[c]	M_w/M_n[c]	$[\alpha]_{435}$[d]
Li^+	CH_2Cl_2	48	99	3,100	1.40	−1.2°
Na^+	CH_2Cl_2	24	88	23,400	1.26	−0.14°
K^+	CH_2Cl_2	24	88	12,500	1.68	−1.1°
Li^+	CH_2Cl_2/toluene (30/70)	48	77	1,700	1.43	−2.3°
Na^+	CH_2Cl_2/toluene (30/70)	48	89	21,000	1.26	−6.9°
K^+	CH_2Cl_2/toluene (30/70)	48	83	54,800	1.68	−4.0°

[a] [Monomer] = 0.23 mol/L, [Monomer]/[Initiator] = 20, Temp. –78 °C.
[b] Hexane-insoluble part.
[c] Determined by GPC as polystyrene standard.
[d] In chloroform.

TABLE 7 Asymmetric Anionic Polymerization of **1b** with ^{i}PrPhOM/(–)-PhBox Initiators[a]

Counter Cation	Solvent	Time/h	Yield/%[b]	M_n[c]	M_w/M_n[c]	$[\alpha]_{435}$[d]
Li^+	CH_2Cl_2	48	96	2,700	1.36	+53.6°
Na^+	CH_2Cl_2	24	49	12,500	1.15	+8.6°
K^+	CH_2Cl_2	24	88	12,500	1.16	−1.1°
Li^+	CH_2Cl_2/toluene (30/70)	48	30	1,600	1.26	+91.8°
Na^+	CH_2Cl_2/toluene (30/70)	236	39	6,200	1.17	−3.0°
K^+	CH_2Cl_2/toluene (30/70)	168	87	17,600	1.24	−3.2°

[a] [Monomer] = 0.23 mol/L, [Monomer]/[Initiator] = 20, Temp. –78 °C.
[b] Hexane-insoluble part.
[c] Determined by GPC as polystyrene standard.
[d] In chloroform.

proceed in slow rate, and afford corresponding polymers in low yields in both solvents. Polymerization with ^{i}PrPhONa/(–)-PhBox initiator yielded a positive specific optical rotation value of +8.6° in dichloromethane and a negative one of –3.0° in a mixture solution of dichloromethane/toluene (30/70 in vol %), respectively, and these values are much smaller than those of the polymers obtained with ^{i}PrPhOLi/(–)-PhBox initiator in both solvents. Moreover, the polymers obtained in both solvents showed an opposite sign each other, and also the optical rotation values became smaller in addition of toluene as a less polar solvent into dichloromethane. It is unclear why the stereochemical result reverses with solvent at present. It is speculated that a counterion Na^+ is brought to the vicinity of the carbanion center by addition of less polar solvent, and the bulkiness of the Na^+ influences to the coordination of a chiral ligand, resulting to less stereoselectivity in the addition reaction. Polymerizations of **1b** with ^{i}PrPhOK/(–)-PhBox initiator in both solvents afford the corresponding polymers with high molecular weights in high yields in comparison with the cases of the polymerizations with ^{i}PrPhONa/(–)-PhBox initiator. However, the polymers obtained with ^{i}PrPhOK/(–)-PhBox initiator in both solvents have much smaller specific optical rotation values relative to those with ^{i}PrPhOLi/(–)-PhBox initiator and ^{i}PrPhONa/(–)-PhBox initiator, and also they have the optical rotation values with negative signs. As ion radius and polarity of K^+ are larger than those of Li^+ and Na^+, K^+ counterion is considered to exist apart from the carbanion, that is, the carbanion that K^+ is a conterion would be present in a free ion state in comparison with Li^+ and Na^+. It is plausible, therefore, that in the addition of the anion to monomer the (–)-PhBox ligand does not work effectively, or there is a possibility that the chiral ligand does not coordinate to K^+ as an extreme case.

From the investigation of the counterion effect in the ^{i}PrPhOM(M = Li, Na, K)/(–)-PhBox initiators for the polymerization of **1b**, it was found that the ^{i}PrPhOLi/(–)-PhBox initiator having Li^+ as a counterion is more effective on the stereocontrol in roder to obtain the optically active polymer in comparison with other two initiators having Na^+ and K^+ as a counterion. Organic lithium initiators are widely used as the stereospecific polymerization catalysts for styrene,[8] 1,3-dienes such as 1,3-butadiene and isoprene,[9] and acrylates.[10] It is pointed out that Li^+ in the asymmetric anionic polymerizations of substituted quinine methides is the most effective counterion.

CONCLUSIONS

Molar optical rotation values of the polymer obtained by the polymerizations of **1a-j** with chiral initiators were significantly dependent upon alkoxy groups, and they decreased with an increase in the bulkiness of the alkoxy groups. Polymerization of **1b** (Et) with ^{i}PrPhOLi/(–)-PhBox afforded the polymer with a maximum value of molar optical rotation, and the ethoxy group was found to be the most suitable substituent for the stereocontrol of the polymer. From optical resolutions of 1-mer and 2-mer in the oligomers obtained by asymmetric oligomerizations of **1** monomers having methoxy(**1a**), ethoxy(**1b**), and *n*-propoxy(**1c**) groups with chiral initiators, stereoselectivity was hardly observed at the initiation reaction, but it was observed at the propagation reaction, where higher stereoselectivity was observed in the monomers with ethoxy and *n*-propoxy groups. In asymmetric anionic polymerizations of **1b** with ^{i}PrPhOM(M = Li, Na, K)/(–)-Sp and ^{i}PrPhOM(M = Li, Na, K)/(–)-PhBox initiators, it was found that the initiator having Na^+ as a counterion is effective for the stereocontrol of the polymer in dichloromethane/toluene (30/70 in vol%) for (–)-Sp as a ligand, and also the initiator having a smaller Li^+ as a counterion is effective in both dichloromethane and dichloromethane/toluene (30/70 in vol%) for (–)-PhBox as a ligand.

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