# Synthesis of Highly Optically Active Polysulfoxides by Asymmetric Oxidation of Polysulfides

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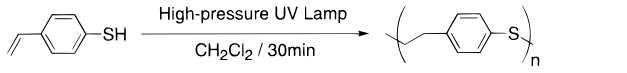
ABSTRACT: Novel highly optically active polysulfoxides having chiral sulfinyl groups in the main chain were prepared by asymmetric oxidation of the corresponding polysulfides by using chiral *N*-sulfonyloxaziridine (**6**). The polysulfoxide with the enantiomeric excess up to 91% ee was obtained in good chemoselectivity when the reaction was carried out with 1 equiv of (−)-*N*-sulfonyloxaziridine, (−)-**6**, in chloroform at room temperature followed by reflux. The enantiomeric excess was estimated from the $^{13}C$ NMR spectrum, and the stereochemistry at the sulfur atom was speculated by comparison of CD spectra of the polysulfoxides with that of the model compound ((*S*)-*p*-tolyl methyl sulfoxide). This asymmetric oxidation is the first example of introduction of chirality in good enantioselectivity into the main chain of a polymer by polymer reaction, that is, the first example of the control of "tacticity" by polymer reaction. In fact, the shift of the glass transition temperature of the polysulfoxide was observed depending on the change of tacticity of the polymer. The obtained polymer is regarded as one of the first examples of the polymers having heteroatom chirality in the main chain.

## Introduction

The sulfoxide is known to have a configurationally stable asymmetric center,[1] and many chiral sulfoxides have been prepared and used in many organic syntheses as chiral synthons since chiral sulfoxides can induce chirality at their α- and/or *β*-carbons.[1,2] Several methods to obtain homochiral sulfoxides have been developed so far. Among them, the synthesis of chiral sulfoxides by asymmetric oxidation is attractive because this method can be potentially applied to every substrate, including polymeric sulfides.[3−7] Both stoichiometric[5] and catalytic[6] oxidations have been studied as the method for the synthesis of optically active sulfoxides. Though catalytic oxidations are potentially better methods, they generally have limitations on substrates and accomplish lower ee so far. On the other hand, the oxidation with modified Sharpless reagent reported by Kagan et al.[5a−d] and the oxidation with chiral *N*-sulfonyloxaziridine invented by Davis et al.[5j] have been extensively investigated as versatile methods for stoichiometric oxidations. Both reagents are known to oxidize *p*-tolyl methyl sulfide to the corresponding sulfoxide in 95% ee or more in good yields.

Therefore, highly optically active polysulfoxides having sulfur asymmetric centers in the main chain can be prepared by the asymmetric oxidation of the corresponding polysulfides.[8] This reaction is considered to be interesting as the first example of the preparation of highly optically active polymers having asymmetric centers in their main chain by polymer reaction;[8a,9] that is, we can control "tacticity" of the polymers by polymer reaction. The resulting polymers are thought to be one of the first polymers having heteroatom chirality in the main chain[8a,10] and are expected to show different properties such as in glass transition temperature based on their stereochemistry. The utilization of chiral polysulfoxides as stationary phases of chiral HPLC column and as polymer reagents is also promising. In this paper, we describe the synthesis of novel optically active polysulfoxides by the asymmetric oxidation of the corresponding polysulfides and the preliminary results about the properties of the obtained polymers.

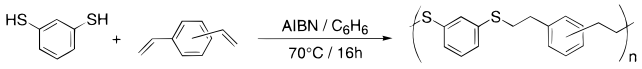
**Scheme 1. Synthesis of Polysulfide 2**




**1** **2**

97%, $M_n$=2400($^1$H-NMR)

**Scheme 2. Synthesis of Polysulfide 5**




**3** **4** (*m*:*p*=2.1:1) **5**

100%, $M_n$=3500($^1$H-NMR)

## Results and Discussion

The oxidizing reagents investigated in this study are known to show better results in the oxidation of aryl alkyl sulfoxides than that of dialkyl sulfoxides. Thus, the polysulfides **2** and **5** having aryl and alkyl groups adjacent to sulfur atoms were prepared by radical polyaddition of the corresponding monomer(s) as shown in Schemes 1 and 2. The monomer **1** for the synthesis of **2** was prepared according to the modified procedure of ref 11. Though **1** contained some oligomers, they did not influence the polymerization to afford the corresponding polymer **2**. The number-average molecular weights of **2** and **5** estimated from $^1$H NMR spectra were 2400[12] and 3500,[13] respectively. Vinylbenzenethiols are known to polymerize by anti-Markovnikov polyaddition between the double bond and mercapto group without vinyl polymerization,[14] and in fact, no grafted chain and Markovnikov addition structure were identified from $^1$H NMR spectra of the polymers. Chiral (−)-*N*-sulfonyloxaziridine ((−)-**6**) was prepared from (+)-camphor by

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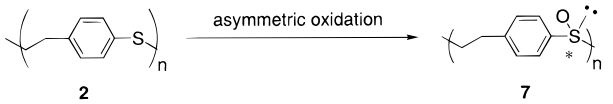
**Table 1. Asymmetric Oxidation of the Polysulfide 2**

| entry | condition[a] | yield (%) | S:S(O):S(O)2[b] | $M_n$ ($M_w/M_n$)[c] | $[\alpha]_D^{20}$($CHCl_3$) | ee (%)[e] |
|---|---|---|---|---|---|---|
| 1 | **a**, $CH_2Cl_2$/−20 °C/32 h | 53 | 39:50:11 | 2500 (2.64) | ≈0° | |
| 2 | **b**, $CHCl_3$/rt (31 h)−reflux (40.5 h) | 79 | 6:89:5 | 3000 (1.39)<br>2400[d] | +9.9°<br>($c$ = 1.11) | 37 (*R*)[f] |
| 3 | **c**, $CHCl_3$/rt (64 h)−reflux (24 h) | 87 | 6:94:0 | 3200 (1.42)<br>3800[d] | −100°<br>($c$ = 1.29) | 91 (*S*)[f] |
| 4 | **c**, $CHCl_3$/reflux (20 h) | 65 | 12:87:1 | 2900 (1.78)<br>4500[d] | −67°<br>($c$ = 1.30) | 84 (*S*)[f] |
| 5 | **c**, $CHCl_3$/rt (7 days)−reflux (24 h) | 72 | 6:93:1 | 2300 (1.45)<br>5000[d] | −84°<br>($c$ = 0.229) | 90 (*S*)[f] |

[a] **a**: Ti(O-*i*-Pr)$_4$/(+)-DET/$H_2O$/*t*-BuOOH (1:2:1:1.6 to the substrate), (DET = diethyl tartrate). **b**: Oxaziridine **8** (see text, 1 equiv). **c**: Oxaziridine (−)-**6** (see text, 1 equiv). [b] Determined by the ratio of integrals of phenyl protons adjacent to sulfur atom in $^1$H NMR spectrum. [c] Determined by GPC. Eluent: $CHCl_3$. Polystyrene was used as the standard for calibration. [d] Determined by ratio of an integral of terminal vinyl protons with that of main-chain methylene protons in $^1$H NMR spectrum. [e] Roughly determined from the integrals of the peaks at the carbon adjacent to sulfur atom in $^{13}$C NMR spectrum.

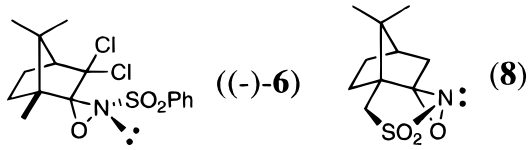
**Scheme 3. Asymmetric Oxidation of Polysulfide 2**




**2** **7**

three steps as reported by Davis et al.[5j] (+)-**6** was also synthesized by the same procedure.

Then, the asymmetric oxidation of the polysulfide **2** was examined (Scheme 3). The results are summarized in Table 1. When modified Sharpless reagent was used as the oxidizing reagent, both selectivity of the oxidation of sulfide units to sulfoxides and enantioselectivity were low (entry 1). The use of the commercially available oxaziridine **8** resulted in poor enantioselectivity, though




((-)-**6**)




(**8**)

the reaction was highly chemoselective (entry 2). On the other hand, optically active polysulfoxides **7** were synthesized in good chemoselectivity and enantioselectivity when Davis's chiral oxaziridine (−)-**6** was utilized (entries 3−5). Especially, the polymer showed high optical rotation when the reaction was carried out at room temperature at first as shown in entry 3. However, elongation of the reaction time at ambient temperature did not improve the enantioselectivity of the reaction (entry 5). In the oxidations by the oxaziridine (−)-**6** (entries 3−5), an increase in the molecular weight of the resulting polysulfoxides compared with the calculated value (2700) was observed. This would be due to the intermolecular reaction of the terminal thiol group with the terminal vinyl group.

The enantiomeric excess of the polysulfoxide **7** was roughly determined from the $^{13}$C NMR spectrum.[15] Figure 1 shows the peaks of the methylene carbons adjacent to sulfinyl groups in $^{13}$C NMR spectra of polymer **7**. As shown in the spectra, two overlapping peaks corresponding to *m* and *r* stereochemistry are observed between 57.5 and 57.7 ppm, and the enantiomeric excess is roughly calculated from the integrals of these two peaks by assuming that the asymmetric oxidation is independent of the oxidation state and the stereochemistry of the neighboring sulfur atoms.[8a,16] In the case of Figure 1a (low $[\alpha]_D$), the enantiomeric excess was estimated to be ca. 37% ee.[16] On the other hand, a sharp *m* peak is observed in the $^{13}$C NMR spectrum of the polymer **7** with high degree of optical rotation (Figure 1b), and the enantiomeric excess was calculated to be 91% ee.[16]

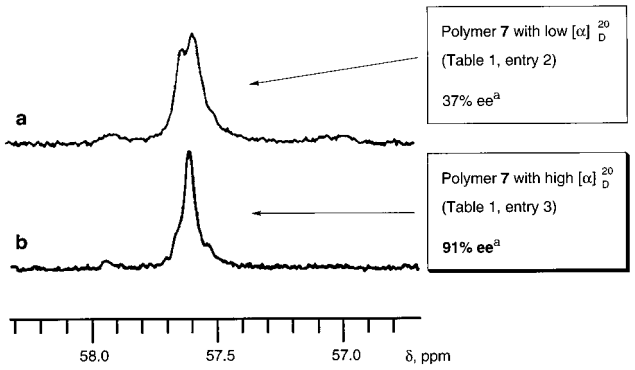



**Figure 1.** $^{13}$C NMR spectra (−S(O)$CH_2$−, 125.7 MHz) of polymer **7** with a low degree of optical rotation (a) and polymer **7** with a high degree of optical rotation (b).

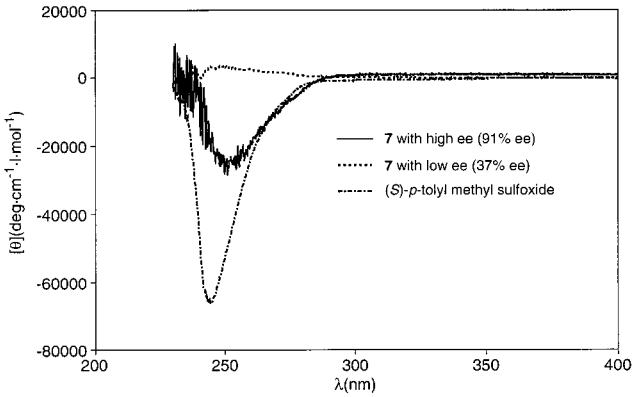
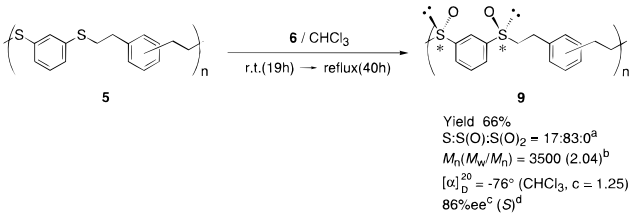



**Figure 2.** CD spectra of polymer **7** with high ee (91% ee, Table 1, entry 3), polymer **7** with low ee (37% ee, Table 1, entry 2), and (*S*)-*p*-tolyl methyl sulfoxide (in $CHCl_3$).

CD spectra of the resulting chiral polysulfoxides **7** in entries 2 and 3 of Table 1 as well as the model compound ((*S*)-*p*-tolyl methyl sulfoxide) are exhibited in Figure 2, and polymer **7** with high ee shows the same negative Cotton effect with that of the model compound ((*S*)-*p*-tolyl methyl sulfoxide) at almost the same wavelength. This result indicates that the stereochemistry of the polysulfoxide asymmetric centers prepared by the chiral oxaziridine (−)-**6** is the same as that of the model compound, that is, the *S*-form. The stereochemistry of other polysulfoxides was also determined from CD spectra. An asymmetric oxidation of the polysulfide **5** was also examined, and the polysulfoxide **9** with $[\alpha]_D$ = −76° (86% ee, *S*-form) was obtained in good yield and

**Scheme 4. Synthesis of the Chiral Polysulfoxide 9**




[a] Determined by the ratio of integrals of methylene protons adjacent to sulfur atom in $^1$H NMR spectrum. [b] Determined by GPC. Eluent: $CHCl_3$. Polystyrene was used as the standard for calibration. [c] Roughly determined from the integrals of the peaks at the carbon adjacent to sulfur atom in the $^{13}$C NMR spectrum. [d] Determined by the CD spectrum.

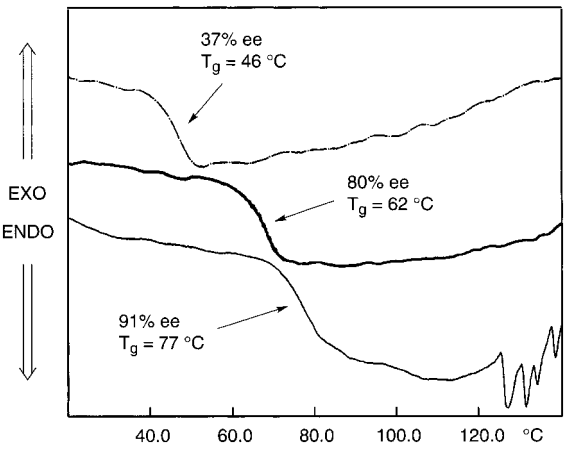



**Figure 3.** DSC thermograms of polysulfoxide **7** with 37% ee, 80% ee, and 91% ee.

chemoselectivity when (−)-**6** was used as the oxidizing reagent (Scheme 4).

The glass transition temperature of the obtained polysulfoxide **7** was measured to investigate the influence of enantiomeric excesses on the properties of the resulting polymers. DSC thermograms of the polymer **7** with different stereoregularity are exhibited in Figure 3. As in the figure, the polysulfoxide with 91% ee showed the glass transition temperature at 77 °C while $T_g$ was observed at 46 °C when the enantiomeric excess of the sulfoxide asymmetric centers was low (37% ee). The polysulfoxide ($M_n$ = 4400 (from $^1$H NMR)) with 80% ee, prepared by using the 1:8 mixture of (−)-**6** with (+)-**6**, showed $T_g$ at 62 °C. This change of the glass transition temperature depending on the enantiomeric excess of the sulfoxide units corresponds to the shift of $T_g$ of vinyl polymers based on their tacticity. Therefore, the synthesis of chiral polysulfoxides by asymmetric oxidation reported here can be regarded as the first example of the control of "tacticity" by polymer reaction. We plan to study more precise control of "tacticity" by using both enantiomers of chiral oxaziridine **6** and the change of other properties depending on "tacticity".

## Conclusion

Novel chiral polysulfoxides were prepared by asymmetric oxidation of the corresponding polysulfides using the chiral oxaziridine **6**. This reaction is the first example of introduction of chirality with high optical activity into the main chain of the polymer by polymer reaction. This means that the tacticity of the polymer can be adjusted by polymer reaction, and in fact, the shift of the glass transition temperature was observed according to the change of the enantiomeric excess of the polymer. The obtained chiral polysulfoxides **7** and **9** are one of the first examples of the polymers having heteroatom chirality in the main chain. Transfer of the asymmetry from sulfur to carbon is under way both from the polymer to low molecular weight compounds and from the polymer to other polymers. We also have a plan to utilize this polymer as chiral stationary phase of HPLC.

## Experimental Section

**General.** $^1$H and $^{13}$C NMR spectra were obtained with a JEOL JNM-EX270 spectrometer (270 MHz for $^1$H NMR and 67.9 MHz for $^{13}$C NMR) or a JEOL JNM-A500 spectrometer (500 MHz for $^1$H NMR and 125.7 MHz for $^{13}$C NMR) in chloroform-*d*. IR spectra were recorded on a Perkin-Elmer 1600 spectrometer. As a ultraviolet light source, 450 W high-pressure mercury lamp (Ushio UM-452) was used with a Pyrex cooler. Gel permeation chromatographic analyses (GPC) by using chloroform as an eluent were carried out on a Tosoh UV-8011 and RI-8000 (Shodex K-803L column) after calibration with standard polystyrene. Optical rotations were measured with a JASCO P-1020 polarimeter by using chloroform as a solvent. CD spectra were recorded on a JASCO J-600 spectropolarimeter with chloroform as a solvent. All DSC analyses were carried out on a Seiko DSC200 instrument by using about 10 mg of exactly weighed samples at heating and cooling rate of 10 °C/min. The midpoint of $T_g$ peak in the thermogram of the second heating scan was adopted as the value of the glass transition temperature.

Unless otherwise noted, the materials were obtained from commercial sources. Chloroform was distilled under nitrogen from $CaH_2$ and dichloromethane also from $CaH_2$. THF and benzene were distilled from sodium diphenylketyl. 2,2′-Azobis-(isobutyronitrile) (AIBN) was recrystallized from methanol.

**Synthesis of *p*-Vinylbenzenethiol (1).** To magnesium shavings (1.64 g, 67.3 mmol) activated with a few crystals of $I_2$ in 14 mL of THF was added slowly a THF (39 mL) solution of *p*-bromostyrene (8.0 mL, 61.2 mmol). The reaction temperature should be maintained at 15−20 °C by occasional cooling with an ice bath. The mixture was then stirred at room temperature for 1 h and cooled to −15 °C. Sulfur (2.16 g, 67.3 mmol) was added to the Grignard reagent during 1 h. The resulting yellow solution was stirred for additional 1 h and allowed to become −5 °C. It was then hydrolyzed with 90 mL of 1.0 N aqueous NaOH solution. The mixture was filtered under nitrogen to remove insoluble materials. The resulting solution was extracted with diethyl ether twice under nitrogen, and the organic layer was then washed by 0.1 M NaOH aqueous solution twice under nitrogen. The aqueous layers were collected and concentrated under vacuum at room temperature. The resulting aqueous solution was neutralized by 0.1 N HCl to be pH = 5−6.5. The solution was extracted with benzene, and the organic layer was dried over $Na_2SO_4$. The mixture was filtered under nitrogen, and the solution was evaporated at room temperature to give *p*-vinylbenzenethiol as a yellow oil in 31% yield. The $^1$H NMR spectrum revealed that the obtained compound was the mixture of monomer with oligomers in the ratio of 1.6:1. A pale yellow solid was obtained after evaporation when the content of oligomers was increased. $^1$H NMR ($\delta$, ppm): 2.86 ($-SCH_2-$, m, 2H of oligomers), 3.13 ($-CH_2Ar-$, m, 2H of oligomers), 3.40 (−SH, s, 1H of oligomers), 3.45 (−SH, s, 1H of monomer), 5.21 ($CH_2=$ , *cis*-proton to phenyl group, dd, $J$ = 10.9, 0.7 Hz, 1H of monomer), 5.23 ($CH_2=$ , *cis*-proton to phenyl group, d, $J$ = 10.9 Hz, 1H of oligomers), 5.70 ($CH_2=$ , *trans*-proton to phenyl group, dd, $J$ = 17.6, 0.7 Hz, 1H of monomer), 5.72 ($CH_2=$ , *trans*-proton to phenyl group, d, $J$ = 17.8 Hz, 1H of oligomers), 6.66 (=CHAr, m, 1H), 7.02−7.38 ($-C_6H_4-$, m, 4H).

**Synthesis of the Polysulfide 2.** A solution of *p*-vinylbenzenethiol, **1** (2.55 g, 18.7 mmol based on monomer unit), in $CH_2Cl_2$ (30 mL) was irradiated with a high-pressure UV lamp for 30 min. The resulting solution was poured into a large

amount of *n*-hexane to give a white sticky solid. After removing *n*-hexane by decantation, the solid was dissolved in $CHCl_3$, and the solution was evaporated to afford the polysulfide **2** as a white solid in 97% yield. $^1$H NMR ($\delta$, ppm): 2.87 ($-SCH_2-$, t, $J$ = 8.0 Hz, 2H), 3.11 ($-CH_2Ar-$, t, $J$ = 8.0 Hz, 2H), 5.23 ($CH_2=$, *cis*-proton to phenyl group, d, $J$ = 10.9 Hz, terminal vinyl group), 5.72 ($CH_2=$, *trans*-proton to phenyl group, d, $J$ = 17.6 Hz, terminal vinyl group), 6.66 (=CHAr, dd, $J$ = 17.6, 10.9 Hz, terminal vinyl group), 7.11 (−Ar−H, d, $J$ = 7.8 Hz, 2H), 7.27 (−Ar−H, d, $J$ = 7.7 Hz, 2H). The number-average molecular weight of the polymer was estimated to be 2400 from the ratio of an integral of terminal vinyl protons with that of main-chain methylene protons in the $^1$H NMR spectrum.

**Synthesis of the Polysulfide 5.** To a mixture of 1,3-benzenedithiol (0.784 g, 5.51 mmol) with divinylbenzene (0.717 g, 5.51 mmol, the ratio of *meta* isomer to *para* isomer was 2.1:1) in benzene (10 mL) was added AIBN (9.05 mg, $5.51 \times 10^{-2}$ mmol), and the solution was stirred at 70 °C for 16 h. The resulting mixture was poured into a large amount of *n*-hexane to give a sticky gum. After freeze-drying of the gum, the polysulfide **5** was obtained as a white solid in a quantitative yield. $^1$H NMR ($\delta$, ppm): 2.89 ($-SCH_2-$, t, $J$ = 7.5 Hz, 4H), 3.14 ($-CH_2Ar-$, t, $J$ = 7.4 Hz, 4H), 3.43 (−SH, s, end group), 7.00−7.28 ($-C_6H_4-$, m, 8H). $^{13}$C NMR ($\delta$, ppm): 34.6, 35.0, 35.3, 126.1, 126.5, 128.5, 128.6, 128.7, 129.1, 137.3, 138.0, 140.1. The number-average molecular weight of the polymer was estimated to be 3500 from the ratio of an integral of terminal thiol protons with that of main-chain methylene protons in the $^1$H NMR spectrum.

**Synthesis of *N*-Sulfonyloxaziridine (6).** The oxaziridine (−)-**6** was prepared from (+)-camphor by three steps according to the procedure described in the literature,[5j] and (−)-**6** was obtained as a white crystal in 15% overall yield. $^1$H NMR ($\delta$, ppm): 0.67 ($-CH_3$, s, 3H), 1.08 ($-CH_3$, s, 3H), 1.43 ($-CH_3$, s, 3H), 1.50 ($-CH_2-$, m, 2H), 1.90 (one of $-CH_2-$, m, 1H), 2.27 (one of $-CH_2-$, m, 1H), 2.70 (−CH−, d, $J$ = 3.9 Hz, 1H), 7.56−7.72 (−Ar−H, m, 3H), 8.09 (−Ar−H, d, $J$ = 7.3 Hz, 2H).

**Oxidation of the Polysulfide 2 by Modified Sharpless Reagent (Ti(O-*i*-Pr)$_4$/(+)-Diethyl Tartrate (DET)/H$_2$O/*t*-BuOOH).** Ti(O-*i*-Pr)$_4$ (0.304 mL, 1.03 mmol) and (+)-DET (0.353 mL, 2.06 mmol) were dissolved in $CH_2Cl_2$ (15 mL) at room temperature. $H_2O$ (0.019 mL, 1.03 mmol) was added slowly to the solution, and the mixture was stirred for 20 min. The polysulfide **2** (0.14 g, 1.03 mmol of sulfide, $M_n$ = 2400) in $CH_2Cl_2$ (5 mL) was added into the yellow solution, and the system was cooled to −20 °C. To this solution was added *t*-BuOOH (ca. 5.5 M in *n*-decane, 0.30 mL, 1.64 mmol), and the mixture was stirred for 32 h. Water (0.19 mL, 10.3 mmol) was added dropwise to the resulting yellow solution, and the mixture was stirred for 1 h at −20 °C and for additional 1 h at room temperature. The mixture was filtered, and the resulting solution was stirred with 5% aqueous NaOH solution and brine for 1 h and then separated. The organic layer was dried over $Na_2SO_4$ and evaporated to give 0.186 g of a pale yellow solid. This solid was dissolved in $CHCl_3$, the insoluble part was filtered off, and the solution was poured into a large amount of *n*-hexane. After suction filtration, the polysulfoxide **7** was obtained as a pale yellow solid (81.1 mg, sulfide:sulfoxide:sulfone = 39:50:11, 53% yield). The ratio among sulfide, sulfoxide, and sulfone was determined by the ratio of integrals of phenyl protons adjacent to the sulfur atom in the $^1$H NMR spectrum. $^1$H NMR ($\delta$, ppm): 2.65−3.13 ($-SCH_2-$ + $-SCH_2CH_2Ar-$ + $-S(O)CH_2-$ + $-S(O)CH_2CH_2Ar-$ + $-S(O)_2CH_2-$, m, 4H), 3.22 ($-S(O)_2CH_2CH_2Ar-$, br, 11% of 2H), 7.00 (−SAr−H, br, 39% of 2H), 7.16−7.33 (−SAr−H + −S(O)-Ar−H, br, 39% of 2H + 50% of 2H), 7.42 (−S(O)Ar−H + $-S(O)_2Ar-$H, br, 50% of 2H + 11% of 2H), 7.70 ($-S(O)_2Ar-$H, br, 11% of 2H). $^{13}$C NMR ($\delta$, ppm): 27.7, 27.9, 35,1, 57.6, 58.1, 124.2, 124.5, 128.3, 129.2, 129.6, 129.8, 130.0, 141.7. GPC (chloroform, polystyrene standard): $M_n$ = 2500 and $M_w/M_n$ = 2.64.

**Synthesis of the Chiral Polysulfoxide 7 by the Oxidation with the Chiral Oxaziridine (−)-6.** In a two-necked flask equipped with a reflux condenser were placed the polysulfide **2** (0.15 g, 1.10 mmol of sulfide, $M_n$ = 2400), the chiral oxaziridine (−)-**6** (0.414 g, 1.10 mmol), and chloroform (30 mL). The mixture was stirred at room temperature for 64 h, and the progress of the reaction was monitored with TLC by checking the decrease of the oxaziridine **6** ($R_f$ = 0.6 ($CH_2Cl_2$:*n*-hexane = 2:1)). The solution was then refluxed for 24 h, and no oxaziridine **6** was observed in TLC after refluxing. The resulting mixture was poured into a large amount of diethyl ether to give a white precipitate. After suction filtration, polymer **7** was obtained in 87% yield (sulfide:slufoxide:sulfone = 6:94:0). The ratio among sulfide, sulfoxide, and sulfone was determined by the ratio of integrals of phenyl protons adjacent to sulfur atom in $^1$H NMR spectrum. The chiral camphorimine was recovered from the diethyl ether solution used in reprecipitation and reoxidized to give the chiral oxaziridine (−)-**6**.[5j] The optical rotation and CD spectrum of the polymer were measured after the polysulfoxide was dissolved in chloroform and reprecipitated again into diethyl ether in order to rule out the possibility of contamination of the chiral oxaziridine (−)-**6**, though no **6** was detected in $^1$H and $^{13}$C NMR spectra of the polymer **7** reprecipitated once. $^1$H NMR ($\delta$, ppm): 2.80−3.21 ($-SCH_2-$ + $-SCH_2CH_2Ar-$ + $-S(O)CH_2-$ + $-S(O)CH_2CH_2$-Ar−, m, 4H), 5.37 ($CH_2=$, *cis*-proton to phenyl group, d, $J$ = 11.2 Hz, terminal vinyl group), 5.84 ($CH_2=$, *trans*-proton to phenyl group, d, $J$ = 17.1 Hz, terminal vinyl group), 6.73 (=CHAr, dd, $J$ = 17.5, 10.9 Hz, terminal vinyl group), 7.10 (−SAr−H, br, 6% of 2H), 7.34 (−SAr−H + −S(O)Ar−H, d, $J$ = 7.9 Hz, 2H), 7.54 (−S(O)Ar−H, d, $J$ = 8.2 Hz, 94% of 2H). $^{13}$C NMR ($\delta$, ppm): 27.8, 57.5−57.7 (two overlapping peaks corresponding to *m* and *r*, respectively, were observed in this region; see the main text and ref 16), 124.4, 127.0, 128.1, 129.2, 129.5, 135.5, 141.6, 142.3. IR (KBr): 2915, 1492, 1410, 1086, 1039, 1012, 915, 807, 728 cm$^{-1}$. The number-average molecular weight of the polymer was estimated to be 3800 from the ratio of an integral of terminal vinyl protons with that of main-chain methylene protons in the $^1$H NMR spectrum. The specific rotation and CD spectrum of the polymer are described in the main text. The asymmetric oxidation of **2** by the mixture of (−)- with (+)-**6** and by the commercial oxaziridine **8** and the oxidation of the polysulfide **5** by the chiral oxaziridine (−)-**6** were also carried out by similar procedures.

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**Supporting Information Available:** $^1$H NMR spectra of **2** and **7** and $^{13}$C NMR spectra of **5**, **7**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

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(16) In the case of asymmetric oxidations independent of the state of adjacent sulfur atoms, the probabilities of generating *m* and *r* diads are described as follows (*S* is the probability in which a sulfur atom is oxidized to (*S*)-sulfoxide): $m = S^2 + (1 - S)^2$ and $r = 2S(1 - S)$. Therefore, two peaks in the $^{13}$C NMR spectrum are assigned to *m* and *r* peaks, respectively, from right to left, because the biggest peak can be identified to be *m* in this asymmetric oxidation. The enantiomeric excess ($q = 2S - 1$ in the case of prevalent pro-(*S*) induction) was calculated from the ratio between *m* and *r* peaks, $m/r = (1 + q^2)/(1 - q^2)$.

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