Synthesis of Optically Active Polymethacrylates Bearing Axially Dissymmetric 1,1′-Binaphthalene Skeleton as a Pendant Group and Their Optical Resolution Ability as Chiral Adsorbent for HPLC

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Optically active polymethacrylates **6** and **8**, which have pendant axially dissymmetric 1,1′-binaphthalene moiety, were synthesized by radical polymerization of (*S*)-2-methacryloyloxy- and (*S*)-2-(3-methacryloyloxypropoxy)-2′-methoxy-1,1′-binaphthalene, respectively. Specific rotation and CD spectrum of **6** are rather different from those of the model compound 2-(2,2-dimethylpropanoyloxy)-2′-methoxy-1,1′-binaphthalene (**7**), while the chiroptical properties of **8** are almost the same as those of the corresponding model compound. The difference of the chiroptical properties between **6** and **7** was attributed to the difference of the dihedral angles between the naphthalene planes of the 1,1′-binaphthalene skeleton. The polymethacrylates **6** and **8** were coated on a spherical silica gel to give HPLC chiral stationary phases (CSP-**6** and CSP-**8**). These CSPs differentiated several enantiomeric 1-aryl-1-alkanols and 1,2-diols as the 3,5-dinitrophenylcarbamates, CSP-**8** showing better resolution than CSP-**6**. Furthermore, (*S*)-2-(5-carboxypentyloxy)-2′-methoxy-1,1′-binaphthalene, a model compound of **8**, was prepared and covalently bonded to an aminopropylsilanized silica gel to afford CSP-**16**, which also resolved these racemates. Thus, the chiral discriminating ability of the polymethacrylate **8** would be based not on the secondary and/or higher-ordered structure, but mainly on the interaction between the individual 1,1′-binaphthalene units of **8** and the racemates.

A wide variety of chiral stationary phases (CSPs) have recently been developed for the separation of enantiomers by means of high-performance liquid chromatography (HPLC).[1] Although many kinds of synthetic chiral polymers have been applied to the CSPs, no polymethacrylates bearing a chiral pendant group have been reported to serve as CSPs for HPLC in spite of their ready availability.[2] The reason seems to be the low chiral recognition ability of the chiral pendant group used and/or the absence of the stable higher-ordered structure of the polymers; optical resolution ability of most polymeric CSPs strongly depends on the secondary or higher-ordered structure of the polymers.[2] It is well known that axially dissymmetric 1,1′-binaphthalene derivatives serve as highly efficient chiral inducers for a wide range of asymmetric reactions,[3] while little is known about the chiral recognition property of their polymers.[4]

In this paper, we wish to report the synthesis and radical polymerization of two new chiral methacrylates bearing axially dissymmetric 1,1′-binaphthalene-2,2′-diol (**1**) derivatives as pendant groups. Also reported are the chiroptical properties of these polymethacrylates and their optical resolution ability as the chiral adsorbents for the CSPs.

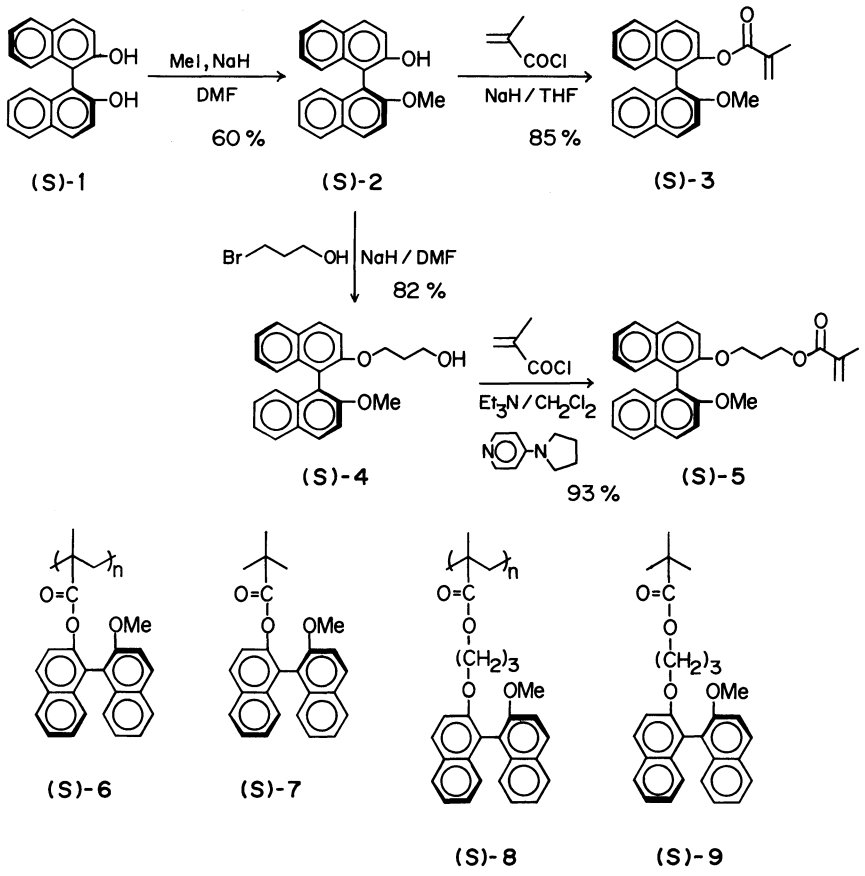
Results and Discussion

Synthesis of Polymethacrylates 6 and 8 and Model Compounds 7 and 9. Scheme 1 shows the synthetic route of polymethacrylates **6** and **8** and their model compounds **7** and **9**. Readily available homochiral (*S*)-**1**[5,6] was converted to 2′-methoxy-1,1′-binaphthalen-2-ol (**2**) in 60% yield by the use of 1 molar equivalent of methyl iodide and sodium hydride in *N*,*N*-dimethylformamide (DMF). Then sodium salt of **2**, prepared by the reaction of sodium hydride and **2** in tetrahydrofuran (THF), was esterified with methacryloyl chloride to afford the homochiral **3** in 85% yield.

Methacrylate **5** which had a spacer group between the 1,1′-binaphthalene moiety and the methacryloyloxyl group was obtained as follows. Treatment of the sodium salt of **2** with 3-bromo-1-propanol in DMF afforded the alcohol **4** in 82% yield. Alcohol **4** was then esterified with methacryloyl chloride in the presence of triethylamine and 4-(1-pyrrolidinyl)pyridine in dichloromethane to yield the homochiral monomer **5** in 93% yield. The model compounds **7** and **9** were prepared from **2** and **4**, respectively, by esterification with 2,2-dimethylpropanoyl chloride in the presence of triethylamine and 4-*N*,*N*-dimethylaminopyridine in dichloromethane (Table 1).

Radical polymerization of the methacrylates **3** and **5** was carried out according to the usual sealed tube technique in benzene (concentration of the monomer=0.4 M, 1 M=1 mol dm^{-3}) at 60 °C for 24 h by use of 3 mol% of 2,2′-azobis(2-methylpropanenitrile) (AIBN) to yield the polymethacrylates **6** and **8**, respectively. The results are shown in Table 1. Although the polymers thus obtained were purified by several reprecipitations from ether, methanol, and benzene–hexane, low molecular weight components remained to result the wide molecular weight distribution of the products.

Attempted hydrolysis of **6** and **8** by treatment with concentrated sulfuric acid[7] or alcoholic potassium hydroxide[8] failed to give the poly(methacrylic acid)s,



Scheme 1.

Table 1. Synthesis of the Polymethacrylates **6** and **8** and the Corresponding Model Compounds **7** and **9**

Product	Yield/%	$[\alpha]_D$[a]/°	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]
6	75	−249	19000	7.6
7	94	−27		
8	73	−64	19000	4.2
9	97	−30		

a) Measured in $CHCl_3$ (c 0.1) at ambient temperature. b) Determined by GPC calibrated with polystyrene standards.

presumably because of the bulky binaphthalene moiety; this prevented the determination of the tacticity of **6** and **8**. However, the ^{13}C NMR spectrum of **8** shown in Fig. 1 exhibited the splitting patterns very similar to those of syndiotactic-rich poly(methyl methacrylate)[9] in the carbonyl and quarternary carbon regions. ^{13}C NMR spectrum of **6** and the ^1H NMR spectra of **6** and **8** showed broad spectral lines providing no significant information about their tacticity.

Comparison of the Chiroptical Properties of the Polymethacrylates 6 and 8 to the Corresponding Model Compounds 7 and 9. The value of the specific rotation of **8** (−64°) was comparable to that of the model compound **9** (−30°). The CD spectrum of **8** in THF was almost comparable to that of **9** as shown in Fig. 2. In contrast, the value of the specific rotation of **6** (−249°) was larger than that of **7** (−27°). Furthermore, CD spectrum of **6** was rather different from that of **7** as shown in Fig. 3. The intensity of the Cotton effects of **6** appeared around the wavelength 230 nm was rather small compared to that of **7**. Theoretical calculation of the CD spectra of 2,2′-disubstituted-1,1′-binaphthalene derivatives revealed that the Cotton effects appeared around 230 nm are derived from the ^1B_b transition of the naphthalene chromophores.[10] Also revealed is that the intensity of the Cotton effects derived from the ^1B_b transition decreases with increase of the dihedral angle between the naphthalene planes of the 1,1′-binaphthalene skeleton.[10] Therefore, the results of the chiroptical studies suggest that the dihedral angle of the binaphthalene residue of the polymer **6** is larger than that of the model compound **7**, presumably because of the steric congestion. Another difference of the CD spectrum between **6** and **7** is the presence of a clear Cotton effect at wavelength 245 nm. Although the origin of this Cotton effect is unknown, it may correspond to the shoulder peak appearing around wavelength 245 nm in the CD spectrum of **7**. Thus, the Cotton effect of **6** around 245 nm becomes apparent with decrease of the intensity

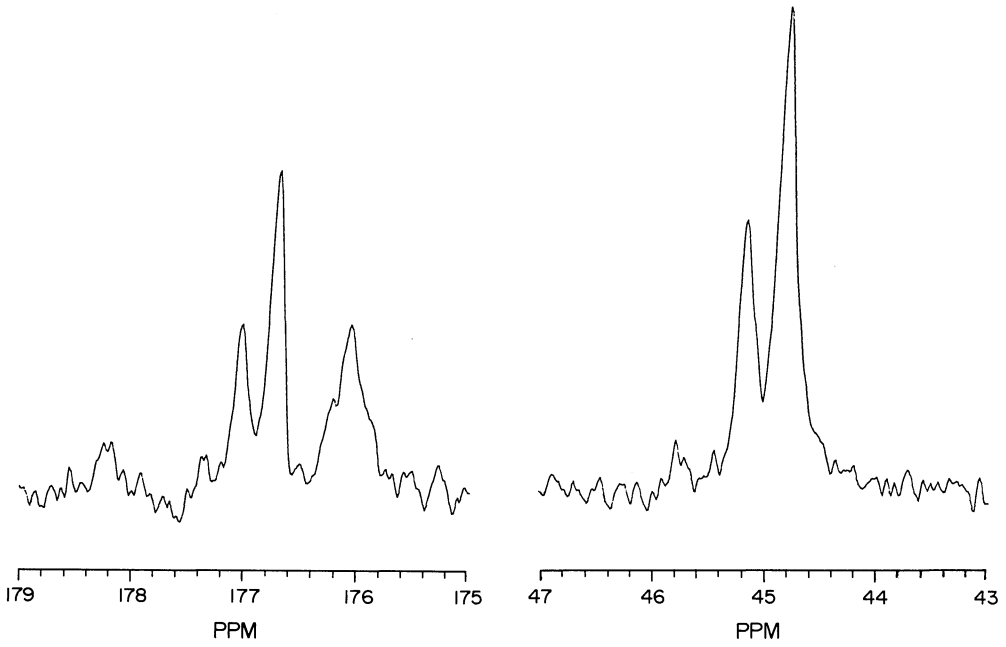


Fig. 1. 62.9 MHz ^{13}C NMR spectrum of **8** in $CDCl_3$ (15 wt/vol%) at 55 °C: left, carbonyl carbon region; right, quarternary carbon region.

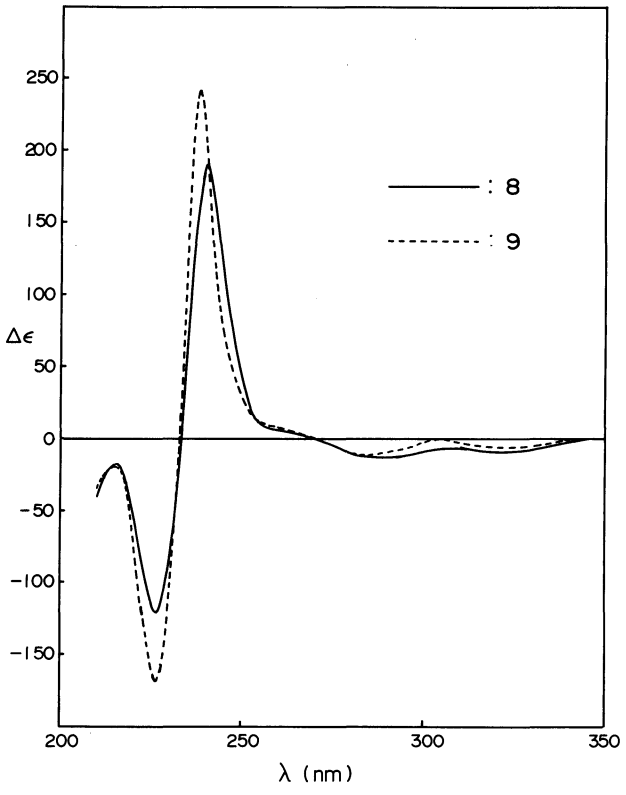


Fig. 2. CD spectra of polymethacrylate **8** and model compound **9** in THF. [**8**]=5.44×10^{-5} mol dm^{-3}, [**9**]= 4.84×10^{-5} mol dm^{-3}.

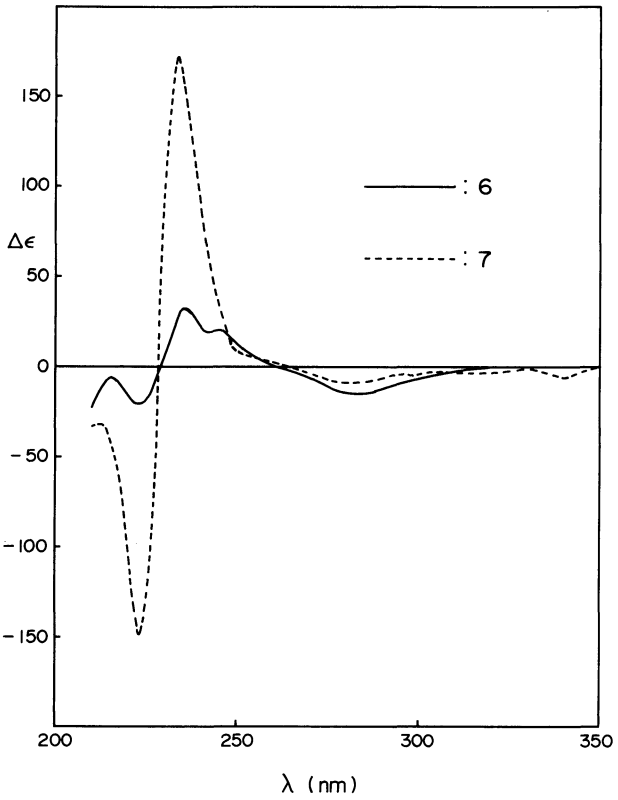
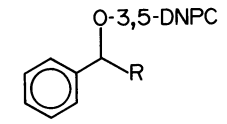


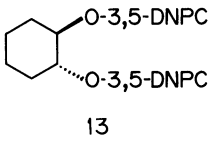
Fig. 3. CD spectra of polymethacrylate **6** and model compound **7** in THF. [**6**]=7.12×10^{-5} mol dm^{-3}, [**7**]= 6.69×10^{-5} mol dm^{-3}.

of the Cotton effect at wavelength 235 nm.

Chiral Recognition Ability of the Polymethacrylates 6 and 8 as the Chiral Adsorbents for the CSPs. To investigate the chiral recognition ability of **6** and **8**, CSP-**6** and CSP-**8** were prepared by coating spherical, macroporous silica gel with THF solutions of **6** and **8**, respectively, using a conventional technique.[11] Polymers **6** and **8** have bulky 1,1′-binaphthalene moieties which can serve as chiral π-electron-donor group. Thus, diastereomeric interaction via π–π interaction is expected between the CSPs and the racemates which have an aromatic group. Table 2 shows the results of the HPLC analyses of such racemic compounds **10**—**15**.



10 : R = Et
11 : R = i-Pr
12 : R = c-Hex



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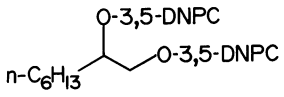

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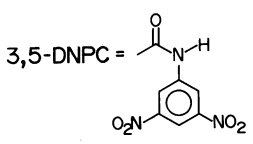

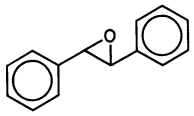

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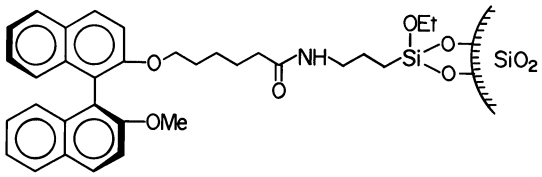
Several 3,5-dinitrophenylcarbamates (3,5-DNPCs) derived from 1-aryl-1-alkanols and aliphatic 1,2-diols were resolved on CSP-**8** column with 3% 2-propanol in hexane as eluent. CSP-**6** resolved only limited 1-aryl-1-alkanol derivatives using 5% 2-propanol in hexane as eluent. As an example, Figure 4 shows the chromatogram of the resolution of **13** on a CSP-**8** column. Relatively broad peaks shown in Fig. 4 might be due to the structural ununiformity of the polymer itself and/or its adsorption state on the silica gel. To examine the difference of the chiral recognition ability between the polymeric chiral selector **8** and the corresponding low molecular weight chiral selector (*S*)-2-(5-carboxypentyloxy)-2′-methoxy-1,1′-binaphthalene (**16**),[12,13] CSP-**16**



CSP-16

was prepared by chemically bonding **16** (0.125 mmol g^{-1} gel) to an aminopropylsilanized silica gel (APS).[14] In addition, for the precise comparison, CSP-**8**APS was prepared by coating the APS with **8** whose binaphthalene unit content is equal to that of CSP-**16**. CSP-**16** and CSP-**8**APS resolved the racemates **10**—**14**, CSP-**8**APS showing slightly better resolution than CSP-**16**, as described in Table 3. Thus, the chiral discriminating ability of the polymethacrylate **8** would be based not on the secondary and/or higher-ordered structure of the polymer, but mainly on the interaction between the

Table 2. Chromatographic Resolution of Racemates **10**—**15** on the CSPs Prepared from Polymethacrylates **6** and **8** Bearing Axially Dissymmetric 1,1′-Binaphthalene Skeleton

Racemates	CSP-**6**[a]			CSP-**8**[b]		
	k_1'[c]	α[d]	R_s[e]	k_1'	α	R_s
10	6.25	1.14	0.46	1.33[f]	1.23	0.33
11	5.14	1.16	0.43	0.93	1.36	0.47
12	3.14	1.0		1.08	1.16	0.25
13	2.02[g]	1.0		3.96	1.65	0.81
14	2.53[g]	1.0		4.78	1.41	0.56
15	1.27[h]	1.08	0.56	0.22[h]	1.0	

a) Eluent: 2-propanol/hexane=5/95, flow rate=1.0 ml min^{-1}. b) Eluent: 2-propanol/hexane=3/97, flow rate=1.0 ml min^{-1}. c) Capacity factor of the enantiomer eluting first=(retention volume of enantiomer−void volume of column)/(void volume of column). d) Separation factor=(k' of more retained enantiomer)/(k' of less retained enantiomer). e) Resolution factor=2×(distance between the peaks of more and less retained enantiomers)/(sum of bandwidth of two peaks). f) Flow rate=0.5 ml min^{-1}. g) Eluent: 2-propanol/hexane=10/90, flow rate=1.0 ml min^{-1}. h) Eluent: methanol, flow rate=0.5 ml min^{-1}.

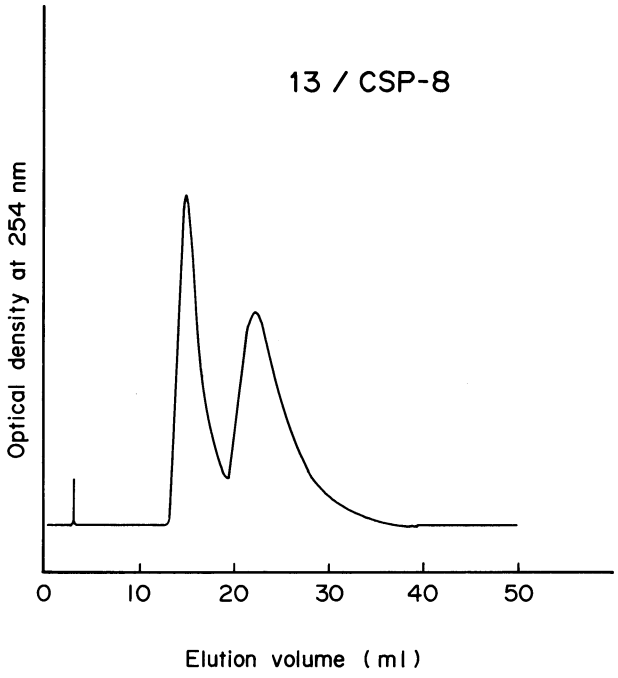


Fig. 4. Chromatographic resolution of racemate **13** on CSP-**8** column. Column: 25×0.46 (i.d.) cm, eluent: 3% 2-propanol in hexane, flow rate: 1.0 ml min^{-1}.

Table 3. Chromatographic Resolution of Racemates **10**—**14** on the CSP-**8**APS and CSP-**16** Having Axially Dissymmetric 1,1′-Binaphthalene Skeleton

Racemates	CSP-**8**APS[a]			CSP-**16**[a]		
	k_1'	α	R_s	k_1'	α	R_s
10	4.33	1.07	0.20	2.63	1.03	0.20
11	3.93	1.08	0.30	2.50	1.04	0.10
12	3.67	1.04	0.10	2.22	1.02	0.10
13	2.74[b]	1.15	0.35	8.94	1.04	0.33
14	3.04[b]	1.07	0.20	14.01	1.02	0.24

a) Eluent: 2-propanol/hexane=3/97, flow rate=1.0 ml min^{-1}. b) Eluent: 2-propanol/hexane=10/90, flow rate=1.0 ml min^{-1}.

individual 1,1′-binaphthalene units of **8** and the racemates. For all of the racemates, CSP-**8** showed larger separation factor and smaller capacity factor compared with those of the CSP-**8**APS and CSP-**16**. Probably, a strong achiral interaction between the racemates and the achiral surface of the APS might prevent the efficient resolution. Because these chiral selectors have no strong hydrogen-bonding site, a main control factor for the chiral discrimination would be donor–acceptor interaction between the binaphthyl moieties of the chiral selectors and the 3,5-dinitrophenyl moieties of the 3,5-DNPCs.

On the other hand, *trans*-stilbene oxide (**15**) which had no strong π-accepting chromophore was partially resolved only by the use of CSP-**6** with methanol as eluent. When a polar eluent like methanol is used, nonpolar interaction between CSP-**6** and **15** would be the driving force for the chiral recognition.

Although the difference of the optical resolution ability between CSP-**6** and CSP-**8** is not clearly explained, the difference of the dihedral angles between the naphthalene planes of the 1,1′-binaphthalene moiety may play an important role.

In conclusion, we have shown here for the first time that the optically active polymethacrylates bearing chiral pendant group (**6** and **8**) prepared by radical polymerization have chiral discriminating ability for 3,5-DNPCs **10**—**14** and *trans*-stilbene oxide (**15**), in spite of having no obvious secondary or higher-ordered structure.

Experimental

Measurements. Melting points were measured on a Yamato MP-21 and uncorrected. Microanalyses were carried out in the Microanalytical Laboratory of the Institute for Chemical Reaction Science, Tohoku University. Optical rotations were obtained at ambient temperature (20—25°C) using a Union Giken PM-101 polarimeter. CD spectra were measured in a 0.10 cm cell at room temperature on a JASCO J-400X spectropolarimeter. HPLC measurements were carried out on a Shimadzu LC-6A, with UV detection at 254 nm. IR spectra were measured on a Shimadzu IR-460 infrared spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL JNM-FX60 instrument or Bruker AC-250T instrument. ^{13}C NMR spectra were recorded on a Bruker AC-250T instrument at 62.9 MHz at 55°C by the inverse-gated proton decoupling method with a recycle delay of 5.0 s. GPC measurements were carried out at 39°C on a Tosoh HLC-802UR instrument equipped with TSK gel G5000H8, G4000H8, and G3000H8 columns using THF as an eluent.

Materials. Homochiral (*S*)-1,1′-binaphthalene-2,2′-diol (**1**) was prepared by a previously reported procedure.[5] Methacryloyl chloride was purchased from Tokyo Kasei Kogyo Co., Ltd. and purified by distillation under reduced pressure over calcium hydride just before use. 3-Bromo-1-propanol was purchased from Tokyo Kasei Kogyo Co., Ltd. and purified by distillation. Other reagents were used as received. DMF, triethylamine, and dichloromethane were purified and dried by using standard procedure. Benzene was purified by washing with concentrated sulfuric acid as usual and distillation over sodium diphenyl ketyl before use. Other solvents were purified by distillation. Reactions were carried out under an N_2 atmosphere with use of standard procedures for the exclusion of moisture unless otherwise noted. Column chromatography was performed by using silica gel (Nacalai Tesque, Inc., Silica Gel 60, 70—230 mesh). Na_2SO_4 was employed for the drying of extracts.

(*S*)-2-Methoxy-1,1′-binaphthalen-2-ol (2). To a stirred solution of (*S*)-**1** (7.85 g, 27.4 mmol) in dry DMF (390 ml) was added sodium hydride (660 mg, 27.4 mmol) by portions at 0°C. After the addition was complete, the resultant solution was stirred for 2 h at ambient temperature. Then methyl iodide (3.90 g, 27.4 mmol) was added to the solution in one portion. The reaction mixture was stirred for another 12 h and then cooled to 0°C. To the mixture was added 2 M (1 M= 1 mol dm^{-3}) hydrochloric acid (60 ml), followed by diluting with distilled water (400 ml). The mixture was extracted with diethyl ether (200 ml×3), washed with brine and dried. After evaporation of the solvents under reduced pressure, the residue was purified by column chromatography (eluent: chloroform) to afford homochiral **2** in 60% yield (4.93 g). Further purification by recrystallization from benzene–cyclohexane gave pure **2** as colorless crystals. Mp 82.0—84.0°C; IR (KBr) 3465 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$) δ=3.75 (3H, s, O–CH_3), 4.61 (1H, br, O–H), 6.95—8.01 (12H, m, Ar-H); $[\alpha]_D$ −40.2° (*c* 1.02, THF) [lit,[15] $[\alpha]_D$ +38.59° (*c* 0.99, THF) for (*R*)-**2**].

2-Methacryloyloxy-2′-methoxy-1,1′-binaphthalene (3). To a stirred solution of (*S*)-**2** (2.19 g, 7.29 mmol) in dry THF (200 ml) was added sodium hydride (260 mg, 10.8 mmol) portionwise. After the addition was complete, methacryloyl chloride (1.17 g, 12.8 mmol) was added to the resultant solution at 0°C in one portion. The reaction mixture was stirred for another 2 h at ambient temperature and then cooled to 0°C. To the mixture was added 2 M hydrochloric acid (5 ml), followed by diluting with distilled water (50 ml). The mixture was extracted with diethyl ether (50 ml×3), washed with brine and dried. After evaporation of the solvents under reduced pressure, the residue was purified by column chromatography (eluent: chloroform) to afford the product **3** in 85% yield (2.28 g). Further purification by recrystallization from chloroform-hexane gave pure **3** as colorless crystals. Mp 104—105°C; IR (KBr) 1724 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=1.55 (3H, s, CH_3), 3.72 (3H, s, O–CH_3), 5.24 (1H, m, vinyl-H), 5.56 (1H, s, vinyl-H), and 6.95—8.01 (12H, m, Ar-H);

$[\alpha]_D$ +1.6° (*c* 1.2, $CHCl_3$). Found: C, 81.48; H, 5.67%. Calcd for $C_{25}H_{20}O_3$: C, 81.50; H, 5.47%.

2-(2,2-Dimethylpropanoyloxy)-2′-methoxy-1,1′-binaphthalene (7). To a stirred solution of (*S*)-**2** (146 mg, 0.486 mmol) in dry dichloromethane (3 ml) were added triethylamine (59 mg, 0.583 mmol) and 4-*N*,*N*-dimethylaminopyridine (59 mg, 0.483 mmol) at ambient temperature. After the addition was complete, 2,2-dimethylpropanoyl chloride (70 mg, 0.581 mmol) was added to the resultant solution at 0°C in one portion. After stirring for another 12 h at ambient temperature, the reaction mixture was directly chromatographed on silica gel (eluent: 20% ethyl acetate in hexane) to afford the product **7** in 94% yield (178 mg) as colorless glass. IR (neat) 1749 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=0.71 [9H, s, C-$(CH_3)_3$], 3.70 (3H, s, O-CH_3), and 7.12—7.96 (12H, m, Ar-H); $[\alpha]_D$ −27.0° (*c* 0.1, $CHCl_3$). Found: C, 81.45; H, 6.33%. Calcd for $C_{26}H_{24}O_3$: C, 81.22; H, 6.29%.

2-(3-Hydroxypropoxy)-2′-methoxy-1,1′-binaphthalene (4). To a stirred solution of (*S*)-**2** (3.10 g, 10.3 mmol) in dry DMF (240 ml) was added sodium hydride (250 mg, 10.3 mmol) by portions at 0°C. After the addition was complete, the resultant solution was stirred for 2 h at ambient temperature. Then, 3-bromo-1-propanol (1.43 g, 10.3 mmol) was added to the solution in one portion. The reaction mixture was stirred for another 1.5 h at ambient temperature and then cooled to 0°C. To the solution was added 2 M hydrochloric acid (20 ml) dropwise, followed by diluting with distilled water (50 ml). The mixture was extracted with diethyl ether (50 ml×3), washed with brine and dried. After evaporation of the solvents under reduced pressure, the residue was purified by column chromatography (eluent: 50% ethyl acetate in hexane) to afford the product **4** in 82% yield (3.04 g) as colorless glass. IR (neat) 3400 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ=1.67 (2H, m, CH_2), 3.23 (2H, t, *J*=5 Hz, O-CH_2), 3.75 (3H, s, O-CH_3), 4.11 (2H, m, ArO-CH_2), and 7.04—8.04 (12H, m, Ar-H); $[\alpha]_D$ −63.2° (*c* 0.9, CH_3OH). Found: C, 80.57; H, 6.29%. Calcd for $C_{24}H_{22}O_3$: C, 80.42; H, 6.19%.

2-(3-Methacryloyloxypropoxy)-2′-methoxy-1,1′-binaphthalene (5). To a stirred solution of **4** (1.22 g, 3.40 mmol) in dry dichloromethane (57 ml) were added triethylamine (781 mg, 7.72 mmol) and 4-(1-pyrrolidinyl)pyridine (250 mg, 1.69 mmol) at ambient temperature. Then, freshly distilled methacryloyl chloride (740 mg, 7.08 mmol) was added to the solution in one portion. After stirring for another 40 h, 2,6-di-*t*-butyl-4-methylphenol (5 mg, 0.023 mmol) was added to the reaction mixture. Then, the volatile components were evaporated under reduced pressure. The residue was purified by column chromatography (eluent:benzene). The eluent containing **5** thus obtained was evaporated in the dark at ambient temperature in vacuo to afford **5** in 93% yield (1.34 g) as colorless glass. IR (neat) 1716 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=1.70—1.81 (2H, m, CH_2), 1.85 (3H, s, CH_3), 3.64—3.86 (2H, m, O-CH_2), 3.72 (3H, s, O-CH_3), 3.96—4.11 (2H, m, ArO-CH_2), 5.46 (1H, m, vinyl-H), 5.97 (1H, s, vinyl-H), and 7.06—7.96 (12H, m, Ar-H); $[\alpha]_D$ −33.0° (*c* 1.3, $CHCl_3$). Found: C, 78.73; H, 6.17%. Calcd for $C_{28}H_{26}O_4$: C, 78.85; H, 6.14%.

2-[3-(2,2-Dimethylpropanoyloxy)propoxy]-2′-methoxy-1,1′-binaphthalene (9). To a stirred solution of (*S*)-**4** (117 mg, 0.326 mmol) in dry dichloromethane (3 ml) were added triethylamine (40 mg, 0.391 mmol) and 4-*N*,*N*-dimethylaminopyridine (40 mg, 0.326 mmol) at ambient temperature. After the addition was complete, 2,2-dimethylpropanoyl chloride (47 mg, 0.391 mmol) was added to the resultant solution at 0°C in one portion. After stirring for another 12 h at ambient temperature, the reaction mixture was directly chromatographed on silica gel (eluent: 20% ethyl acetate in hexane) to afford the product **9** in 97% yield (140 mg) as colorless glass. IR (neat) 1726 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=1.11 [9H, s, C-$(CH_3)_3$], 1.60—1.80 (2H, m, CH_2), 3.61—3.83 (2H, m, O-CH_2), 3.72 (3H, s, O-CH_3), 3.93—4.08 (2H, m, ArO-CH_2), and 7.07—7.95 (12H, m, Ar-H); $[\alpha]_D$ −30.0° (*c* 0.1, $CHCl_3$). Found: C, 78.49; H, 6.63%. Calcd for $C_{29}H_{30}O_4$: C, 78.70; H, 6.83%.

Radical Polymerization of 3. **3** (668 mg, 1.81 mmol), AIBN (9.9 mg, 0.06 mmol), and freshly distilled benzene (4.5 ml) were degassed in a glass tube by the freeze-pump-thaw technique and sealed under vacuum. The polymerization was conducted in a thermostat at 60°C with shaking for 24 h. Then, the reaction mixture was cooled to ambient temperature. The polymeric products were precipitated by pouring the reaction mixture into ether (300 ml) with stirring. The polymers thus obtained were purified by reprecipitation of the chloroform solution (10 ml) from methanol (300 ml), and dried at 60°C for 24 h in vacuum (0.1 mmHg, 1 mmHg=133.322 Pa) to afford **6** in 75% yield (501 mg) as a white powder. IR (KBr) 1736 cm^{-1} (C=O); ^1H NMR (15 wt/vol% in $CDCl_3$ at 55°C) δ=−2.0—1.5 (5H, br, CH_3 and CH_2), 1.5—4.4 (3H, br, O-CH_3), and 5.0—9.0 (12H, br, Ar-H); $[\alpha]_D$ −249° (*c* 0.1, $CHCl_3$). Found: C, 81.41; H, 5.68%. Calcd for $C_{25}H_{20}O_3$: C, 81.50; H, 5.47%.

Radical Polymerization of 5. According to the procedure described for the polymerization of **3**, **5** (876 mg, 2.06 mmol) was polymerized in freshly distilled benzene (5.0 ml) in the presence of AIBN (10.0 mg, 0.061 mmol) to afford **8** in 73% yield (636 mg) as a white powder. IR (KBr) 1726 cm^{-1} (C=O); ^1H NMR (15 wt/vol% in $CDCl_3$ at 55°C) δ=0.5—1.0 (3H, br, CH_3), 1.3—2.0 (4H, br, CH_2), 3.46 (5H, br.s, O-CH_3 and O-CH_2), 3.75 (2H, br.s, ArO-CH_2), and 6.9—7.9 (12H, br.m, Ar-H); $[\alpha]_D$ −64° (*c* 0.1, $CHCl_3$). Found: C, 78.83; H, 6.17%. Calcd for $C_{28}H_{26}O_4$: C, 78.85; H, 6.14%.

Preparation of Packing Material and Column Packing. Macroporous silica gel, (Merck, LiChrospher SI 1000: mean particle size, 10 μm; pore size, 100 nm), was silanized with dichlorodiphenylsilane according to the literature method.[11] A chiral polymer (0.50 g) was dissolved in 20 ml of THF. Then, the silanized silica gel (2.5 g) was wetted with the polymer solution (ca. 10 ml, about a half of the total volume). After irradiation of the resultant mixture with ultrasound for 1 min, the solvent was evaporated in vacuo at ambient temperature. Obtained polymer-coated silica gel was again wetted with the remaining polymer solution and treated as same as the first coating process. The chiral packing material thus obtained was packed in a stainless steel HPLC column (i.d., 0.46 cm; length, 25 cm) by a slurry method. CSP-**8**APS was prepared by coating **8** (150 mg) to an aminopropylsilanized silica gel (3.0 g: mean particle size, 5 μm; pore size, 10 nm)[14] according to the method described above. The aminopropyl groups uncovered with the polymer were then converted to the trifluoroacetic acid (TFA) salts by passing 15% hexane solution of 2-propanol containing 0.2% TFA through the column. The plate number of the columns packed CSP-**6**, CSP-**8**, CSP-**8**APS, and CSP-**16** were about 1700, 3000, 7500, and 11000, respectively, for 1,3,5-tri-*t*-butylbenzene using 5% 2-propanol in hexane as the eluent at flow rate of 1.0 ml min^{-1} at ambient temperature.

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