Synthesis of Novel Polymethacrylate Bearing an (S)-(+)-1-Cyclohexylethyl Urea Group in the Side Chain and Its Chiral Recognition Ability

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ABSTRACT: A new chiral methacrylate, (S)-(+)-1-cyclohexylethyl-(2-methacryloyloxyethyl)urea (CEMOU), was synthesized from 2-methacryloyloxyethyl isocyanate (MOI) and (S)-(+)-cyclohexylethylamine. Radical homopolymerization of CEMOU was performed in several solvents to obtain the corresponding chiral polymers having hydrogen bonds based on urea moieties. Specific optical rotations of poly(CEMOU) were slightly changed by the measurement temperature, which may be attributed in part to a change of conformation caused by hydrophobic interaction between the cyclohexyl groups. From the results of radical copolymerization of CEMOU (M_1) with styrene (ST, M_2) or methyl methacrylate (MMA, M_2), monomer reactivity ratios (r_1, r_2) and Alfrey–Price Q–e values were determined: $r_1 = 0.89$, $r_2 = 0.12$, $Q_1 = 2.45$, $e_1 = 0.68$ for the CEMOU–ST system; $r_1 = 0.48$, $r_2 = 0.18$, $Q_1 = 8.39$, $e_1 = 1.97$ for the CEMOU–MMA system. The chiroptical property of the poly(CEMOU-co-ST) was slightly influenced by the co-units. Poly(CEMOU)-bonded silica gel as the chiral stationary phase (CSP) was prepared for high-performance liquid chromatography (HPLC). The CSP resolved *trans*-2-dibenzyl-4,5-di(o-hydroxyphenyl)-1,3-dioxolane in normal phase such as *n*-hexane/2-propanol by HPLC. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1018–1025, 2003

Key words: chiral; radical polymerization; copolymerization; high-performance liquid chromatography

INTRODUCTION

The authors investigated synthesis and polymerizations of some chiral methacrylates from 2-methacryloyloxy isocyanate (MOI) and chiral alcohols or amines such as cholesterol, L-menthol, amino acid derivatives, 2-hydroxy-2'-methoxy 1,1'-binaphthalene, (S)-methylbenzylamine, and L-phenylalanine methyl ester and the chiroptical properties of these polymers.[1–4] MOI is a bifunctional monomer with both a reactive isocyanate group and a polymerizable double bond; it is convenient and widely used for crosslinking agents and materials for the molecular design of new polymers.[5] Many kinds of MOI derivatives have been synthesized from several alcohols and amino compounds and polymerized.[6] However, there have been few reports on the synthesis of MOI derivatives bearing an optically active group.[7,8] To our knowledge, no chiroptical properties of MOI derivatives with optically active groups have been reported. MOI is also useful for the preparation of macromonomers.[9] We synthesized and polymerized N-substituted maleimide (RMI) macromonomers and examined the thermal stability of the polymers obtained.[10] Optically active acrylamide macromonomers were also synthesized and polymerized and were applied to the chiral stationary phase (CSP) for high-performance liquid chromatography (HPLC).[11]

Recently, a wide variety of CSPs have been developed for the separation of enantiomers by HPLC.[12] There have been few reports on the preparation of CSPs for HPLC from polymethacrylate bearing a chiral pendant group, although many kinds of synthetic chiral polymers have been applied to CSPs.[13] This may be because of the low chiral recognition ability of the chiral pendant group used and/or the absence of stable higher-order structures of the polymers.[13] We have previously reported on the preparation of new CSPs with chiral polymethacrylate having urethane or urea bonds in the side chain and their chiral recognition abilities by HPLC.[2–4] Miyano et al.[14] synthesized optically active polymethacrylate bearing a 1,1'-binaphthalene moiety as the pendant group and investigated the optical resolution ability as a chiral adsorbent for HPLC. Liu et al.[15] reported on the optical resolution of racemates by chiral polymethacrylate having (+)-5-oxobornyl moieties.

This article describes the synthesis and polymerization of a new chiral methacrylate bearing urea bonds from MOI and (S)-(+)-1-cyclohexylethylamine; the chiroptical properties of the polymers obtained are

discussed. The CSP for HPLC was prepared from silica gel and chiral polymethacrylate having urea bonds, and its optical resolution ability was also investigated.

EXPERIMENTAL

Materials

MOI (Showa Denko Co., Ltd., Tokyo, Japan) was purified by distillation under reduced pressure. Styrene (ST) and methyl methacrylate (MMA) were purified by ordinary methods.[16] Tetrahydrofuran (THF) and toluene were dried over sodium metal and then used after distillation. N,N–Dimethylformamide (DMF) and chloroform were used after distillation. 2,2'-Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol.

(S)-(+)-1-Cyclohexylethyl-(2-methacryloyloxyethyl)urea (CEMOU) was synthesized as follows (Scheme 1): A solution of MOI (3.7 g, 2.4×10^{-2} mol) in THF (20 mL) was added dropwise to a stirred solution of (S)-(+)-cyclohexylethylamine (3.0 g, 2.4×10^{-2} mol) in THF (180 mL) under nitrogen at room temperature. The solution was heated at 40°C and stirred for 90 h under nitrogen. The reaction mixture was evaporated under reduced pressure to give the crude product. Purification by recrystallization from dichloromethane/n-hexane gave pure CEMOU as white powder: yield 88.4%; mp. 125°C–127°C; $[\alpha]_{435}^{25}$ +31.2° ($c = 1.0$ g/dL, $l = 10$ cm, DMF); ^{1}H-NMR (δ, ppm from TMS in CDCl$_3$) 6.12 [s, 1H (trans) CH$_2$=C], 5.59 [s, 1H (cis) CH$_2$=C], 4.86–4.82 (t, $J = 5.61$, 1H, CH$_2$—NH), 4.50–4.47 (d, $J = 8.90$, 1H, C*—NH), 4.24–4.21 (t, $J = 5.28$, 5.61, 2H, O—CH$_2$), 3.62–3.47 (m, 3H, C*—H and N—CH$_2$), 1.95 (s, 3H, =C—CH$_3$), 1.76—0.92 (m, 14H, in cyclohexyl group and C*—CH$_3$); ^{13}C-NMR (δ, ppm from TMS in CDCl$_3$), 167.48 (C=O), 157.93 (NH—CO), 136.03 (CH$_2$=C), 125.56 (CH$_2$=C), 64.21 (O—CH$_2$), 50.33 (C*—H), 43.61, 29.04, 28.75, 26.42, 26.24, 26.20 (in cyclohexyl group), 39.37 (N—CH$_2$), 18.42 (=C—CH$_3$), 18.22 (C*—CH$_3$).

Other reagents were used without further purification.

Radical polymerization

Radical homopolymerization and copolymerization were performed with AIBN as initiator in a suitable solvent in a sealed tube at 60°C. After polymerization

Scheme 2
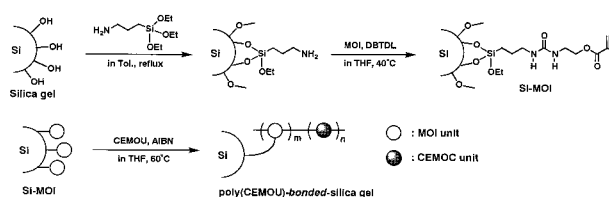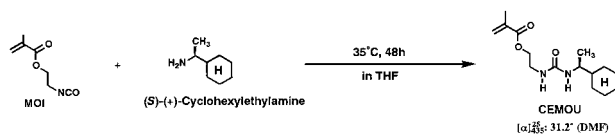
the polymer solutions were poured into a large amount of methanol to precipitate the polymers and were centrifuged. The polymers were purified by reprecipitating it twice from chloroform solution to excess n-hexane. The polymers were dried in vacuum for 3 days. The composition of the copolymer was calculated from elemental analysis (N).

Preparation of CSP for HPLC and column packing

Poly(CEMOU)-bonded silica gel as CSP for HPLC was prepared by the synthetic routes shown in Scheme 2 . Macroporous silica gel (TOSOH, TSK-GEL SI100; mean particle size, 5 μm; pore size, 100 Å) was silanized with 3-aminopropyl triethoxysilane according to the method described in the literature.[17] MOI (16 mL) was added to a slurry of the silanized silica gel (8.0 g) under nitrogen. The mixture was heated to 35°C, stirred for 45 h under nitrogen, and then cooled to room temperature. The reaction mixture was filtered, washed with dichloromethane, acetone, and methanol, and then dried in vacuo to obtain silica gel containing vinyl groups on the surface (Si100–MOI; C, 13.02%; H, 2.24%; N, 3.05%).

One gram of Si100–MOI and 0.5 g of monomer (CEMOU) were weighed in a Schlenk reaction tube. A solution of 3 mol % AIBN (against CEMOU)) in 10 mL of THF was added to the mixture in a Schlenk reaction tube under nitrogen. The slurry was shaken at 60°C for 24 h and cooled to room temperature. The reaction mixture was filtered, washed with DMF, THF, acetone, and methanol, and then dried in vacuo to afford poly(CEMOU)-bonded silica gel (CSP; C, 22.14%; H, 3.54%; N, 4.31%). The content (16.2 wt %) of the poly(CEMOU) segment on the CSP was examined by IR.

The CSP was packed in a stainless-steel HPLC column (i.d., 2 mm; length, 15 cm) using a slurry method. Theoretical plate numbers of the columns packed CSP was 1630, which was measured for toluene in eluent at a flow rate of 0.1 mL/min at 25°C.

Measurements

NMR spectra were recorded at 25°C using a JEOL EX-270 (Jeol, Ltd.). Infrared spectra were recorded using a Shimadzu FTIR-8100A (Shimadzu, Ltd.). Elemental analysis was carried out with a 2400II CHN

Scheme 1

TABLE I
Radical Homopolymerizations of CEMOU for 24 h at 60° C[a]

Run	Monomer	Polymer solvent (mL)	Yield[b] %	$\bar{M}_n$[c] $(\times 10^{-4})$	$\bar{M}_w/\bar{M}_n$[c]	$[\alpha]_{435}^{25}$[d] (deg)
1	CEMOU	THF (5)	77.6	1.54	1.55	21.5
2	CEMOU	CHCl$_3$ (5)	87.3	1.38	1.90	21.4
3	CEMOU	DMF (5)	79.6	3.33	1.31	20.9
4	CEMOU	Toluene (5)	71.1	—[e]	—[e]	24.1

[a] Monomer = 0.5 g, initiator; AIBN, [AIBN] [monomer] = 0.03
[b] Runs 1–4: *n*-hexane insoluble part
[c] By GPC with polystyrene standard in THF
[d] c = 1.0 g/dL l = 10 cm, runs 1–4 in DMF
[e] THF insoluble.

(Perkin–Elmer). Gel permeation chromatography (GPC) measurements were carried out at 50°C using THF or DMF as an eluent on a Shimadzu SPD-10A (Shimadzu, Ltd.) equipped with a UV detector; HSG-40, HSG-20, HSG-15, and HSG-10 columns for THF or HSG-60 columns for DMF; and a Jasco-OR 990 (Japan Spectroscopic Co.) with a polarimetric detector. Specific optical rotations were measured with a Jasco DIP-140 (5- and 10-cm quartz cell lengths, c = 1.0 gd/L in DMF). HPLC measurements were carried out on a Shimadzu LC-10AT (Shimadzu, Ltd.) equipped with UV detection at 254 nm.

RESULT AND DISCUSSION

Radical homopolymerization of CEMOU

Radical homopolymerization of CEMOU was performed with AIBN as an initiator at 60°C in various solvents, as summarized in Table I. The polymerization proceeded homogeneously for runs 2 and 3 (Table I), and precipitate was observed with propagating polymerization for run 1. For run 4 polymerization in toluene was heterogeneous throughout. All obtained polymers were white powders, though they were sticky and rubbery in methanol and *n*-hexane. The polymers were soluble in organic solvents such as THF, chloroform, and DMF, except for the polymer obtained in toluene, which was insoluble in THF. It is difficult to explain clearly, but the polymer obtained in toluene may have a higher number-average molecular weight (M_n) than the other polymers. The M_n and specific optical rotation ($[\alpha]_{435}^{25}$) values of poly(CEMOU) ranged from 13,800 to 33,300 and from 20.9° to 24.1°, respectively. The M_n for the polymer obtained in DMF was higher than that for the polymer obtained in THF. This may have been a result of precipitate appearing when polymerization proceeded in THF, whereas DMF was a good solvent for poly(CEMOU). Figure 1 shows the ^{1}H-NMR spectra of CEMOU and poly(CEMOC). The peaks at 6.08 and 5.52 ppm assigned to vinyl groups [$\underline{CH}_2$=C(CH$_3$)—] disappeared

after polymerization, indicating that the radical polymerization proceeded completely.

Expanded IR spectra for CEMOU and poly(CEMOU) determined in chloroform are shown in Figure 2. CEMOU exhibited absorption because of stretching vibration of the N—H from 3680 to 3180 cm^{-1}, with a top peak at 3440 cm^{-1}. Poly(CEMOU) showed a broad peak from 3780 to 3140 cm^{-1}, with a top peak at 3400 cm^{-1}. The top peak for poly(CEMOU) shifted from 3440 to 3400 cm^{-1}. Thus, poly(CEMOU) may have hydrogen bonds caused by the urea segments.

Figure 3 shows the relationships between specific optical rotations of poly(CEMOU) and measured temperatures in chloroform. For poly(CEMOU), absolute
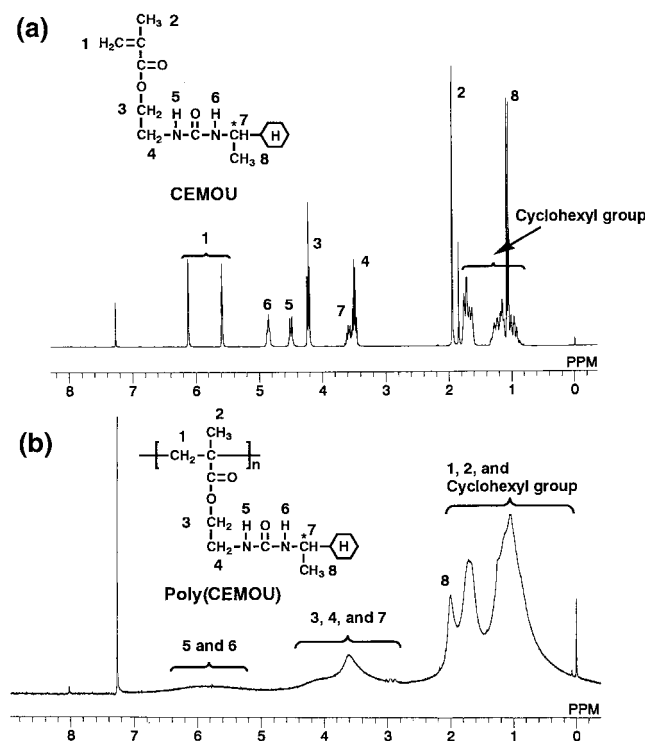

Figure 1 ^{1}H-NMR spectra of (a) CEMOU and (b) poly(CEMOU) in CDCl$_3$ at 23.5°C (270 MHz).
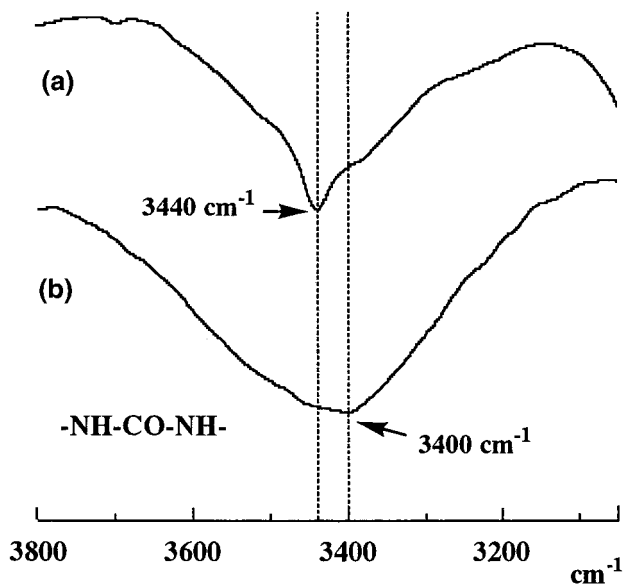
Figure 2 Expanded IR spectra of (a) CEMOU and (b) poly(CEMOU) in CHCl₃.

values of specific optical rotations slightly decreased with increasing temperature $[|\Delta(\alpha)/\Delta T| = 0.12]$. These changes, which were reversible, may be attributed to the change of conformation caused by hydrogen bonding as a result of the urea segments and/or the interaction between the cyclohexyl groups. We previously reported[1] that temperature dependence of a specific optical rotation of poly{cholesteryl-(2-methacryloyloxyethyl)carbamate [CHMOC]} having urethane and cholesteryl groups in the side chain might be a
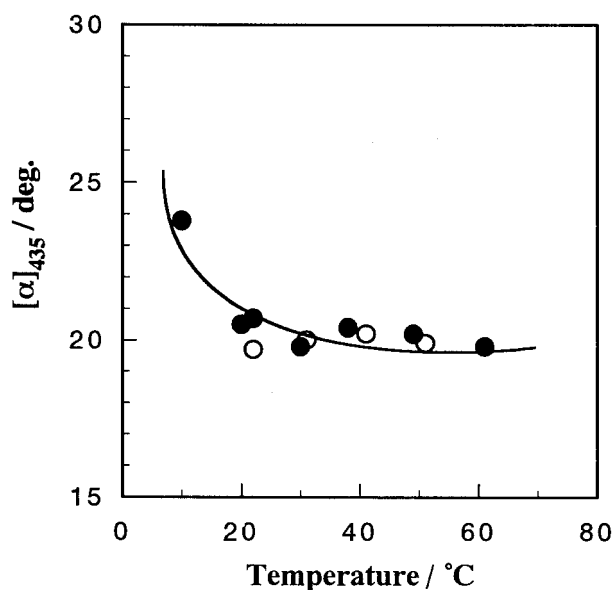

Figure 3 Dependence of specific optical rotation of (●, ○) poly(CEMOU) on the measurement temperature in DMF: c = 1.0 g/dL, l = 10 cm (●: increasing temperature; ○: decreasing temperature).
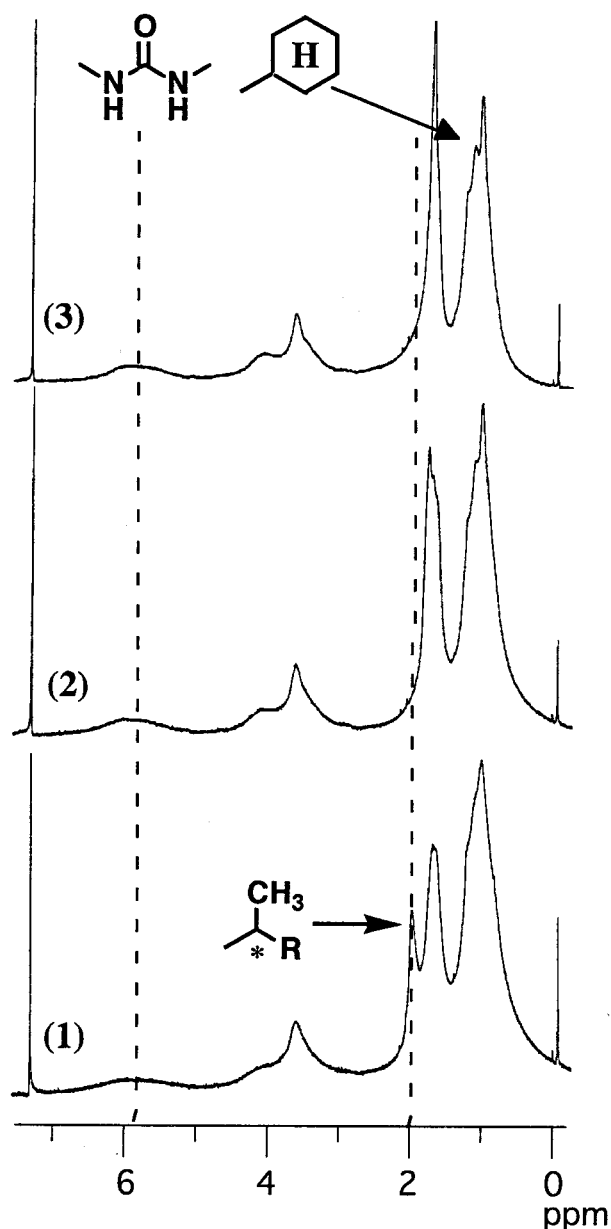
Figure 4 ¹H-NMR for poly(CEMOU) in CDCl₃ at (1) 20°C, (2) 40°C, and (3) 50°C.

result in part of the conformation change from both strong hydrogen bonds based on the urethane groups and interaction between the cholesteryl groups.

Figure 4 shows the ¹H-NMR spectra of poly(CEMOU) at various temperatures. A change was not observed with increasing temperature in the broad peak from the N—H, whereas the peak from the methyl group neighboring to the chiral carbon shifted to a high magnetic field with increasing temperature. Furthermore, the peak resulting from the cyclohexyl groups for poly(CEMOU) partially split into two bands with increasing temperature. These results suggest that the temperature dependence of specific optical rotation of poly(CEMOU), as shown in Figure 3,

TABLE II
Radical Copolymerization of CEMOU (M_1) with ST (M_2) and MMA (M_2) in THF (4 mL) at 60°C[a]

Run	M_2	M_1 in monomer (mol %)	Polymerization time (h)	Yield[b] %	M_1 in copolymer[c] (mol %)	(wt %)	$\bar{M}_n$[d] ($\times 10^{-4}$)	$\bar{M}_w/\bar{M}_n$[d]	$[\alpha]_{435}^{25}$[e] (deg)
1	ST	20.1	6.5	10.5	40.7	65.0	0.24	1.31	17.3
2	ST	40.5	4.5	15.8	57.1	78.3	4.97	1.92	25.2
3	ST	60.0	3.5	24.4	71.5	87.2	1.34	3.34	22.2
4	ST	80.4	3.5	22.2	79.9	91.5	2.07	2.09	18.6
5	MMA	20.3	22.0	22.4	31.7	56.7	0.59	1.57	12.1
6	MMA	39.1	7.4	26.6	55.0	77.5	0.97	1.83	17.0
7	MMA	59.4	3.7	19.0	63.5	83.1	3.63	2.64	20.7
8	MMA	80.3	3.7	46.1	73.2	88.5	1.90	2.35	21.8

[a] $M_1 + M_2 = 0.5$ g, initiator: 2,2-α-azobisisobutyronitrile (0.03 mol/L), THF 4 mL
[b] MeOH—insoluble part
[c] By elemental analysis
[d] By GPC with standard polystyrene in DMF
[e] $c = 1.0$ g/dL, $l = 5$ cm, in DMF.

might be in part due to conformation change from hydrophobic interaction between cyclohexyl groups rather than from hydrogen bonds based on the urea groups.

Radical copolymerization of CEMOU with ST or MMA

The results of radical copolymerization of CEMOU (M_1) with ST (M_2) or MMA (M_2) using AIBN in THF at 60°C are summarized in Table II. All copolymerizations proceeded heterogeneously, that is, precipitate was obtained with the copolymerization proceeding. The obtained copolymers were not soluble in acetone, toluene, ethyl acetate, THF, and so on, but they did dissolve in chloroform and DMF.

The copolymer composition curves for the polymerization of CEMOU with ST or MMA are shown in Figure 5. The monomer reactivity ratios (r_1, r_2) were calculated using the high-conversion method,[18] and Alfrey–Price Q–e values[19] for CEMOU were determined as follows: $r_1 = 0.89$, $r_2 = 0.12$, $Q_1 = 2.45$, $e_1 = 0.68$ in the CEMOU–ST system; $r_1 = 0.48$, $r_2 = 0.18$, $Q_1 = 8.39$, $e_1 = 1.97$ in the CEMOU–MMA system. The Q_1 and e_1 values in the M_1–ST system were apparently different from those in the M_1–MMA system. This may have occurred because the steric effect is not considered in the Alfrey–Price Q and e theory. It seems that CEMOU had a relatively high steric hindrance because of a large substituent group such as cinchona alkaloid. In addition, the copolymerization results may have been strongly affected by the heterogeneous course of the copolymerization.

Figure 6 shows the relationship of a specific optical rotation with monomeric unit content (wt %) of CEMOU in poly(CEMOU-co-M_2). The line connecting 0° with the $[\alpha]_{435}^{25}$ of poly(CEMOU) refers to the relationship between the specific optical rotation and mono-

meric unit contents (wt %) of in a mixture of poly(CEMOU) and poly(ST) [or poly(MMA)]. In Figure 6 the specific optical rotation of poly(CEMOU-co-ST) showed a small deviation from the line, suggesting that the chiroptical property of the copolymers depended slightly on the co-units (ST monomeric units).

Optical resolution ability of poly(CEMOU)

To investigate the chiral recognition ability of poly(CEMOU), the chiral stationary phase (CSP)—poly(CEMOU)-bonded silica gel—was prepared according to synthetic routes shown in Scheme 2. Figure 7 depicts the IR spectra of poly(CEMOU), silica gel
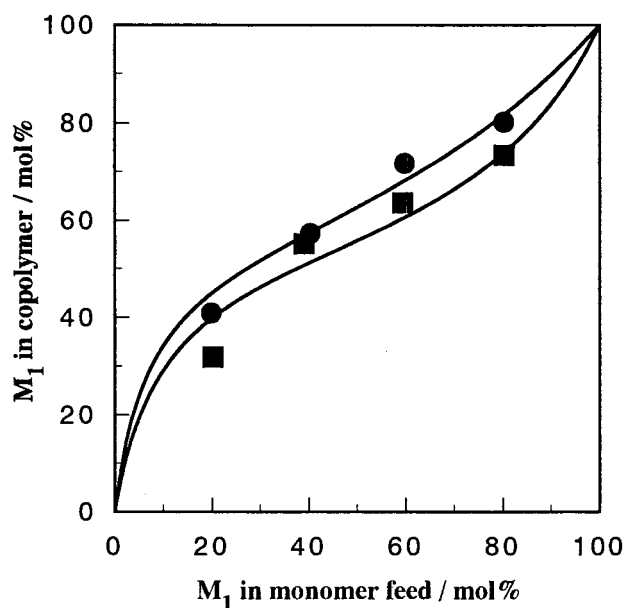
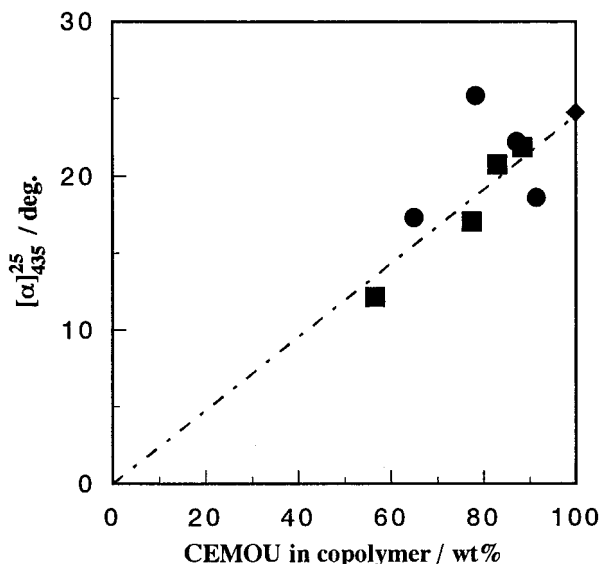**Figure 5** Copolymer composition curves of poly(CEMOU-co-M_2); $M_2 = $ (●) ST and (■) MMA.

Figure 6 Relationships between specific optical rotations ($[\alpha]_{435}^{25}$) and the content (wt %) of monomeric units of CEMOU in poly(CEMOU-*co*-M$_2$); M$_2$ = (●) ST and (■) MMA; (◆) poly(CEMOU).

Figure 8 Calibration curve of content (wt %) of poly(CEMOU) segment in poly(CEMOU)-bonded silica gel.

(Si100–MOI), and poly(CEMOU)-bonded silica gel. For poly(CEMOU)-bonded silica gel, absorptions from the alkyl chain (—CH$_2$—) in the CEMOU units and the Si—O— in silica gel were observed clearly at 2925 and 800 cm^{-1}, respectively. The content (16.2 wt %) of poly(CEMOU) segment on CSP-II was determined by a calibration curve obtained from the ratios (A$_{2925}$ cm^{-1}/A$_{800}$ cm^{-1}) of absorbance at 2925 and 800 cm^{-1} in the IR spectra of suitable mixtures of silica gel and chiral polymers, as shown in Figure 8.

Poly(CEMOU) has urea bonds; so hydrogen bonding is expected between the CSP and racemates having a carbonyl and a hydroxyl group. The ability of the CSP to do chiral recognition of racemates **1–22**
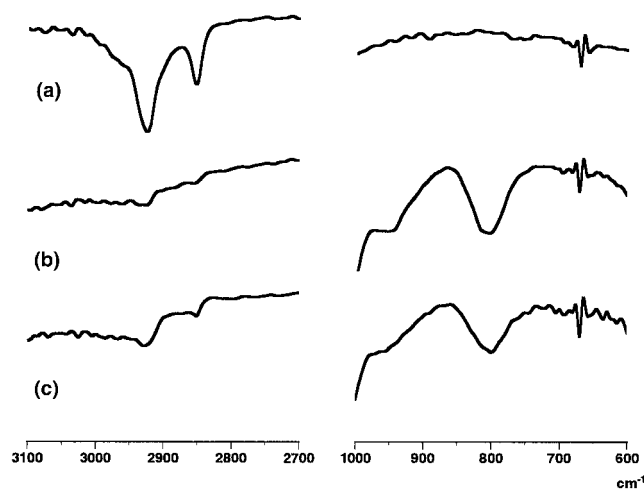
(Scheme 3) was examined with HPLC. The results of chromatographic resolution, summarized in Tables III and IV, show that the CSP resolved racemate **7** in normal phase, such as *n*-hexane/2-propanol, but did not resolve all racemates in reversed phase such as methanol–water. A typical chromatogram of the resolution of racemate **7** on CSP is shown in Figure 9. In a previous work,[4] the CSP prepared from poly{(s)-methylbenzyl-(2-methacryloyloxyethyl) urea[MBMOU]}-bearing (*S*)-methylbenzyl urea groups could resolve racemate **2** in normal phase. Table III shows that racemate **7** was not resolved using 20% 2-propanol in *n*-hexane as eluent but was resolved using 10% and 5% 2-propanol in *n*-hexane as eluent. The enantiomer capacity (k_1, k_2) and separation (α) factors using 5% 2-propanol in *n*-hexane as eluent were larger than those using 10% 2-propanol in *n*-hexane as eluent. This indicates that hydrogen bonding may be the main interaction between CSP and racemate **7**.

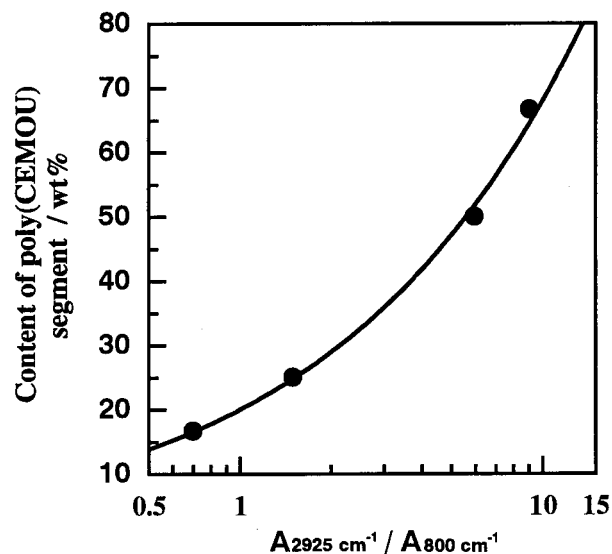**Figure 7** Expanded IR spectra of (a) poly(CEMOU), (b) Si100-MOI, and (c) poly(CEMOU)-bonded silica gel.

CONCLUSIONS

1. A new chiral methacrylate–bearing urea moiety, CEMOU, was synthesized from MOI and (*S*)-(+)-cyclohexylethylamine.
2. Radical homopolymerizations of CEMOU were carried out in various solvents to obtain the corresponding chiral polymers having hydrogen bonds based on urea units.
3. From the results of the copolymerization of CEMOU with ST or MMA, monomer reactivity ratios and *Q* and *e* values were determined. The chiroptical property of poly(CEMOU-*co*-ST)

1: trans-Stilbene oxide   **2:** 1,2,3,4-Tetrahydro-1-naphthyl alcohol   **3:** 1,1'-Bi-2-naphthyl alcohl   **4:** *trans*-3, 4-Dimethyl-N-phenylsuccinimide   **5:** Madellic acid   **6:** Mandelic acid ethyl ester

7: *trans*-2-Dibenzyl-4,5-di (o-hydroxyphenyl)-1,3-dioxolane   **8:** *trans*-2-Cyclohexanespiro-4,5-di (o-hydroxyphenyl)-1,3-dioxolane   **9:** *trans*-Epoxy-1-phenyl-3-phenylpropane-3-one   **10:** *trans*-Epoxy-1-(4-fluoro phenyl)- 4,4-dimethyl pentane- 3-one   **11:** *trans*-Epoxy-1-4-(chloro phenyl)- 4,4-dimethyl pentane- 3-one

12: 2-Benzoylocmethyl-pyran-4-one   **13:** 2-Ethoxycarbonyl-pyran 4-one   **14:** Methoxycarbonyl-2, 2-dimethyl-1-phenyl ethanol   **15:** 2-Ethoxycarbonyl-N-(p-methoxyphrnyl)-4-pyridine   **16:** 2-phenyl-N-(p-(phenyl sulufonyl) phrnyl)-4-pyridine   **17:** N-Benzyl-1-(1-methyl-2-methoxycarbonyl) ethylamine

18: *trans*-Epoxy-1-(2-fluoro phenyl)- 4,4-dimethyl pentane- 3-one   **19:** *trans*-Epoxy-1-(3-fluoro phenyl)- 4,4-dimethyl pentane- 3-one   **20:** Methoxycarbonyl-2, 2-dimethyl-1-phenylethanol   **21:** α-hydroxybenzyl methylamid   **22:** Ketprophene

Scheme 3

TABLE III
Chromatographic Resolution of Racemates 1–22 on Poly(CEMOU)-Bonded Silica Gel at 0.1 mL/min
of Flow in Normal Phase Such as *n*-Hexane/2-Propanol

	n-hexane/2-propanol											
	(9.5:0.5$_{volume}$)				(9:1$_{volume}$)				(8:2$_{volume}$)			
Racemate	k_1^a	k_2^a	α^b	R_S^c	k_1	k_2	α	R_S	k_1	k_2	α	R_S
1	0.14	0.14	1.0		0.13	0.13	1.0		0.11	0.11	1.0	
2	0.60	0.60	1.0		0.54	0.54	1.0		0.38	0.38	1.0	
3	0.33	0.33	1.0		3.55	3.55	1.0		2.33	2.33	1.0	
4	0.70	0.70	1.0		3.25	3.25	1.0		0.44	0.44	1.0	
5	1.11	1.11	1.0		0.77	0.77	1.0		0.37	0.37	1.0	
6	0.36	0.36	1.0		0.34	0.34	1.0		0.26	0.26	1.0	
7	0.44	0.64	1.43	0.35	0.40	0.56	1.35	0.34	1.20	1.20	1.0	
8	2.18	2.18	1.0		2.88	2.88	1.0		0.13	0.13	1.0	
9	2.01	2.01	1.0		1.34	1.34	1.0		0.80	0.80	1.0	
10	0.68	0.68	1.0		0.35	0.35	1.0		0.18	0.18	1.0	
11	0.37	0.37	1.0		0.36	0.36	1.0		0.75	0.75	1.0	
12	2.18	2.18	1.0		1.32	1.32	1.0		ND	ND	ND	
13	2.80	2.80	1.0		1.72	1.72	1.0		0.68	0.68	1.0	
14	1.44	1.44	1.0		0.76	0.76	1.0		0.34	0.34	1.0	
15	0.63	0.63	1.0		0.56	0.56	1.0		0.97	0.97	1.0	
16	0.50	0.50	1.0		0.42	0.42	1.0		1.23	1.23	1.0	
17	0.18	0.18	1.0		0.54	0.54	1.0		0.38	0.38	1.0	
18	0.51	0.51	1.0		3.81	3.81	1.0		0.82	0.82	1.0	
19	1.17	1.17	1.0		1.11	1.11	1.0		2.50	2.50	1.0	
20	0.41	0.41	1.0		0.28	0.28	1.0		0.16	0.16	1.0	
21	0.59	0.59	1.0		0.31	0.31	1.0		0.18	0.18	1.0	
22	1.22	1.22	1.0		2.60	2.60	1.0		0.89	0.89	1.0	

[a] Capacity factor of enantiomer eluting first (k_1) and second (k_2) = (retention time of enantiomer–void time of column)/(retention time of 1,3,5-*t*-butylbenzene)

[b] Separation factor: $\alpha = k_2/k_1$

[c] Resolution factor = 2 × (distance between peaks of more and ress retained enantiomers)/(sum of bandwidth of two peaks); ND = not determined.

TABLE IV
Chromatographic Resolution of Racemates 5–9, 11–14, 17, and 19–21 on Poly(CEMOU)-Bonded Silica Gel
at 0.1 mL/min of Flow in a Reversed Phase such as Methanol/Water

	Methanol/water							
	(7:3$_{volume}$)				(5:5$_{volume}$)			
Racemate	k_1	k_2	α	R_S	k_1	k_2	α	R_S
5	3.78	3.78	1.0		2.67	2.67	1.0	
6	0.19	0.19	1.0		2.38	2.38	1.0	
7	0.31	0.31	1.0		2.57	2.57	1.0	
8	0.59	0.59	1.0		1.54	1.54	1.0	
9	3.99	3.99	1.0		2.61	2.61	1.0	
11	1.94	1.94	1.0		2.69	2.69	1.0	
12	0.61	0.61	1.0		2.78	2.78	1.0	
13	1.09	1.09	1.0		1.60	1.60	1.0	
14	0.27	0.27	1.0		3.01	3.01	1.0	
17	0.31	0.31	1.0		2.51	2.51	1.0	
19	2.21	2.21	1.0		1.58	1.58	1.0	
20	0.29	0.29	1.0		2.59	2.59	1.0	
21	3.95	3.95	1.0		2.83	2.83	1.0	

[a] Capacity factor of enantiomer eluting first (k_1) and second (k_2) = (retention time of enantiomer–void time of column)/(retention time of 1,3,5-t-butylbenzene);
[b] Separation factor: $\alpha = k_2/k_1$;
[c] Resolution factor = 2 × (distance between peaks of more and ress retained enantiomers)/(sum of bandwidth of two peaks).

was slightly influenced by the comonomer units.

4. CSPs prepared from silica gel and poly(CEMOU) resolved racemate **7** by HPLC in a normal phase such as n-hexane/2-propanol.

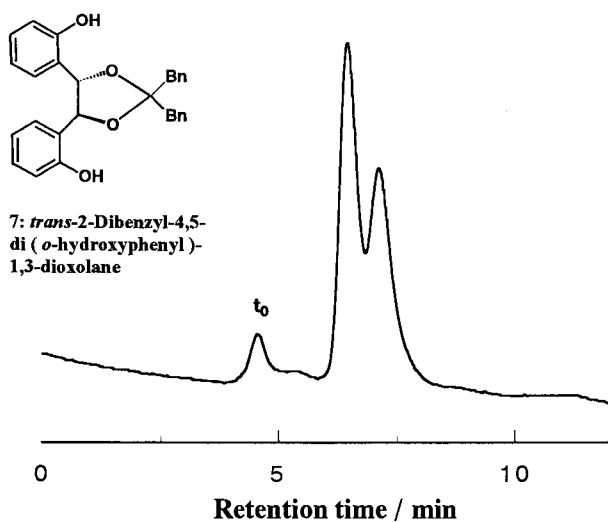**7**: *trans*-2-Dibenzyl-4,5-di(*o*-hydroxyphenyl)-1,3-dioxolane

Figure 9 Typical HPLC chromatogram of racemate **7** with poly(CEMOU)-bonded silica gel in n-hexane:2-propanol (9.0:1.0$_{volume}$) mobile phase; racemate **7**: *trans*-2-dibenzyl-4,5-di(*o*-hydroxyphenyl)-1,3-dioxolane; column size: 150 mm × 2 mm; flow: 0.1 mL/min.

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