Synthesis and ring-opening polymerization of optically pure mesogenic malolactonates

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Synthesis and ring-opening polymerization of optically pure mesogenic malolactonates

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Optically pure malolactonate monomers containing biphenyl mesogenic groups with either an ethylene or a hexamethylene spacer were prepared from optically pure malic acid and polymerized with alkylaluminoxane catalysts to form a series of new chiral side chain liquid-crystalline polymers, which contained the chiral centres in the backbone. The mesogenic malolactonate monomers were determined to be optically pure by ^{1}H NMR spectroscopy of the β-lactone complexed with a chiral europium shift reagent. Both the methylaluminoxane and isobutylaluminoxane catalysts gave polymers having bimodal molecular weight distributions, the latter catalyst yielded a larger amount of the higher molecular weight fraction than the former. The polymers showed high optical rotations, high degrees of isotactic stereoregularity, and enantiotropic liquid-crystalline properties, all of which were influenced by the molecular weight distribution. Copolymers of malolactonate monomers with different spacers were also prepared and characterized.

1. Introduction

Low molar mass compounds and polymers with chiral liquid-crystalline phases, either the cholesteric (Ch*) or the chiral smectic C (S$_C^*$) phase, have become of great interest in the last decade. Interest in the Ch* phase comes from its optical properties, including thermochromism at selective wavelengths of the reflected light and circularly polarized light, whereas the S$_C^*$ phase is of interest for its ferroelectric properties and for its fast switching times in electric fields [1]. Liquid-crystalline side chain polymers have been studied most intensively because these polymers can be oriented under magnetic fields and the molecular orientation can be frozen in below their glass transition temperatures, so they do not require a separate matrix to form liquid crystal devices [2].

Although a number of different structural families of chiral side chain liquid crystalline polymers have been studied, most of them have had their chiral centres in the terminal group of the pendent mesogenic units [3]. In contrast, Hong and Stupp [4] prepared and characterized a somewhat different structural system of chiral side chain liquid-crystalline polymers in which the chiral centres were located between the polymer backbones and the mesogenic units. Ujiie and Iimura [5] studied another system of chiral side chain liquid-crystalline polyesters in which the chiral centres were located in the backbones, and the pendent mesogenic units were linked to the chiral centres by the spacers. Both of these systems can be expected to exhibit larger values of

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spontaneous polarization of the S_C^* phase than those of the conventional side chain liquid-crystalline polymer systems because mobilities of the chiral centres in the former are relatively lower due to their inclusion in or near the macromolecular backbones. The system reported by Ujiie and Iimura formed the expected S_C^* phase, which had a very large value of spontaneous polarization, but the system reported by Hong and Stupp formed a smectic A phase.

The chiral side chain liquid-crystalline polyesters of Ujiie and Iimura were prepared by the step growth polymerization of optically active tartarate or malate monomers, which contained pendent mesogenic units, with appropriate aliphatic diols [5]. In the present study, a somewhat different type of liquid-crystalline polyesters was investigated in which the chiral centres were located in the backbones and the mesogenic units were linked to the chiral centres by spacers. The present polymers, I, were prepared by ring-opening polymerization of optically active malolactonate monomers containing mesogenic units, II.

$$n = 2, 6 \text{ or } 11.$$
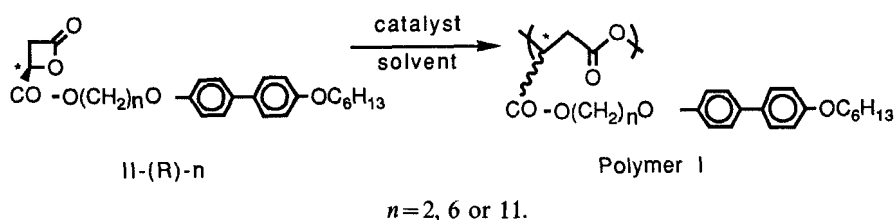
Arnold and Lenz established the synthetic route for the preparation of optically pure benzyl and isopropyl malolactonates [6], and Lenz and co-workers have developed a series of alkylaluminoxane catalysts for the polymerization of β-lactones, including malolactonates [7]. These procedures were used to design and prepare the chiral polymers, I. The procedure developed by Arnold and Lenz [6] was modified for preparation of a series of optically pure mesogenic malolactonate monomers, II.
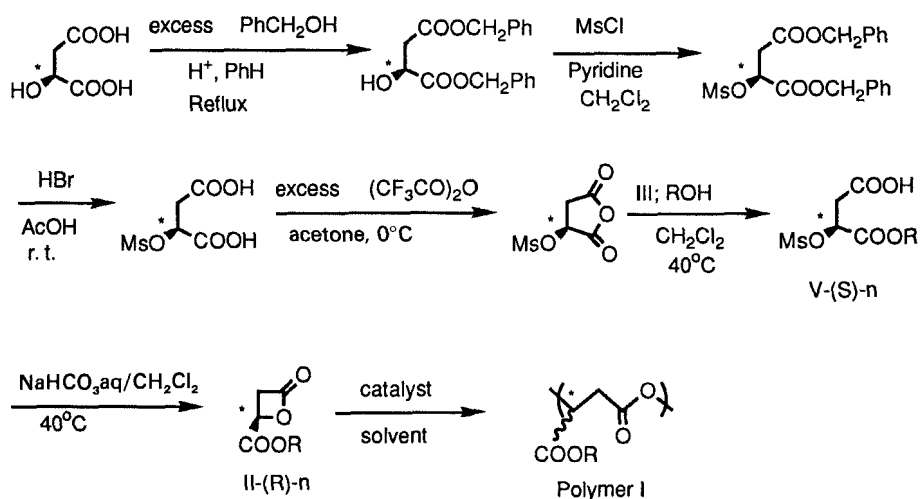
For III: $R = (CH_2)_n O$ —⟨O⟩—⟨O⟩—OC_6H_{13} and $n = 2$, 6 or 11; $Ms = OSO_2CH_3$, $Ph = C_6H_5$, and (S) and (R) are the absolute configurations of the chiral centres in II and V.

Because the mesogenic alcohols, ROH, which contained a biphenyl moiety and alkyl spacer, III, are relatively high melting compounds, an appropriate solvent had to be used for this procedure. The series of the mesogenic alcohols, III, used for the synthesis of the monomer as previously described are shown in the following scheme [8].

$$HO-\bigcirc-\bigcirc-OH \xrightarrow[\text{2)HCl}]{\text{1) }C_6H_{13}Br,\ NaOH/EtOH} HO-\bigcirc-\bigcirc-OC_6H_{13}$$

IV

$$\xrightarrow[\text{EtOH-KOHaq}]{HO(CH_2)nCl} HO(CH_2)_nO-\bigcirc-\bigcirc-OC_6H_{13}$$

III-n
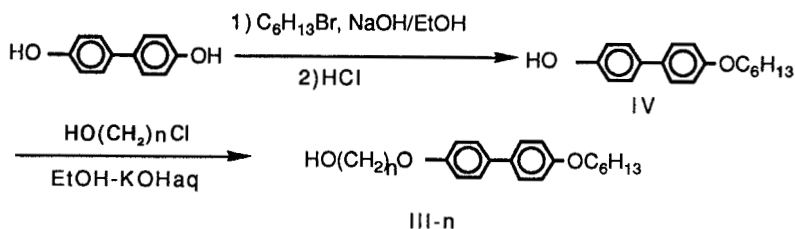
2. Experimental

2.1. *Precursors and monomers*

2.1.1. *4-hexyloxy-4′-hydroxybiphenyl IV*

Mp, 156–158°C; Elemental analysis for $C_{18}H_{22}O_2$: found C, 79·39 per cent, H, 8·14 per cent; calculated C, 80·01 per cent, H, 8·14 per cent.

2.1.2. *4-(6-Hydroxyhexyloxy)-4′-hexyloxybiphenyl III-6*

Mp 144–145°C. ^{1}H NMR (DMSO-d_6) $\delta = 0·88$ (3H, t, $J = 6·6$ Hz), 1·3–1·5 (12 H, m), 1·6–1·8 (4 H, m), 3·39 (2 H, t, $J = 6·0$ Hz), 3·98 (4 H, t, $J = 6·5$ Hz), 4·20 (1 H, t, $J = 5·2$ Hz), 6·95 (4 H, d, 8·6 Hz), 7·49 (4 H, d, $J = 8·6$ Hz). Elemental analysis for $C_{24}H_{34}O_3$: found C, 77·90 per cent, H, 9·10 per cent; calculated C, 77·85 per cent, H, 9·18 per cent.

2.1.3. *4-(2-Hydroxyethoxy)-4′-hexyloxybiphenyl III-2*

Mp 161–162°C. ^{1}H NMR (DMSO-d_6) $\delta = 0·88$ (3 H, t, $J = 6·6$ Hz), 1·3–1·5 (6 H, m), 1·6–1·8 (2 H, m), 3·7–3·8 (2 H, m), 3·9–4·1 (4 H, m), 4·57 (1 H, m), 6·9–7·1 (4 H, m), 7·50 (4 H, d, $J = 8·7$ Hz). Elemental analysis for $C_{20}H_{26}O_3$: found C, 76·21 per cent, H, 8·32 per cent; calculated C, 76·45 per cent, H, 8·27 per cent.

2.1.4. *4-(11-Hydroxydodecyloxy)-4′-hexyloxybiphenyl III-11*

Mp 135–137°C. ^{1}H NMR (DMSO-d_6) $\delta = 0·88$ (3 H, t, $J = 5·8$ Hz), 1·2–1·5 (22 H, m), 1·6–1·8 (4 H, m), 3·36 (2 H, t, $J = 5·3$ Hz), 3·99 (4 H, t, $J = 6·6$ Hz), 4·20 (1H, t, $J = 5·2$ Hz), 6·96 (4 H, d, 8·6 Hz), 7·49 (4 H, d, $J = 8·6$ Hz). Elemental analysis for $C_{29}H_{44}O_3$: found C, 79·07, H, 9·82 per cent; calculated C, 79·11 per cent, H, 9·99 per cent.

2.1.5. *1-[6-(4′-hexyloxy-4-biphenylyloxyhexyl] hydrogen (S)-O-mesylmalate V-(S)-6*

In 50 ml of dry dichloromethane (distilled over P_2O_5) were dispersed 3·21 g of III-6 and 2·07 g of (S)-O-mesylmalic anhydride prepared as previously described. The heterogeneous solution was refluxed for 12 h, the reaction mixture was evaporated *in vacuo* and the residue dissolved in chloroform at 25°C. After insoluble material was removed by filtration, the solution was evaporated *in vacuo* to yield 5·30 g of a powder. ^{1}H NMR (CDCl$_3$) $\delta = 0·91$ (3 H, t, $J = 6·8$ Hz), 1·2–1·5 (10 H, m), 1·6–2·0 (6 H, m), 3·05 (2 H, d, $J = 5·5$ Hz), 3·17 (3 H, s), 4·0 (4 H, m), 4·24 (2 H, t, $J = 6·6$ Hz), 5·36 (1 H, t, $J = 6·4$ Hz), 6·93 (4 H, d, $J = 8·6$ Hz), 7·45 (4 H, d, $J = 8·6$ Hz), 9·7 (1 H, sb). Elemental

analysis for $C_{29}H_{40}O_9S$: found C, 59·25 per cent, H, 6·91 per cent, S, 5·41 per cent (a small amount of solvent was detected by ^1H NMR); calculated for C, 61·72 per cent, H, 7·09 per cent, S, 5·68 per cent. $[\alpha]_D^{20} = -28·1°$ ($c = 10$, $CHCl_3$).

The other monomesogenic (S)-O-mesylmalates, V-(S)-2 and V-(S)-11, were prepared by the same procedure from III-2 and III-11, respectively. This series of half esters formed liquid-crystalline phases above the melting point. The liquid-crystalline properties of these compounds will be discussed in the future.

2.1.6. *1-[2-(4'-hexyloxy-4-biphenylyl)ethyl] hydrogen (S)-O-mesylmalate V-(S)-2*

^1H NMR ($CDCl_3$) $\delta = 0·91$ (3 H, t, $J = 6·8$ Hz), 1·2–1·6 (6 H, m), 1·7–1·9 (2 H, m), 3·06 (2 H, d, $J = 5·6$ Hz), 3·18 (3 H, s), 3·98 (2 H, t, $J = 6·6$ Hz), 4·23 (2 H, t, $J = 4·2$ Hz), 4·5–4·7 (2 H, m), 5·36 (1 H, t, $J = 6·2$ Hz), 6·9–7·0 (4 H, m), 7·4–7·5 (4 H, d, $J = 8·6$ Hz). Elemental analysis for $C_{25}H_{32}O_9S$: found C, 58·14 per cent, H, 6·23 per cent, S, 6·45 per cent (a little amount of solvent was detected by ^1H NMR); calculated C, 59·07 per cent, H, 6·30 per cent, S, 6·30 per cent. $[\alpha]_D^{20} = -28·2°$ ($c = 10$, $CHCl_3$).

2.1.7. *1-[11-(4'-hexyloxy-4-biphenylyl)oxydodecyl] hydrogen (S)-O-mesylmalate V-(S)-11*

^1H NMR ($CDCl_3$) $\delta = 0·91$ (3 H, t, $J = 6·8$ Hz), 1·2–1·9 (26 H, m), 3·07 (2 H, d, $J = 5·6$ Hz), 3·18 (3 H, s), 3·98 (4 H, t, $J = 6·6$ Hz), 4·24 (2 H, t, $J = 6·6$ Hz), 5·3–5·4 (1 H, m), 6·93 (4 H, d, $J = 8·6$ Hz), 7·45 (4 H, d, $J = 8·6$ Hz). Elemental analysis for $C_{34}H_{50}O_9S$: found C, 62·44 per cent, H, 7·64 per cent, S, 4·92 per cent (a small amount of solvent was detected by ^1H NMR); calculated C, 64·37 per cent, H, 7·88 per cent, S, 5·05 per cent. $[\alpha]_D^{20} = -21·9°$ ($c = 10$, $CHCl_3$)

2.1.8. *6-(4'-Hexloxy-4-biphenylyl)oxyhexyl (R)-malolactonate II-(R)-6*

A solution of 2·29 g of V-(S)-6 in 25 ml of dichloromethane was heated at 40°C, and a solution of 0·40 g of sodium bicarbonate in 15 ml of water was added to the former solution. After the reaction mixture was heated at 40°C for 4 h, it was extracted with dichloromethane. Because the mixture formed an emulsion during the extraction, the organic solvent fraction was collected, filtered and dried over anhydrous sodium sulphate. After filtration, the dichloromethane solution was evaporated *in vacuo* to yield 0·85 g of colourless crystals (yield 45 per cent). Mp 90–93°C. IR (KBr) 1845 and 1730 cm^{-1} for the carbonyl groups. ^1H NMR ($CDCl_3$) $\delta = 0·91$ (3 H, t, $J = 3·8$ Hz), 1·2–1·7 (10 H, m), 1·7–1·95 (6 H, m), 3·61 (2 H, dd, $J = 16·8$ Hz, 4·6 Hz), 3·77 (1 H, dd, $J = 16·4$ Hz, 6·4 Hz), 3·99 (4 H, m), 4·27 (2 H, t, $J = 6·8$ Hz), 4·85 (1 H, dd, $J = 6·4$ Hz, 4·6 Hz), 6·93 (4 H, d, $J = 8·8$ Hz), 7·45 (4 H, d, $J = 8·8$ Hz). Elemental analysis for $C_{28}H_{36}O_6$: found C, 71·93 per cent, H, 7·55 per cent; calculated C, 71·81 per cent, H, 7·55 per cent. $[\alpha]_D^{20} = +6·8°$ ($c = 5·0$, $CHCl_3$).

2.1.9. *2-(4'-hexyloxy-4-biphenylyl)oxyethyl (R)-malolactonate II-(R)-2*

This monomer was prepared by the same procedure from V-(S)-2, but V-(S)-11 did not yield the corresponding malolactonate (yield 38 per cent). ^1H NMR ($CDCl_3$) $\delta = 0·91$ (3 H, t, $J = 6·4$ Hz), 1·2–1·6 (6 H, m), 1·7–1·95 (2 H, m), 3·60 (1 H, dd, $J = 16·6$ Hz, 4·5 Hz), 3·77 (1 H, dd, $J = 16·6$ Hz, 6·5 Hz), 3·98 (4 H, t, $J = 6·6$ Hz), 4·25 (2 H, t, $J = 4·8$ Hz), 4·61 (1 H, t, $J = 4·5$ Hz), 4·89 (1 H, m), 6·93 (4 H, d, $J = 7·0$ Hz), 7·47 (4 H, m). Elemental analysis for $C_{24}H_{26}O_6$: found C, 70·16 per cent, H, 6·55 per cent; calculated C, 70·26 per cent, H, 6·34 per cent. $[\alpha]_D^{20} = +9·4°$ ($c = 5·0$, $CHCl_3$). To determine the optical purities of this series of malolactonate monomers, the optical isomers were also prepared from (R)-malic acid by the same procedure. The data are collected in table 1.

2.2. *Optical purities of malolactonate monomers*

^{1}H NMR spectra of II-(*R*)-6, II-(*S*)-6 and the appropriate mixtures of II-(*R*)-6 and II-(*S*)-6 were obtained in solutions of mixed solvents of benzene-d$_6$ and carbon tetrachloride containing 33 mol% of tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate]europium(III) [6]. The spectra were recorded on a Varian XL-300 at 35°C.

2.3. *Polymerization (general procedure)*

In 3 ml of dry toluene (distilled over lithium aluminium hydride powder) was dissolved 0·25 g of the monomer, II-(*S*)-6, under an argon atmosphere. After dissolution was completed, 8–10 mol% of the isobutylaluminoxane catalyst in hexane solution based on the monomer was injected by a syringe. The reaction mixture was stirred at 90°C for 8–10 days, after which the reaction mixture was poured into 20 ml of methanol. The obtained precipitate was filtered, washed with methanol, and dried *in vacuo*. The dried precipitate was dispersed in 3 ml of acetyl acetone for 8 h. The insoluble product was dried at 50°C *in vacuo*. The alkylaluminoxane catalysts were prepared as previously reported [7].

2.4. *Characterization*

The specific rotations of the optically active compounds in chloroform were measured with an Autopol polarimeter (Rudolph Research Co.). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian XL-300 and a JOEL EX-400, respectively. The molecular weights of the polymers were determined by a Waters GPC instrument with a reflective index detector and Ultrastyragel linear and Ultrastyragel 500A columns using chloroform as the eluent and polystyrene standards for calibration. The thermal analysis was obtained on a Perkin–Elmer DSC-2 at a scanning rate of 20°C min^{-1}.

3. Results and discussion

3.1. *Monomer synthesis*

Yield and optical rotation data for the series of mesogenic half ester precursor compounds, V, and malolactonate monomers, II, are collected in table 1. The esterification reaction of the mesogenic alcohols, III, with O-mesylmalic anhydride gave quantitative yields of the half ester products, V, but the yields of the malolactonate monomers, II, from these precursors were much lower and varied with the length of the alkyl group spacer between the chiral centre and the mesogenic unit as shown in table 1. Indeed, V-(*S*)-11 did not form the malolactonate in measurable amounts under the reaction conditions described, but it formed only insoluble products instead in both water and dichloromethane. During the lactonization of V to II, the sign of the specific rotation changed as expected because the reaction occurs by an intramolecular S$_N$2 mechanism in which the asymmetric carbon atom undergoes a configurational inversion, but the absolute values of optical rotations of the (*S*) and (*R*) isomers of V and II were almost identical indicating that both optical isomers were essentially pure for both compounds.

The optical purities of the malolactonate monomers were measured by 300 MHz ^{1}H NMR spectroscopy for the lactones complexed with a chiral europium shift reagent, Eu(hfc)$_3$. The NMR spectra of the mixtures of II-(*R*)-6 and II-(*S*)-6 with this reagent are shown in figure 1. Eu(hfc)$_3$ interacted with each compound to cause a split of both the methine proton peak in the lactone ring at 4·41 ppm and the methylene protons peaks in the spacers at 4·04 ppm, into two distinct peaks in each case, with peak separations of

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Table 1. Yields and specific rotations of a series of precursor compounds and malolactonate monomers.

Compounds	Yields/%	$[\alpha]_D$ (a)/°
Precursor compounds		
V-(S)-6	100	−28·1
		(c = 10, 20°C)
V-(S)-2	100	−28·2
		(c = 10, 20°C)
V-(S)-11	100	−21·9
		(c = 10, 20°C)
V-(R)-6	100	+26·1
		(c = 9·6, 25°C)
Malolactonate monomers		
II-(R)-6	45	+6·8
		(c = 5·0, 20°C)
II-(R)-2	38	+9·4
		(c = 5·0, 20°C)
II-(R)-11	0	
II-(S)-6	50	−6·4
		(c = 5·0, 25°C)

(*a*) Optical rotations measured for chloroform solutions.
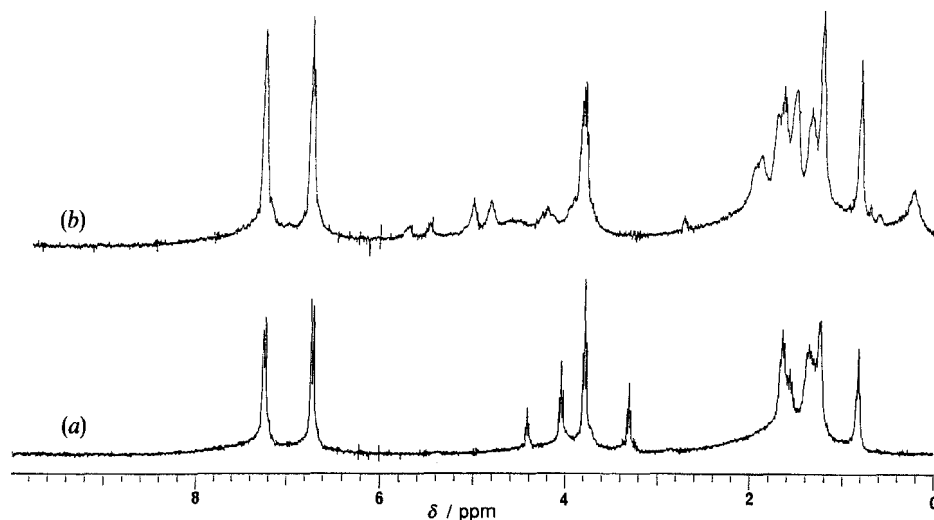
Figure 1. ^{1}H NMR spectra (solvent; $C_6D_6/CCl_4 = 1/9$ volume ratio) of II-6. (*a*) A mixture of II-(R)-6 and II-(S)-6, (*b*) a mixture of II-(R)-6 and II-(S)-6 in the presence of Eu(hfc)$_3$.

72 Hz and 57 Hz, respectively. Conversely, with this shift reagent, the peaks of monomers, II-(R)-6 and II-(S)-6, showed no splitting in the spectra in figure 2. The new peaks were identified from the integrated values of the peaks at different enantiomeric purities of the lactones.

Similarly, as shown by the spectra in figure 3, mixtures of II-(R)-2, II-(S)-2 and Eu(hfc)$_3$ also gave splitting peaks for both the methine protons of the lactone ring at 4·56 ppm and the methylene protons of the spacer at 4·44 ppm. The two distinct peaks
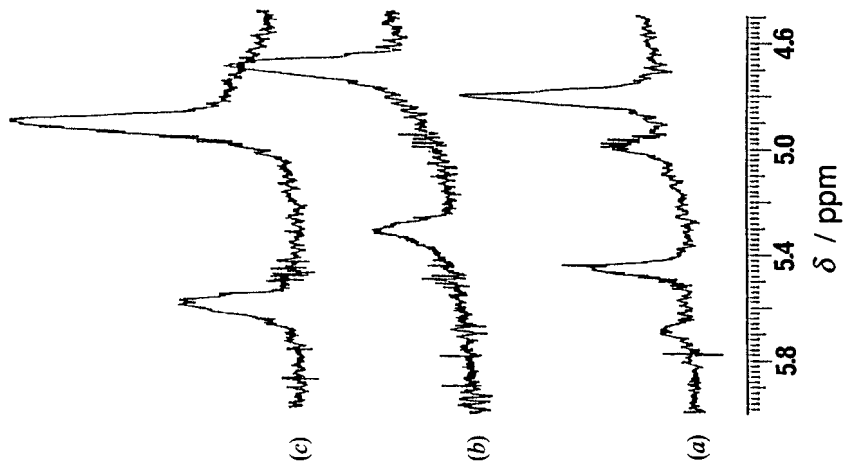
Figure 3. ¹H NMR spectra of II-2 in the presence of Eu(hfc)₃ (solvent; C₆D₆/CCl₄ = 1/9 volume ratio): (*a*) a mixture of II-(*R*)-2 and II-(*S*)-2 without Eu(hfc)₃, (*b*) a mixture of II-(*R*)-2 and II-(*S*)-2 (3:7 weight ratio), (*c*) II-(*R*)-2, (*d*) II-(*S*)-2.

Figure 2. ¹H NMR spectra of II-6 in the presence of Eu(hfc)₃ (solvent; C₆D₆/CCl₄ = 1/9 volume ratio): (*a*) a mixture of II-(*R*)-6 and II-(*S*)-6 (7:3 weight ratio), (*b*) II-(*R*)-6, (*c*) II-(*S*)-6.

Table 2. Polymerization conditions, yields and characterization of the series of polymers (a).

Monomer	Polymer	Catalyst (b)	Solvent	Yield/%	Molecular weight (c)				$[\alpha]_D^{25}$ (d)/°
						M_n	M_w	M_w/M_n	
II-(R)-6	I-1	MAO	Toluene	48	(W)	1600	5000	3·1	−3·2
					(H)	9000	15000	1·7	(c=7·0)
II-(R)-6	I-2	IBAO	Toluene	39	(W)	4000	18000	4·5	−3·3
					(H)	16000	23000	2·1	(c=5·5)
II-(R)-6	I-3	IBAO	Toluene/hexane (e)	35	(W)	3500	22000	6·5	−2·9
					(H)	—	—(f)		(c=3·0)
II-(S)-6	I-4	IBAO	Toluene	30	(W)	3300	12000	3·9	+5·9
					(H)	10000	19000	1·9	(c=2·9)

(a) The polymerization was carried out at 90°C for 10 days to yield polymers I-1, I-2 and I-3, and for 8 days to yield polymer I-4.
(b) MAO: methylaluminoxane, IBAO: isobutylaluminoxane.
(c) Molecular weights were determined by GPC based on polystyrene standards. W is the value calculated for the entire GPC chromatogram; H is the value calculated for the higher molecular weight peak only.
(d) Measured in chloroform solution.
(e) Toluene/hexane=1/1 volume ratio.
(f) The molecular weight distribution was not bimodal.

were separated by 82 Hz and 66 Hz, respectively, for these monomers, but no splitting was observed for the optical isomers, II-(R)-2 and II-(S)-2, in the presence of this shift reagent. From these data, the optically active monomers, II, were determined to be optically pure within experimental error.

3.2. *Polymer synthesis and characterization*

The optically pure lactone monomer, II-(R)-6, was polymerized in either a toluene or a toluene/hexane solution with two different alkylaluminoxane catalysts. The results obtained are listed in table 2, and the GPC chromatograms of the polymers obtained are shown in figure 4. The chromatograms generally contained a bimodal molecular weight distribution, as seen in figure 4, with one peak at a number average molecular weight, $\bar{M}_n$, of approximately 20 000 and the other at approximately 1500. The specific molecular weights observed for the higher peak, H, of these two peaks are listed in table 2, as is the $\bar{M}_n$ value calculated for the entire chromatograms, W.

The isobutylaluminoxane catalyst (IBAO, see figure 4(b)) yielded a higher molecular weight polymer than methylaluminoxane (MAO, see figure 4(a)). The molecular weight distribution of the polymer in a hexane/toluene mixed solvent was broader than that prepared in toluene, and the GPC chromatograms of the former did not show a clear bimodal distribution (see figure 4(c)).

The signs of the specific optical rotations of the polymers obtained from the two monomers were different, as shown in table 2, and the absolute values were also different between polymers I-2 ($-3\cdot3°$) and I-4 ($+5\cdot9°$). This difference is presumably caused by the difference in the specific rotations on two different fractions of the bimodal molecular weight distribution, which is formed in these polymerization reactions. The polymerization of β-butyrolactone with alkylaluminoxane catalysts always yields a bimodal molecular weight distribution, and in the polymerization of
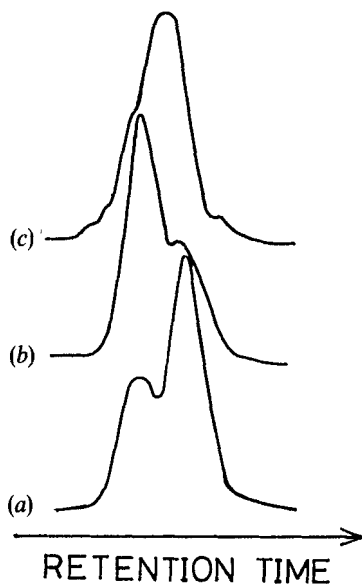

Figure 4. GPC chromatograms of a series of polymers: (a) polymer I-1 prepared with MAO in toluene, (b) polymer I-2 prepared with IBAO catalyst in toluene, (c) polymer I-3 prepared with IBAO catalyst in a mixture of toluene and hexane (1:1 volume ratio).

(*S*)-*β*-butyrolactone we found that the high molecular weight fraction, which was isolated by solvent extraction, exhibited a lower specific rotation than the low molecular weight fraction [9]. This difference is believed to result from the simultaneous occurrence of two different reaction mechanisms in the ring-opening polymerization reaction; namely, both acyl cleavage and alkyl cleavage as we previously described. However, propagation occurs predominantly by acyl cleavage rather than alkyl cleavage with the alkylaluminoxane catalyst [9]. Acyl cleavage results in retention of the configuration, while alkyl cleavage results in either inversion of configuration or racemization. In our system, the same combination of mechanisms probably occurs, but the two different molecular weight fractions of these mesogenic polymers could not be fractionated by extraction with acetone.

Earlier studies carried out by Guerin and co-workers on poly(benzyl malolactonate) showed that high resolution ^{13}C NMR could be used for studying the microstructure of the polymers [10]. The ^{13}C NMR spectra for polymer I-2, which was obtained by a distortionless enhancement by the polarization transfer (DEPT) technique, are shown in figure 5. All peaks in the spectra could be assigned, as shown in figure 5, by DEPT spectra and C–H COSY techniques. The peak intensities assigned to
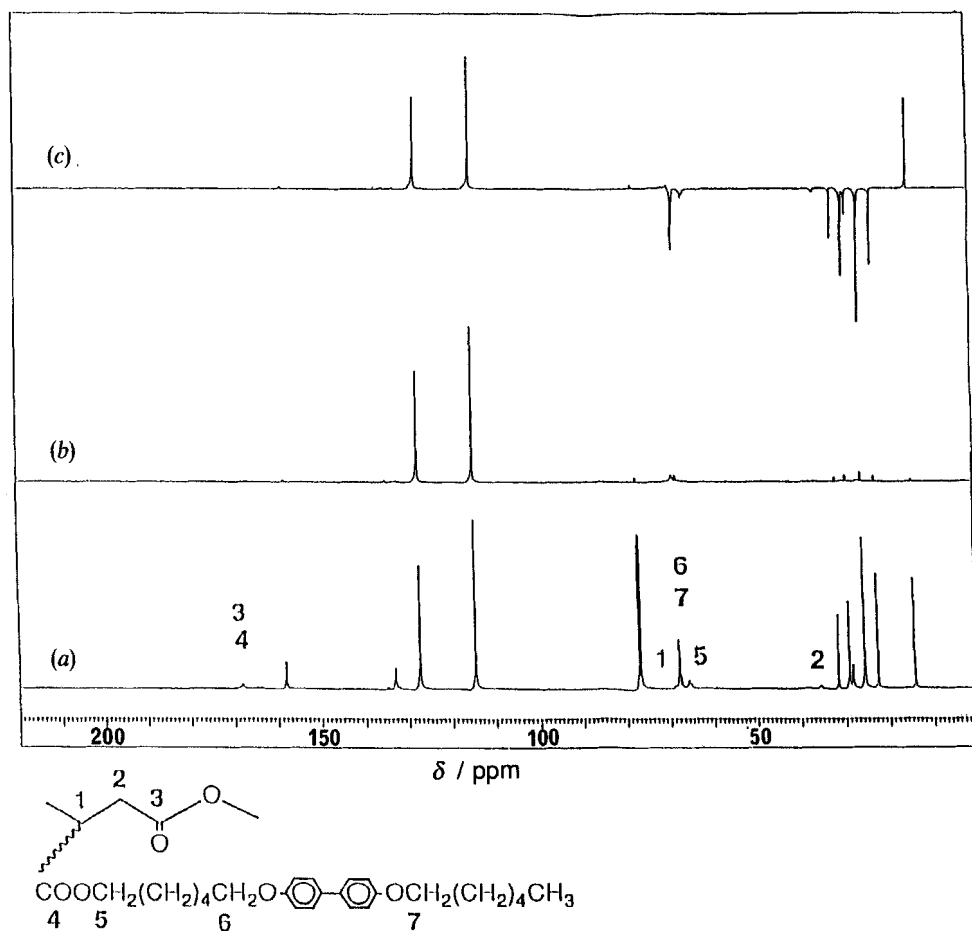

Figure 5. ^{13}C NMR spectra of polymer I-2 (solvent; CDCl$_3$). (*a*) $\theta = 45°$, (*b*) $\theta = 90°$, (*c*) $\theta = 135°$.
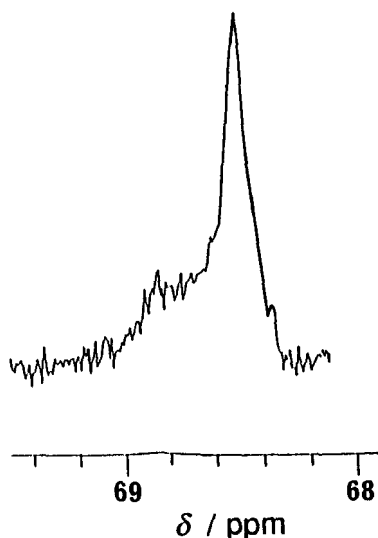
Figure 6. ^{13}C NMR spectra at $\theta = 90°$ of methine carbon in the backbone of polymer I-2.

the main chain carbons were low relative to the others. Furthermore, the peak for the methine carbon at 68·5 ppm, which is expected to show the effects of the triad configurational sequence in the main chain, was very close to that of the methylene carbons next to the biphenol moiety, so the DEPT spectra in figure 5 (*b*) ($\theta = 90°$) which contained only methine carbon peaks could be used to determine polymer tacticity. The expanded region of the methine carbon signal is shown in figure 6. The relative weight of the higher field peak, which was assigned to the isotactic signal by Guerin and co-workers, was dominant indicating that this polymer had a high degree of isotactic stereoregularity.

The second heating DSC thermograms of polymers with different molecular weight distributions are shown in figure 7. For polymers I-1 and I-3 several endotherms were detected in the second heating scans, while for polymer I-2 a small endotherm at 98°C and a broad endotherm around 157°C were observed. Schlieren textures were observed for all polymers placed on a hot stage of a polarized light microscope, and no changes were observed for the textures of polymers I-1 and I-3 in the temperature range between the first and the last endotherm.

The polymer obtained from the (*S*)-lactone, polymer I-4, was also examined by ^{13}C NMR (DEPT) and DSC. The ^{13}C spectrum of polymer I-4 contained the same relative weight of the higher field peak, which was again dominant in the methine carbon signal as did polymer I-2, but any differences between the two polymers was obscure because of both relatively broad methine signals. In the DSC second heating scan of polymer I-4, the phase transition behaviour was the same as that for polymer I-2, but the isotropization transition of polymer I-4 appeared at higher temperature, by 11°C, than that for I-2. Both the higher transition temperature [10] and the higher absolute value of specific optical rotation, as seen in table 2, indicate that polymer I-4 had a higher stereoregularity than polymer I-2.

The data for the copolymers of II-(*S*)-6 and II-(*S*)-2 are given in table 3. The molar ratios of the monomers in the copolymers were estimated by ^{1}H NMR spectroscopy based on the integrated values of the methylene protons in the alkyl spacers of II-(*S*)-6
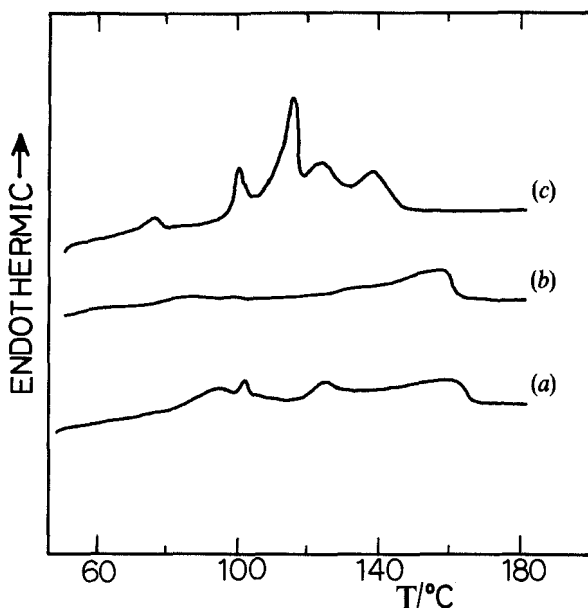
Figure 7.   DSC thermograms of a series of polymer I. (*a*) Polymer I-1, (*b*) polymer I-2, (*c*) polymer I-3.

Table 3.   Yields and characterization of copolymers.

Composition (*a*)			Molecular weights (*b*)		
x	*y*	Yields/%	$\bar{M}_{\mathrm{n}}$	$\bar{M}_{\mathrm{w}}$	$\bar{M}_{\mathrm{w}}/\bar{M}_{\mathrm{n}}$
75	25	29	(*W*) 4100	17000	4·1
			(*H*) 16000	24000	1·5
25	75	20	(*W*) 2800	20000	7·3
			(*H*) 13000	25000	1·9

(*a*) Determined from the ^{1}H NMR spectra of the copolymer; *x* is the content of II-(*R*)-6, *y* is the content of II-(*R*)-2 in the copolymer.

(*b*) Molecular weights were determined by GPC based on polystyrene standards; *W* is the value calculated for the entire GPC chromatogram; *H* is the value calculated for the higher molecular weight peak only.

and II-(*S*)-2 at 4·12 ppm and 4·45 ppm, respectively. These copolymers also showed the bimodal molecular weight distributions on analysis by GPC and contained dominantly a higher molecular weight polymer. The second heating DSC thermograms for both copolymers contained only two endotherms corresponding to the melting and isotropization transitions. Both copolymers also exhibited schlieren textures in the temperature range between the melting transition and the isotropization transition.

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