Macromolecules 1993, 26, 5494-5502

Synthesis and Liquid Crystallinity of Stereoregular Polymethacrylates with Mesogenic Ester Groups

Tamaki Nakano, Tsuyoshi Hasegawa, and Yoshio Okamoto*

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan

Received March 9, 1993; Revised Manuscript Received June 29, 1993•

ABSTRACT: 2-[4-(4′-Methoxyphenyl)phenoxy]ethyl, 3-[4-(4′-methoxyphenyl)phenoxy]propyl, 4-[4-(4′-methoxyphenyl)phenoxy]butyl, 5-[4-(4′-methoxyphenyl)phenoxy]pentyl, and 6-[4-(4′-methoxyphenyl)-phenoxy]hexyl methacrylates were synthesized and polymerized. Anionic polymerization of these monomers was carried out with *tert*-butylmagnesium bromide in toluene, chloroform, and tetrahydrofuran at low temperature, and radical polymerization was conducted with α,α'-azobis(isobutyronitrile) in toluene at 60 °C. Highly isotactic (mm 90–97%) and syndiotactic (rr 79–86%) polymers were obtained by anionic polymerization in chloroform and tetrahydrofuran, respectively, and polymers rich in syndiotacticity (rr 56–66%) were obtained by radical polymerization. Thermal properties and liquid crystallinities of the polymers depended greatly on both the tacticity of the main chain and the length of the methylene chain (spacer) in the side group. These observations were interpreted in terms of zigzag (*all-trans*) and helical conformations of the main chain of syndio- and isotactic polymers, respectively, and the *all-trans* conformation of the spacer chain.

Introduction

Liquid crystalline polymers have attracted growing interest because of their potentiality as materials for recording and electrooptic devices.[1] For these purposes, various side-chain liquid crystalline polymers with several types of main chains such as poly(meth)acrylate, polysiloxane, and poly(vinyl ether) have been synthesized.[2] As for the polymers with asymmetric centers in the main chain, it is considered important to get information on the relation between the tacticity of the main chain and the liquid crystallinity in order to obtain high-performance liquid crystalline material. However, only a few investigations have been done on this point so far. As the first example of such a study, Ringsdorf and co-workers reported the influence of main-chain tacticity on the liquid crystallinity for poly[6-[4-(4′-methoxyphenyl)phenoxy]-hexyl methacrylate] (poly-1).[3] Differences in thermal properties have also been shown for iso- and syndiotactic poly(*p*-biphenyl acrylate)s.[4] Further, Duran and co-workers have suggested that the smectic phase should be more unfavorable for isotactic side-chain mesogenic polymethacrylates than for syndiotactic ones on the basis of their consideration of the conformational difference of stereoregular polymers.[5] However, the value of the stereoregularity of the polymers in these studies is moderate or low.

Recently, we synthesized highly isotactic (mm >91%) and syndiotactic (rr >84%) poly-1's and poly[6-[4-[4′-[(*S*)-2-methylbutoxy]phenyl]phenoxy]hexyl methacrylate]s (poly-2's) by anionic polymerization and reported preliminary results on the relationship between the tacticities and liquid crystallinities of the obtained polymers; as for poly-1, only the syndiotactic polymer showed liquid crystallinity, while, as for poly-2, only the isotactic one showed liquid crystallinity.[6] In the present paper, we report on the stereoregular polymerization and thermal properties of the resulting polymers of 2-[4-(4′-methoxyphenyl)phenoxy]ethyl methacrylate (3), 3-[4-(4′-methoxyphenyl)phenoxy]propyl methacrylate (4), 4-[4-(4′-methoxyphenyl)phenoxy]butyl methacrylate (5), 5-[4-(4′-methoxyphenyl)phenoxy]pentyl methacrylate (6), and 1. The monomers were polymerized anionically with *tert*-butylmagnesium bromide (*t*-BuMgBr) and radically with α,α'-azobis(isobutyronitrile) (AIBN); the anionic polymerization gave highly stereoregular polymers. Thermal properties of the polymers were investigated with differential scanning calorimetry (DSC); polarizing optical microscopic observation of some of the polymers gave information on their liquid crystalline phase.[7] On the basis of the observations, the influence of both the stereoregularity of the main chain and the length of the methylene chain (spacer) in the side group on the thermal properties and liquid crystallinities of the polymers will be discussed.

Experimental Section

Materials. Toluene was purified in the usual manner and dried with a small amount of *n*-BuLi. Tetrahydrofuran (THF) was dried over a Na wire and distilled onto $LiAlH_4$. Chloroform was dried over CaH_2 and distilled onto CaH_2. Diethyl ether was dried over a Na wire and distilled onto CaH_2. These solvents were distilled under high vacuum just before use.

t-BuMgBr was prepared from Mg powder and *tert*-butyl bromide in diethyl ether ([MgC] = 0.245 M, [Mg] = 0.646 M).[8] AIBN was purified by recrystallization from methanol.

Triethylamine was distilled and dried on KOH under a nitrogen atmosphere. Methacryloyl chloride was synthesized from methacrylic acid and trichlorophosphorus and purified by distillation.

4,4′-Biphenol (TCI), 2-chloro-1-ethanol (Kishida), 3-chloro-1-propanol (Aldrich), 1,4-dibromobutane (Wako), 1,5-dibromopentane (TCI), and 6-chloro-1-hexanol (Nakalai Tesque) were used as commercially obtained.

Monomer Synthesis. The methods of monomer synthesis are shown in Scheme I.

4-Hydroxy-4′-methoxybiphenyl (7; Eq 1 in Scheme I). Dimethyl sulfate (9.09 g, 72.1 mmol) was added dropwise to a water (200 mL) solution of 4,4′-dihydroxybiphenyl (31.3 g, 0.17 mol) and NaOH (15.2 g, 0.38 mol) at room temperature. The resulting precipitate was collected by filtration, neutralized by aqueous HCl, and dried under vacuum. The product was purified by recrystallization from ethanol. Yield: 10.2 g, 71%. Mp: 183.0–184.0 °C (lit.[9,10] mp 182–183 °C).

4-(2-Hydroxyethoxy)-4′-methoxybiphenyl (8; Eq 2). 8 was prepared from 2-chloro-1-ethanol (1.34 g, 16.6 mmol) and 7 (2.65 g, 13.2 mmol) in the presence of KOH (0.82 g, 14.6 mmol) and KI[9] (0.62 g, 3.73 mmol) in a manner similar to the method described in the literature.[11] Yield: 2.00 g, 62%. Mp: 169.4–170.2 °C (lit.[12] mp 170–172 °C). IR (KBr): 3296 cm^{-1} (OH). ^1H

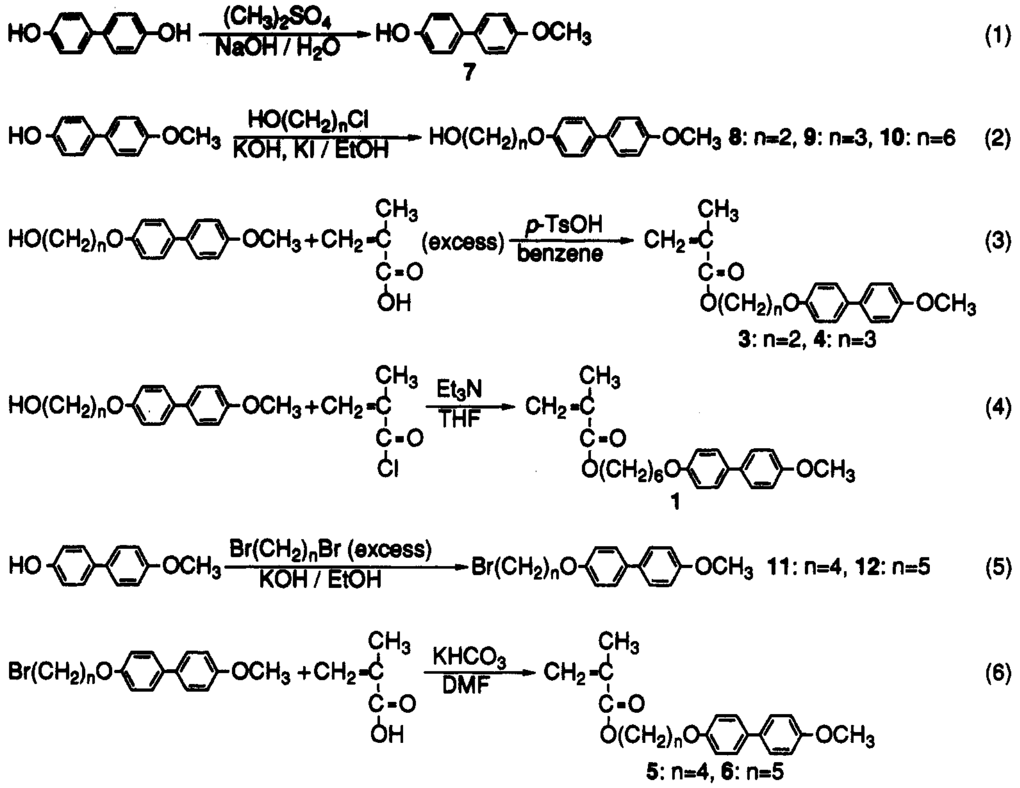
---

* To whom all correspondence should be addressed.

• Abstract published in *Advance ACS Abstracts*, September 1, 1993.

0024-9297/93/2226-5494$04.00/0

Scheme I. Synthesis of Monomers



NMR ($CDCl_3$, 200 MHz): δ 6.9, 7.5 (m, aromatic, 8H), 4.1 (m, $PhOCH_2$, 2H), 4.0 (m, $C\mathit{H}_2OH$, 2H), 3.8 (s, OCH_3, 3H), 2.1 (t, OH, 1H).

4-(3-Hydroxypropoxy)-4′-methoxybiphenyl (9; Eq 2). 9 was prepared by the same method used for the synthesis of 8 from 3-chloro-1-propanol (8.16 g, 86.3 mmol) and 7 (13.1 g, 65.5 mmol). Yield: 12.3 g, 69%. Mp: 170.7–171.3 °C. IR (KBr): 3284 cm^{-1} (OH). ^1H NMR ($CDCl_3$, 200 MHz): δ 6.9, 7.5 (m, aromatic, 8H), 4.2 (t, $PhOCH_2$, 2H), 3.9 (q, $C\mathit{H}_2OH$, 2H), 3.8 (s, OCH_3, 3H), 2.1 (quint, $PhOCH_2C\mathit{H}_2$, 2H), 1.8 (t, OH, 1H).

4-(6-Hydroxyhexoxy)-4′-methoxybiphenyl (10; Eq 2). 10 was prepared from 6-chloro-1-hexanol (1.47 g, 10.8 mmol) and 7 (2.50 g, 12.5 mmol) in the presence of KOH (0.60 g, 10.8 mmol) in a manner similar to the method described in the literature.[11] Yield: 1.18 g, 40%. Mp: 150.8–151.5 °C (lit.[12] mp 134–136 °C). IR (KBr) 3300 cm^{-1} (OH). ^1H NMR ($CDCl_3$, 270 MHz): δ 6.9, 7.5 (m, aromatic, 8H), 4.2 (t, $PhOCH_2$, 2H), 3.8 (s, OCH_3, 3H), 3.6 (t, $C\mathit{H}_2OH$, 2H), 1.8 (quint, $PhOCH_2C\mathit{H}_2$, 2H), 1.4–1.7 (m, $C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2CH_2O\mathit{H}$, 7H).

2-[4-(4′-Methoxyphenyl)phenoxy]ethyl Methacrylate (3; Eq 3). 8 (16.1 g, 68.3 mmol), methacrylic acid (31.6 g, 0.37 mol), *p*-toluenesulfonic acid (*p*-TsOH) (1.54 g, 8.94 mmol), and hydroquinone (0.39 g, 3.54 mmol) were dissolved in benzene (500 mL). After the solution was refluxed with azeotropic removal of water for 12 h,[10] benzene was removed to give white crystals. The product was recrystallized from a mixture of THF and diethyl ether (60/40 (v/v)). Yield: 10.6 g, 50%. Mp: 94.2–95.0 °C. IR (KBr): 1721 (C=O), 1640 cm^{-1} (C=C). ^1H NMR ($CDCl_3$, 200 MHz): δ 6.9, 7.5 (m, aromatic, 8H), 5.6, 6.1 (s, $CH_2=C$, 2H), 4.5, 4.3 (t, OCH_2, 4H), 3.8 (s, OCH_3, 3H), 2.0 (s, CCH_3, 3H). Anal. Calcd for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 72.81; H, 6.46. FD-MS: *m/z* 312 (M$^+$).

3-[4-(4′-Methoxyphenyl)phenoxy]propyl Methacrylate (4; Eq 3]. 4 was prepared from 9 (35.5 g, 0.14 mol) and methacrylic acid (60.0 g, 0.70 mol) by the same method used for the synthesis of 3. Yield: 19.2 g, 43%. Mp: 88.4–89.2 °C. IR (KBr): 1721 (C=O), 1638 cm^{-1} (C=C). ^1H NMR ($CDCl_3$, 200 MHz): δ 6.9, 7.5 (m, aromatic, 8H), 5.6, 6.1 (s, $CH_2=C$, 2H), 4.4, 4.1 (t, OCH_2, 4H), 3.8 (s, OCH_3, 3H), 2.2 (quint, $PhOCH_2C\mathit{H}_2$, 2H), 2.0 (s, OCH_3, 3H). Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.50; H, 6.79. FD-MS: *m/z* 326 (M$^+$).

6-[4-(4′-Methoxyphenyl)phenoxy]hexyl Methacrylate (1; Eq 4). 1 was prepared from 10 (30.0 g, 0.10 mol) and methacryloyl chloride (13.6 g, 0.13 mol) in the presence of triethylamine (13.1 g, 0.13 mol) in a manner similar to the method described in the literature.[12] 1 can be prepared also from 10 and methacrylic acid according to the method by Finkelmann.[11] Yield: 20.4 g, 61%. Mp: 74.5–75.5 °C. IR (KBr): 1720 (C=O), 1640 cm^{-1} (C=C). ^1H NMR ($CDCl_3$, 200 MHz): δ 6.9, 7.5 (m, aromatic, 8H), 4.2, 4.0 (t, OCH_2, H), 3.8 (s, OCH_3, 3H), 2.0 (s, CCH_3, 3H), 1.8, 1.7 (quint, $OCH_2C\mathit{H}_2$, 4H), 1.4–1.6 (m, $PhOCH_2CH_2C\mathit{H}_2C\mathit{H}_2$, 4H). Anal. Calcd for $C_{23}H_{28}O_4$: C, 74.97; H, 7.66. Found: C, 74.71; H, 7.62. FD-MS: *m/z* 368 (M$^+$).

4-(4-Bromobutoxy)-4′-methoxybiphenyl (11; Eq 5). An ethanol (600 mL) solution of 7 (25.8 g, 0.13 mol) and KOH (8.06 g, 0.14 mol) was added dropwise to an ethanol (150 mL) solution of 1,4-dibromobutane (93.6 g, 0.43 mol) and KI (2.21 g, 13.3 mmol). The reaction mixture was refluxed for 12 h. After ethanol was evaporated, the residue was dissolved in chloroform and washed with water. The organic layer was dried on $MgSO_4$, and the solvent was evaporated. To remove unreacted 1,4-dibromobutane, the product was washed with hexane. The hexane-insoluble part was purified by column chromatography (silica gel; Wakogel C-1000; eluent, chloroform). Yield: 21.2 g, 49%. Mp: 127.5–128.4 °C. IR (KBr): 1276 cm^{-1} (CH_2Br). ^1H NMR ($CDCl_3$): δ 6.9, 7.5 (m, aromatic, 8H), 4.0 (t, $PhOCH_2$, 2H), 3.8 (s, OCH_3, 3H), 3.5 (t, CH_2Br, 2H), 1.9–2.2 (m, $PhOCH_2C\mathit{H}_2C\mathit{H}_2$, 4H).

4-(5-Bromopentoxy)-4′-methoxybiphenyl (12; Eq 5). 12 was prepared from 7 (22.2 g, 0.11 mol) and 1,5-dibromopentane (80.8 g, 0.35 mol) by the same method used for the synthesis of 11. Yield: 16.2 g, 42%. Mp: 90.0–91.0 °C. IR (KBr): 1276 cm^{-1} (CH_2Br). ^1H NMR ($CDCl_3$, 200 MHz): δ 6.9, 7.5 (m, aromatic, 8H), 4.0 (t, $PhOCH_2$, 2H), 3.8 (s, OCH_3, 3H), 3.5 (t, CH_2Br, 2H), 1.8–2.0 (m, $PhOCH_2C\mathit{H}_2CH_2C\mathit{H}_2$, 4H), 1.6–1.7 (m, $PhOCH_2$-$CH_2C\mathit{H}_2$, 2H).

4-[4-(4′-Methoxyphenyl)phenoxy]butyl Methacrylate (5; Eq 6). Methacrylic acid (6.57 g, 76.3 mmol) was reacted with $KHCO_3$ (7.30 g, 72.9 mmol) to form potassium methacrylate. This salt was allowed to react with 11 (19.9 g, 59.3 mmol) in the presence of hydroquinone (0.15 g, 1.36 mmol) in *N,N′*-dimethylformamide (600 mL) with stirring at 100 °C for 12 h. After the solvent was removed, the residue was dissolved in chloroform and washed with 5% aqueous NaOH and water. The chloroform solution was dried on $MgSO_4$. Removal of solvent gave a white crystal. The product was purified by recrystallization from a mixture of THF and diethyl ether (60/40 (v/v)). Yield: 14.6 g, 72%. Mp: 82.6–83.3 °C. IR (KBr): 1717 (C=O), 1638 cm^{-1} (C=C). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.9, 7.5 (m, aromatic, 8H), 5.6, 6.1 (s, CH_2=C, 2H), 4.2, 4.0 (t, OCH_2, 4H), 3.8 (s, OCH_3, 3H), 2.0 (s, CCH_3, 3H), 1.9 (m, $PhOCH_2\mathit{CH_2}\mathit{CH_2}$, 4H). Anal. Calcd for $C_{21}H_{24}O_4$: C, 74.09; H, 7.11. Found: C, 74.08; H, 7.12. FD-MS: *m/z* 340 (M$^+$).

5-[4-(4′-Methoxyphenyl)phenoxy]pentyl Methacrylate (6; Eq 6). **6** was prepared from **12** (16.0 g, 45.7 mmol) and methacrylic acid (4.87 g, 56.6 mmol) by the same method used for the synthesis of **5**. Yield: 9.65 g, 60%. Mp: 89.5–90.2 °C. IR (KBr): 1715 (C=O), 1638 cm^{-1} (C=C). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.9, 7.5 (m, aromatic, 8H), 5.6, 6.1 (s, CH_2=C, 2H), 4.2, 4.0 (t, OCH_2, 4H), 3.8 (s, OCH_3, 3H), 2.0 (s, CCH_3, 3H), 1.7–1.9 (m, $PhOCH_2\mathit{CH_2}CH_2\mathit{CH_2}$, 4H), 1.5–1.7 (m, $PhOCH_2CH_2\mathit{CH_2}$, 2H). Anal. Calcd for $C_{22}H_{26}O_4$: C, 74.55; H, 7.39. Found: C, 74.36; H, 7.38. FD-MS: *m/z* 354 (M$^+$).

Anionic Polymerization. Anionic polymerization was carried out in a dry glass ampule under a dry nitrogen atmosphere. Monomer (0.5 g) was placed in a dry glass ampule, which was then evacuated with a vacuum line and flushed with dry nitrogen. After this procedure, a three-way stopcock was attached to the ampule and a solvent was added with a hypodermic syringe to dissolve the monomer. The monomer solution was then cooled to the prescribed temperature, and a prescribed amount of *t*-BuMgBr in diethyl ether was added to the monomer solution with a syringe. The polymerization was terminated by the addition of a small amount of methanol. After termination, the solution was poured into a large amount of methanol. The precipitates were collected with a centrifuge and dried under vacuum.

Radical Polymerization. Radical polymerization was done under a nitrogen atmosphere. To a toluene solution of monomer (0.5 g) in a dry glass ampule equipped with a three-way stopcock was added with a syringe at room temperature a toluene solution of AIBN (0.2 M). The solution was heated to 60 °C to initiate the reaction. The reaction was terminated by cooling the reaction mixture to −30 °C. The polymerization product was treated by the same method used for anionic polymerization.

Measurement. ^{1}H NMR spectra were measured in $CDCl_3$ on Varian VXR-500 (500 MHz), Gemini 200 (200 MHz), and JEOL GSX-270 (270 MHz) spectrometers. IR spectra were recorded with a Jasco FT/IR-7000 spectrophotometer. Gel permeation chromatography (GPC) was performed by a Tosoh HLC 802A chromatograph equipped with TSK-G3000H and G5000H GPC columns connected in series by using chloroform as an eluent. A calibration curve was obtained with standard polystyrenes. DSC measurements were carried out with a Seiko DSC100 apparatus at a heating rate of 5 °C/min and at a cooling rate of 2 °C/min. Field desorption mass (FD-MS) spectra were taken on JEOL DX-HF303 and JMS-AX505HA spectrometers. Microscopic investigation was performed by a Nikon OPTIPHOT-POL polarized optical microscope equipped with a Mettler FP90 central processor and a FP82HT hot stage. The melting point was determined with samples placed in a glass capillary tube by using a Büchi apparatus at a heating rate of 1 °C/min.

Results and Discussion

Thermal Properties and Liquid Crystallinities of Monomers. In the DSC measurements of monomers, **3**, **4**, and **6** showed only one endothermic peak at 96, 90, and 91 °C, respectively. In contrast, **1** showed two endothermic peaks at 59 and 70 °C[11-13] and **5** at 80 and 84 °C, suggesting that **1** and **5** each have a mesophase at these temperature ranges. In the polarizing microscopic investigation, **1** and **5** exhibited a mosaic texture which appears to be attributed to a smectic phase (Figure 1). The property of monomer **1** in the present study was similar to that previously reported.[11]

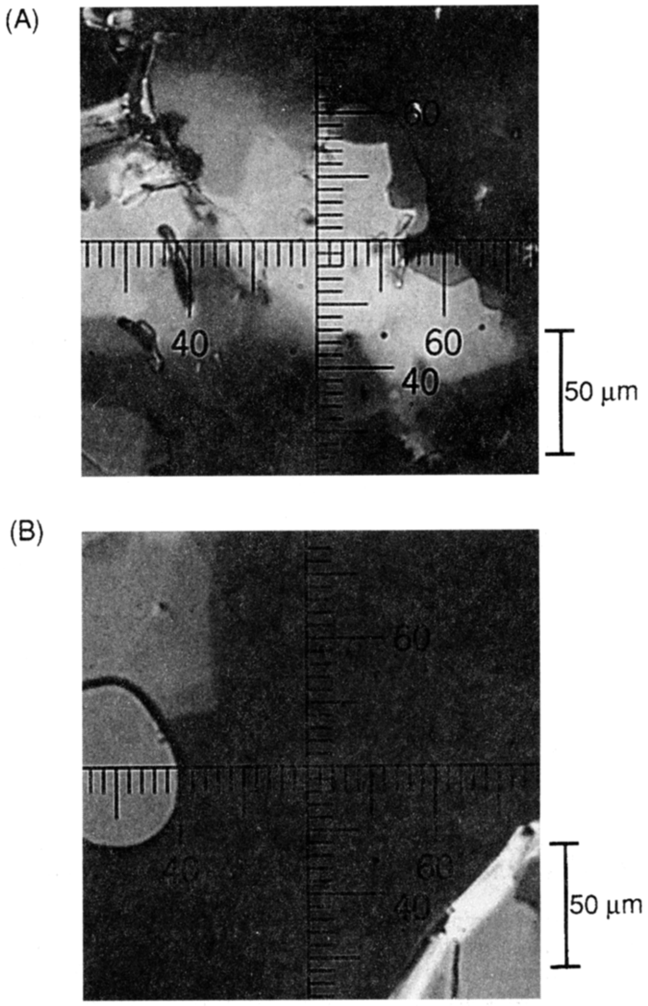


Figure 1. Polarized optical micrographs of **1** (A) and **5** (B): (A) annealing at 69.5 °C for 5 min; (B) annealing at 81.6 °C for 7 h.

Polymerization. The results of polymerization are summarized in Tables I–V. Anionic polymerizations in toluene and chloroform were isotactic specific, and that in THF was syndiotactic specific. The polymers obtained by anionic polymerization are considered to have the same chemical structure with a *tert*-butyl group at the α-end and a hydrogen at the ω-end (Scheme II). The length of the spacer appeared to have little influence, if any, on the polymerization chemistry in the present study, although a significant effect of the spacer length has been reported on radical polymerization stereochemistry for the methacrylates with methoxybiphenyl as the mesogen and oxyethylene units as the spacer.[10]

The polymerization of methyl methacrylate (MMA) with *t*-BuMgBr in toluene at −78 °C is known to afford a highly isotactic polymer (triad isotacticity (mm) ~97%).[8,14] Since, in the present study, polymerization in toluene could not be accomplished at −78 °C because of the low solubility of the monomer, it was conducted at 0 °C (run 1 in Tables I, II, and V and runs 1 and 2 in Tables III and IV). However, the polymerization in toluene at 0 °C still presented the problem that the product precipitated in the course of reaction. This resulted in rather low yields and low molecular weights of the products. Furthermore, the values of isotacticity of the obtained polymers were much lower than that reported for poly(MMA) prepared with the same initiator and solvent.[8,14]

In order to improve the solubility problem, we used chloroform as a polymerization solvent (runs 2 and 3 in Tables I and II, runs 3 and 4 in Tables III and IV, and run 2 in Table V).[6,15] Both the monomers and polymerization products showed better solubility in chloroform than in toluene, and the reaction was possible at −30 °C for **3** and **4**, at −20 °C for **5** and **6**, and at −60 °C for **1**. At these

Table I. Polymerization of 3 for 24 h[a]

								DP[c]		tacticity (%)		
run	initiator	[monomer]/[initiator]	solvent	temp (°C)	yield (%)	$\bar{M}_n{}^b \times 10^{-3}$	$\bar{M}_w/\bar{M}_n{}^b$	GPC	NMR	mm	mr	rr
1	*t*-BuMgBr	20	toluene	0	25	4.6	2.09	15	24	81	17	2
2	*t*-BuMgBr	20	$CHCl_3$	−30	63	11.7	2.35	37	46	94	6	0
3	*t*-BuMgBr	10	$CHCl_3$	−30	87	6.2	1.79	20	19	90	8	2
4	*t*-BuMgBr	20	THF	−78	55	7.3	1.43	23	28	2	19	79
5	*t*-BuMgBr	10	THF	−78	78	6.4	1.23	20	17	1	20	79
6	AIBN	20	toluene	60	86	13.4	2.36			8	33	59
7	AIBN	50	toluene	60	80	22.4	2.08			5	33	62

[a] Conditions: monomer, 0.5 g; solvent, 10 mL (runs 1, 2, 6, and 7), 15 mL (runs 3–5). [b] Determined by GPC. [c] Degree of polymerization calculated from M_n estimated by GPC and that directly determined by ^{1}H NMR spectra.

Table II. Polymerization of 4 for 24 h[a]

								DP[b]		tacticity (%)		
run	initiator	[monomer]/[initiator]	solvent	temp (°C)	yield (%)	$\bar{M}_n{}^b \times 10^{-3}$	$\bar{M}_w/\bar{M}_n{}^b$	GPC	NMR	mm	mr	rr
1	*t*-BuMgBr	20	toluene	0	11	2.4	1.11	7	6	78	19	3
2	*t*-BuMgBr	20	$CHCl_3$	−30	57	22.2	2.80	68	129	97	3	0
3	*t*-BuMgBr	10	$CHCl_3$	−30	85	12.8	1.54	39	42	90	7	3
4	*t*-BuMgBr	20	THF	−78	46	10.8	2.08	33	43	5	12	83
5	*t*-BuMgBr	10	THF	−78	24	6.8	2.27	21	16	5	14	81
6	AIBN	20	toluene	60	84	13.2	1.82			8	35	57
7	AIBN	50	toluene	60	78	20.0	1.83			6	38	56

[a] Conditions: monomer, 0.5 g; solvent, 10 mL (runs 1, 2, 6, and 7), 15 mL (runs 3–5). [b] See Table I.

Table III. Polymerization of 5 for 25 h[a]

								DP[b]		tacticity (%)		
run	initiator	[monomer]/[initiator]	solvent	temp (°C)	yield (%)	$\bar{M}_n{}^b \times 10^{-3}$	$\bar{M}_w/\bar{M}_n{}^b$	GPC	NMR	mm	mr	rr
1	*t*-BuMgBr	20	toluene	0	35	3.9	1.72	11	14	79	16	5
2	*t*-BuMgBr	10	toluene	0	65	3.5	1.54	10	10	77	21	2
3	*t*-BuMgBr	20	$CHCl_3$	−20	89	8.1	3.22	24	39	95	4	1
4	*t*-BuMgBr	10	$CHCl_3$	−20	94	6.1	1.86	18	15	93	6	1
5	*t*-BuMgBr	20	THF	−78	80	8.7	1.23	26	21	2	12	86
6	*t*-BuMgBr	10	THF	−78	95	4.8	1.45	14	11	5	15	80
7	AIBN	20	toluene	60	87	10.2	2.21			8	34	58
8	AIBN	50	toluene	60	82	22.2	1.98			6	38	56

[a] Conditions: monomer, 0.5 g; solvent, 15 mL (runs 1, 2, 5, and 6), 20 mL (runs 3 and 4), 10 mL (runs 7 and 8). [b] See Table I.

Table IV. Polymerization of 6 for 24 h[a]

								DP[b]		tacticity (%)		
run	initiator	[monomer]/[initiator]	solvent	temp (°C)	yield (%)	$\bar{M}_n{}^b \times 10^{-3}$	$\bar{M}_w/\bar{M}_n{}^b$	GPC	NMR	mm	mr	rr
1	*t*-BuMgBr	20	toluene	0	33	4.8	2.67	14	10	77	19	4
2	*t*-BuMgBr	10	toluene	0	70	4.1	1.88	12	9	77	20	3
3	*t*-BuMgBr	20	$CHCl_3$	−20	78	12.7	14.02	36	59	96	3	1
4	*t*-BuMgBr	10	$CHCl_3$	−20	90	4.7	3.06	13	12	91	8	1
5	*t*-BuMgBr	20	THF	−60	34	6.7	1.57	19	24	2	18	80
6	*t*-BuMgBr	10	THF	−60	68	6.2	1.46	17	21	3	18	79
7	AIBN	20	toluene	60	79	13.9	1.59			14	28	58
8	AIBN	50	toluene	60	74	15.6	2.17			9	31	60

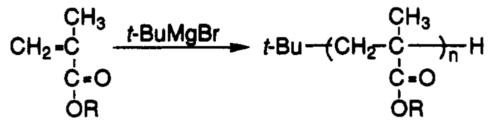
[a] Conditions: monomer, 0.5 g; solvent, 2.0 mL (runs 1–4), 15 mL (runs 5–8). [b] See Table I.

Table V. Polymerization of 1 for 24 h[a]

								DP[b]		tacticity (%)		
run	initiator	[monomer]/[initiator]	solvent	temp (°C)	yield (%)	$\bar{M}_n{}^b \times 10^{-3}$	$\bar{M}_w/\bar{M}_n{}^b$	GPC	NMR	mm	mr	rr
1	*t*-BuMgBr	20	toluene	0	31	1.9	4.25	5	8	73	21	6
2	*t*-BuMgBr	20	$CHCl_3$	−60	78	7.3	2.21	20	27	90	9	1
3	*t*-BuMgBr	20	THF	−78	44	10.4	1.41	28	24	1	14	85
4	AIBN	20	toluene	60	81	12.6	2.26			2	32	66

[a] Conditions: monomer, 0.5 g; solvent, 10 mL (runs 1, 2, and 4), 15 mL (run 3). Most data are taken from ref 6. [b] See Table I.

Scheme II. Polymerization of Methacrylates with *t*-BuMgBr



temperatures, the reaction systems were homogeneous throughout the polymerization. The polymerization in chloroform afforded highly isotactic polymers with higher molecular weights in higher yields in comparison with the polymerization in toluene. It is noteworthy that the isotacticity is higher at the [monomer]/[initiator] ratio of 20 than at that of 10 for the polymerization of monomers **3**–**6**. This may be due to ligation (complexation) of the monomer to Mg cation existing at the growing end. At higher [monomer]/[initiator] ratios, larger amounts of growing species ligated by a monomer may exist in the

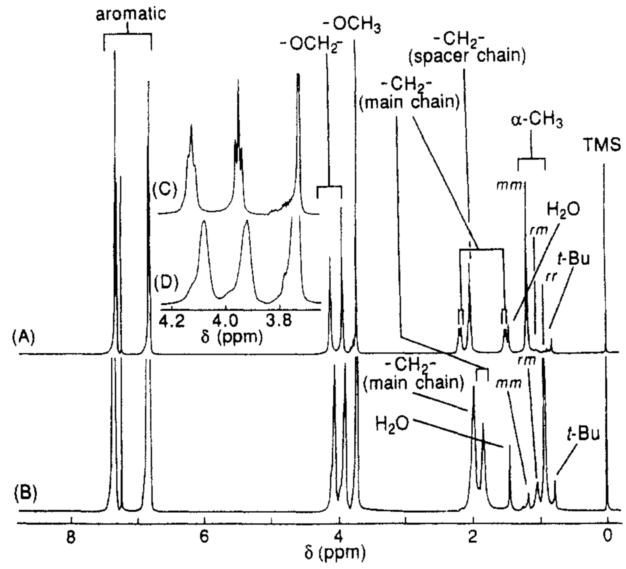


Figure 2. ^{1}H NMR spectra of iso- (A and C) and syndiotactic (B and D) poly-4's (runs 2 and 4 in Table II) (500 MHz, $CDCl_3$, 60 °C).

reaction system, and such species may give polymers with higher isotacticity.

Anionic polymerization in THF afforded highly syndiotactic polymers (runs 4 and 5 in Tables I and II, runs 5 and 6 in Tables III and IV, and run 3 in Table V).[16] The value of the syndiotacticity was rather lower than that of poly(MMA) obtained in THF with the same initiator system.[17] Radical polymerization gave polymers rich in syndiotacticity similarly to the polymerization of a number of methacrylates (runs 6 and 7 in Tables I and II, runs 7 and 8 in Tables III and IV, and run 4 in Table V).[18]

The tacticity of the polymers was determined by ^{1}H NMR spectroscopic analysis. As an example, the spectra of the poly-4's with different values of tacticity are shown in Figure 2. For the isotactic polymer (Figure 2A), the main-chain methylene signals showed AB quartet splitting similarly to isotactic poly(MMA).[14b] The α-methyl signal split into three peaks which were assigned to mm, mr, and rr triad stereosequences as shown in the figure, and no signal based on the side chain overlapped on the peaks. Spectral differences depending on tacticity were also seen for side-chain signals. It was most remarkable for oxymethylene signals as shown in the expanded spectra, although one of the oxymethylene groups is much more remote from the main chain than is the α-methyl group (Figure 2C,D).[19] This contrasts with the fact that the side-chain methoxy signal of poly(MMA) is less sensitive to the difference in tacticity of main chain.[20] Furthermore, the spectral pattern of the side-chain protons varied depending on the temperature of measurement.[19] These observations suggest that the side chains may be forced to be in a position sensitive to main-chain tacticity in solution owing to steric interaction of the side chains or the π–π interaction of the neighboring mesogenic groups. This may be related to the conformational stiffness of the polymer chain reported for liquid crystalline polymethacrylates similar to those in the present study.[21]

In the spectra of the polymers prepared with *t*-BuMgBr (Figure 2A,B), the signal due to the *tert*-butyl group attached to the α-end was observed separately from other peaks. The degree of polymerization (DP) of the polymers was directly determined by comparing the area of the *tert*-butyl signal with that of the main-chain α-methyl signal. The DPs determined by ^{1}H NMR analysis did not necessarily agree with those by GPC analysis. The discrepancy between the molecular weight estimated by GPC and that by more direct methods has already been pointed out for a series of side-chain mesogenic polymethacrylates.[21]

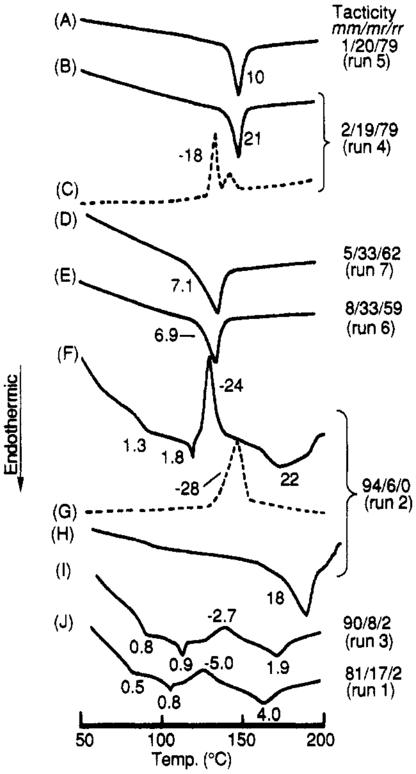


Figure 3. DSC thermograms of syndio- (A–E) and isotactic (F–J) poly-3's. Solid traces A, B, D–F, I, and J correspond to those on the second heating scan (5 °C/min), solid trace H corresponds to that on the third heating scan (5 °C/min), and dotted traces correspond to those on the second cooling scan (2 °C/min). The transition enthalpy values (J/g) for the peaks and tacticities of the samples are printed in the figure. Run numbers in parentheses correspond to those in Table I.

Thermal Properties and Liquid Crystallinities of the Polymers. The obtained polymers showed remarkably different DSC patterns depending on their tacticity. The difference in the DSC patterns is not considered to be based on varying molecular weight in most cases as clarified for poly-1 with a number-average molecular weight (M_n) of 5700–48 900.[6] The details will be described later. The DSC traces shown in the figures are those of the second heating scan and the second cooling scan. The trace patterns of the third heating scan were almost the same as those of the second heating scan except for an isotactic poly-3.

On the second heating scan, the syndiotactic poly-3's showed only one endothermic peak, while the isotactic polymers showed a complex pattern with three endothermic peaks and one exothermic peak (Figure 3A,B,D–F,I,J). The temperature for the endothermic transition on the heating scan for the iso- and syndiotactic polymers appears to decrease with a decrease in the value of the tacticity. The thermal property of poly-3 prepared via radical polymerization in dioxane has already been reported by Rodriguez-Parada and Percec; the polymer showed one broad and one sharp endothermic peak at 112 and 150 °C, respectively.[12] The discrepancy between the present results and their results may be due to a slight difference in the tacticity of the polymers. On the second cooling scan, the syndiotactic poly-3 with a triad syndiotacticity (rr) of 79% showed two exothermic peaks (Figure 3C) although this polymer showed only one endothermic

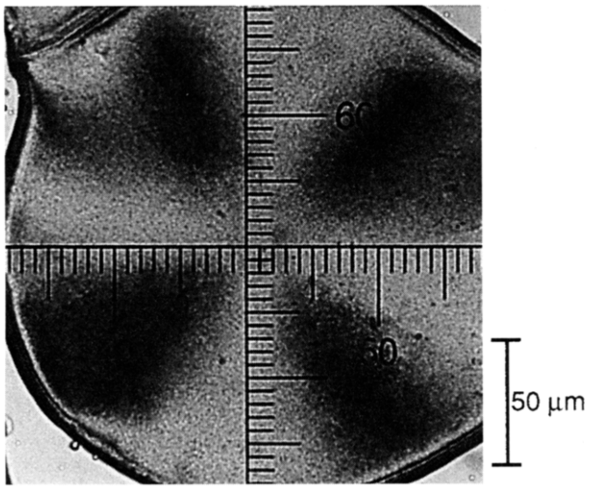


Figure 4. Optical polarization micrograph of isotactic poly-**3** (run 2 in Table I) after being annealed at 149.6 °C for 1 day.

peak on the second heating scan (Figure 3B) and also on the second and third heating scans at a lower rate of heating (2 °C/min). This suggests a monotropic phase transition of this polymer. The thermal property of the isotactic poly-**3** with mm of 94% was characteristic (Figure 3F–H); this polymer showed only one broad exothermic peak on the second cooling scan (Figure 3G) and one broad endothermic peak on the third heating scan (Figure 3H) after being annealed at 210 °C for 1 h and being cooled to room temperature at the rate of ca. 0.5 °C/min. The exothermic peaks on the second heating and cooling scans may be due to crystallization of the polymer. This polymer showed an optical texture in polarizing microscopic observation by annealing at 149.6 °C in the course of heating (10 °C/min); however, the texture was not clear enough to be identified (Figure 4).

Poly-**4**'s showed no clear dependence of the DSC pattern on the main-chain tacticity on both heating and cooling scans (Figure 5); however, the transition temperature was higher for syndiotactic polymers. This is consistent with the fact that most isotactic polymethacrylates possess higher chain flexibility than syndiotactic ones.[22] The much lower transition temperature for the polymer with mm of 78% than those for others may be due to its low molecular weight, which corresponds to DP = 7. Although one of the syndiotactic poly-**4**'s showed a shoulder peak accompanying the main peak on the heating scan (Figure 5B), no clear optical texture was observed for this polymer.

The iso- and syndiotactic poly-**5**'s showed different patterns of DSC thermograms (Figure 6). On the heating scan, the syndiotactic polymers showed two endothermic peaks, while the isotactic polymers showed only one endothermic peak. The poly-**5** with rr of 86% showed two exothermic peaks on the second cooling scan, suggesting that this polymer may undergo an enantiotropic phase transition. The transition temperatures of syndio- and isotactic polymers did not show a clear dependence on the change in tacticity. No clear optical texture was observed for the syndiotactic poly-**5** with the highest syndiotacticity in polarizing microscopic analysis.

A remarkable dependence of thermal properties on the polymers' tacticity was observed for poly-**6** (Figure 7). The syndiotactic polymer showed two endothermic peaks on both the heating and the cooling scans. With a decrease in the value of the syndiotacticity, one of the peaks of the higher temperature became clearer and the temperature for the peak increased, while the other peak remained at almost the same position. On the heating scan for the isotactic polymers, the polymer with mm of 96% showed only one endothermic peak (Figure 7G) and the other polymer showed two endothermic peaks (Figure 7H,J,K). For the latter polymers, the peak of lower temperature became clearer as the value of the isotacticity decreased. The transition temperatures for the isotactic polymers appeared to decrease with a decrease in the value of the isotacticity. Comparing the DSC traces of the heating and cooling scans for the two syndiotactic and an isotactic polymer (Figure 7A with B, E with F, and H with I), the poly-**6**'s seem to undergo an enantiotropic phase transition. The syndiotactic poly-**6** of rr 80% (Figure 7A) exhibited a batnet texture at 164.7 °C and a fan-shaped texture at 162.9 °C, which may be due to a smectic phase, by annealing at these temperatures in the course of slow cooling (0.2 °C/min) (Figure 8).

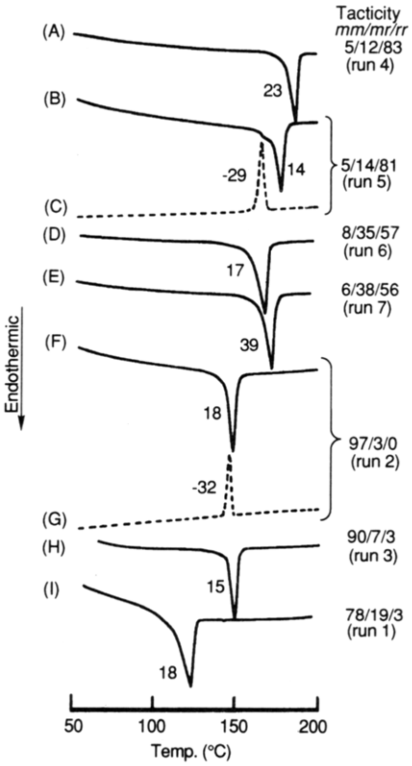


Figure 5. DSC thermograms of syndio- (A–E) and isotactic (F–I) poly-**4**'s. Solid traces correspond to those on the second heating scan (5 °C/min) and dotted traces those to on the second cooling scan (2 °C/min). The transition enthalpy values (J/g) for the peaks and tacticities of the samples are printed in the figure. Run numbers in parentheses correspond to those in Table II.

The poly-**1** also showed marked dependence of the DSC pattern on their tacticity (Figure 9). The syndiotactic polymer showed complex DSC patterns, while the isotactic polymer showed only one endothermic peak. The isotactic poly-**1** showed one exothermic peak (126.3 °C) also on the second cooling scan. The higher transition temperature for the isotactic polymer is in contrast to the higher flexibility of most isotactic polymethacrylates in comparison with syndiotactic ones.[22] The thermal properties of the iso- and syndiotactic poly-**1**'s have been reported by other researchers, and the results differed somewhat from ours. Ringsdorf and co-workers[3] reported that the syndiotactic poly-**1** (rr 63%) showed a DSC pattern that was more similar to poly-**1** with rr of 85% rather than to poly-**1** with rr of 66% prepared in the present study, and isotactic poly-**1** (mm 65%) showed two endothermic peaks. Moreover, Rodriguez-Parada and Percec have prepared poly-**1** by radical polymerization in dioxane and observed two transition temperatures for the polymer.[12] These

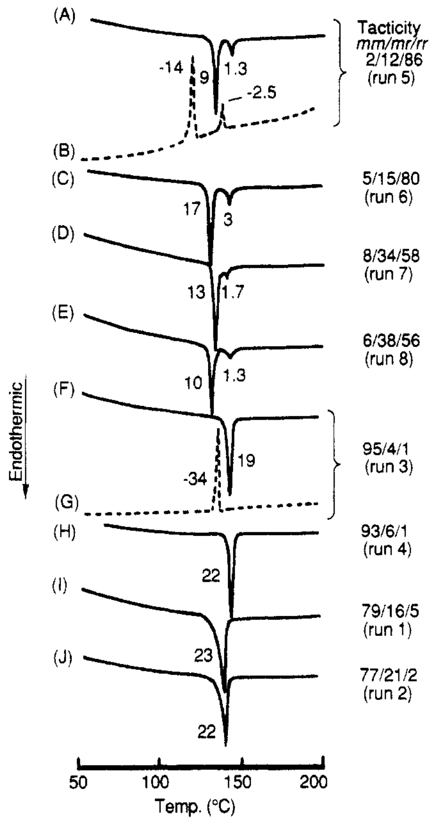


Figure 6. DSC thermograms of syndio- (A–E) and isotactic (F–J) poly-**5**'s. Solid traces correspond to those on the second heating scan (5 °C/min) and dotted traces to those on the second cooling scan (2 °C/min). The transition enthalpy values (J/g) for the peaks and tacticities of the samples are printed in the figure. Run numbers in parentheses correspond to those in Table III.

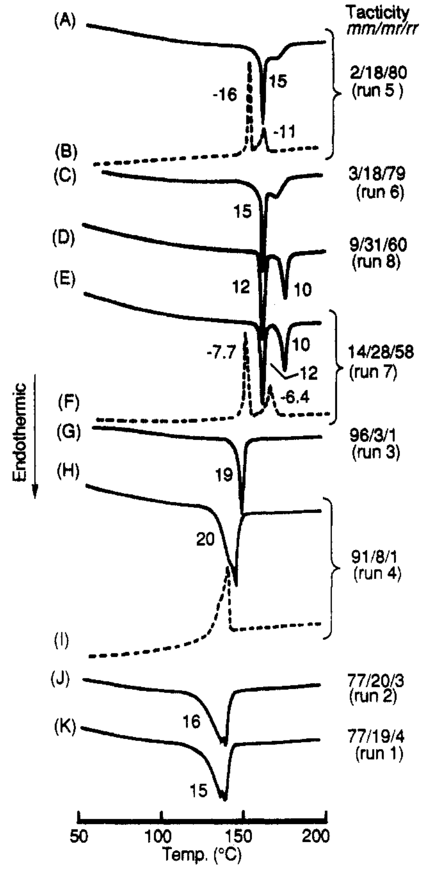


Figure 7. DSC thermograms of syndio- (A–F) and isotactic (G–K) poly-**6**'s. Solid traces correspond to those on the second heating scan (5 °C/min) and dotted traces to those on the second cooling scan (2 °C/min). The transition enthalpy values (J/g) for the peaks and tacticities of the samples are printed in the figure. Run numbers in parentheses correspond to those in Table IV.

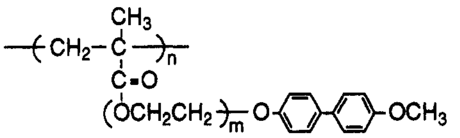
discrepancies suggest that slight differences in tacticity can affect the thermal property of the polymer. In polarizing microscopic analysis of poly-**1**'s, the polymer with rr of 85% showed an optical texture which seemed to be a schlieren texture by annealing at 134.5 °C in the course of slow cooling (0.2 °C/min) (Figure 10),[23] while the isotactic polymer (Figure 9C) did not show any clear texture.[24]

In order to get information on the influence of molecular weight and its distribution on thermal properties, the isotactic poly-**1** was separated by GPC into four fractions with narrow molecular weight distribution, and their thermal properties were investigated (Table VI). The obtained polymers, having different M_n's, showed only one endothermic peak (clearing point) on DSC analysis similarly to the original polymer, although the transition temperatures were slightly lower than that of the original polymer. These results suggest that the thermal property of the isotactic polymer is not greatly affected by molecular weight and its distribution within the range shown in the table.

Figure 11 shows the plot of clearing temperature (T_i) against the number of methylene groups in the spacer chain (n). An obvious odd–even effect is seen for the clearing temperature for highly syndiotactic polymers and the polymers rich in syndiotacticity in the range of n = 2–6, whereas the effect was not as remarkable for isotactic polymers as for the others.

Structural Model of the Polymers. The thermal properties and liquid crystallinities of a series of the polymethacrylates synthesized in the present study were greatly affected by the tacticity of the main chain and the length of the spacer chain as described above. We give some consideration to the relation between the properties and the stereostructure of the polymers.

Duran, Skoulios, and co-workers have proposed a ribbon-like structure with *all-trans* planar zigzag conformation of the main chain (Figure 12) in a solid state for a series of polymethacrylates with a general structure, poly-**13**'s,



$$-\!\left(CH_2-\overset{CH_3}{\underset{\underset{(OCH_2CH_2)_m-O-C_6H_4-C_6H_4-OCH_3}{C=O}}{C}}\right)_n-$$

poly-**13s** (m=0-4)

which are rich in syndiotacticity prepared by radical polymerization on the basis of X-ray diffraction data.[5,25] Their model is consistent with the results of theoretical and experimental studies on the conformation of syndiotactic poly(MMA),[26,27] and it explained liquid crystallinity (smectic phase) of the poly-**13**'s. This model seems reasonably applicable to the syndiotactic polymers prepared in the present study because the chemical structure of the polymers is similar to that of poly-**13s**. On the other hand, most isotactic polymers, including poly(MMA), are known to take a helical conformation in the solid state.[28,29] This conformation may be applicable also for the isotactic polymers in the present study.

The remarkable tacticity dependence of the thermal property as presented in this paper may be based on the conformational difference postulated above. The conformational difference of the main chain should cause a

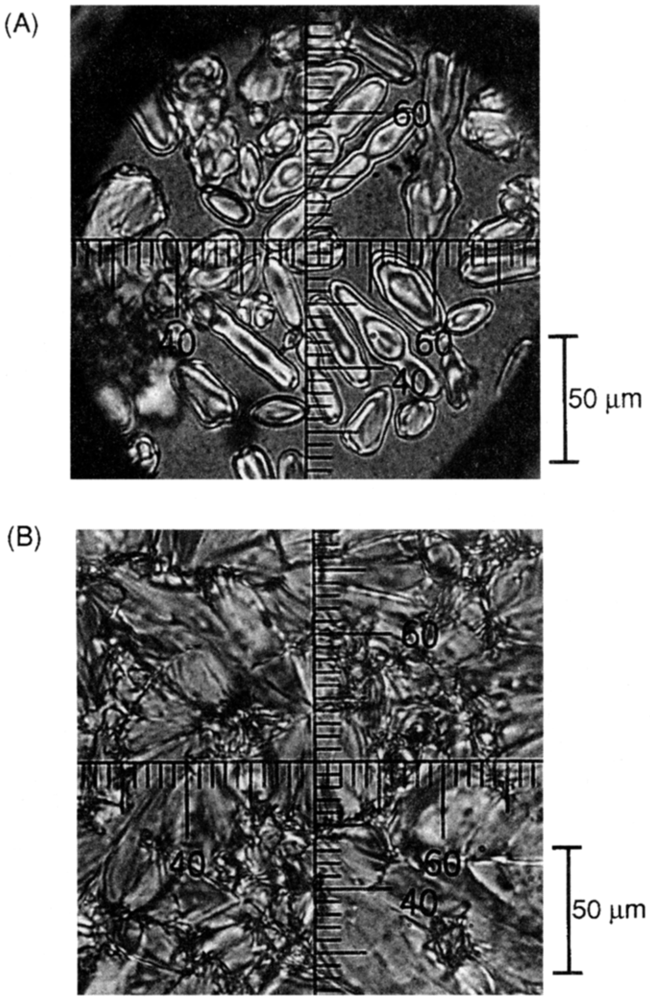


Figure 8. Optical polarization micrographs of syndiotactic poly-**6** (run 2 in Table IV) after bein annealed at 164.7 °C for 2 h (A) and at 162.9 °C for 1 day (B).

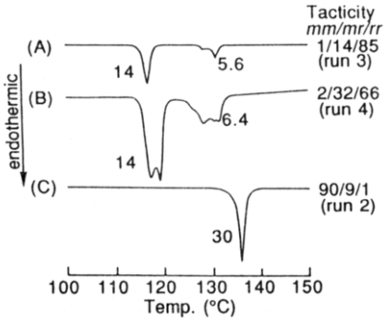


Figure 9. DSC thermograms of syndio- (A and B) and isotactic (C) poly-**1s** on the second heating scan (5 °C/min). The transition enthalpy values (J/g) for the peaks and tacticities of the samples are printed in the figure. Run numbers in parentheses correspond to those in Table V.

great difference in the location of mesogenic groups with respect to the main chain; for a syndiotactic polymer, the side groups are aligned on the one side of a zigzag backbone (Figure 12), while for an isotactic polymer, the side groups should radiate from the helical main chain. These differences should affect the assembly of mesogenic groups. The unusual pattern seen in ^{1}H NMR spectra of iso- and syndiotactic polymers in solution (Figure 2) may possibly have a connection with the conformational difference in solid state which is discussed above.

The spacer length is considered to affect the local conformation of the side chain as well as mechanical decoupling of the mesogenic group from the main chain. Assuming an *all-trans* conformation of the side chain for a syndiotactic polymer, the direction of the mesogenic groups with respect to the main chain differs depending on the odd–even number of methylene groups (Figure 13). Although the number of methylene groups may affect the location of the mesogenic groups also in isotactic polymers with the postulated helical conformation, such an effect is considered to be larger for syndiotactic polymers as the mobility of the side chain seems less a result of the steric hindrance and π–π interaction between the neighboring side groups. These assumptions account fairly well for the different effect of the spacer length of iso- and syndiotactic polymers on the clearing temperature shown in Figure 11.

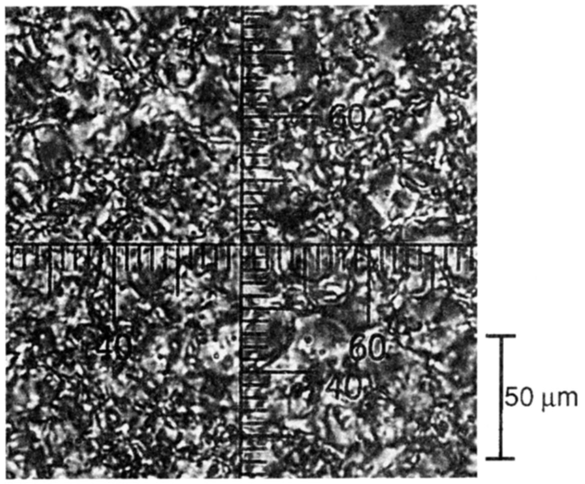


Figure 10. Optical polarization micrograph of syndiotactic poly-**1** (run 3 in Table V) after being annealed at 134.5 °C for 2 days.

Table VI. Thermal Properties of Polymer Obtained by GPC Fractionation of Isotactic Poly-1[a]

fraction	$\bar{M}_n{}^b \times 10^{-3}$	$\bar{M}_w/\bar{M}_n{}^b$	T_i (°C)	ΔH (J·g^{-1})
1	48.9	1.16	131.1	23.9
2	27.6	1.24	132.2	26.0
3	11.2	1.21	130.3	25.8
4	5.7	1.17	128.8	27.9

[a] Original polymer; run 2 in Table V. [b] Determined by GPC.

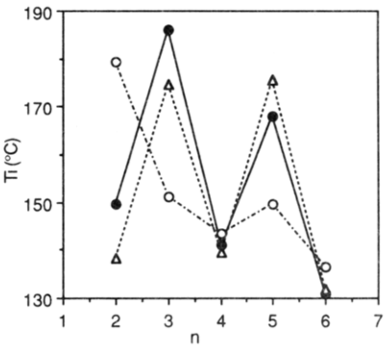


Figure 11. Dependence of clearing temperature (T_i) of the polymers on the number of methylene groups (n) of spacer: (–●–) syndiotactic polymers prepared by anionic polymerization in THF; (- - -Δ- - -) polymers rich in syndiotacticity prepared by radical polymerization; (–·○–·) isotactic polymers prepared by anionic polymerization in $CHCl_3$. The polymers were prepared at [monomer]/[initiator] = 20.

Conclusion

The highly stereoregular polymers were prepared by anionic polymerization of the methacrylates having mesogenic ester groups, **1** and **3**–**6**, with *t*-BuMgBr. The

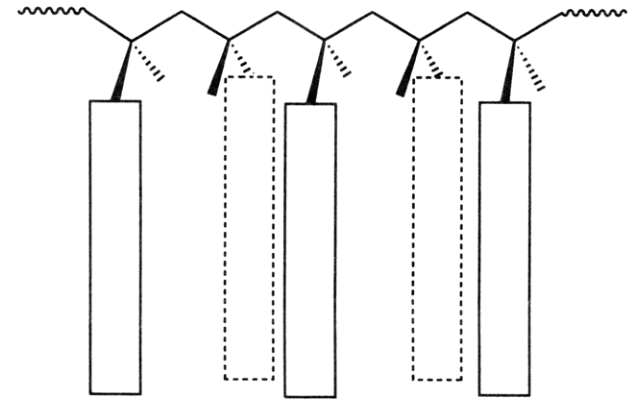


Figure 12. Ribbon-like structure of syndiotactic polymers with a *all-trans*, planar zigzag conformation of the main chain. The open rectangle represents a mesogenic side chain.

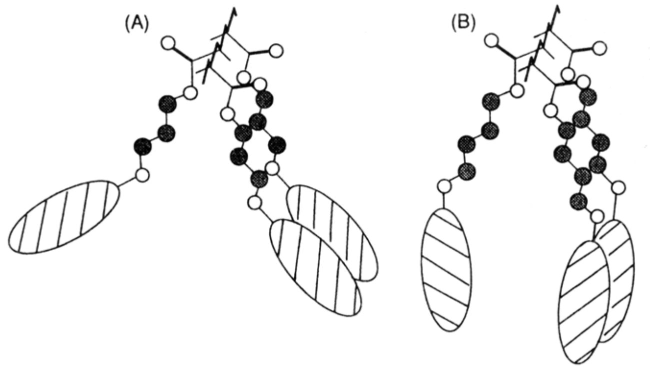


Figure 13. Model syndiotactic triad sequences with a odd (A) and even (B) number of methylene groups of the spacer. Open circles, filled circles, and shaded ellipses represent respectively oxygen atoms, methylene groups of the spacer, and mesogenic groups.

thermal properties and liquid crystallinities depended remarkably on the main-chain tacticity and the number of methylene groups in the side chain. These findings were attributed to the postulated conformational difference between iso- and syndiotactic polymers (a helical and a zigzag main-chain conformation for the isotactic ones and syndiotactic ones, respectively) with an *all-trans* conformation assumed for the side chain. The unusual features of ^{1}H NMR spectra of the polymers suggested some specific conformation of the polymer chain also in solution.

Acknowledgment. The present work was supported partly by a Grant-in-Aid for Scientific Research (Nos. 04403021 and 04855184) of the Ministry of Education, Science, and Culture and a grant from the Asahi Glass Foundation. The authors are grateful to Messrs. T. Asakura and K. Nishimura for their experimental assistance.

References and Notes

(1) For review, see: (a) Krongauz, V. In *Applied Photochromic Polymer Systems*; Mcardle, C. B., Ed.; Blackie & Sons: London, 1992; pp 121–173. (b) *Polymer Liquid Crystals*; Ciferri, A., Krigbaum, W. R., Meyer, R. B., Eds.; Academic Press: New York, 1982.
(2) For review, see: *Comb-Shaped Polymers and Liquid Crystals*; Plate, N. A., Shibaev, V. P., Eds.; Plenum: New York, 1987.
(3) Hahn, B.; Wendorff, J. H.; Portugall, M.; Ringsdorf, H. *Colloid Polym. Sci.* **1981**, *259*, 875.
(4) Frosini, V.; Levita, G.; Lupinacci, D.; Magagnini, P. L. *Mol. Cryst. Liq. Cryst.* **1981**, *66*, 21.
(5) Duran, R.; Guillon, D.; Gramain, P.; Skoulios, A. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 181.
(6) Okamoto, Y.; Asakura, T.; Hatada, K. *Chem. Lett.* **1991**, 1105.
(7) In the present study, the phase transitions of the polymers were analyzed only by DSC and microscopic observation. The analyses of the other technics are scheduled for the future, and the results will be described elsewhere.
(8) Hatada, K.; Ute, K.; Tanaka, K.; Kitayama, T.; Okamoto, Y. *Polym. J.* **1985**, *17*, 977.
(9) Allcock, H. R.; Kim, C. *Macromolecules* **1990**, *23*, 3881.
(10) Duran, R.; Gramain, P. *Makromol. Chem.* **1987**, *188*, 2001.
(11) Finkelmann, H.; Happ, M.; Portugal, M.; Ringsdorf, H. *Makromol. Chem.* **1978**, *179*, 2541.
(12) Rodriguez-Parada, J. M.; Percec, V. *J. Polym. Sci., Part A: Polym. Chem.* **1986**, *24*, 1363.
(13) Ando, M.; Uryu, T. *J. Polym. Sci., Part C: Polym. Lett.* **1989**, *27*, 325.
(14) (a) Hatada, K.; Ute, K.; Tanaka, K.; Okamoto, Y.; Kitayama, T. *Polym. J.* **1986**, *18*, 1037. (b) Hatada, K.; Ute, K.; Tanaka, K.; Imanari, M.; Fujii, N. *Polym. J.* **1987**, *19*, 425.
(15) Nishioka, A.; Watanabe, H.; Abe, K.; Sono, K. *J. Polym. Sci.* **1960**, *48*, 241.
(16) Although the polymerization of 1 with *t*-BuMgBr in THF has already been reported, the tacticity of the obtained polymer was not described. Koide, N.; Kumada, T.; Iimura, K. *The 14th Japanese Symposium on Liquid Crystals (Sendai) Abstr.* **1988**, 264 (No. 3D310).
(17) Cao, Z.-K.; Ute, K.; Kitayama, T.; Okamoto, Y.; Hatada, K. *Konbunshi Ronbunshu (Jpn.)* **1986**, *43*, 435.
(18) For a review of polymerization stereochemistry of methacrylates, see: Hatada, K.; Kitayama, T.; Ute, K. *Prog. Polym. Sci.* **1988**, *13*, 189.
(19) The unusual feature of the ^{1}H NMR spectra was seen also for the other polymers. The details of the NMR analysis will be reported elsewhere.
(20) Bovey, F. A. In *Chain Structure and Conformation of Macromolecules*; Academic Press: New York, 1982; pp 47–50.
(21) Duran, R.; Strazielle, C. *Macromolecules* **1987**, *20*, 2853.
(22) For a review of the tacticity dependence of polymer properties, see: Yuki, H.; Hatada, K. *Adv. Polym. Sci.* **1979**, *31*, 1.
(23) We reported in the previous paper[6] that the syndiotactic poly-**1** (run 3 in Table V) showed a smectic phase in addition to a nematic phase with a schlieren texture. However, we were unsuccessful in reproducing the result in repeated experiments for the same sample and were able to observe only a schlieren texture.
(24) A fan-shaped optical texture has been reported for poly-1 with isotacticity of mm 68%.[3]
(25) (a) Duran, R.; Guillon, D.; Gramain, Ph.; Skoulios, A. *J. Phys. (Paris)* **1988**, *49*, 121. (b) Duran, R.; Guillon, D.; Gramain, Ph.; Skoulios, A. *J. Phys. (Paris)* **1988**, *49*, 1455. (c) Duran, R.; Guillon, D.; Gramain, Ph.; Skoulios, A. *J. Phys. (Paris)* **1987**, *48*, 2043. (d) Duran, R.; Guillon, D.; Gramain, Ph.; Skoulios, A. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 321.
(26) Sundararajan, P. R.; Flory, P. J. *J. Am. Chem. Soc.* **1974**, *96*, 5025.
(27) Lovell, R.; Windle, A. H. *Polymer* **1981**, *22*, 175.
(28) Natta, G.; Corradini, P. *J. Polym. Sci.* **1959**, *39*, 29.
(29) Vogl, O.; Jaycox, G. D. *Polymer* **1987**, *28*, 2179.