

SYNTHESIS AND PROPERTIES OF NEW MESOGEN-JACKETED LIQUID CRYSTALLINE POLYMERS^{*}

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Abstract Some new mesogen-jacketed liquid crystalline polymers (MJLCP) with polymer backbones, spacers, and mesogenic units of different structures were synthesized by radical polymerization. The mesomorphic behavior of these polymers was examined using differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). Their liquid crystallinity is influenced by the variation of polymer backbone, spacer, mesogenic unit and its terminal groups. The results show that 1) a more flexible polymer main-chain is more favorable to the formation of a liquid crystal phase, while 2) a flexible spacer will decrease the "Jacket Effect" and the liquid crystallinity and 3) a subtle modification of the terminal groups on the mesogenic unit may also have a significant influence on properties of the polymers.

Keywords Mesogen-jacketed liquid crystalline polymers, Polymer backbones, Spacers, Mesogenic units, Liquid crystallinity

INTRODUCTION

The side-chain liquid crystalline polymers (SCLCPs) in which the mesogenic units are laterally attached to the polymer main-chain have been synthesized and studied in recent years^[1-18]. All of them but a few^[8-11] have only a nematic mesophase independent of the nature of the backbone, the length of the flexible spacers, and the length of the terminal groups on the mesogenic units. Finkelmann^[1] reasoned that, since the side chains are bonded to the backbone at a site close to the centre of the mesogenic unit, the structure would clash with the smectic mesophase. On the other hand, Zhou *et al.*^[2, 5] reasoned that the bonding of the mesogenic unit to the polymer backbone is at the centre of gravity or a nearby position of the mesogenic unit, so the motion of the backbone should have only minor effects on the motions of the mesogenic units. Therefore, the use of flexible spacers, which is required for the conventional SCLCPs with terminally attached mesogenic units to "decouple" the motions of the backbone and the side-chain segments^[19], is of less importance for these SCLCPs to form a stable liquid crystalline phase. The most distinct feature of the SCLCPs with a polyethylene main chain studied by Zhou *et al.*^[5] is that only a single covalent bond is used to connect the mesogenic units and the main chain. Because of the spatial requirement of the bulky and rigid mesogenic units, the side-chain mesogenic units are organized around the polymer backbone so as to form a mesogen-jacketed structure (MJLCP). This idea has been repeatedly supported by Hardouin^[7], Gray^[20], Richardson^[21], Mauzac^[22], Xu^[23] and Zhou^[24-26].

In this paper, we present some new MJLCPs with different polymer backbones, spacers and mesogenic units. In addition, the relationship of the polymer structure and liquid crystallinity is also studied.

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EXPERIMENTAL

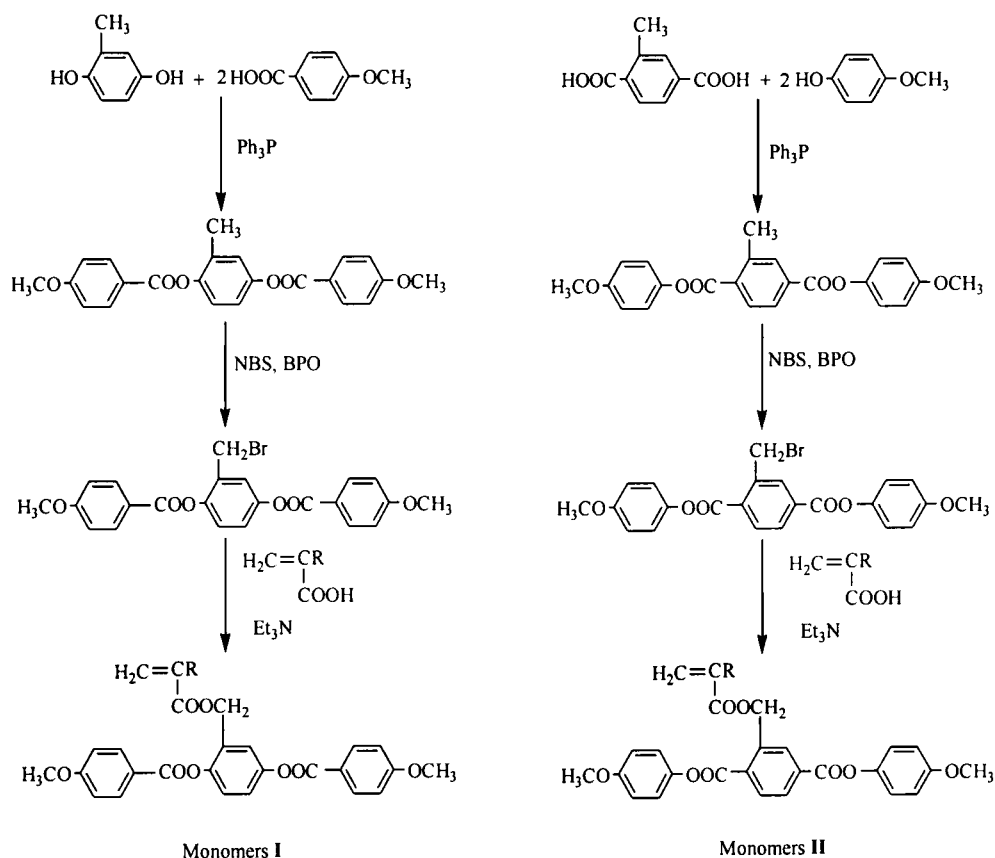
Materials

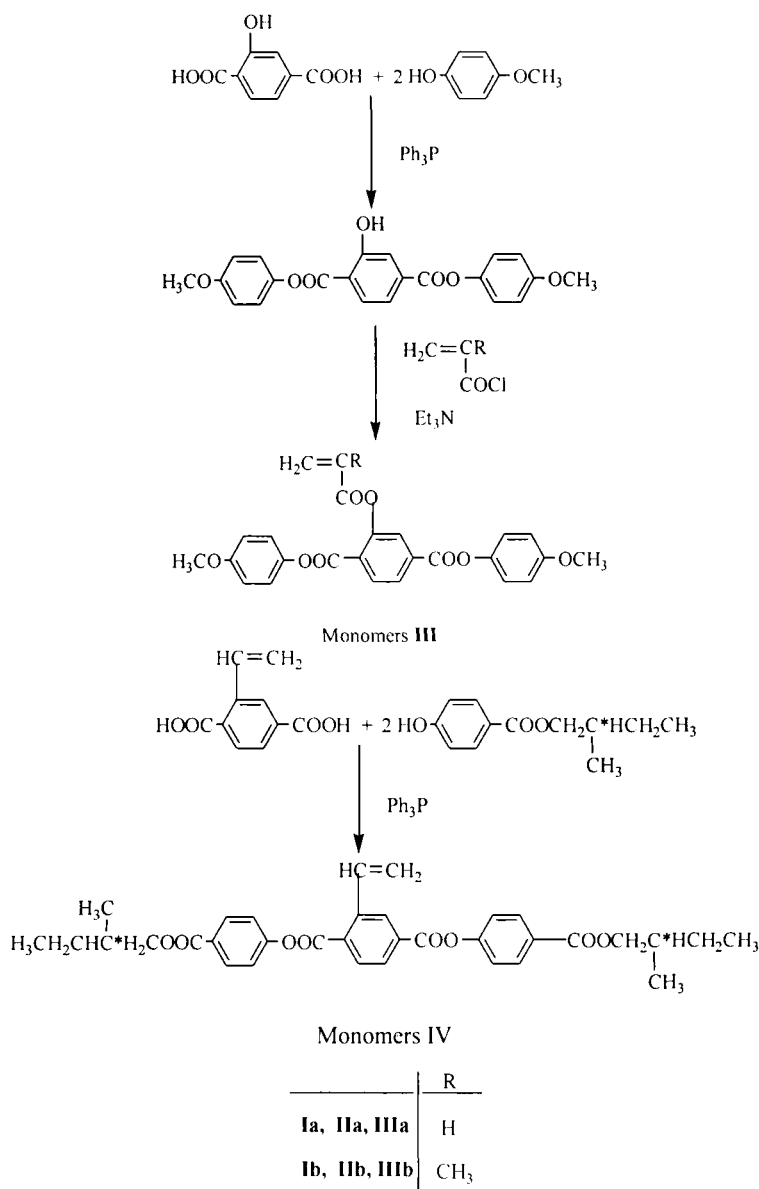
Methylhydroquinone, *p*-methoxybenzoic acid and *p*-methoxyphenol were used as received from Aldrich. Methylterephthalic acid was prepared by oxidation of acetyl-*m*-xylene. Hydroxyterephthalic acid was prepared as described in the literature^[27]. (*S*)-4-(2'-Methyl-*n*-butoxy)phenol was prepared as described in the literature^[28]. Vinylterephthalic acid was prepared as described in the literature^[18]. All other reagents and solvents were commercial products.

Measurements

¹H-NMR spectra were recorded on a Bruker ARX400 spectrometer by using CDCl₃ as solvent. The elemental analyses were carried out on an Elemental Vario EL instrument. The mass spectra (EI) were recorded on a VG-ZAB-HB mass spectrometer. Thermal analyses were carried out under a nitrogen atmosphere by means of a Perkin Elmer DSC 7 apparatus. The liquid crystallinity was also studied by means of a Leitz Laborlux 12 Pol polarizing optical microscope (POM) with a Leitz hot stage.

Synthesis of Monomers (Scheme 1)





Scheme 1. Synthesis of monomers I-IV

2,5-Bis[(4'-methoxybenzoyl)oxy]toluene

p-Methoxybenzoic acid (12.2 g, 80 mmol) and triphenylphosphine (22 g, 84 mmol) were dissolved in 80 mL dried pyridine to get the solution A. Methylhydroquinone (5.0 g, 40 mmol) and hexachloroethane (21 g, 88 mmol) were dissolved in 80 mL dried pyridine to get the solution B. Then solution B was added slowly to solution A. After addition, the mixture was stirred at room temperature for 4 h. Then the mixture was added to a methanol/water (1:3) solution. The precipitate was filtered and purified using column chromatography on silica gel with methylene chloride as eluent. The resultant product was recrystallized in benzene/*n*-hexane mixture solvents to yield 11.1 g (yield 70%) of the product as colorless crystals. DSC: k 169.1 n 253 i; M.S.: 392; ¹H-NMR (δ): 8.21 (m, 4H), 7.18 (m, 3H), 7.04 (m, 4H), 3.94 (s, 6H), 2.30 (s, 3H).

2,5-Bis[(4'-methoxyphenoxy)carbonyl]toluene

The procedure was the same as used above but the methoxybenzoic acid was replaced by methylterephthalic acid

and methylhydroquinone was replaced by *p*-methoxyphenol. The yield was 82%. DSC: k 133.1 n 211.8 i; M.S.: 392; $^1\text{H-NMR}$ (δ): 7.84~7.96 (*m*, 3H), 7.20~7.31 (*m*, 8H), 3.94 (*s*, 3H), 3.92 (*s*, 3H), 2.63 (*s*, 3H).

2,5-Bis[(4'-methoxyphenoxy)carbonyl]phenol

Hydroxyterephthalic acid (3.6 g, 20 mmol) and triphenylphosphine (11 g, 42 mmol) were dissolved in 40 mL dried pyridine to get the solution A. *p*-Methoxyphenol (5.0 g, 40 mmol) and hexachloroethane (11 g, 44 mmol) were dissolved in 40 mL dried pyridine to get the solution B. Then solution A was added slowly to solution B. After addition, the mixture was stirred at room temperature for 4 h. Then the mixture was added to a methanol/water (1: 3) solution. The precipitate was filtered. The product was purified using column chromatography on silica gel with methylene chloride as eluent to yield 1.9 g (yield 35%) of the product. DSC: k 162.2 n 242.1 i; $^1\text{H-NMR}$ (δ): 10.60 (*s*, 1H), 8.20 (*d*, 1H, J = 8.2 Hz), 7.85 (*s*, 1H), 7.74 (*d*, 1H, J = 8.2 Hz), 7.10~7.20 (*m*, 4H), 6.89~7.01 (*m*, 4H), 3.85 (*s*, 3H), 3.84 (*s*, 3H).

2,5-Bis[(4'-methoxybenzoyloxy)benzyl bromide

A mixture of 2,5-bis[(4'-methoxybenzoyloxy)toluene (7.9 g, 20 mmol), *N*-bromo-succinimide (3.7 g, 21 mmol), BPO (0.2 g) and anhydrous benzene (80 mL) was refluxed with stirring for 6 h and then cooled. The mixture was filtered and then the solvent was stripped off by a rotatory evaporator. The resultant solid was recrystallized from an ethanol/benzene mixture to yield 6.1 g (65%) of the product. $^1\text{H-NMR}$ (δ): 8.15~8.25 (*m*, 4H), 7.25~7.36 (*m*, 3 H), 6.90~7.10 (*m*, 4H), 4.45 (*s*, 2H), 3.90 (*s*, 6H).

2,5-Bis[(4'-methoxyphenoxy)carbonyl]benzyl bromide

The same bromination procedure was used for 2,5-bis[(4'-methoxyphenoxy)carbonyl]toluene to yield the product. The recrystallization was from acetone and the yield was 75%. $^1\text{H-NMR}$ (δ): 8.19~8.31 (*m*, 3H), 7.15~7.24 (*m*, 4H), 6.90~7.00 (*m*, 4H), 5.20 (*s*, 2H), 3.82 (*s*, 6H).

2,5-Bis[(4'-methoxybenzoyloxy)benzyl acrylate (Ia) or methacrylate (Ib)

Et_3N (1 mL) was dropped slowly into methylene chloride (2 mL) containing acrylic or methacrylic acid (0.2 g), to which the 2,5-bis[(4'-methoxybenzoyloxy)benzyl bromide (1.9 g, 4 mmol) in methylene chloride (8 mL) was dropped with stirring at 0°C. The reaction was continued at 0°C for 4 h. The solvent was stripped off by a rotatory evaporator. The residue was purified by column chromatography on silica gel with methylene chloride as eluent, followed by recrystallization in benzene/*n*-hexane.

Ia: Yield: 38%; M.S.: 462; $^1\text{H-NMR}$ (δ): 8.16 (*d*, 2H, J = 8.8 Hz), 8.15 (*d*, 2H, J = 8.8 Hz), 7.36 (*d*, 1H, J = 2.1 Hz), 7.30 (*d*, 1H, J = 8.8 Hz), 7.26 (*dd*, 1H, J = 8.8 Hz, J = 2.1 Hz), 7.00 (*d*, 2H, J = 8.8 Hz), 6.99 (*d*, 2H, J = 8.8 Hz), 6.37 (*dd*, 1H, J = 17.2 Hz, J = 1.3 Hz), 6.08 (*dd*, 1H, J = 17.2 Hz, J = 10.4 Hz), 5.8 (*dd*, 1H, J = 10.4 Hz, J = 1.3 Hz), 5.23 (*s*, 2H), 3.92 (*s*, 6H).

Anal. calcd for $\text{C}_{26}\text{H}_{22}\text{O}_8$: C, 67.53; H, 4.762. Found: C, 67.28; H, 4.468.

Ib: Yield: 50%; M.S.: 476; $^1\text{H-NMR}$ (δ): 8.16 (*d*, 2H, J = 8.8 Hz), 8.15 (*d*, 2H, J = 8.8 Hz), 7.36 (*d*, 1H, J = 2.5 Hz), 7.30 (*d*, 1H, J = 8.8 Hz), 7.28 (*dd*, 1H, J = 8.8 Hz, J = 2.5 Hz), 7.00 (*d*, 2H, J = 8.8 Hz), 6.99 (*d*, 2H, J = 8.8 Hz), 6.07 (*s*, 1H), 5.53 (*p*, 1H, J = 1.5 Hz), 5.22 (*s*, 2H), 3.91 (*s*, 6H), 1.87 (*s*, 3H).

Anal. calcd for $\text{C}_{27}\text{H}_{24}\text{O}_8$: C, 68.07; H, 5.042. Found: C, 67.89; H, 5.837

2,5-Bis[(4'-methoxyphenoxy)carbonyl]benzyl acrylate (IIa) or methacrylate (IIb)

The procedure was the same as for **Ia** and **Ib** but the precursor was 2,5-bis[(4'-methoxyphenoxy)carbonyl]benzyl bromide.

IIa: Yield: 55%; M.S.: 462; $^1\text{H-NMR}$ (δ): 8.37 (*d*, 1H, J = 1.0 Hz), 8.33 (*d*, 1H, J = 8.0 Hz), 8.26 (*dd*, 1H, J = 8.0 Hz, J = 1.0 Hz), 7.16 (*d*, 4H, J = 8.0 Hz), 6.97 (*d*, 4H, J = 8.0 Hz), 6.51 (*dd*, 1H, J = 17.2 Hz, J = 1.3 Hz), 6.24 (*dd*, 1H, J = 10.4 Hz, J = 17.2 Hz), 5.91 (*dd*, 1H, J = 10.4 Hz, J = 1.3 Hz), 5.72 (*s*, 2H), 3.843 (*s*, 3H), 3.841 (*s*, 3H). Anal. calcd for $\text{C}_{26}\text{H}_{22}\text{O}_8$: C, 67.53; H, 4.762. Found: C, 67.30; H, 4.620.

IIb: Yield: 60%; M.S.: 476; $^1\text{H-NMR}$ (δ): 8.38 (*s*, 1H, J = 0.8 Hz), 8.31 (*d*, 1H, J = 8.0 Hz), 8.25 (*dd*, 1H, J = 8.0 Hz, J = 0.8 Hz), 7.16 (*d*, 4H, J = 8.8 Hz), 6.96 (*d*, 4H, J = 8.8 Hz), 6.22 (*s*, 1H), 5.71 (*s*, 2H), 5.63 (*p*, 1H, J = 1.4 Hz), 3.84 (*s*, 6 H), 2.0 (*s*, 3 H). Anal. calcd for $\text{C}_{27}\text{H}_{24}\text{O}_8$: C, 68.07; H, 5.042. Found: C, 68.09; H, 5.74.

2,5-Bis[(4'-methoxyphenoxy)carbonyl]phenyl acrylate (IIIa)²⁹ or methacrylate (IIIb)

2,5-Bis[(4'-methoxyphenoxy)carbonyl]phenol (1 g, 2.5 mmol) was dissolved in 20 mL methylene chloride and 2.5 mL Et₃N, to which 1 mL acryloyl or methacryloyl chloride in 5 mL methylene chloride was added dropwise with stirring at 0°C. The reaction was continued at that temperature for 4 h. The Et₃N-HCl salt was precipitated. It was filtered and then the solvent was stripped off by a rotatory evaporator. The residue was purified by column chromatography on silica gel with methylene chloride as eluent, followed by recrystallization in benzene/*n*-hexane.

IIIa: Yield: 70%; M.S.: 448; ¹H-NMR (δ): 8.32 (*d*, 1H, *J* = 8.0 Hz), 8.19 (*dd*, 1H, *J* = 8.0 Hz, *J* = 1.6 Hz), 8.03 (*d*, 1H, *J* = 1.6 Hz), 7.15 (*d*, 2H, *J* = 7.2 Hz), 7.09 (*d*, 2H, *J* = 7.2 Hz), 6.95 (*d*, 2H, *J* = 7.2 Hz), 6.92 (*d*, 2H, *J* = 7.2 Hz), 6.65 (*d*, 1H, *J* = 17.2 Hz), 6.36 (*dd*, 1H, *J* = 17.2 Hz, *J* = 10.4 Hz), 6.04 (*d*, 1H, *J* = 10.4 Hz), 3.83 (*s*, 3H), 3.81 (*s*, 3H). Anal. calcd for C₂₅H₂₀O₈: C, 66.96; H, 4.464. Found: C, 66.90; H, 4.587.

IIIb: Yield: 63%; M.S.: 462; ¹H-NMR (δ): 8.31 (*d*, 1H, *J* = 8.0 Hz), 8.18 (*dd*, 1H, *J* = 8.0 Hz, *J* = 1.6 Hz), 8.02 (*d*, 1H, *J* = 1.6 Hz), 7.15 (*d*, 2H, *J* = 6.8 Hz), 7.09 (*d*, 2H, *J* = 7.2 Hz), 6.95 (*d*, 2H, *J* = 7.2 Hz), 6.92 (*d*, 2H, *J* = 7.2 Hz), 6.40 (*s*, 1H), 5.76 (*s*, 1H), 3.83 (*s*, 3H), 3.81 (*s*, 3H), 2.05 (*s*, 3H). Anal. calcd for C₂₆H₂₂O₈: C, 67.53; H, 4.762. Found: C, 67.34; H, 4.513.

2,5-Bis{[(*S*)-4'-(2''-methyl-*n*-butoxy)phenoxy]carbonyl}styrene (IV)

Vinylterephthalic acid (3.9 g, 20 mmol) and triphenylphosphine (11 g, 42 mmol) were dissolved in 40 mL dried pyridine to get the solution A. (*S*)-4-(2'-Methyl-*n*-butoxy)phenol (8.4 g, 40 mmol) and hexachloroethane (10.5 g, 44 mmol) were dissolved in 40 mL dried pyridine to get the solution B. Then solution B was slowly added to solution A. After addition, the mixture was stirred at room temperature for 4 h. Then the mixture was added to a methanol/water (1:3) solution. The precipitate was filtered and purified using column chromatography on silica gel with methylene chloride as eluent. The resultant product was recrystallized in *n*-hexane to yield 7.4 g (yield 64%) of the product. m.p: (by DSC) 69.1°C; M.S.: 572; [α]_D²⁵ (*c*, 0.5, THF) = +3.1°; ¹H-NMR (δ): 8.46 (*d*, 1H, *J* = 1.6 Hz), 8.26 (*d*, 1H, *J* = 8.2 Hz), 8.23 (*dd*, 1H, *J* = 8.2 Hz, *J* = 1.6 Hz), 8.17 (*d*, 2H, *J* = 8.4 Hz), 8.16 (*d*, 2H, *J* = 8.8 Hz), 7.55 (*dd*, 1H, *J* = 17.0 Hz, *J* = 10.6 Hz), 7.34 (*d*, 2H, *J* = 8.8 Hz), 7.33 (*d*, 2H, *J* = 8.4 Hz), 5.86 (*d*, 1H, *J* = 17.6 Hz), 5.53 (*d*, 1H, 11 Hz), 0.9~4.9 (*m*, 22H). Anal. calcd for C₃₄H₃₆O₈: C, 71.33; H, 6.293. Found: C, 70.98; H, 6.492.

Polymerization

All polymerizations were carried out in THF or toluene using 0.5% equivalent moles AIBN as initiator at 60°C for 48 h. The polymers were precipitated in methanol. The precipitate was redissolved in THF, and then reprecipitated in methanol. This procedure was repeated three times.

RESULTS AND DISCUSSION

Synthesis

The synthetic procedure for monomers **I-IV** is shown in Scheme 1. **I** and **II** were synthesized in three steps by the condensation reaction of methylhydroquinone and *p*-methoxybenzoic acid (or methylterephthalic acid and *p*-methoxyphenol), followed by the bromomethylation of the resultant 2,5-bis[(4'-methoxybenzoyl)oxy]toluene (or 2,5-bis[(4'-methoxyphenoxy)carbonyl]toluene), and then by the esterification of the 2,5-bis[(4'-methoxybenzoyl)oxy]benzyl bromide (or 2,5-bis[(4'-methoxyphenoxy)carbonyl]benzyl bromide) with acrylic or methacrylic acid. The final esterifying step was improved by using a direct reaction of the benzyl bromides with acrylic or methacrylic acid instead of the conventional esterification of benzyl bromides with the salts of the two acids, which simplified the synthetic procedure. **III** was synthesized in two steps by the condensation reaction of hydroxyterephthalic acid and *p*-methoxyphenol, and then by the esterification of the 2,5-bis[(4'-methoxyphenoxy)carbonyl]phenol with acrylic^[29] or methacrylic acid. In order to prevent the auto-condensation of hydroxyterephthalic acid in the condensation procedure, we changed the order of addition, i.e. the solution of hydroxyterephthalic acid and triphenylphosphine was slowly added to the solution of *p*-methoxyphenol and hexachloroethane. **IV** was synthesized by the condensation reaction of vinylterephthalic acid and (*S*)-4'-(2''-

methyl-*n*-butoxy)-phenol.

All the structures of monomers were identified by $^1\text{H-NMR}$, elemental analysis, and mass spectrometry described in the experimental section. The results are in good agreement with the expected structures.

The radical polymerizations of monomers **I-IV** in THF or toluene yielded the desired polymers shown in Chart 1. All polymers were purified by repeated dissolution in THF and precipitation in methanol, and were then dried in vacuum. Molecular weights of polymers were determined relative to polystyrene by gel permeation chromatography (GPC) at room temperature in THF on PL-GPC 210 (England). The results were summarized in Table 1, together with the results of elemental analysis.

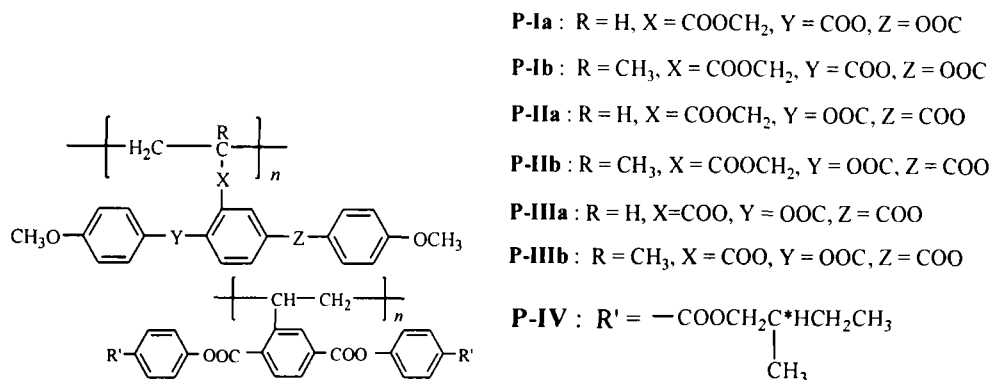


Chart 1 Laterally attached SCLCPs prepared by radical polymerization of I-IV

Table 1. Characterization of the resulted polymers ^a

Polymers	Yield (%)	M_n^b ($\times 10^{-4}$)	M_w/M_n	C	Elemental analyses		
					found	calcd ^c	H
P-Ia	82	1.2	1.91	67.45	4.780	67.53	4.762
P-Ib	69	3.1	2.34	68.21	5.028	68.07	5.042
P-IIa	90	1.3	3.05	67.61	4.809	67.53	4.762
P-IIb	88	1.1	3.31	67.92	5.057	68.07	5.042
P-IIIa	70	1.1	2.22	66.88	4.481	66.96	4.464
P-IIIb	59	0.4	2.06	67.46	4.795	67.53	4.762
P-IV^d	81	7.4	3.57	71.28	6.325	71.33	6.293

a) all polymerizations were conducted in THF except **P-IV** in toluene,

b) molecular weights were determined by GPC in THF based on polystyrene standards,

c) infinite degree of polymerization was assumed,

d) $[\alpha]_{365}^{25}$ (c, 0.5, THF) = +20°

Phase Behavior of Monomers

All the monomers **I-IV** except **IIIb** and **IV** form a nematic mesophase. The phase transition temperatures as well as the liquid-crystal-to-isotropic transition enthalpy and entropy of the monomers are summarized in Table 2.

Ia and **Ib** form an enantiotropic liquid crystal phase while **IIa** and **IIb** form only a monotropic liquid crystal phase, although **I** and **II** have similar structure except for the interconnecting order of the two ester groups in mesogenic units. This result agrees well with that of Dewar^[30, 31]. Dewar studied the phase transition behavior of 1,4-bis[(*p*-methoxybenzoyl)oxy]benzene and 1,4-bis[(*p*-methoxyphenoxy)carbonyl]benzene and found that the former had a more stable mesophase than the latter. He reasoned that in the former there was a mutual conjugation between the methoxy group and carboxyl group which should increase the polarity of the carbonyl oxygen and help to stabilize the mesophase, while in the latter there was not such mutual conjugation so that the mesophase stability was lower. However, due to the bulk lateral substituent on **I** and **II**, the clearing temperatures are all much lower than what Dewar obtained for the two non-laterally-substituted parent compounds, e.g., that of **Ib** is 129.1°C and that of **IIb** is only 51°C. In fact, the metastable nematic mesophase of **IIb** was not detected by

DSC because of its very low stability. However, POM of **IIb** did show the presence of this metaphase (see Fig. 1).

Table 2. Thermal transitions and thermodynamic parameters of monomers I-IV ^a

Monomers	Phase transition(°C)	ΔH (kJ · mol ⁻¹)	ΔS (J · mol ⁻¹ · K ⁻¹)
Ia	k 120.6 n 125.1 i	0.93	2.46
	i 121.5 n	-1.55	3.92
Ib	k 124.6 n 129.1 i	–	–
	i 104.1 n	-1.58	4.19
IIa	k 91.4 (n 70.4 i)	–	–
	i 68.2 n	-0.68	1.99
IIb	k 119.9 (n 51 ^b i)	–	–
	i 68.0 k (i 48 ^b n)	–	–
IIIa	k 122.7 (n 53.8 i)	0.40	1.22
	i 49.8 n	-0.79	2.45
IIIb	k 115.0 i	–	–
IV	k 69.1 i	–	–

a) k = crystalline, n = nematic, i = isotropic, (monotropic), thermal transitions were read from reproducible first or second heating scans with a heating rate of 20 K/min and first cooling scans with a cooling rate of 20 K/min, b) transition temperature was determined by polarizing optical microscopy (POM)

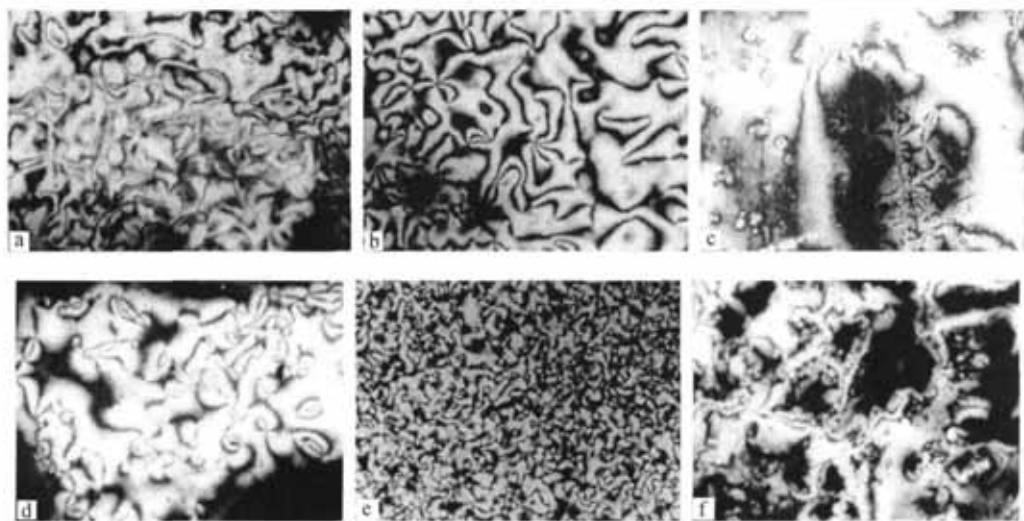


Fig. 1 Polarizing optical micrographs of the schlieren nematic textures obtained on cooling a) monomer **Ia**, 52°C (×320); b) monomer **Ib**, 22°C (×320); c) monomer **IIa**, 52°C (×100); d) monomer **IIb**, 32°C (×320); e) monomer **IIIa**, 30°C (×320) and f) polymer **P-Ia**, 165°C (×100)

III has a very similar structure to **II** except that there is an additional methylene in the lateral substituent of **II**. However, **III** has much lower potential to form a mesophase; for instance, **IIb** forms a metastable monotropic liquid crystal phase while **IIIb** does not. The possible reason is that the introduction of a CH₂ in between the phenylene and the acryloyloxy group may have diminished the steric effect imposed on the mesogenic core by the acryloyloxy group, such that the central phenylene and the other parts of the mesogenic core will have a higher coplanarity. In addition, the acrylates have a more stable mesophase than the methacrylates because the size of acryloyloxy is smaller than that of the methacryloyloxy and thus the steric effect of the former is less than that of the latter.

No liquid crystallinity of **IV** was detected by DSC or POM although its homologous compound 2,5-bis[(*p*-methoxyphenoxy)carbonyl]styrene did form a stable enantiotropic mesophase^[18]. This indicated that the liquid crystallinity of this series of rod-like compounds is very sensitive to the change in the terminal groups.

Phase Behavior of Polymers

The DSC traces obtained on heating and on cooling are presented in Fig. 2. The phase transition temperatures and liquid-crystal-to-isotropic transition enthalpy and entropy of polymers **P-I** ~ **P-IV** are summarized in Table 3.

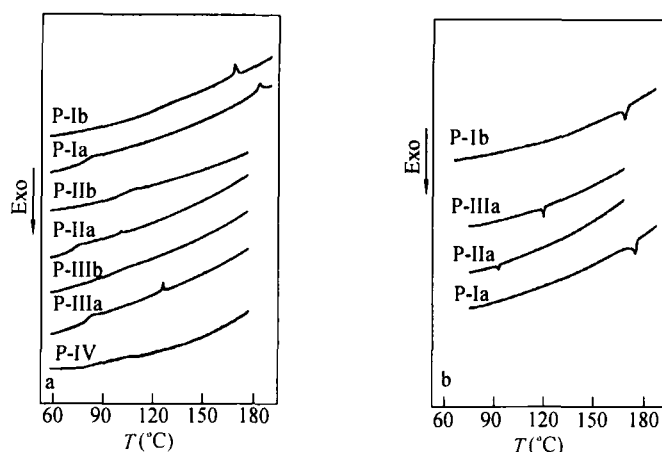


Fig. 2 DSC curves of P-I~P-IV in a) heating and b) cooling processes

P-IIb, **P-IIIb** and **P-IV** do not form a liquid crystal phase while the others all form an enantiotropic liquid crystal phase. The clearing temperature of these liquid crystal side-chain polymers is higher than that of their corresponding monomers. In other words, the polymers have higher mesophase stability compared with their corresponding monomers. This indicates that the linkage of the laterally substituted nematic monomer units to the polymer backbone “stabilizes” the liquid crystalline state^[1]. The textures obtained by polarizing optical microscopy and the small enthalpy changes (about $1 \text{ kJ} \cdot \text{mol}^{-1}$) are characteristic of a nematic phase^[1].

P-Ia and **P-Ib** have a similar structure with identical mesogenic units and spacers but have different main chains. The former is a polyacrylate while the latter is a polymethacrylate. **P-Ia** has a lower T_g but a higher T_i than **P-Ib**, although the latter has a higher molecular weight. This implies that a more flexible polymer main chain is more desirable for the formation of a liquid crystalline phase. The same was obtained for **P-IIa** and **P-IIb** as well as for **P-IIIa** and **P-IIIb**. However, if the polymer has a much longer spacer (*i.e.* $n = 11$), due to the “decoupling” effect, the polymer backbone will have less influence on the mesophase^[1].

Table 3. Thermal Transitions and Thermodynamic Parameters of Polymers^a

Polymers	Phase transition (°C)	$\Delta H^b (\text{kJ} \cdot \text{mol}^{-1})$	$\Delta S^b (\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$
P-Ia	g 73.1 n 178.3 i	1.14	2.53
	i 176.7 n	-1.40	3.11
P-Ib	g 120.3 n 172.8 i	0.92	2.06
	i 170.4 n	-1.18	2.66
P-IIa	g 67.1 n 97.8 i	0.14	0.36
	i 95.0 n	-0.16	0.43
P-IIb	g 95.1 i	-	-
P-IIIa	g 76.2 n 124.1 i	0.26	0.65
	i 122.2 n	-0.36	0.91
P-IIIb	g 94.0 i	-	-
P-IV	g 88 i	-	-

a) g = glassy, n = nematic, i = isotropic, (monotropic), thermal transitions were read from reproducible second or third heating scans with a heating rate of 10 K/min and first or second cooling scans with a cooling rate of 10 K/min , b) relative to monomer unit

P-I and **P-II** are structurally identical with only a difference in the interconnecting order of the two ester

groups in the mesogenic units. The clearing temperature of **P-Ia** is 178.3°C while that of **P-IIa** is only 97.8°C, and the clearing temperature of **P-Ib** is 172.8°C while **P-IIb** has no liquid crystallinity. These results may also be explained with Dewar's argument^[30, 31] as we just demonstrated for the monomers.

P-IIa and **P-IIIa** have similar structure except for an additional methylene in the spacer for **P-IIa**, but the clearing temperature of the former ($T_i = 97.8^\circ\text{C}$) is lower than that of the latter ($T_i = 124.1^\circ\text{C}$). Recently, we reported the properties of a polymer which has a similar structure to **P-IIa** and **P-IIIa** but without any spacer (**P1**)^[18] (see Chart 2.). No clearing temperature of **P1** was observed below 320°C. On the other hand, as shown in Chart 2, **P2**, **P-Ia** and **P3** also have the similar structures with identical polymer backbone and mesogenic units but different spacers. The clearing temperature of **P3** is only 49°C^[1], and that of **P-Ia** is 178.3°C while that of **P2** is higher than 300°C^[5]. These results show that if a spacer is introduced, the "Jacket Effect" and polymer liquid crystallinity will decrease with increasing length and flexibility of the spacer. This result is in good agreement with what Hardouin^[32] and Gray^[21] have obtained.

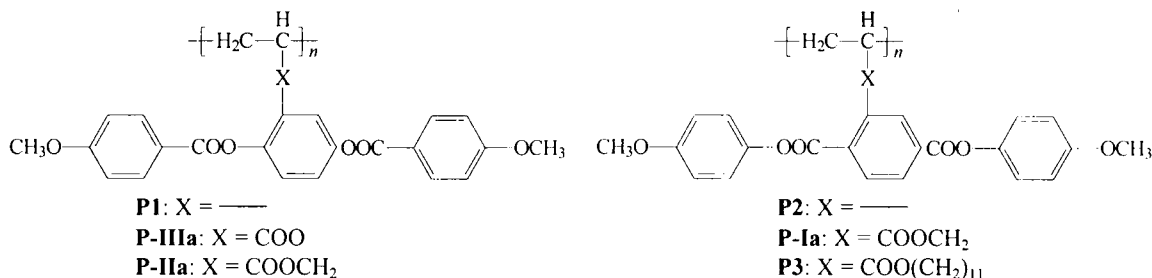


Chart 2 MJLCP with different spacers

P-IV and **P1** have similar structures with identical polymer backbone, spacers and mesogenic cores except that the terminal groups of **P-IV** have a methyl branch. However, **P-IV** has no liquid crystallinity, while **P1** forms a very stable mesophase with T_i higher than 320°C. In addition, we have found that if the two methoxyl groups in **P1** are changed into hexyloxy or pentyloxy groups the resulting polymers are also liquid crystalline with T_i higher than 300°C. These results show that a subtle modification of the terminal groups of the mesogenic units of the MJLCP may have a very significant influence on the liquid crystallinity of the polymers^[1, 33].

CONCLUSIONS

The liquid crystallinity of the mesogen-jacketed liquid crystalline polymers is influenced by variations in the polymer backbone, the spacer, the mesogenic unit and its terminal groups. A more flexible polymer main chain is more favorable to the formation of a liquid crystal phase while a flexible spacer will decrease the "Jacket" effect and the liquid crystallinity; and a subtle modification of the terminal groups on the mesogenic unit may also have a significant influence on properties of the polymers.

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