

Synthesis and Thermal Behavior of Side-Chain Liquid Crystalline Polymethacrylates Containing Tolane-Based Mesogenic Side Groups

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SYNOPSIS

The synthesis and characterization of nine polymethacrylates containing 4-alkoxy-4'-trifluoromethyltolane, 4-alkoxy-4'-cyanotolane, and 4-alkoxy-4'-nitrotolane side groups were described in this study. The phase behavior of the prepared monomers and polymers was characterized by differential scanning calorimetry, optical polarizing microscopy, and x-ray diffraction. All of the obtained monomers exhibit no mesophase, while most of the synthesized polymers reveal enantiotropic mesomorphism. The polymethacrylate containing 4-propoxy-4'-nitrotolane side groups was the only one which shows no mesomorphic behavior. Both the spacer length and the nature of terminal groups have profound influence on the phase transition temperatures and thermal stability of the mesophase. The polymers with longer spacers tend to form a more ordered mesophase with a wider temperature range. Among three polymers with the same spacer length, the polymer with a trifluoromethyl terminal end group is inclined to form a more ordered mesophase than the other two polymers. No side chain crystallization occurred for all obtained polymers. © 1994 John Wiley & Sons, Inc.

Keywords: liquid crystal polymer • polymethacrylate • tolane

INTRODUCTION

Side-chain liquid crystalline polymers (side-chain LCPs) are of both theoretical and practical interest because they combine the anisotropy of liquid crystals with properties of the polymeric backbone. Some new applications based on these materials have been reported.¹⁻⁵ Examining the relationship between their chemical structures and mesomorphic properties has been one very important for the study of side-chain LCPs.

Tolane, which possesses extended conjugation, has been widely used for the synthesis of low molar mass liquid crystals with high birefringence.⁶⁻¹⁰ Recently, Percec et al. reported some new tolane-based liquid crystals and liquid crystalline polymers by using phase transfer Pd(O)/Cu(I) catalyzed coupling

reactions.¹¹⁻¹⁷ This study is to present the synthesis and characterization of side-chain liquid crystalline polymethacrylates containing 4-alkoxy-4'-trifluoromethyltolane, 4-alkoxy-4'-cyanotolane and 4-alkoxy-4'-nitrotolane in the mesogenic side groups. Both the monomers and the polymers were characterized by differential scanning calorimetry, optical polarized microscopy, and x-ray diffractometry. The effects of terminal groups as well as spacer length on the mesomorphic properties of the obtained polymers are discussed.

EXPERIMENTAL

Materials

Bis(triphenylphosphine)palladium(II) chloride, triphenylphosphine, 2-methyl-3-butyn-2-ol (all from Janssen, Belgium), copper(I) iodide (from Merck) and all other reagents (from Aldrich) were used as received. Tetrahydrofuran (THF) was first refluxed

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over potassium and then distilled under nitrogen. Chloroform was dried by refluxing over calcium hydride followed by distillation. 2,2'-Azoisobutyronitrile (AIBN) (from Janssen) was freshly recrystallized from methanol (below 40°C).

Techniques

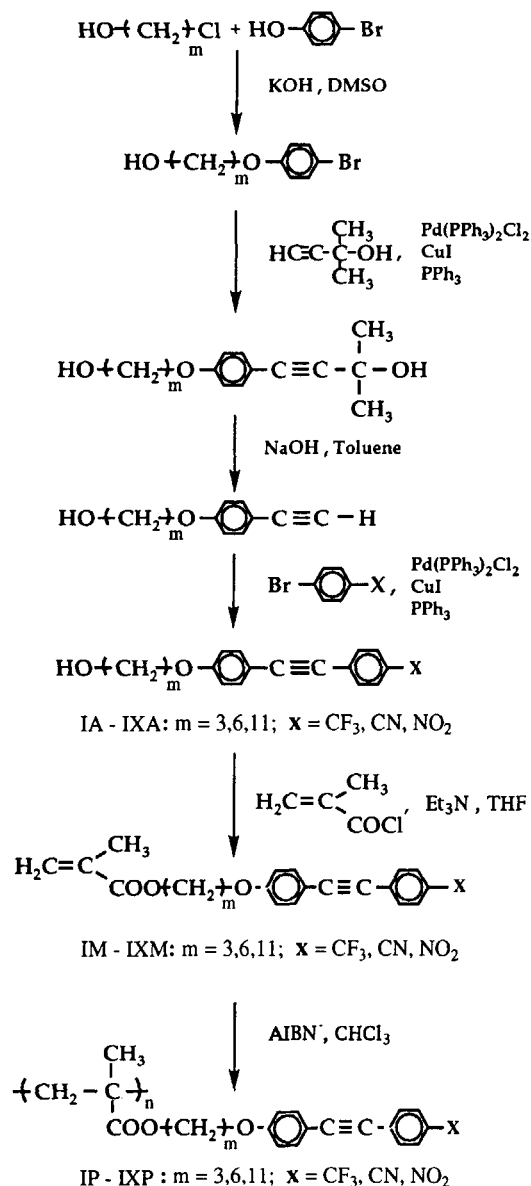
¹H-NMR spectra were obtained with a Bruker AM-400 spectrometer. All spectra were recorded in CDCl₃ solution with TMS as the internal standard, unless otherwise stated. IR spectra were measured on a Perkin-Elmer 842 infrared spectrometer. Purity was determined by high-performance liquid chromatography (HPLC) with a Spectra-Physics LC instrument. Preparative gel permeation chromatography (GPC) was run on a Spectra-Physics LC instrument for separating unreacted monomers from polymers. The molecular weights of the polymers were determined by a Viscotek 200 GPC equipped with a differential refractometer and a viscometer. A set of four Ultrastaygel linear columns was used with THF as eluent at a flow rate of 1 mL/min. The number- and weight-average molecular weight (\bar{M}_n and \bar{M}_w) were determined relative to polystyrene standards. A Dupont 910 differential scanning calorimeter (DSC), equipped with a 9900 computer system, was used for determination the thermal transitions which were read at the maximum of their endothermic or exothermic peaks. Heating and cooling rates were 10°C/min in all of these cases. Glass transition temperatures (T_g) were read at the middle of the change in heat capacity. The transitions were collected from the second heating and cooling scans, unless otherwise specified. A Nikon Microphot-FX optical polarized microscope equipped with a Mettler FP 82 hot stage and a Mettler FP 80 central processor were applied toward observing thermal transitions and anisotropic textures. X-ray diffraction measurements were performed with a Rigaku powder diffractometer using nickel-filtered CuK α radiation.

Synthesis of Monomers and Polymers

The synthesis of monomers and polymethacrylates is outlined in Scheme 1.

4-Bromo-1-(3-hydroxypropanyloxy)benzene, 4-Bromo-1-(6-hydroxyhexanyloxy)benzene and 4-Bromo-1-(11-hydroxyundecanyloxy)benzene

All three compounds were synthesized by the etherification of 4-bromophenol with corresponding ω -bromoalkan-1-ol or ω -chloroalkan-1-ol. An example



Scheme 1. Synthesis of polymethacrylates IP-IXP.

of this procedure is given below. A mixture of 4-bromophenol (10.0 g, 57.8 mmol), potassium hydroxide (3.20 g, 57.8 mmol), and dimethyl sulfoxide (100 mL) was heated to 65°C. Then 6-chloro-1-hexanol (8.70 g, 63.6 mmol) was added dropwise. The obtained solution was stirred at 65°C for 18 h, and cooled to room temperature. The solvent was distilled under reduced pressure. The obtained crude product was dissolved in ethyl acetate and washed with dilute potassium hydroxide, water, and dried over anhydrous magnesium sulfate. After the solvent was removed in a rotary evaporator, the residue was purified by column chromatography [silica gel, a

mixture of chloroform and THF (10 : 1 v/v) as eluent] to yield 13.4 g (85.2%) of colorless oily product. $^1\text{H-NMR}$ (CDCl_3): $\delta = 1.34\text{--}1.77$ [m; 8H, $-(\text{CH}_2)_4-$], 3.60 (t; 2H, $\text{HO}-\text{CH}_2-$), 3.86 (t; 2H, $-\text{CH}_2-\text{O}-$), 6.70 and 7.30 (q; 4H, aromatic protons). 4-Bromo-1-(3-hydroxypropanyloxy)benzene was obtained with 82.0% yield, colorless oily product. $^1\text{H-NMR}$ (CDCl_3): $\delta = 1.96$ (m; 2H, $-\text{CH}_2-$), 3.70 (t; 2H, $\text{HO}-\text{CH}_2-$), 3.90 (t; 2H, $-\text{CH}_2-\text{O}-$), 6.75 and 7.32 (q; 4H, aromatic protons). 4-Bromo-1-(11-hydroxyundecanyloxy)benzene was obtained with 89.4% yield, mp 43°C . $^1\text{H-NMR}$ (CDCl_3): $\delta = 1.30\text{--}1.82$ [m; 18H, $-(\text{CH}_2)_9-$], 3.63 (t; 2H, $\text{HO}-\text{CH}_2-$), 3.88 (t; 2H, $-\text{CH}_2-\text{O}-$), 6.70 and 7.31 (q; 4H, aromatic protons).

4-(3-Hydroxy-3-methyl-1-butynyl)-1-(3-hydroxypropanyloxy)benzene, 4-(3-Hydroxy-3-methyl-1-butynyl)-1-(6-hydroxyhexanyloxy)benzene, and 4-(3-Hydroxy-3-methyl-1-butynyl)-1-(11-hydroxyundecanyloxy)benzene

All three compounds were synthesized by coupling reaction of 2-methyl-3-butyn-2-ol with corresponding aryl bromides. An example is outlined below. To a solution of 4-bromo-1-(6-hydroxyhexanyloxy)benzene, (18.0 g, 66.0 mmol), 2-methyl-3-butyn-2-ol (6.70 g, 79.0 mmol), and dry triethylamine (50 mL) in THF (100 mL). Bis(triphenylphosphine)palladium(II) chloride (0.33 g), copper (I) iodide (0.33 g), and triphenylphosphine (0.66 g) were added.¹⁸ The mixture was heated to 60°C for 8 h. After cooling to room temperature, the solution was filtered and the solvent was evaporated under reduced pressure to dryness. The obtained crude product was purified by column chromatography [silica gel, a mixture of chloroform and THF (6 : 1 v/v) as eluent] to yield 12.4 g (68.0%) of white crystals. mp 83°C . MS: 276 (M^+). $^1\text{H-NMR}$ (CDCl_3): $\delta = 1.40\text{--}1.81$ [m; 8H, $-(\text{CH}_2)_4-$], 1.60 [s; 6H, $-(\text{CH}_3)_2$], 3.66 (t; 2H, $\text{HO}-\text{CH}_2-$), 3.95 (t; 2H, $-\text{CH}_2-\text{O}-$), 6.79 and 7.36 (q; 4H, aromatic protons). 4-(3-Hydroxy-3-methyl-1-butynyl)-1-(3-hydroxypropanyloxy)benzene was obtained with 70.2% yield, mp 112°C . $^1\text{H-NMR}$ (CDCl_3): $\delta = 1.60$ [s; 6H, $-(\text{CH}_3)_2$], 1.95 (m; 2H, $-\text{CH}_2-$), 3.71 (t; 2H, $\text{HO}-\text{CH}_2-$), 4.01 (t; 2H, $-\text{CH}_2-\text{O}-$), 6.79 and 7.36 (q; 4H, aromatic protons). 4-(3-Hydroxy-3-methyl-1-butynyl)-1-(11-hydroxyundecanyloxy)benzene was obtained with 73.5% yield, mp 79°C . $^1\text{H-NMR}$ (CDCl_3): $\delta = 1.31\text{--}1.82$ [m; 18H, $-(\text{CH}_2)_9-$], 1.61

[s; 6H, $-(\text{CH}_3)_2$], 3.65 (t; 2H, $\text{HO}-\text{CH}_2-$), 3.95 (t; 2H, $-\text{CH}_2-\text{O}-$), 6.80 and 7.35 (q; 4H, aromatic protons).

[4-(3-Hydroxypropanyloxy)phenyl]acetylene, [4-(6-Hydroxyhexanyloxy)phenyl]acetylene, and [4-(11-Hydroxyundecanyloxy)phenyl]acetylene

All compounds were synthesized by deprotection of the protected aryl acetylides. An example is given as follows. 4-(3-Hydroxy-3-methyl-1-butynyl)-1-(6-hydroxyhexanyloxy)benzene (12.0 g, 43.0 mmol) was dissolved in dried toluene (150 mL) in a reaction vessel equipped with a Dean-Stark trap and a reflux condenser; then the sodium hydroxide (1.70 g, 43.0 mmol) was added.¹⁸ The mixture was heated to reflux for 3 h. After the reaction time, the reaction mixture was cooled to room temperature, washed with water, and dried over anhydrous magnesium sulfate. The toluene was removed and the resulting solid was purified by column chromatography [silica gel, a mixture of chloroform and THF (12 : 1 v/v) as eluent] to yield 6.40 g (68.3%) of light yellow crystals; mp 49.0°C . MS: 218 (M^+). $^1\text{H-NMR}$ (CDCl_3): $\delta = 1.42\text{--}1.80$ [m; 8H, $-(\text{CH}_2)_4-$], 2.97 (s; 1H, $-\text{C}\equiv\text{C}-\text{H}$), 3.64 (t; 2H, $\text{HO}-\text{CH}_2-$), 3.94 (t; 2H, $-\text{CH}_2-\text{O}-$), 6.79 and 7.40 (q; 4H, aromatic protons). [4-(3-Hydroxypropanyloxy)phenyl]acetylene was obtained with 72.0% yield, mp 55°C . $^1\text{H-NMR}$ (CDCl_3): $\delta = 1.94$ (m; 2H, $-\text{CH}_2-$), 2.97 (s; 1H, $-\text{C}\equiv\text{C}-\text{H}$), 3.70 (t; 2H, $\text{HO}-\text{CH}_2-$), 4.05 (t; 2H, $-\text{CH}_2-\text{O}-$), 6.80 and 7.41 (q; 4H, aromatic protons). [4-(11-Hydroxyundecanyloxy)phenyl]acetylene was obtained with 75.3% yield, mp 53°C . $^1\text{H-NMR}$ (CDCl_3): $\delta = 1.30\text{--}1.80$ [m; 18H, $-(\text{CH}_2)_9-$], 2.98 (s; 1H, $-\text{C}\equiv\text{C}-\text{H}$), 3.65 (t; 2H, $\text{HO}-\text{CH}_2-$), 3.95 (t; 2H, $-\text{CH}_2-\text{O}-$), 6.79 and 7.40 (q; 4H, aromatic protons).

1-[4-(ω -Hydroxyalkanyloxy)phenyl]-2-(4-trifluoromethylphenyl)acetylene (IA-III A), 1-[4-(ω -Hydroxyalkanyloxy)phenyl]-2-(4-cyanophenyl)acetylene (IV A-VI A), and 1-[4-(ω -Hydroxyalkanyloxy)phenyl]-2-(4-nitrophenyl)acetylene (VII A-IX A)

All nine compounds were prepared by the same method. An example of this procedure is given below. To a solution of [4-(6-hydroxyhexanyloxy)phenyl]acetylene (2.20 g, 10.0 mmol) and 4-bromobenzonitrile (2.20 g, 12.0 mmol) in dry triethylamine (10 mL) and tetrahydrofuran (40 mL), bis(triphenylphosphine)palladium(II) chloride (0.05 g), copper(I) iodide (0.05 g) and triphenyl-

phosphine (0.10 g) were added. The mixture was heated to reflux for 5 h, then cooled to room temperature. After filtration to remove precipitated material, the solvent of the filtered solution was evaporated under reduced pressure. The obtained crude product was purified by column chromatography [silica gel, a mixture of chloroform and THF (30 : 1 v/v) as eluent] to yield 2.30 g (71.4%) of white crystals. The $^1\text{H-NMR}$ chemical shifts for all synthesized compounds together with their melting temperatures and yields are presented in Table I.

1-[4-(ω -Methacryloyloxyalkanyloxy)phenyl]-2-(4-trifluoromethylphenyl)acetylene (IM–IIIM), 1-[4-(ω -Methacryloyloxyalkanyloxy)phenyl]-2-(4-cyanophenyl)acetylene (IVM–VIM), and 1-[4-(ω -Methacryloyloxyalkanyloxy)phenyl]-2-(4-nitrophenyl)acetylene (VIIM–IXM)

All methacrylate monomers IM–IXM were synthesized by the esterification of the corresponding alcohols IA–IXA, with methacryloyl chloride. An example is given as follows. 1-[4-(6-Hydroxyhexanyloxy)phenyl]-2-(4-cyanophenyl)acetylene (1.50 g,

4.70 mmol) was dissolved in a mixture of dried THF (30 mL) and triethylamine (1.01 g, 9.98 mmol). After the solution was cooled in an ice-water bath to 0°C , and methacryloyl chloride (0.74 g, 7.05 mmol) was added dropwise. The reaction mixture was allowed to warm slowly to room temperature and stirred overnight. The product was obtained by being poured into water, filtered, dried under vacuum, and purified by column chromatography (silica gel, chloroform as eluent) to yield 1.51 g (83%) of white crystals. The yields and $^1\text{H-NMR}$ chemical shifts of all monomers are summarized in Table II.

Synthesis of Polymethacrylates IP–IXP

The free radical polymerizations of the monomers were carried out in a Schlenk tube under nitrogen. The polymerization tube, which contained a chloroform solution of a monomer (10%, wt/vol) and an initiator (AIBN, 1 wt% vs. monomer), was degassed under vacuum, and finally filled with nitrogen. All polymerizations were carried out at 65°C for 24 h. After the reaction time, the obtained polymers were precipitated in methanol, filtered, purified

Table I. Characterization of 4-(ω -Hydroxyalkanyloxy)tolanes (IA–IXA)

Compound	Yield (%)	mp ($^\circ\text{C}$)	400 MHz $^1\text{H-NMR}$ (CDCl_3 , TMS, δ , ppm)
IA	75	139	1.97 (m; 2H, $-\text{CH}_2-$), 3.74 (t; 2H, $\text{HO}-\text{CH}_2-$), 4.10 (t; 2H, $-\text{CH}_2-\text{OPh}$), 6.85–7.48 and 7.57 (q and s; 8H, aromatic protons)
IIA	82	115	1.40–1.83 [m; 8H, $-(\text{CH}_2)_4-$], 3.66 (t; 2H, $\text{HO}-\text{CH}_2-$), 3.98 (t; 2H, $-\text{CH}_2-\text{OPh}$), 6.84–7.47 and 7.57 (q and s; 8H, aromatic protons)
IIIA	70	110	1.30–1.81 [m; 18H, $-(\text{CH}_2)_9-$], 3.65 (t; 2H, $\text{HO}-\text{CH}_2-$), 3.97 (t; 2H, $-\text{CH}_2-\text{OPh}$), 6.84–7.48 and 7.57 (q and s; 8H, aromatic protons)
IVA	73	123	1.96 (m; 2H, $-\text{CH}_2-$), 3.75 (t; 2H, $\text{HO}-\text{CH}_2-$), 4.12 (t; 2H, $-\text{CH}_2-\text{OPh}$), 6.85–7.61 (2q; 8H, aromatic protons)
VA	71	127	1.42–1.81 [m; 8H, $-(\text{CH}_2)_4-$], 3.65 (t; 2H, $\text{HO}-\text{CH}_2-$), 3.97 (t; 2H, $-\text{CH}_2-\text{OPh}$), 6.85–7.61 (2q; 8H, aromatic protons)
VIA	81	102	1.32–1.80 [m; 18H, $-(\text{CH}_2)_9-$], 3.64 (t; 2H, $\text{HO}-\text{CH}_2-$), 4.10 (t; 2H, $-\text{CH}_2-\text{OPh}$), 6.85–7.60 (2q; 8H, aromatic protons)
VIIA	63	89	1.96 (m; 2H, $-\text{CH}_2-$), 3.75 (t; 2H, $\text{HO}-\text{CH}_2-$), 4.10 (t; 2H, $-\text{CH}_2-\text{OPh}$), 6.86–8.22 (2q; 8H, aromatic protons)
VIIIA	74	123	1.43–1.82 [m; 8H, $-(\text{CH}_2)_4-$], 3.65 (t; 2H, $\text{HO}-\text{CH}_2-$), 4.00 (t; 2H, $-\text{CH}_2-\text{OPh}$), 6.87–8.22 (2q; 8H, aromatic protons)
IXA	68	100	1.32–1.80 [m; 18H, $-(\text{CH}_2)_9-$], 3.64 (t; 2H, $\text{HO}-\text{CH}_2-$), 3.99 (t; 2H, $-\text{CH}_2-\text{OPh}$), 6.88–8.22 (2q; 8H, aromatic protons)

Table II. Characterization of Monomers IM–IXM

Monomer	Yield (%)	400 MHz ¹ H-NMR (CDCl ₃ , TMS, δ, ppm)
IM	88	1.95 (s; 3H, —CH ₃), 2.16 (m; 2H, —CH ₂ —CH ₂ —CH ₂ —), 4.10 (t; 2H, —CH ₂ —OPh), 4.34 (t; 2H, —COO—CH ₂ —), 5.57 and 6.11 (2s; 2H, CH ₂ =), 6.85–7.47 and 7.57 (q and s; 8H, aromatic protons)
IIM	74	1.45–1.82 [m; 8H, —(CH ₂) ₄ —], 1.95 (s; 3H, —CH ₃), 3.98 (t; 2H, —CH ₂ —OPh), 4.16 (t; 2H, —COO—CH ₂ —), 5.55 and 6.11 (2s; 2H, CH ₂ =), 6.84–7.47 and 7.57 (q and s; 8H, aromatic protons)
IIIM	76	1.29–1.81 [m; 18H, —(CH ₂) ₉ —], 1.95 (s; 3H, —CH ₃), 3.97 (t; 2H, —CH ₂ —OPh), 4.14 (t; 2H, —COO—CH ₂ —), 5.55 and 6.10 (2s; 2H, CH ₂ =), 6.84–7.47 and 7.57 (q and s; 8H, aromatic protons)
IVM	71	1.95 (s; 3H, —CH ₃), 2.17 (m; 2H, —CH ₂ —CH ₂ —CH ₂ —), 4.10 (t; 2H, —CH ₂ —OPh), 4.35 (t; 2H, —COO—CH ₂ —), 5.57 and 6.11 (2s; 2H, CH ₂ =), 6.87–7.63 (2q; 8H, aromatic protons)
VM	83	1.46–1.84 [m; 8H, —(CH ₂) ₄ —], 1.95 (s; 3H, —CH ₃), 3.99 (t; 2H, —CH ₂ —OPh), 4.17 (t; 2H, —COO—CH ₂ —), 5.55 and 6.10 (2s; 2H, CH ₂ =), 6.87–7.63 (2q; 8H, aromatic protons)
VIM	62	1.30–1.83 [m; 18H, —(CH ₂) ₉ —], 1.94 (s; 3H, —CH ₃), 3.98 (t; 2H, —CH ₂ —OPh), 4.14 (t; 2H, —COO—CH ₂ —), 5.55 and 6.10 (2s; 2H, CH ₂ =), 6.87–7.63 (2q; 8H, aromatic protons)
VIIM	66	1.95 (s; 3H, —CH ₃), 2.18 (m; 2H, —CH ₂ —CH ₂ —CH ₂ —), 4.11 (t; 2H, —CH ₂ —OPh), 4.36 (t; 2H, —COO—CH ₂ —), 5.58 and 6.11 (2s; 2H, CH ₂ =), 6.90–8.22 (2q; 8H, aromatic protons)
VIIIM	65	1.47–1.82 [m; 8H, —(CH ₂) ₄ —], 1.95 (s; 3H, —CH ₃), 4.00 (t; 2H, —CH ₂ —OPh), 4.17 (t; 2H, —COO—CH ₂ —), 5.55 and 6.10 (2s; 2H, CH ₂ =), 6.88–8.22 (2q; 9H, aromatic protons)
IXM	50	1.30–1.81 [m; 18H, —(CH ₂) ₉ —], 1.94 (s; 3H, —CH ₃), 3.98 (t; 2H, —CH ₂ —OPh), 4.14 (t; 2H, —COO—CH ₂ —), 5.55 and 6.10 (2s; 2H, CH ₂ =), 6.89–8.22 (2q; 8H, aromatic protons)

by several reprecipitations from THF solutions into methanol, and further purified by preparative GPC if deemed necessary.

RESULTS AND DISCUSSION

The synthesis of the methacrylate monomers and intermediary compounds is outlined in Scheme 1. All of the rigid rod-like tolans were prepared via the coupling reaction of [4-(ω-hydroxyalkanyloxy)phenyl]acetylenes and aryl halides in the presence of a palladium complex and a copper(I) salt. The methacrylate monomers IM–IXM were synthesized by a simple esterification reaction of the corresponding alcohols of tolane compounds with methacryloyl chloride. The purity of the obtained products was demonstrated via column chromatography as being high after purification. Typical thermal behavior of the monomers is shown in Figure 1 with VIM functioning as an example. The monomer exhibited only melting and crystallization transi-

tions on both heating and cooling when the sample was heated to around 110°C (curves A and B). If the heating temperature was raised to as high as 180°C (curve C), one exothermic peak (148°C) would be observed. This exothermic peak was attributed to the thermal polymerization of the monomer. Two distinct transitions at 12 and 104°C were observed both in the subsequent cooling and heating scans. One was the glass transition and the other was the liquid crystalline-isotropic transition, as observed by a batonnet smectic A texture found on the optical polarized microscope. On the other hand, the isotropization temperature of the thermally polymerized sample was lower than that of the polymer obtained by free radical polymerization. This lower temperature could have been due to a much lower molecular weight achieved by the thermally polymerized sample. Table III summarizes the thermal transitions and the corresponding enthalpy changes of all monomers without thermal polymerization. All of the monomers exhibited no mesomorphic behavior.

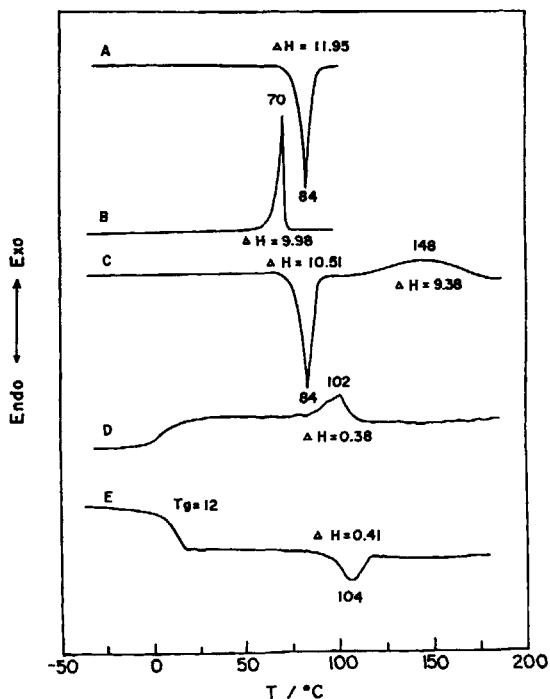


Figure 1. DSC thermograms (10°C/min) of monomer **VIM**: (A) and (B), heating to 100°C (A) then cooling down (B); (C), heating to 180°C and then isothermal for 24 h; (D) and (E), cooling and heating scans after the thermal treatment of (C); ΔH unit in kcal/mol.

The free radical polymerization of the methacrylate monomers was performed in chloroform using AIBN as initiator (Scheme 1). The unreacted monomers were first removed by several reprecipitations from tetrahydrofuran solution into methanol and then separated by preparative GPC if necessary. The polymers were therefore obtained with a high purity. The polymers were therefore obtained with a high purity. The molecular weights and thermal transitions of all obtained polymers are reported in Table IV. The degree of polymerization (\overline{DP}) of all synthesized polymers was observed in this table as being higher than 35. Thermotropic behavior of a side-chain LCP has been well-documented as normally being molecular weight independent when its \overline{DP} is higher than 10.¹⁹ All of the polymers except for **VIIIP** showed mesomorphic behavior. Among three polymers containing three methylene units in their spacers, both polymers **IP** and **IVP** exhibited respectively an enantiotropic nematic phase while polymer **VIIIP** showed no mesomorphic behavior. The nature of the terminal group obviously played a very important role in the formation of mesomorphic behavior. The characteristic schlieren ne-

matic texture exhibited by polymer **IVP** is presented in Figure 2.

Figure 3 depicts the DSC traces of the three polymers containing six methylene units in their spacers. All of the three polymers exhibited a glass transition and a liquid-crystalline to isotropic phase transition on both DSC heating and cooling scans. Polymer **IIP** containing a trifluoromethyl terminal group exhibited a smectic phase which could not be discriminated by optical microscopy observation. Polymer **VP** containing a cyano terminal group presents a smectic A phase; meanwhile, polymer **VIIIP** containing a nitro terminal group shows a nematic phase. The nature of the terminal groups apparently has a pronounced effect on the mesophases formed. Among those three polymers with the same spacer length, the polymer with trifluoromethyl terminal group tends to form a more ordered mesophase. This result also sufficiently correlates with the low molar mass LCs for the same terminal groups as those in previous reports.^{20,21}

Table III. Phase Transitions^a and the Corresponding Enthalpy Changes of Monomers **IM–IXM**

Monomer	m^b	X^b	Phase Transitions [°C (corresponding enthalpy changes, kcal/mol)]	
			Heating	Cooling
IM	3	CF ₃	k 93.2 (8.40) i i 64.8 (7.34) k	
IIM	6	CF ₃	k 75.2 (11.22) i i 60.4 (10.83) k	
IIIM	11	CF ₃	k 73.9 (13.77) i i 55.0 (13.52) k	
IVM	3	CN	k 78.0 (7.57) i i 31.3 (1.87) k	
VM	6	CN	k 88.1 (8.84) i i 65.7 (8.77) k	
VIM	11	CN	k 83.7 (11.95) i i 70.3 (9.98) k	
VIIIM	3	NO ₂	k 105.1 (5.52) i i 71.7 (5.22) k	
VIIIM	6	NO ₂	k 74.0 (8.10) i i 47.0 (8.31) k	
IXM	11	NO ₂	k 89.5 (11.69) i i 73.3 (12.30) k	

^a k = Crystalline, i = isotropic.

^b m , X , according to Scheme 1.

Table IV. Molecular Weight, Phase Transitions,^a and the Corresponding Enthalpy Changes of Polymers **IP–IXP**

Polymer	m^c	X^c	GPC			Phase transitions [°C (corresponding enthalpy changes, kcal/mru ^b)] Heating Cooling
			\bar{M}_n	\bar{M}_w/\bar{M}_n	\bar{DP}	
IP	3	CF ₃	14,130	2.0	36	g 78.2 n 98.0 (0.12) i i 89.2 (0.12) n 72.2 g
IIP	6	CF ₃	17,390	1.4	40	g 52.6 s 102.8 (1.96) i i 89.5 (1.99) s 49.7 g
IIIP	11	CF ₃	24,660	2.1	49	g 34.5 s 122.9 (3.49) i i 113.8 (3.53) s 28.6 g
IVP	3	CN	22,540	1.3	65	g 75.4 n 102.4 (0.11) i i 92.7 (0.12) n 71.4 g
VP	6	CN	39,110	1.4	101	g 50.0 s _A 123.8 (0.42) i i 118.9 (0.40) s _A 44.5 g
VIP	11	CN	40,130	1.9	88	g 29.6 s _A 133.0 (0.79) i i 125.4 (0.76) s _A 22.2 g
VIIP	3	NO ₂	12,910	1.9	35	g 77.0 i i 71.3 g
VIIIP	6	NO ₂	36,500	1.6	90	g 47.7 n 78.6 (0.14) i i 70.3 (0.15) n 42.7 g
IXP	11	NO ₂	18,230	2.1	38	g 19.7 s _A 111.7 (0.60) i i 104.7 (0.56) s _A 12.6 g

^a g = glassy, s = smectic, n = nematic, i = isotropic.

^b mru = mole repeating unit.

^c m, X, according to Scheme 1.

Figure 4 illustrates the DSC traces of the polymers containing 11 methylene units in their spacers. All of the three polymers exhibited a glass transition and an enantiotropic smectic phase. Polymer **IIIP** displayed a smectic phase, while **VIP** and **IXP** exhibited a smectic A phase. The typical focal-conic

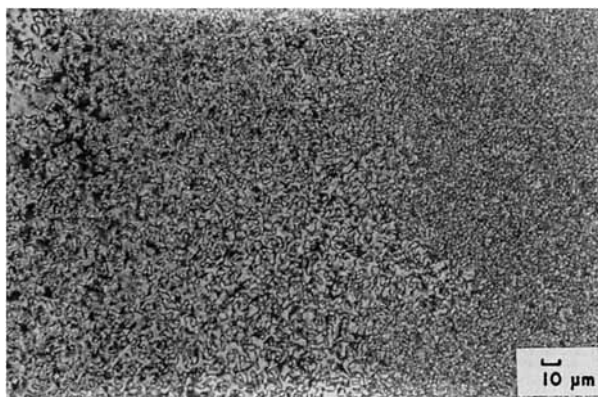


Figure 2. Optical polarizing micrograph displayed by polymer **IVP**: typical texture obtained at 90°C.

smectic A texture exhibited by polymer **VIP** is shown in Figure 5. Figure 6 presents the x-ray diffraction diagrams obtained from powder sample **IXP** at 30°C. A broad reflection was observed at about 4.49 Å which corresponds to lateral spacing of two mesogenic side groups. Additionally, a sharp first-order reflection was found at 42.0 Å along with a second-order reflection at 21.3 Å which correspond to smectic layers. An additional interesting remark refers to the fact that the average layer spacing is approximately 1.4 times larger than the actual molecular length. It is well-known that interdigitated bilayer smectic A structures usually occur for the smectogens that have molecular structures containing a terminal cyano or nitro group.^{22,23} Furthermore, among three different polymers with the same spacer length, the one with cyanotolane-based mesogen notably has the highest isotropization temperature. This phenomena could be due to the conjugating effect induced by the cyano group with the tolane moiety, leading to a longer mesogenic core than the others.^{19,24}

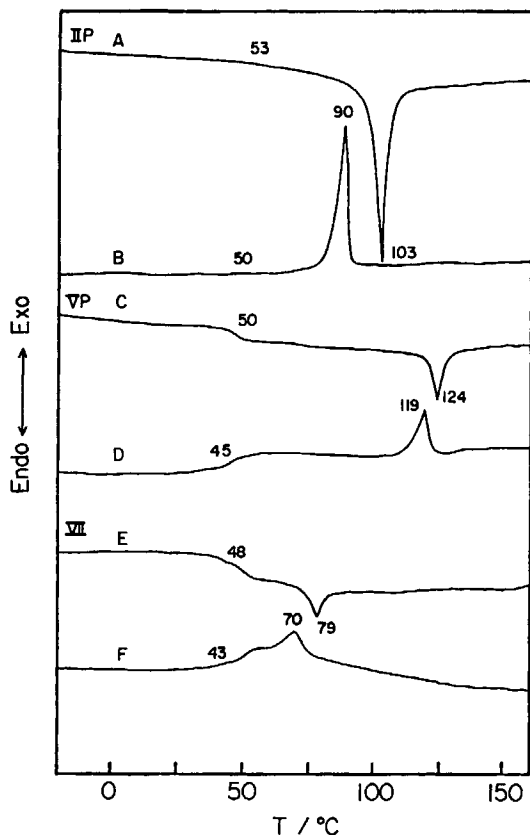


Figure 3. Normalized DSC traces of (A) IIP, second heating scan; (B) IIP, second cooling scan; (C) VP, second heating scan; (D) VP, second cooling scan; (E) VIIIP, second heating scan; and (F) VIIIIP, second cooling scan.

In this study, only three varieties of spacer length, i.e., $m = 3, 6,$ and 11 , were used for preparing each series of polymers containing a same terminal group. An investigation of the true spacer effect on the mesomorphic behavior of the obtained polymers would be insufficient. However, according to the data reported in Table IV, among each series of polymers, the one with 11 methylene units in the spacers always exhibits a more orderly mesophase with a wider temperature range and has a large value for the enthalpy of isotropization than the others. Furthermore, no side chain crystallization occurred in all cases of polymer—even though 11 methylene units were used as spacers. This is especially important for a side-chain liquid crystalline polymer containing such a rigid rod-like mesogen.

In conclusion, a series of new polymethacrylates containing 4-alkoxy-4'-trifluoromethyltolane, 4-alkoxy-4'-cyanotolane, and 4-alkoxy-4'-nitrotolane side groups were prepared. Most of the obtained

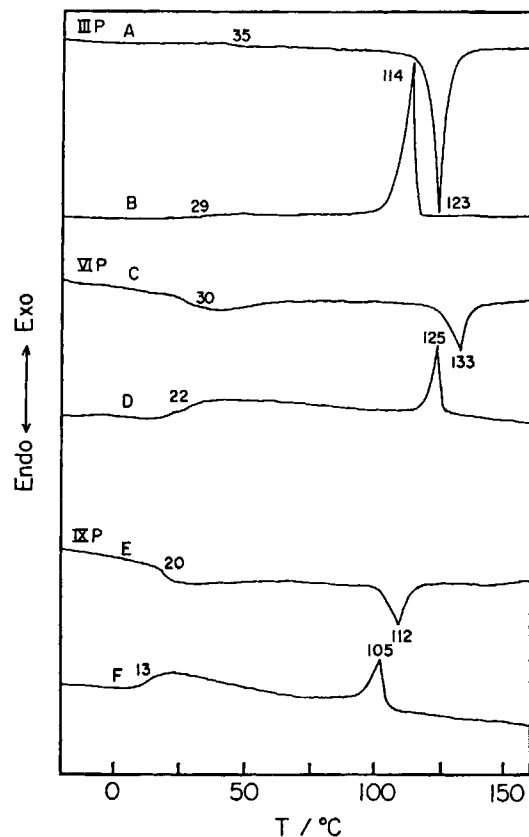


Figure 4. Normalized DSC traces of (A) IIIP, second heating scan; (B) IIIP, second cooling scan; (C) VIIP, second heating scan; (D) VIIP, second cooling scan; (E) IXIP, second heating scan; and (F) IXIP, second cooling scan.

polymers exhibited enantiotropic mesophases. Both the spacer length and the terminal group played quite significant roles on the nature of mesophase

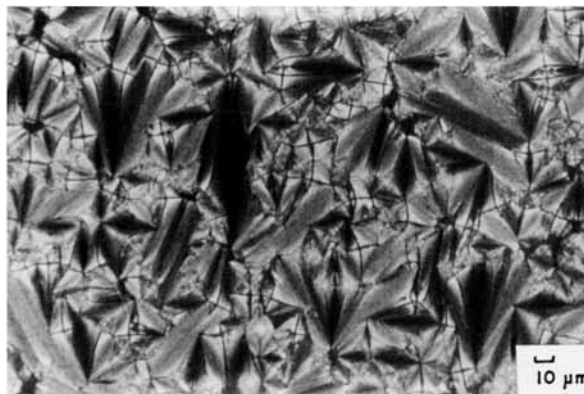


Figure 5. Optical polarizing micrograph displayed by polymer VIP: typical texture obtained at 120°C.

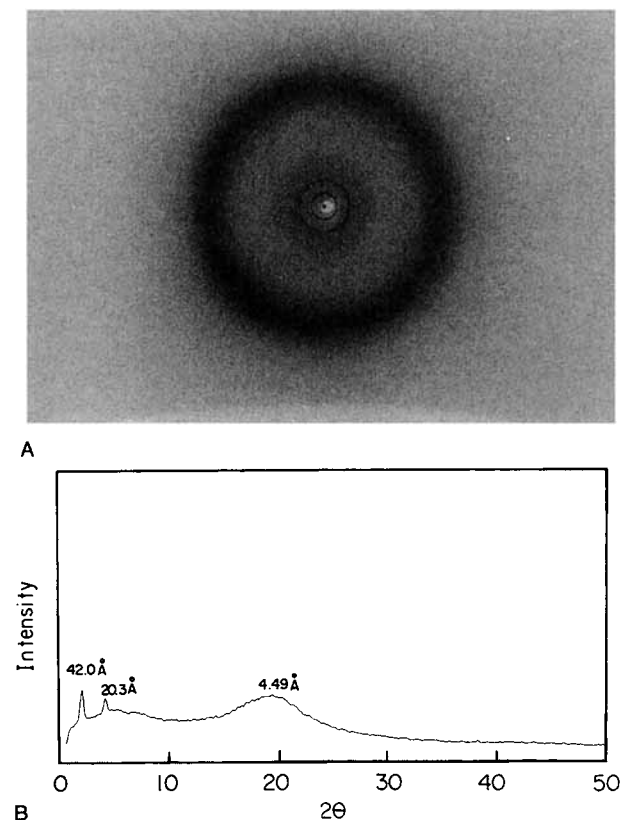


Figure 6. (A) Wide-angle x-ray diffraction pattern of polymer IXP at 30°C; (B) x-ray diffractometer diagram of polymer IXP at 30°C.

formed. The polymers with a trifluoromethyl terminal group were found to tend to form a more orderly mesophase. The polymers with 11 methylene units in their spacers, revealed a more orderly mesophase with a wider temperature range of mesophase than the others. Furthermore, side chain crystallization did not occur for all of the polymers prepared in this study.

The authors are grateful to the National Science Council of the Republic of China (NSC-82-0511-E007-01) for its financial support of this work.

REFERENCES AND NOTES

1. L. L. Chapoy, *Recent Advances in Liquid Crystalline Polymers*, Elsevier, London and New York, 1985.

2. C. B. McArdle, *Side Chain Liquid Crystal Polymers*, Blackie, Glasgow and London, 1989.
3. B. A. Jones, J. S. Bradshaw, M. Nishioka, and M. L. Lee, *J. Org. Chem.*, **49**, 4947 (1984).
4. M. A. Apfel, H. Finkelmann, G. M. Janini, R. J. Lamb, B. H. Luhmann, A. Price, W. L. Roberts, T. J. Shaw, and C. A. Smith, *Anal. Chem.*, **57**, 651 (1985).
5. J. S. Bradshaw, C. Schregenberg, H. C. Karen, K. E. Markides, and M. L. Lee, *J. Chromatogr.*, **358**, 95 (1986).
6. H. Kelker and R. Hatz, *Handbook of Liquid Crystals*, Verlag Chemie, Weinheim, 1980, p. 91.
7. G. Bauer, *Mol. Cryst. Liq. Cryst.*, **63**, 45 (1981).
8. Y. Goto, K. Kitano and T. Ogawa, *Liq. Cryst.*, **5**, 225 (1989).
9. C. Viney, D. J. Brown, C. M. Dannels, and R. T. Twieg, *Liq. Cryst.*, **13**, 95 (1993).
10. S. Greenfield, D. Coates, E. Brown, and R. Hittich, *Liq. Cryst.*, **13**, 301 (1993).
11. C. Pugh and V. Percec, *J. Polym. Sci. Part A: Polym. Chem.*, **28**, 1101 (1990).
12. C. Pugh and V. Percec, *Mol. Cryst. Liq. Cryst.*, **178**, 193 (1991).
13. C. Pugh, C. Tarnstrom, and V. Percec, *Mol. Cryst. Liq. Cryst.*, **195**, 185 (1991).
14. C. Pugh and V. Percec, *Chem. Mater.*, **3**, 107 (1991).
15. C. Pugh, S. K. Andersson, and V. Percec, *Liq. Cryst.*, **10**, 229 (1991).
16. V. Percec and R. Rodenhouse, *J. Polym. Sci. Part A: Polym. Chem.*, **29**, 15 (1991).
17. V. Percec, G. Johansson, and R. Rodenhouse, *Macromolecules*, **25**, 2563 (1992).
18. D. E. Ames, D. Bull, and C. Takundwa, *Synthesis*, 364 (1981).
19. V. Percec and C. Pugh, *Side Chain Liquid Crystal Polymers*, C. B. McArdle, Ed., Blackie, Glasgow and London, 1989, chapter 3.
20. G. H. W. Milburn, C. Campbell, A. J. Shand, and A. R. Werninck, *Liq. Cryst.*, **8**, 623 (1990).
21. C. J. Hsieh and G. H. Hsiue, *Liq. Cryst.*, in press.
22. G. W. Gray and J. W. Goodby, *Smectic Liquid Crystals, Textures and Structures*, Leonard Hill, 1984, chapter 1.
23. A. J. Leadbetter, J. L. A., Durrant, and M. Rugman, *Mol. Cryst. Liq. Cryst.*, **34**, 231 (1977).
24. G. W. Gray and J. W. Goodby, *Smectic Liquid Crystals, Textures and Structures*, Leonard Hill, 1984, chapter 10.

Received May 13, 1993

Accepted October 4, 1993