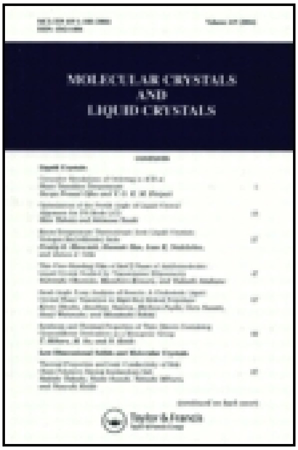

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Synthesis and Characterization of Side-Chain Liquid Crystalline Polymethacrylates Containing Fluorinated Diphenyldiacetylene Side-Groups

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Version of record first published: 24 Sep 2006.

To cite this article: Y.-H. Lu , K.-T. Tsay , C.-S. Hsu & H.-L. Chang (1994): Synthesis and Characterization of Side-Chain Liquid Crystalline Polymethacrylates Containing Fluorinated Diphenyldiacetylene Side-Groups, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 250:1, 85-97

To link to this article: http://dx.doi.org/10.1080/10587259408028195

Mol. Cryst. Liq. Cryst., 1994, Vol. 250, pp. 85–97
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Printed in the United States of America

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(Received 27 July, 1993; in final form September 19, 1993)

The synthesis of four side-chain liquid crystalline polymethacrylates containing either 4-alkanyloxy-4′-flourodiphenyldiacetylenes or 4-alkanyloxy-3′,4′-difluorodiphenyldiacetylenes side groups is presented. The phase behavior of both monomeric and polymeric liquid crystals was characterized by differential scanning calorimetry and optical polarizing miocroscopy. All synthesized polymethacrylates present nematic mesomorphism. The glass transition temperature of the obtained polymers decreases as the spacer length increases.The mesomorphic behavior of the prepared polymers depends very much on the degree of substitution of the mesogenic side groups on the polymer backbones.

Keywords: Fluorinated diphenyldiacetylene, side-chain LC polymer, polymethacrylate, mesomorphic properties

1. INTRODUCTION

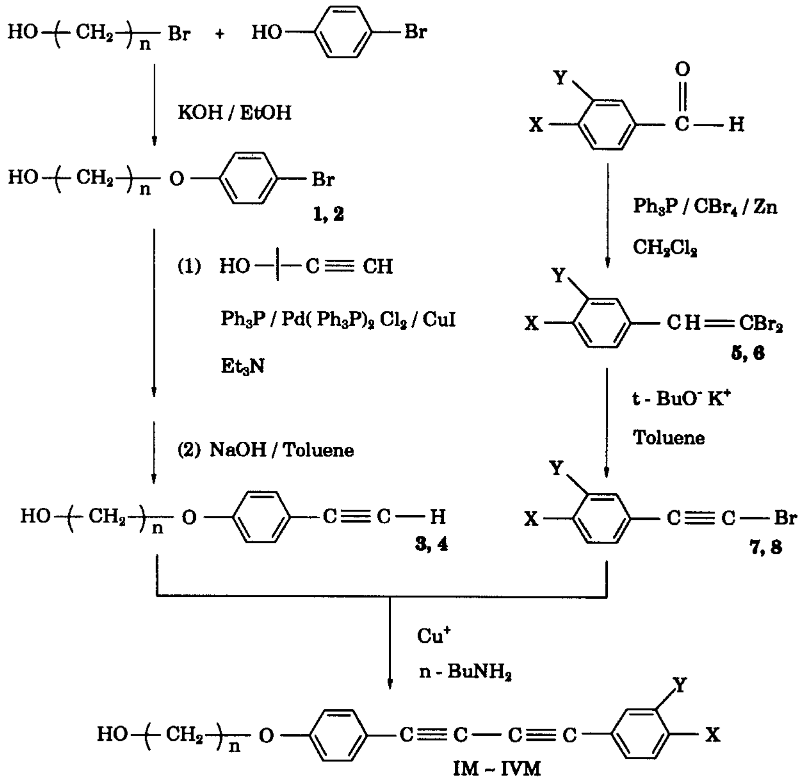
The synthesis and characterization of diphenyldiacetylenic liquid crystals (LCs) have been extensively studied in recent years.[1–9] These LCs which have extended n-conjugation and perfect linear rod-like structure, exhibit extraordinarily high birefringence and relatively low viscosity and have been demonstrated as having a potential application in infrared spatial light modulators.[10] Furthermore, the unsymmetrically diphenyldiacetylenic LCs which contain an electron donating group at one end of the molecule and an electron withdrawing group at the other, have been found to possess pronounced second-order nonlinear optical properties.[4,5]

Fluorinated LC compounds are known for their modest dielectric anisotropy and low viscosity and are useful for formulating LC mixtures.[10,11] Recently, we prepared several series of fluorinated diphenyldiacetylene liquid crystals.[12] The particular examples refer to 4-alkylphenyl-4′-fluorophenyldiacetylenes and 4-alkoxyphenyl-4′-

fluorophenyldiacetylenes. Most of them present an enantiotropic nematic phase and are useful for display application. The goal of this study is to present the synthesis and characterization of four side-chain liquid crystalline polymethacrylates containing either 4-alkanyloxy-4′-fluorodiphenyldiacetylenes or 4-alkanyloxy-3′,4′-difluorodiphenyldiacetylenes side groups. The thermal behavior of the prepared monomers and polymers are described.

2. RESULTS AND DISCUSSION

The synthetic routes used to prepare the monomers IM–IVM are outlined in Scheme I. All the unsymmetrical diacetylenes were prepared by the Cadiot–Chodkiewicz coupling of the terminal acetylene with 1-bromoacetylene.[13,14] Both terminal acetylene and



	IM	IIM	IIIM	IVM
n	6	6	11	11
X	F	F	F	F
Y	H	F	H	F

SCHEME I Synthesis of monomers IM ~ IVM

TABLE I

Characterization of Monomers IM ~ IVM

Monomer	Yield (%)	300 MHz ^{1}H-NMR (CDCl$_3$, δ, ppm)
IM	51%	1.40 ~ 1.90 (m, 8H, HO—CH$_2$—(CH_2)$_4$—), 3.66 (t, 2H, HO—CH_2-) 3.97 (t, 2H, —CH_2—O—Ph) 6.80 ~ 7.60 (m, 8H, aromatic protons)
IIM	46%	1.40 ~ 1.90 (m, 8H, HO—CH$_2$—(CH_2)$_4$—), 3.66 (t, 2H, HO—CH_2—) 3.97 (t, 2H, —CH_2—O—Ph) 6.80 ~ 7.60 (*m*, 7H, aromatic protons)
IIIM	58%	1.20 ~ 1.90 (m, 18H, HO—CH$_2$—(CH_2)$_9$—), 3.64 (t, 2H, HO—CH$_2$—) 3.98 (t, 2H, —CH_2—O—Ph) 6.80 ~ 7.60 (m, 8H, aromatic protons)
IVM	62%	1.20 ~ 1.90 (m, 18H, HO—CH$_2$—(CH_2)$_9$—), 3.64 (t, 2H, HO—CH_2—) 3.98 (t, 2H, —CH_2—O—Ph) 6.80 ~ 7.60 (m, 7H, aromatic protons)

1-bromoacetylene were synthesized according to the same procedures reported by Corey and Fuchs.[15] In addition to the cross-coupling products, a trace amount of homocoupling products was also formed. Therefore, the products should be purified several times by column chromatography. Table I summarized the yields and ^{1}H NMR chemical shifts of the synthesized diphenyldiacetylenic monomers IM–IVM.

The thermal transitions and the corresponding enthalpy changes of the fluorinated diphenyldiacetylenic monomers IM–IVM are summarized in Table II. All monomers exhibit liquid crystalline properties even though they contain respectively a hydroxy group in their alkoxy terminal group. For both monomers, which contain six methyl-

TABLE II

Phase Transitions and Phase Transition Enthalpies for Monomers IM ~ IVM

Monomer	Phase transitions, °C (Corresponding enthalpy changes, Kcal/mol)[a]	
	Heating	Cooling
IM	K 111 (10.85) N 131 (0.40) I	I 130 (10.52) N 194 (0.36) K
IIM	K 115 (11.34) I	I 107 N 104 (10.72)[b] K
IIIM	K 107 (12.04)[b] N 112 I	I 110 (0.47) N 103 (0.34) S$_A$ 97 (10.77) K
IVM	K 85 (9.25) S$_A$ 99 (1.88) I	I 96 (2.10) S$_A$ 69 (5.07) K

[a] K = crystalline, N = nematic, S$_A$ = smectic, A, I = isotropic.

[b] Overlapped transitions, $\Delta H = \Delta H_1 + \Delta H_2$

ene units in their alkoxy terminal groups, IM displays an enantiotropic nematic phase while IIM exhibits a monotropic nematic phase. Furthermore, monomer IM shows a wider temperature range of nematic phase than monomer IIM. For both monomers which contain eleven methylene units in their alkoxy terminal groups, IIIM presents an enantiotropic nematic phase and a monotropic smectic A phase while IVM reveals only an enantiotropic smectic A phase. Figure 1 presents the representative DSC thermograms of monomer IIIM. It shows a melting transition at 107°C and a nematic to isotropic phase transition at 112°C on the heating scan. Upon the cooling scan, it presents an isotropic to nematic phase transition at 110°C, a nematic to smestic A phase transition at 103°C and a crystallization transition at 97°C. Figure 2 shows the nematic and smectic A textures displayed by monomer IIIM.

Thermal polymerization of the synthesized diphenyldiacetylenic monomers were investigaed by DSC and optical polarizing microscopy equipped with a heating stage. Figure 3 shows the DSC thermograms of monomers IM–IVM which were heated to 350°C. A big exothermic transition corresponding to the thermal polymerization of the diphenyldiacetylenic monomer was observed in each DSC heating curve. The exothermic changes begin near 200°C. The subsequent DSC scans show no exothermic peak

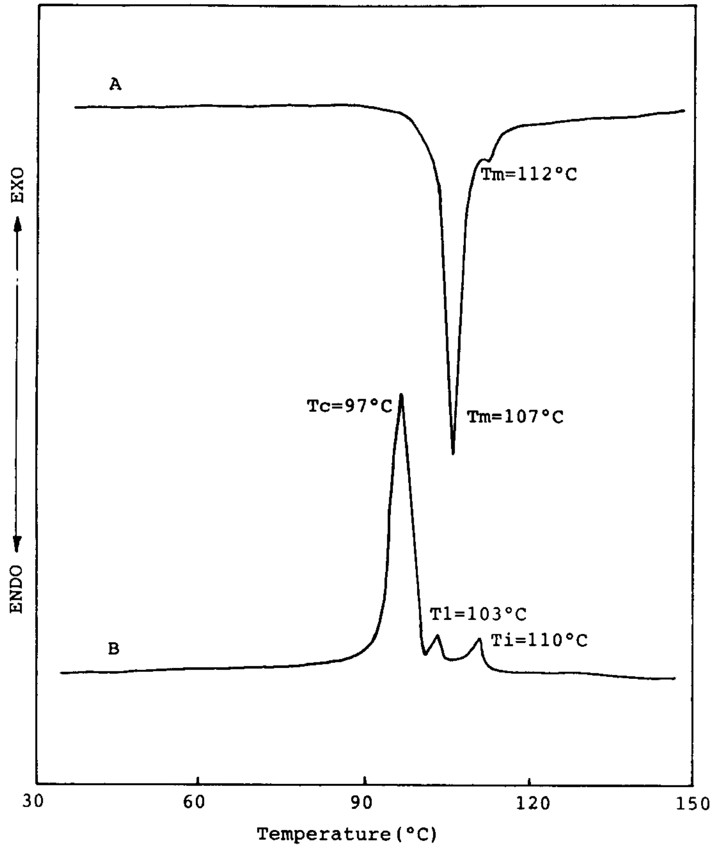


FIGURE 1 DSC thermograms (10°C/min) of monomer IIIMH: A) Heating scan, B) Cooling scan.

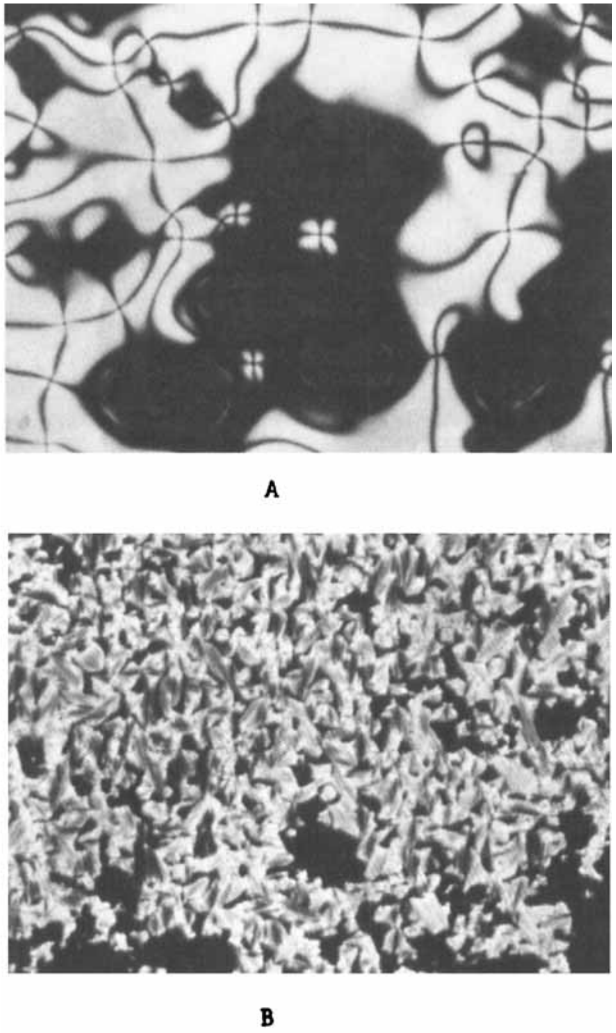


FIGURE 2 Optical polarizing micrographs displayed by monomer IIIM (320X): A) The nematic texture was obtained at 110°C, B) The smectic A texture was obtained at 103°C. See Color Plate I.

for all mononers. This means that thermal polymerization could be complete at 350°C. The enthalpy changes vary in the range from 221 $\mathrm{KJ\,mol^{-1}}$ to 248 $\mathrm{KJ\,mol^{-1}}$. The polymerization of diacetylenic compounds occurs in the solid state by a 1,4-addition, followed by a photochemical mechanism described previously.[16,17] The polymerization of diacetylenic liquid crystals has been proven to easily occur in a smectic or even a nematic mesophase.[4-9] Evidence for the formation of polymers was also obtained by optical polarizing microscopy. On initial heating at 200°C, the monomer underwent reversible phase transition at temperatures which have only a few degrees difference with those which have been shown in DSC scans. Further heating to higher temperature formed the dark red or brown polymers of low solubility in common solvents.

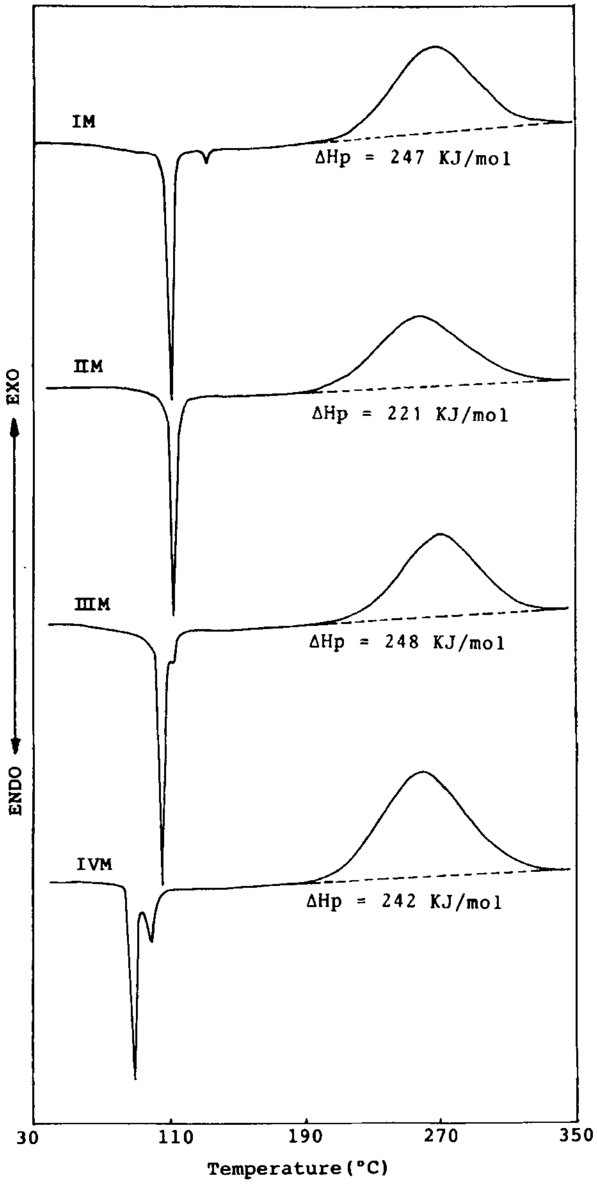
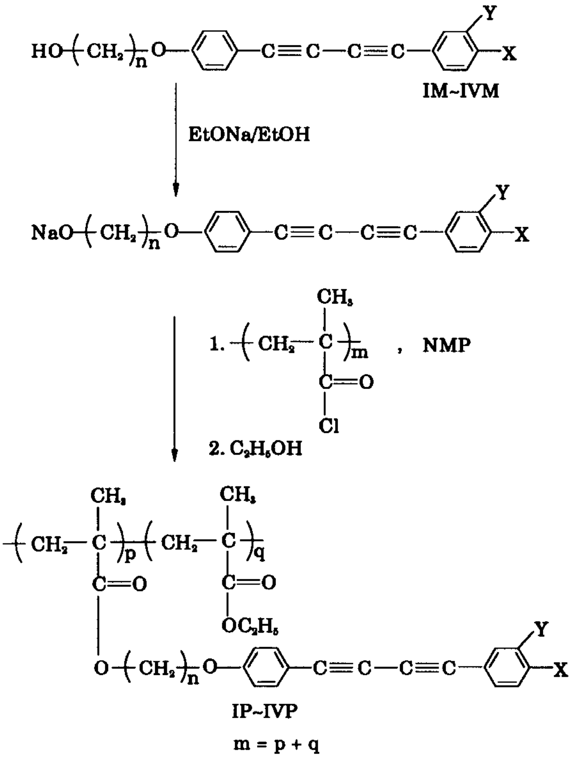


FIGURE 3 DSC heating thermograms (10°C/min) of monomers IM–IVM.

Scheme II outlines the synthetic route used to prepare the side-chain liquid crystalline polymethacrylates. The sodium salts of fluorinated diphenyldiacetylenic monomers were reacted with poly(methacryloyl chloride) in NMP to form the polymers. Table III summarizes the molecular weights and degree of substitution for polymers IP–IVP. The molecular weights of the obtained polymers which are in the range of 3736–8274, have been determined by GPC using a calibration based on polystyrene



	IP	IIP	IIIP	IVP
n	6	6	11	11
X	F	F	F	F
Y	H	F	H	F

SCHEME II Synthesis of polymers IP ~ IVP

standards and therefore have only a relative meaning. The degree of substitution of the mesogenic side groups in the resultant polymers was determined by the integration of the NMR signals presented by aromatic protons in the mesogenic side groups and both methyl and methylene protons in the polymethacrylate backbones. The degree of substitution of about 70% has been achieved for polymers IP and IIP. However both polymers containing eleven methylene units in their mesogenic side groups have showed much lower degrees of substitution, i.e., only 30% for IIIP and 40% for IVP. This could be due to the lesser solubility of the sodium salts of their monomers in NMP. In view of the fact that the monomers are relatively bulky, there is little surprise that complete conversion (i.e., 100% degree of substitution) has not been achieved in any of the polymers listed in Table III.

TABLE III

Molecular Weights, Phase Transitions and Phase Transition Enthalpies for Polymers **IP–IVP**

Polymer	$\overline{Mn}$[a]	$\overline{Mw}$[a]	Degree of substitution[b] (%)	Phase transitions, °C (Corresponding enthalpy changes, Kcal/mru)[c] Heating Cooling
IP	8274	18243	72.7	G 56 N 151 (0.77) 134 (0.51) N 51 G
IIP	6991	22214	70.9	G 34 N 135 (0.36) 126 (0.14) N 33 G
IIIP	3736	7513	30.1	G 22 N 113 (0.19) I I 106 (0.13) N 18 G
IVP	3944	8214	40.3	G 30 N 98 (0.46) I I 97 (0.44) N 27 G

[a] Data determined by GPC using a calibration based on the polystyrene standard.
[b] Data calculated from NMR spectra of polymers.
[c] mru = mole repeating units, G = glassy, N = nematic, I = isotropic.

The thermal transitions and the corresponding enthalpy changes of polymers IP–IVP have been reported in Table III. All four polymers show nematic mesomorphism. Both polymers IP and IIP, respectively, present a glass transition temperature at 56°C and 34°C and an enantiotropic nematic phase. It is no surprise that both isotropization temperature and isotropization enthalpy changes of polymer IP are higher than those of polymer IIP which contain a lateral fluoro-substituent in its mesogenic side groups. Polymer IIIP exhibits a glass transition at 22°C and an enantiotropic nematic phase. It is well documented that in many cases the mesophase formed by a side-chain liquid crystalline polymer is more organized than the one exhibited by the corresponding monomers. As can be seen from Table II, monomer IIIM displays an enantiotropic nematic and a monotropic smectic A phase. However polymer IIIP reveals only an enantiotropic nematic phase. The reason could be due to the very low degree of substitution achieved in this polymer. Figure 4 illustrates the representative DSC traces of polymer IVP. A glass transition presents at 30°C is displayed here, followed by a nematic to isotropic phase transition at 98°C on the heating scan (curve A). The cooling scan (curve B) looks almost identical to the heating scan, except that a few degrees of supercooling are observed for both transitions. Figure 5 presents the nematic texture exhibited by polymer IVP. The wide-angle X-ray diffraction diagram obtained from powder samples of polymers of IIIP and IVP show only a broad reflection at the wide-angle region (associated with the lateral packings), which indicates the formation of a nematic phase.

In conclusion, four new side-chain liquid crystalline polymethacrylates containing fluorinated diphenyldiacetylenic side groups are synthesized. All of the obtained polymers reveal respectively an enantiotropic nematic mesophase. The glass temperature of the obtained polymers decreases as the spacer length increases. Both polymers containing eleven methylene units in their spacers, have achieved only 30–40% degree of substitution and therefore display only an enantiotropic nematic phase.

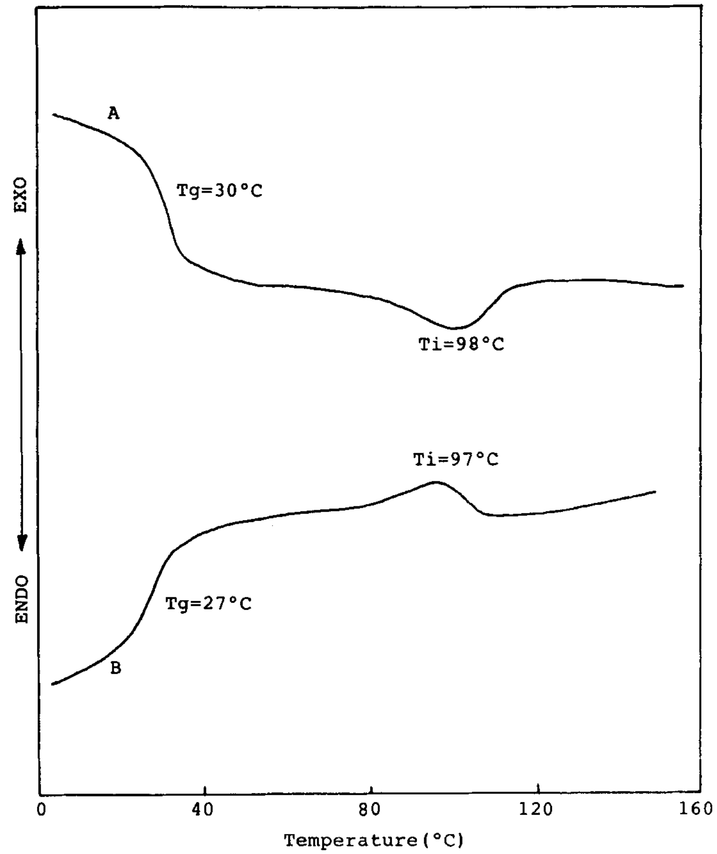


FIGURE 4 DSC thermograms (10°C/min) of polymer IVP: A) Heating scan, B) Cooling scan.

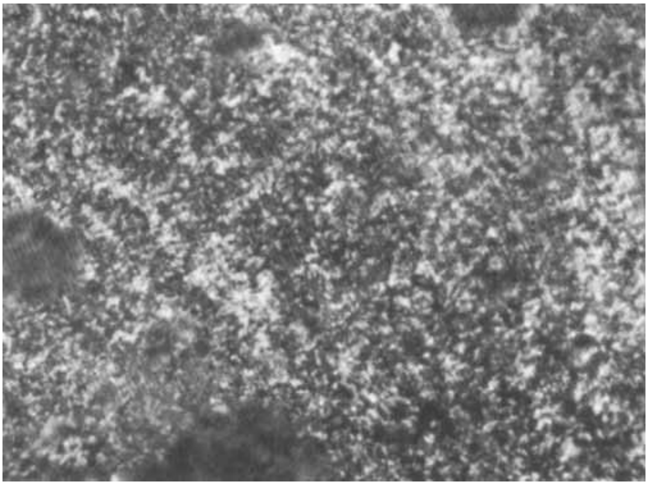


FIGURE 5 Typical nematic texture exhibited at 90°C by polymer IVP. See Color Plate II.

3. EXPERIMENTAL

3.1. Materials

Poly(methacryloyl chloride) was obtained from Polysciences, Inc. (Warrington, PA, USA) and used as received. All other reagents were obtained from Aldrich and also used as received. *N*-Methyl-2-pyrrolidinone used as a solvent in the polymerization reaction was first heated to reflux over calcium hydride and then distilled under nitrogen.

3.2. Techniques

^{1}H NMR spectra (300 MHz) were recorded on a Varian VXR-300 spectrometer. FT–IR spectra were measured on a Nicolet 520 FT–IR spectrometer. Thermal transitions and thermodynamic parameters were determined by using a Seiko SSC/5200 differential scanning calorimeter equipped with a liquid nitorgen cooling accessory. Heating and cooling rates were 10°C min^{-1}. Thermal transitions reported were collected during the second heating and cooling scans. A Carl–Ziess Axiphot optical polarized microscope equipped with a Mettler FP 82 hot stage and a FP 80 central processor was used to observe the thermal transitions and to analyze the anisotropic textures. Preparative gel permeation chromatography (GPC) was run on a Waters 510 LC instrument equipped with a 4410 differential refractometer and a preparative GPC column (22.5 mm x 60 cm) supplied by American Polymer Standard Co. X-ray diffraction measurements were performed with nickel-filtered Cu, Kα radiation with a Rigaku powder diffractometer.

3.3. Synthesis of Monomers and Polymers

The synthesis of fluorinated diphenyldiacetylenic monomers is outlined in Scheme I.

4-Bromo-1-(6-hydroxyhexan-1-yloxy)benzene (1),
4-Bromo-1-(11-hydroxyundecan-1-yloxy)benzene (2)

Both compounds were prepared by etherification of 4-bromophenol with corresponding 6-chlorohexanol or 11-bromoundecanol. The synthesis of compound **1** is described below.

4-Bromophenol (25 gm, 0.144 mol) was added to a stirred solution of KOH (9.3 g, 0.166 mol) KI (0.2 g) in 300 mL of 95% ethanol. 6-Chlorohexanol (2.7 g, 0.166 mol) was added when dissolution was complete. The solution was heated under reflux for 12 h and cooled to room temperature. The solvent was then removed in a rotary evaporater. The residue was washed with water, dried and purified by column chromatography (silica gel, ethyl acetate/*n*-hexane = 1:1 as eluent) to yield 33.2 g (84.5%) of pale yellow liquid. ^{1}H NMR (CDCl$_3$, δ, ppm): 1.25–1.80 (m, 8H, —$(CH_2)_4$—), 3.62 (t, 2H —CH_2OH), 3.96 (t, 2H, —CH_2OPh—), 6.83–7.44 (m, 4 aromatic protons).

4-Ethynyl-1-(6-hydroxyhexane-1-yloxy)benzene (3),
4-Ethynyl-1-(11-hydroxy-undecan-1-yloxy)benzene (4)

Both compounds were synthesized by the same method. The synthesis of compound **3** is described below. To a homogeneous solution of 4-bromo-(6-hydroxyhexane-1-yloxy)benzene (7 g, 0.026 mol) and 2-methyl-3-butyn-2-ol (2.39 g, 0.028 mol) in triethylamine (50 ml) was added bis(triphenylphosphine)palladium (II) chloride (70 mg), cuprous iodide (70 mg) and triphenylphosphine (140 mg). The reaction mixture was heated under reflux for 8 h, cooled to room temperature and treated with saturated ammoniun chloride. The obtained product was extracted with methylene chloride. The collected organic solution was washed with water and dried with anhydrous $MgSO_4$. After removal of the solvent, the remaining solid was purified by column chromatography (silica gel, ethyl acetate: *n*-hexane = 1:1 as eluent) to yield 3.0 g (42.3%) of 1-[(6-hydroxyhexane-1-yloxy)phenyl]-2-(isopropanol)acetylene. The obtained 1-[(6-hydroxyhexane-1-yloxy)phenyl]-2-(isopropanol)acetylene (3.0 g, 0.011 mol) dissolved subsequently in toluene (70 ml) an NaOH (0.877 g, 0.022 mol) aqueous solution was then added. The reaction mixture was heated under reflux for 4 h, cooled and filtered. After the solvent in the filtrate was removed, the crude product was purified by column chromatography (silica gel, ethyl acetate: *n*-hexane = 1:1 as eluent) to yield 1.45 g (60.5%) of white crystals; mp = 51.6°C. ^1H NMR ($CDCl_3$, δ, ppm): 1.25–1.80 (m, 8H, $-(CH_2)_4-$), 3.00 (s, 1H, $-C{\equiv}C-H$), 3.62 (t, 2H, $-CH_2-OH$), 3.96 (t, 2H, $-CH_2-OPh-$) 6.83–7.44 (m, 4 aromatic protons).

4-Fluoro-β,β′-dibromostyrene (5), 3,4-Difluoro-β,β′-dibromostyrene (6)

Both compounds were prepared by the same method. The synthesis of compound **5** is described below.

Triphenylphosphine (64 g, 0.25 mol) was added in portions to a stirred mixture of carbon tetrabromide (83 g, 0.25 mol) and zinc powder (16.25 g, 0.25 mol) in dichloromethane (300 ml). The suspension was stirred for 48 h until a purple color developed. 4-Fluorobenzaldehyde (15.3 g, 0.125 mol) was then added to this mixture and stirring was continued for 3 h. A deep brown color developed as the reaction proceeded and the solution was filtered. After the solvent in the filtrate was removed, the crude product was purified by column chromatography (silica gel, ethyl acetate: *n*-hexane = 1:2 as eluent) to yield 57.3 g (82%) of pale yellow liquid.

2-(4-Fluorophenyl)-bromoacetylene (7), 2-(3,4,-Difluorophenyl)-1-bromoacetylene (8)

Both compounds **7** and **8** were prepared by dehydrobromination of compounds **5** and **6** respectively. The synthetic procedure of compound **7** is given as follows.

4-Fluoro-β,β′-dibromostyrene (27.8 g, 0.1 mol) and potassium *t*-butoxide (11.2 g, 0.1 mol) in toluene (100 ml) were heated at reflux temperature for 8 h. The reaction mixture was cooled to room temperature and filtered. The solvent in the filtrate was removed and the obtained product was purified by column chromatography (silica gel, *n*-hexane as eluent) to yield 16.1 g (81%) of pale yellow liquid.

4-(6-Hydroxyhexan-1-yloxy)-4′-fluorodiphenyldiacetylene (IM), 4-(6-Hydroxyhexan-1-yloxy)-3′,4′-difluorodiphenyldiacetylene (IIM), 4-(11-Hydroxyundecan-1-yloxy)-4′-fluorodiphenyldiacetylene (IIIM),

4-(11-Hydroxyundecan-1-yloxy)-3′,4′-difluorodiphenyldiacetylene (IVM).

The monomers IM–IVM were prepared by the Cadiot–Chodkiewicz coupling of the terminal acetylenes (**3** and **4**) with 1-bromoacetylenes (**7** and **8**) respectively.[13,14] The synthesis of monomer IM is described below.

To an ethanolic solution (30 ml) of compound **3** (0.68 g, 3.12 mmol) containing a large excess of *n*-butylamine (4 ml, 40 mmol) was added a catalytic quantity of cuprous chloride (0.5 g) to reduce any cupric ion formed.

1-(4-Fluorophenyl)-2-bromoacetylene (0.62 g, 3.12 mmol) in 30 ml of ethanol was then added and the reaction mixture was stirred at room temperature for 2 h. The product was isolated by filtration and purified by column chromatography (silica gel, ethyl acetate: *n*-hexane = 1 : 1 as eluent, to yield 0.53 g (51%) of white crystals. The yields and ^{1}H NMR chemical shifts of monomers IM–IVM are recorded in Table 1.

3.4. Synthesis of Polymethacrylates

The synthetic route used to prepare the polymethacrylates IP–IVP is outlined in Scheme II. The polymethacrylates were prepared by etherification of sodium salt derived from monomers with poly(methacryloyl chloride). The detailed synthetic procedure is described below. There was 0.069 g (3 mmol) of freshly cut sodium dissolved in 30 mL of absolute ethyl alcohol. After the sodium was completely dissolved, (3 mmol) of monomer IM was added all at once. The ethyl alcohol was removed by a rotary evaporater to form the sodium salt of monomer IM, and 30 mL of dried *N*-methyl-2-pyrrolidinone (NMP) were added into the same flask. When the sodium salt was completely dissolved, the proper amount of poly(methacryloyl chloride) (3 mmol acid chloride presented in the polymer) in NMP was added to the reaction mixture. The reaction was stirred at 80°C under a nitrogen atmosphere for 5 hr. After this reaction time, absolute ethyl alcohol was added to consume the unreacted acid chloride. The solution was filtered and the polymer was isolated in *n*-hexane, purified by several reprecipitations from THF into *n*-hexane at 60°C to remove the unreacted monomer, further purified by preparative GPC and then dried under vaccum.

Acknowledgement

The authors are grateful to the National Science Council of the Republic of China for financial support of this work (Grant NSC 18-0405-E009-01)

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