

Side-Chain Liquid-Crystalline Polymers with a Limonene-*co*-Methyl Methacrylate Main Chain: Synthesis and Characterization of Polymers with Phenyl Benzoate Mesogenic Groups

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ABSTRACT: A new series of liquid-crystalline polymers with a polymer backbone of limonene-*co*-methyl methacrylate were synthesized and characterized, and the spacer length was taken to be nine methylene units. The chemical structures of the obtained olefinic compound and polymers were confirmed with elemental analysis and proton nuclear magnetic resonance spectroscopy. The thermal behavior and liquid crystallinity of the polymers were characterized with differential scanning calorimetry and polarized optical microscopy. The polymers exhibited thermotropic liquid-crystalline behavior and displayed a glass-transition temperature at 48°C. The

appearance of the characteristic schlieren texture confirmed the presence of a nematic phase, which was observed under polarized optical microscopy. These liquid-crystalline polymers exhibited optical activity. A comparison was also made with polyacrylates and polymethacrylate-based materials. This revealed that the nature of the polymer backbone had a major effect on the liquid-crystalline properties. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4595–4600, 2006

Key words: crystallization; differential scanning calorimetry (DSC); liquid-crystalline polymers (LCP)

INTRODUCTION

During the last 20 years, increasing interest has been devoted to side-chain liquid-crystalline polymers (SCLCPs) because SCLCPs have great potential as new materials for electronic devices, nonlinear optic information storage, and display devices. SCLCPs were reported first by Ringsdorf¹ and Finkelmann and further work was performed by Shibaev and Plate.² The extent to which the mesophase can develop in the systems is influenced by the flexibility of the backbone chain and by whatever mesogen is attached directly to the chain or pushed further away by the insertion of a flexible spacing unit.

Polymer liquid crystals combine the properties of a polymer with those of liquid crystals. These hybrids show the same mesophase characteristics of ordinary liquid crystals yet retain many of the versatile properties of polymers. An SCLCP is often composed of three basic components: a polymer backbone, a mesogenic

unit, and a flexible spacer that bridges the mesogenic unit and the polymer backbone. The properties may be affected by variations in the chemical structures of these components.

In this series, different SCLCPs have been synthesized by the variation of the backbone, such as polysiloxanes,^{3–7} polyacrylates,⁸ polymethacrylates,⁹ polyacetylenes,¹⁰ polyphosphazenes,^{11,12} polyepichlorohydrins,¹³ poly(phenylene oxide),¹⁴ and polysulfones.¹⁵ Among these, the polysiloxane backbone, because of its low glass-transition temperature (T_g), is particularly favored; it can permit the formation of a mobile mesophase at room temperature, but the use of these polymers in electrooptic display devices is limited because of their high local viscosities even in the nematic state.

In this respect, the largest set of such data exists for polymers containing 4-cyanobiphenyl as the mesogenic unit. This has been attached to a wide range of polymer backbones: poly(vinyl ether),^{16–18} polystyrene,^{19,20} polynorbornene, polyacrylates, polysiloxanes,^{21–23} and polymethacrylates.²⁴

In the synthesis of SCLCPs, the backbone plays an important role. It is the flexibility of the backbone that matters; backbones such as polyacrylates, polymethacrylates, and polysiloxanes are quite flexible and possess low T_g values. Similarly, copolymers of terpenes with vinyl monomers also show low T_g values, but research on their behavior as backbones is still in its infancy, with no examples of such poly-

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mers being documented in the literature. This is the first report highlighting terpene copolymers as new backbones because terpene copolymers have been reported to have low T_g values.

The synthesis and characterization of terpene copolymers with vinyl monomers constitute a recent area of green chemistry. Terpene polymerization was initiated by Roberts and Day²⁵ when they polymerized α,β -pinene and limonene with a Friedel–Crafts catalyst. Terpenes have been introduced as economic monomers for the synthesis of homopolymers and copolymers with functional groups and optical activity. The synthesis and characterizations of copolymers of terpenes with vinyl monomers have been reported by this laboratory.^{26–33} A search of the literature has revealed that liquid-crystalline polymers (LCPs) have been prepared by the variation of the mesogenic group or polymer backbone. These have not been introduced into a mesogenic group or used as a backbone for the synthesis of SCLCPs. Therefore, it is worthwhile to examine the copolymers of terpene as backbones.

In this article, we report the synthesis and characterization of a new LCP with a polymer backbone of limonene-*co*-methyl methacrylate attached via polymethylene spacers to a phenyl benzoate mesogenic group. A comparison is also made with LCPs of terpene and corresponding polyacrylate and methacrylates. These LCPs show liquid-crystalline properties with a nematic phase.

Furthermore, the thermotropic liquid-crystalline properties were studied with differential scanning calorimetry (DSC) and polarized optical microscopy (POM).

EXPERIMENTAL

Materials

4-Hydroxybenzoic acid (Acros), 4-hydroxyphenol (Lancaster), 11-bromo-1-undecene (Lancaster), and thionyl chloride (Merck) were used as received. Triethylamine was refluxed over potassium hydroxide and distilled. Azobisisobutyronitrile (AIBN) was recrystallized twice by methanol. Other reagents and solvents were used without further purification.

Instrumental analysis

The proton nuclear magnetic resonance (¹H-NMR) spectrum was recorded with a Varian 100HA JEOL LA 400 spectrophotometer with CDCl₃ as the solvent and tetramethylsilane as the internal reference. The Fourier transform infrared (FTIR) spectrum was recorded with a PerkinElmer 599B with KBr pellets. Thermal transitions were measured with a PerkinElmer DSC-7 differential scanning calorimeter at heating and cooling rates of 10°C/min. The anisotropic textures were observed

with a Censico optical polarized microscope in conjunction with an Instec HS1 hot stage.

Synthesis of the monomer and copolymer

The vinyl-terminated mesogen, containing the phenyl benzoate mesogenic core, was prepared according to the procedure reported by Itoh and Lenz³⁴ (see Scheme 1).

ANAL. Calcd: C, 77.22%; H, 9.07%. Found, C, 77.2%; H, 8.09%. Yield: 5.86 g (12.6 mmol, 51%).

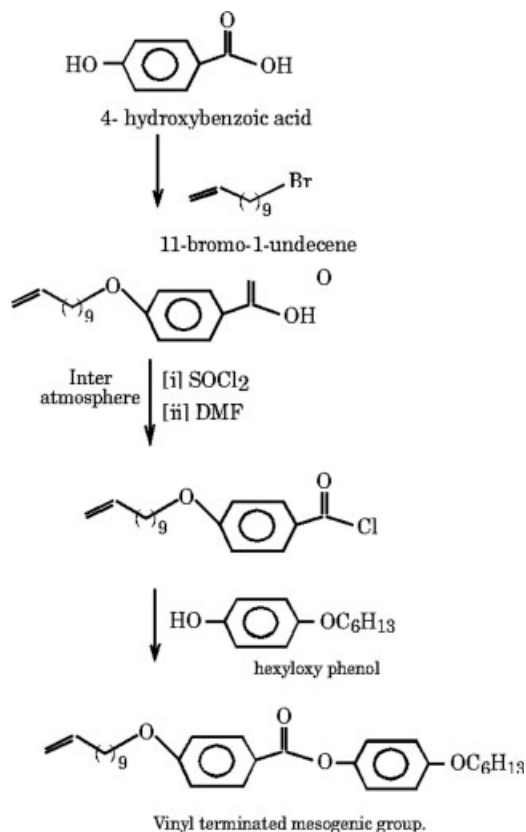
Characterization of the mesogen

Nuclear magnetic resonance spectroscopy (Fig. 1)

¹H-NMR (CDCl₃, δ , ppm): 0.92 (t, 3H, CH₃), 1.32–2.05 (m, 24H, CH₂), 3.87–4.04 (t, 4H, OCH₂), 5.00 (m, 2H, CH₂=), 5.82 (m, 1H, =CH), 6.74–7.26 (aromatic protons).

POM

The mesogen formed liquid-crystalline phases.³⁴ Upon cooling from the isotropic state at 81°C, the mesogen exhibited a nematic droplet texture, which was followed by Schlieren texture formation at 79.7°C; then, a mosaic texture appeared at 78°C, and finally a homeotropic texture formed upon further cooling.



Scheme 1

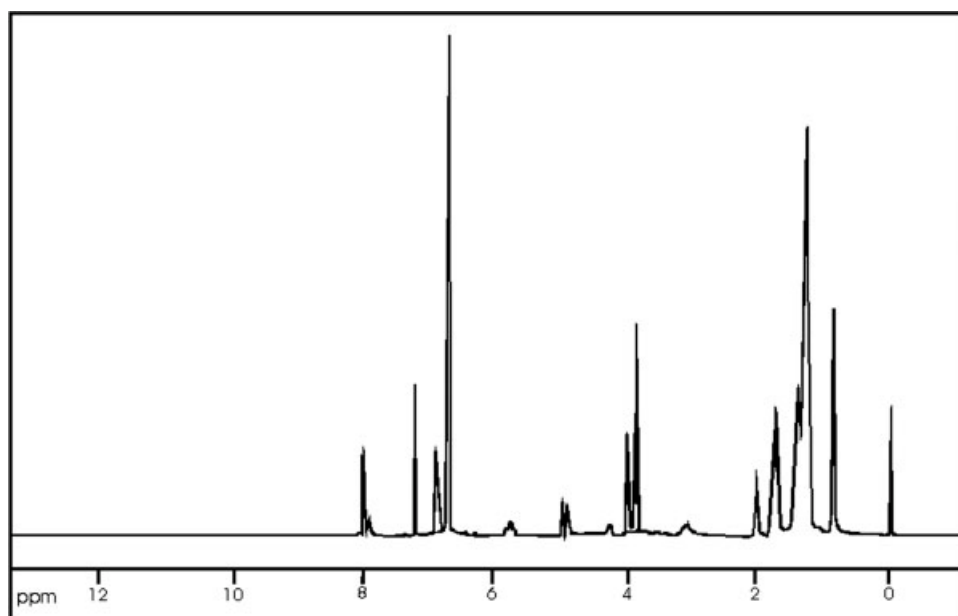
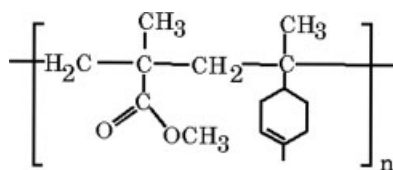


Figure 1 $^1\text{H-NMR}$ spectrum of the mesogen.

Synthesis of the copolymer

The synthesis and general characterization of the copolymer of limonene with methyl methacrylate (MMA) have been reported elsewhere.³⁵ Briefly, a solution containing limonene, MMA, and BPO (benzoyl peroxide) as the initiator in xylene were polymerized for 1 h at $80 \pm 0.1^\circ\text{C}$ under an inert atmosphere of nitrogen. The copolymer was precipitated in methanol and dried to a constant weight. The structure of the copolymer of limonene with MMA was as follows:



Limonene-*co*-methyl methacrylate copolymer characterization

FTIR spectroscopy³⁵

The FTIR spectrum of the copolymer(s) showed the characteristic frequencies at 2951.40 cm^{-1} due to the C—H stretching band of the aromatic ring of limonene and at 1732.40 cm^{-1} due to the $-\text{OCH}_3$ group of MMA (Fig. 2).

Nuclear magnetic resonance spectroscopy³⁵

The $^1\text{H-NMR}$ spectrum of the copolymer showed singlets at $\delta = 5.3\text{--}5.6$ and $\delta = 3.8\text{--}4.1$ due to trisubstituted olefinic protons (double bond between C-1 and C-2) of limonene and $-\text{OCH}_3$ of MMA, respec-

tively. The disappearance of the peak at $\delta = 4.6$ indicated that external double bonds were involved in the bond formation with MMA (Fig. 3).

Copolymer composition and values of the reactivity ratios³⁵

The relative peak areas of methoxy and trisubstituted olefinic protons of MMA and limonene at $\delta = 3.8\text{--}4.1$ and $\delta = 5.3\text{--}5.6$, respectively, in the copolymers were used to calculate the copolymer composition. The reactivity ratios for MMA ($r_1 = 0.07$) and limonene ($r_2 = 0.012$) were calculated with the Kelen-Tüdös method. The product of $r_1 r_2$ was nearly zero, which was a sign of alternating copolymerization. Therefore, the possibility of coexistence of graft, block, and random copolymers was ruled out.

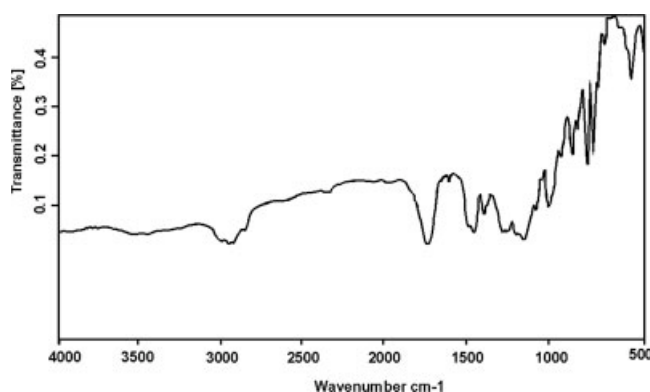


Figure 2 IR spectrum of the limonene-*co*-methyl methacrylate copolymer.

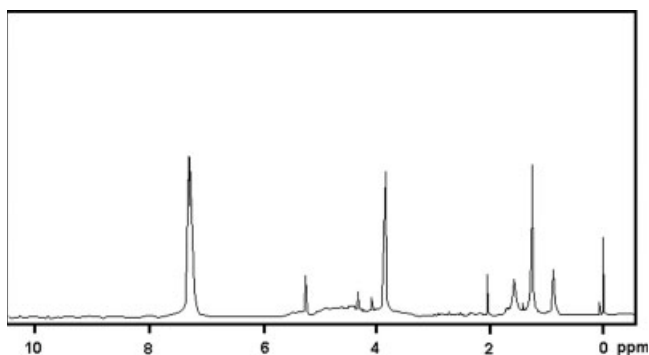


Figure 3 $^1\text{H-NMR}$ spectrum of the limonene-co-methyl methacrylate copolymer.

Synthesis of the LCPs

The polymerization was carried out in dimethylformamide (DMF) at $80 \pm 0.1^\circ\text{C}$ for 18 h under an inert atmosphere of nitrogen with 6.15 mmol of (limonene-co-methyl methacrylate)_{base} M_r , 0.160 mmol of the mesogen, and 0.121 mmol of AIBN. The LCPs were precipitated in methanol and vacuum-dried until a constant weight was obtained (Scheme 2).

RESULTS AND DISCUSSION

$^1\text{H-NMR}$

The $^1\text{H-NMR}$ spectrum of the polymer (Fig. 4) showed multiplets at 8.01–7.50, a singlet at 5.3, and triplets at 0.89 and 1.25–2.17 ppm corresponding to aromatic pro-

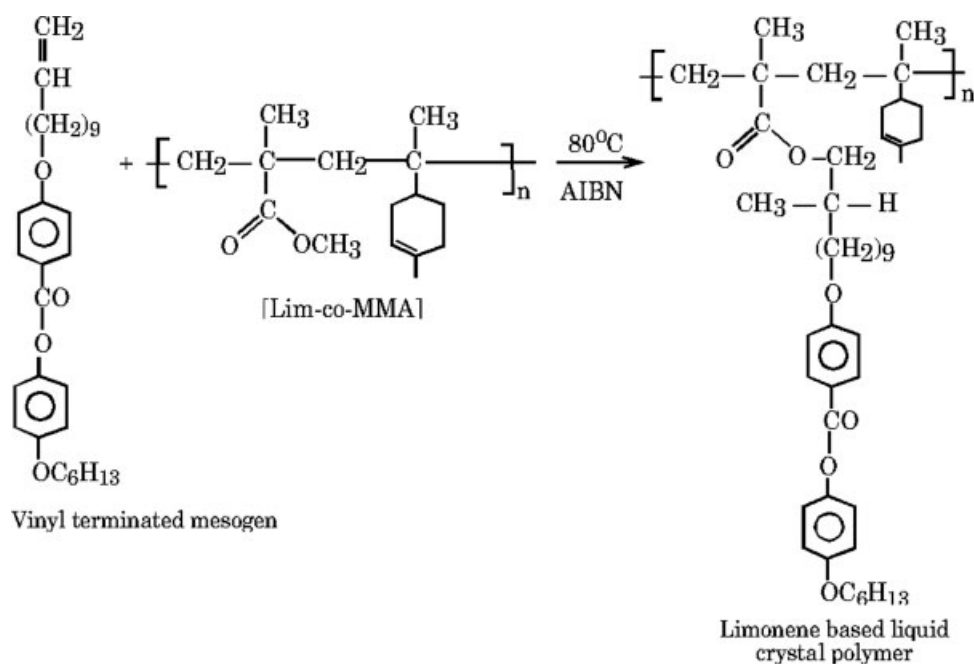
tons, olefinic protons present in limonene, and methyl and methylene protons, respectively.

Thermal and texture analysis

Liquid-crystalline phases are normally birefringent and show periodic structures or other textures under cross-polarizers. The color in these images is caused by the spatial periodicity of the order of the wavelength of light and interference of the transmitted polarized light. Typical textures include nematic and smectic textures caused by discontinuities in the orientation.

In general, the polymer backbone, the rigidity of the mesogenic unit, and the length of the flexible spacer have major effects on the phase behavior of SCLCPs. The polysiloxane polymer backbones account for the majority of SCLCPs because they show mesomorphic properties at moderate temperatures. The flexible spacer plays a vital role in this because it decouples to some extent the ordering tendencies of the mesogenic unit from those of the backbones to adopt random coil conformations. Its presence endows the polymer with a unique duality of properties.

The LCPs were semicrystalline at room temperature but showed liquid crystallinity at higher temperatures. The thermotropic mesomorphism of the polymer was investigated with a combination of DSC and POM. The phase-transition temperatures, being relevant thermodynamic parameters, were determined by DSC measurements, and the liquid-crystalline behavior was elucidated with POM. The polymer



Scheme 2

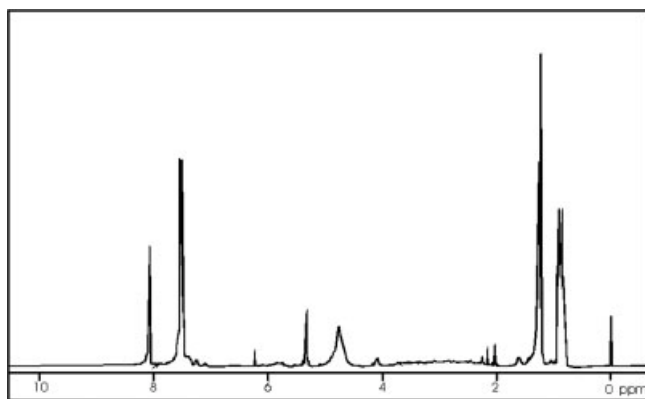


Figure 4 ^1H -NMR spectrum of an LCP.

was previously heated to a temperature higher than the isotropization point to channel any effect of the former thermal history on the phase transitions.

The polymer exhibited an enantiotropic nematic mesophase (Fig. 5). The first heating scan exhibited T_g at 48°C and a melting endotherm at 97°C , which was followed by a nematic mesophase that underwent isotropization at 119°C . Under POM, the nematic phase displayed a characteristic schlieren texture for the nematic mesophase (Fig. 6). The first cooling and second heating scans were almost identical and displayed T_g at 46 and 47°C , respectively, whereas the isotropization temperatures were 114 and 120°C , respectively. From the first heating scan of DSC, it seems that the polymer underwent side-chain crystallization, but this was not confirmed by the first cooling and second heating. According to the literature, a phenyl benzoate based mesogenic group generally does not undergo side-chain crystallization.³⁴

A comparison³⁶ of the liquid-crystalline polyacrylates with the corresponding polymethacrylates showed that T_g of the polyacrylates ($T_g = 25\text{--}78^\circ\text{C}$) was lower than T_g of the polymethacrylate series ($T_g = 47\text{--}97^\circ\text{C}$). This tendency was expected because poly(methyl methacrylate) (PMMA) has a T_g value of 105°C , whereas poly(methyl acrylate) (PMA) has a T_g value of 10°C . It is generally assumed that the T_g values of liquid-crystalline polyacrylates are higher than that of PMA, whereas the T_g values of the corresponding polymethacrylates are lower than that of PMMA. In this case, T_g of the LCP was 48°C , which was quite low; the T_g values of the terpene polymers^{37,38} were also low ($35^\circ\text{C} \leq T_g < 100^\circ\text{C}$).

A comparison was also made of the polyacrylate and polymethacrylate LCPs with six spacer units and a phenyl benzoate mesogenic group because no data were available for nine spacer units for the analogous mesogenic group. The phase transitions of the liquid-crystalline polyacrylate³⁶ were g 20 s 130°C i, whereas for the analogous mesogenic group, the phase transitions of the liquid-crystalline polymethacrylates^{36,39}

were g 47 s 115°C i (where g is glass transition, s is smectic and i is isotropic).

In this study, poly(limonene-*co*-methyl methacrylate) was used as a backbone instead of polymethacrylate. The phase transitions observed for these LCPs were quite similar to those of polymethacrylate, but these polymers showed a schlieren texture for the nematic phase under hot-stage polarized light microscopy. The phase transitions shown by limonene-*co*-methyl methacrylate LCPs were g 48 n 119°C i (where n is nematic).

It is widely believed that the polymer backbone has a major effect on the liquid-crystalline behavior. The aforementioned data are in good agreement with that idea. Besides their phase behavior, these polymers are also optically active. The general prediction that the introduction of a spacer will lead to the formation of liquid-crystalline phases with the properties of low-molecular-weight liquid crystals has also been verified. On the other hand, the complete decoupling model, in which the liquid-crystalline behavior is governed only by the mesogenic group and T_g is governed only by the main chain, has to be modified.

CONCLUSIONS

We synthesized a new LCP with limonene-*co*-methyl methacrylate as the backbone and a phenyl benzoate mesogenic group attached to the polymer backbone via a polymethylene spacer. A comparison of the thermal and liquid-crystalline properties of polymethacrylates and poly(limonene-*co*-methyl methacrylate)-based SCLCPs containing phenyl benzoate mesogenic

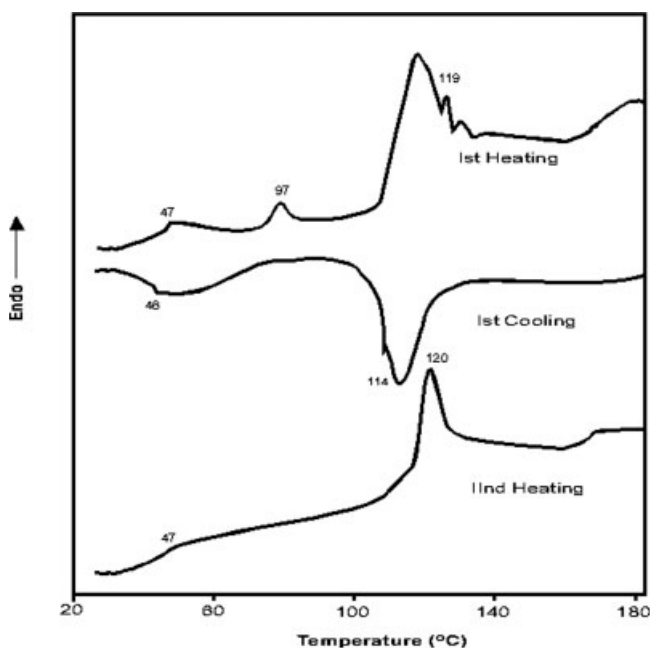


Figure 5 DSC curves for the polymer upon the first heating, first cooling, and second heating (heating rate = $10^\circ\text{C}/\text{min}$).

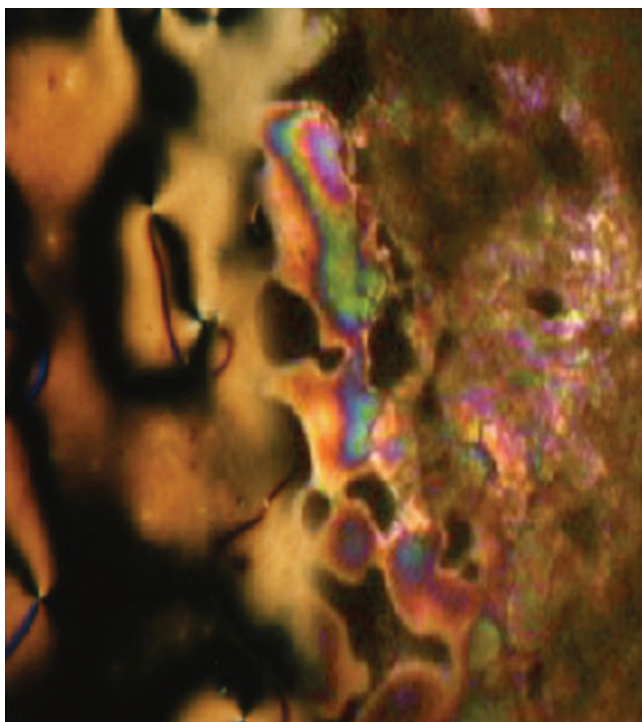


Figure 6 Polarizing optical micrograph displayed by the LCP nematic phase. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

groups showed similar transition behaviors but different mesophases. The polymer was semicrystalline but formed a liquid-crystalline phase at temperatures above T_g . The LCPs were optically active and showed T_g at 48°C.

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References

- Finkelmann, H.; Happ, M.; Portugal, M.; Ringsdorf, H. *Makromol Chem* 1978, 179, 2541.
- Shibaev, V. P.; Plate, N. A. *Adv Polym Sci* 1984, 60, 173.
- Finkelmann, H.; Rehage, G. *Makromol Chem Rapid Commun* 1980, 1, 31.
- Finkelmann, H.; Rehage, G. *Makromol Chem Rapid Commun* 1980, 1, 733.
- Jones, B. A.; Bradshaw, J. S.; Nishioka, M.; Lee, M. L. *J Org Chem* 1984, 49, 4947.
- Mauzac, M.; Hardouin, F.; Richard, H.; Achard, M. F.; Sigaud, G.; Gasparoux, H. *Eur Polym J* 1986, 22, 137.
- Richard, H.; Mauzac, M.; Nguyen, H. T.; Sigaud, G.; Achard, M. F.; Hardouin, F.; Gasparoux, H. *Mol Cryst Liq Cryst* 1988, 155, 141.
- Portgull, M.; Ringsdorf, H.; Zentel, R. *Makromol Chem* 1982, 183, 2311.
- Paleos, C. M.; Margomonou, L. G.; Filippakis, S. E.; Mallaris, A. *J Polym Sci Polym Chem Ed* 1982, 20, 2267.
- Lam Jacky, W. Y.; Kong, X.; Dong, Y.; Cheuk, K. K. L.; Xu, K.; Tang, B. Z. *Macromolecules* 2000, 33, 5027.
- Kim, C.; Allock, H. R. *Macromolecules* 1987, 20, 1726.
- Singler, R. E.; Willingham, R. A.; Lenz, R. W.; Furukawa, A.; Finkelmann, H. *Macromolecules* 1987, 20, 1727.
- Pugh, C.; Percec, V. *Polym Bull* 1986, 16, 521.
- Pugh, C.; Percec, V. *Polym Bull* 1986, 16, 513.
- Braun, D.; Herr, R. P.; Arnold, N. *Makromol Chem Rapid Commun* 1987, 8, 359.
- Percec, V.; Lee, M. *Macromolecules* 1991, 24, 2780.
- Percec, V.; Lee, M. *Macromolecules* 1991, 24, 1017.
- Percec, V.; Lee, M.; Ackerman, C. *Polymer* 1992, 33, 703.
- Imrie, C. T.; Karasaz, F. E.; Attard, G. S. *J Macromol Sci Pure Appl Chem* 1994, 31, 1221.
- Imrie, C. T.; Karasaz, F. E.; Attard, G. S. *Macromolecules* 1993, 26, 3803.
- Percec, V.; Lee, M. *Macromol Sci Chem* 1991, 28, 651.
- Hsu, C. S.; Percec, V. *Polym Bull* 1987, 18, 91.
- Nestor, G. N.; White, M. S.; Gray, G. W.; Lacey, D.; Toyne, K. J. *Makromol Chem* 1987, 188, 2759.
- Kostromin, S. G.; Sinityn, V. V.; Talroze, R. V.; Shibaev, V. P. *Polym Sci USSR* 1984, 26, 370.
- Roberts, W. J.; Day, A. R. *J Am Chem Soc* 1950, 72, 1226.
- Pandey, P.; Srivastava, A. K. *Ind J Chem Technol* 2002, 10, 192.
- Sharma, S.; Srivastava, A. K. *J Polym Plast Technol Eng* 2003, 42, 485.
- Sharma, S.; Srivastava, A. K. *J Appl Polym Sci* 2004, 91, 2343.
- Shukla, A.; Srivastava, A. K. *High Perform Polym* 2003, 15, 243.
- Yadav, S.; Srivastava, A. K. *J Polym Plast Technol Eng* 2004, 43, 1229.
- Shukla, A.; Srivastava, A. K. *Polym Adv Technol* 2004, 15, 445.
- Shukla, A.; Srivastava, A. K. *J Appl Polym Sci* 2004, 92, 1134.
- Sharma, S.; Srivastava, A. K. *Eur Polym J* 2004, 40, 2235.
- Itoh, M.; Lenz, R. W. *J Polym Sci Part A: Polym Chem* 1992, 30, 803.
- Sharma, S.; Srivastava, A. K. *J Macromol Sci Pure Appl Chem* 2004, 40, 593.
- Portugall, M.; Ringsdorf, H.; Zentel, R. *Makromol Chem* 1982, 183, 2311.
- Sharma, S.; Srivastava, A. K. *Ind J Chem Technol* 2005, 12, 62.
- Shukla, A.; Srivastava, A. K. *Polym Plast Technol Eng* 2002, 41, 777.
- Finkelmann, H.; Ringsdorf, H.; Wendorff, J. H. *Makromol Chem* 1978, 179, 273.