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Synthesis and characterization of 6-[4-(trans -4-pentylcyclohexyl)phenoxy]hexyl acrylate homopolymer and copolymers

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Online publication date: 11 November 2010

To cite this Article Sainath, A. V. Sesha , Yonetake, K. , Aita, T. , Inoue, T. and Koyama, K.(2003) 'Synthesis and characterization of 6-[4-(trans -4-pentylcyclohexyl)phenoxy]hexyl acrylate homopolymer and copolymers', Liquid Crystals, 30: 5, 565 — 570

To link to this Article: DOI: 10.1080/0267829031000105079
URL: http://dx.doi.org/10.1080/0267829031000105079

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LIQUID CRYSTALS, 2003, VOL. 30, NO. 5, 565–570

Synthesis and characterization of 6-[4-(*trans*-4-pentylcyclohexyl)phenoxy]hexyl acrylate homopolymer and copolymers

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(*Received 18 July 2002; accepted 20 January 2003*)

The compound 6-[4-(*trans*-4-pentylcyclohexyl)phenoxy]hexyl acrylate (**2**) was prepared and homopolymerized. The block copolymer and copolymer of **2** with styrene were synthesized by photopolymerization and solution techniques, respectively. These polymers were characterized by IR and ^{1}H NMR spectra and size exclusion chromatography. Polarizing optical microscopy (POM) and X-ray diffraction (XRD) studies revealed that these polymers exhibited smectic A (SmA) phases. POM showed that the homopolymer showed a higher order SmA phase than did the block copolymer and copolymer. After magnetically forced alignment the samples exhibited similar optical texture but the domain size of the liquid crystalline phase increased. Differential scanning calorimetry, POM and XRD data suggest that the SmA domain size decreased in the order hompolymer > block copolymer > copolymer.

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1. Introduction

Side chain liquid crystalline polymers (SCLCPs) have attracted much attention due to their potential application in numerous areas, especially in the field of electronics and optical materials [1–12]. Many SCLCPs, and their copolymers with amorphous or semi-crystalline segments, have been synthesized in recent years, since many variations on the structures of SCLCPs are possible. Copolymers bearing amorphous or semi-crystalline and liquid crystalline (LC) segments can exhibit different morphological behaviours; moreover copolymers have created new possibilities for fabricating high modulus and high strength polymeric materials. Recently LC elastomers have been found to be useful as artificial muscle materials [13, 14].

Adams and Gronski reported, for the first time, the synthesis of an LC side chain block copolymer, using two successive polymer-analogous reactions on a styrene/butadiene block copolymer, that exhibited LC behaviour as well as phase separation [15]. Block and graft LC polymers could be made via living polymerizations [16, 17]. LC side chain block copolymers were prepared consisting of a non-LC block and LC block by using GTP [18] and photopolymerization [19].

Arnold and coworkers reported on the synthesis of LC block copolymers consisting of an amorphous A-block and an LC block. Their results showed, in the case of a lamellar structure, a dependence of the LC behaviour on the type of monomer in the A-block. They worked on varying the block length ratios for the AB block copolymer to obtain different volume ratios of the two block parts and their associated change in morphology [20, 21]. First the time, the influence of triblock (amorphous/LC/amorphous) copolymer and amorphous/LC block morphology and microstructure on phase behaviours was reported by Adams *et al.* [22].

In this study, we report the variation of mesomorphic properties in the presence of a non-LC material component of a liquid crystalline polymer, and compare the thermal properties and morphology of homopolymer, LC–non-LC–LC triblock copolymer and copolymer by thermal analysis, polarizing optical microscopy (POM) and X-ray diffraction (XRD).

2. Experimental

2.1. *Material*

Tetraethylthiuram disulfide (TD), tetrahydrofuran (THF), α,α′-azobisisobutyronitrile (AIBN), *p*-(*trans*-4-pentylcyclohexyl)phenol and methanol were purchased from Kanto Chemical Co., Inc. 6-Bromo-1-hexanol and

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Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2003 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/0267829031000105079

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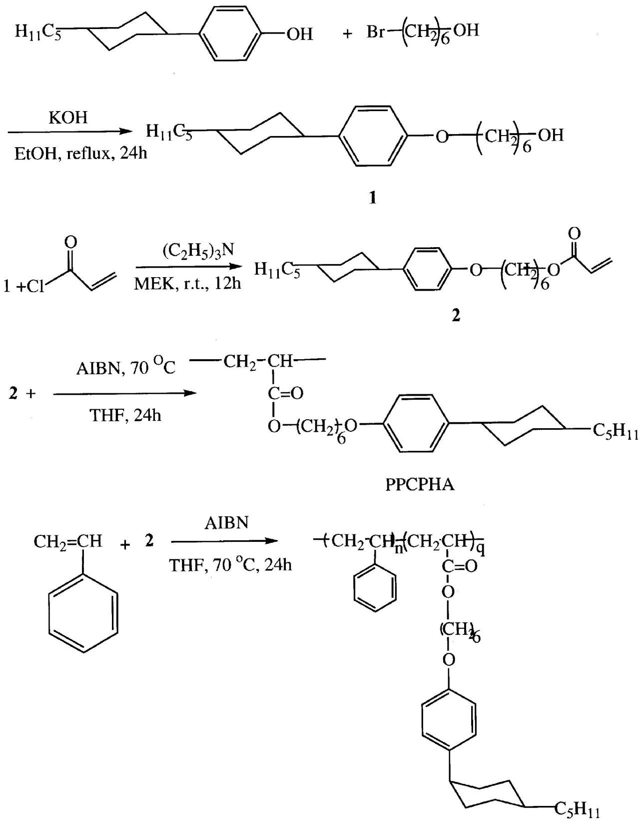
acryloyl chloride were obtained from Acrocs Organics; styrene, methylethylketone (MEK) and triethylamine (TEA) were from Wako. Styrene was distilled under reduced pressure to remove the inhibitor. All reagent grade materials used in this study were used as received.

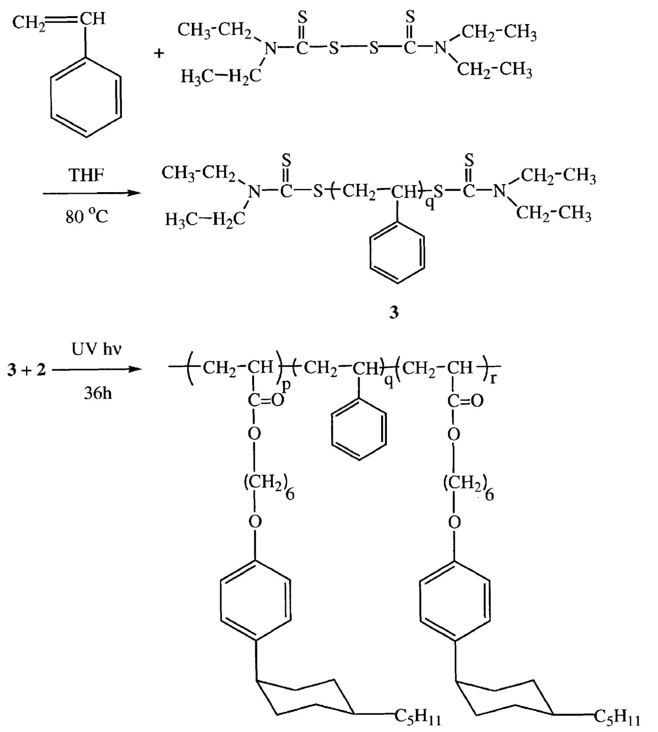
Synthetic methods are illustrated in schemes 1 and 2.

2.1.1. *4-(6-Hydroxyhexyloxy)-4-(trans-4-pentylcyclohexyl)-phenyl 1*

A mixture of *p*-(*trans*-4-pentylcyclohexyl)phenol (6.35 g, 0.026 mol) and KOH (1.46 g, 0.026 mol) in ethanol (30 ml) was heated under reflux for 15 min. To this solution was added dropwise a solution of 6-bromo-1-hexanol (5.0 g, 0.028 mol) in ethanol (5 ml) at room temperature. After addition, reflux was continued for 24 h, and the solvent was evaporated. The residue was extracted with diethyl ether, and the ether layer washed with aqueous saturated sodium carbonate solution and dried over anhydrous magnesium sulfate. The solvent was evaporated to produce a white solid which was purified by column chromatography; yield 61%. T_m: 86–89.8°C. IR (KBr): 3394 (OH), 2923 and 2854 (CH), and 1250 cm^{-1} (aryl C–O). ^{1}H NMR ($CDCl_3$): δ 7.0 (2d, Ar–H, 4H), 3.9 (t, –O–CH_2, 2H), 3.7 (q, –CH_2–O–, 2H), 2.4 (m, Ar–cyclohexane CH, 1H), 0.95–1.95 (m, normal and cyclohexane –CH_2 and CH, 25H) and 0.9 (t, –CH_3, 3H). Anal: calc for $C_{23}H_{38}O_2$ C 79.71, H 11.05; found C 79.86, 11.36%.



Scheme 1. Preparation of compound **1**, compound **2**, homopolymer and copolymer.



Scheme 2. Preparation of block copolymer.

2.1.2. *6-[4-(trans-4-pentylcyclohexyl)phenoxy]hexyl acrylate 2*

A solution of acryloyl chloride (0.5 ml, 0.006 mol) was added dropwise to an ice-cooled solution of compound **1** (1.5 g, 0.00435 mol) and TEA (0.84 ml, 0.006 mol) in MEK. After addition, the mixture was stirred for 12 h at room temperature, and the solvent was evaporated. The residue was extracted with diethyl ether, and the ether layer was washed with water and dried over anhydrous magnesium sulfate. The solvent was evaporated. Recrystallization from methanol at 0°C gave white needles; yield 70%. T_m: 38–39.5°C. IR (KBr): 2916 and 2854 (CH), 1712 (ester C=O), 1620 (CH_2=CH), and 1250 cm^{-1} (aryl C–O). ^{1}H NMR ($CDCl_3$): δ 8.7 (2d, Ar–H, 4H), 6.1 (m, CH_2=CH–, 3H), 4.15 (t, –O–CH_2, 2H), 3.93 (t, –CH_2–O–, 2H), 2.2 (m, Ar–cyclohexane CH, 1H), 0.95–1.95 (m, normal and cyclohexane –CH_2 and CH, 25H) and 0.89 (t, –CH_3, 3H). Anal: calcd for $C_{26}H_{40}O_3$ C 77.95, H 10.07; found C 77.68, H 10.43%.

2.1.3. *Homopolymerization of 6-[4-(trans-4-pentylcyclohexyl)phenoxy]hexyl acrylate (PPCPHA)*

Compound **2** (0.9 g) was polymerized as a solution in THF (3 ml) using AIBN (0.011 g) as an initiator at 70°C under argon atmosphere. The polymer was isolated after polymerization for 24 h by adding the reaction solution to excess of methanol; it was purified by reprecipitation from THF solution on addition to methanol, and dried under vacuum. The yield of PPCPHA was about 80%. IR (KBr): 2924 and 2854 (CH), 1736 (ester C=O) and 1250 cm^{-1} (aryl C–O). ^{1}H NMR (CDCl$_3$): δ 7.0 (Ar–H, 4H), 4.0 (–O–CH$_2$, 2H), 3.86 (–CH$_2$–O–, 2H), 2.2 (Ar–cyclohexane CH and backbone –CH, 2H), 0.95–1.95 (normal and cyclohexane –CH$_2$, –CH and backbone –CH$_2$, 27H) and 0.89 (–CH$_3$, 3H).

2.1.4. *Synthesis of copolymer*

Compound **2** (1.8 g, 0.0045 mol) and styrene (0.239 g, 0.0023 mol) were copolymerized as a solution in THF using AIBN as initiator at 70°C under argon atmosphere. The copolymer was isolated after polymerization for 24 h by adding the reaction solution to excess of methanol; it was purified by reprecipitation from THF solution on addition to methanol, and dried under vacuum. The yield of copolymer was about 70%. IR (KBr): 2916 and 2846 (CH), 1728 (ester C=O) and 1242 cm^{-1} (aryl C–O). ^{1}H NMR (CDCl$_3$): δ 6.6–7.2 (Ar–H, 9H), 3.9 (–O–CH$_2$ and –CH$_2$–O–, 4H), 2.4 (Ar–cyclohexane CH and backbone –CH, 3H), 0.95–2.0 (normal and cyclohexane –CH$_2$, –CH and backbone –CH$_2$, 29H) and 0.89 (–CH$_3$, 3H).

2.1.5. *Synthesis of telechelic polystyrene (TD-PS)*

1 g of TD and 15 ml of styrene were dissolved in 15 ml of THF in a stainless steel reactor. The solution was purged with argon for 20 min, and the reactor was immersed in a water bath at 80°C. After polymerizing for 3 h, the polymer was recovered by precipitation on addition to a large excess of methanol and drying. The resulting polymer was purified twice by dissolving in THF and reprecipitating with methanol. The yield was about 20%. The functionality of the end groups was determined by UV analysis as described previously [23, 24]. GPC data: M_n: 4522, M_w/M_n: 1.53. The functionality was 1.9.

2.1.6. *Synthesis of block copolymer*

TD-PS (0.3 g) and **2** (2.5 g) were dissolved in THF (8 ml) in a pear-shaped pyrex flask. A 140 W Hanovia medium pressure mercury lamp was set at an 8 cm distance from the reaction solution. The photopolymerization was continued for 24 h after which the solution was poured into a large excess of methanol to precipitate the polymer. The block copolymer was purified three times by dissolving in THF and reprecipitating with methanol. IR (KBr): 2924 and 2854 (CH), 1736 (ester C=O) and 1250 cm^{-1} (aryl C–O). ^{1}H NMR (CDCl$_3$): δ 6.2–7.2 (Ar–H, 9H), 4.0 (–O–CH$_2$, 2H), 3.9 (–CH$_2$–O–, 2H), 2.4 (Ar–cyclohexane CH and backbone –CH, 3H), 0.95–1.95 (normal and cyclohexane –CH$_2$, –CH and backbone –CH$_2$, 29H) and 0.9 (–CH$_3$, 3H).

2.2. *Characterization*

FTIR spectra were measured on a Horiba FT-210 spectrophotometer at a resolution of 2 cm^{-1} for KBr specimens at room temperature. ^{1}H NMR spectra were recorded in CDCl$_3$ on a JEOL EX 270 spectrometer. Thermal analyses were performed by a differential scanning calorimeter, Perkin-Elmer DSC7 at a heating rate of 20°C min^{-1} under nitrogen, and followed by cooling to −30°C at a rate of 10°C min^{-1}.

Thermogravimetry data were recorded on a Seiko SSS 5000 TG-DTA 220 thermal analyser at a heating rate of 10°C min^{-1}. Optical texture of the samples were examined under nitrogen using a polarizing optical microscope equipped with a hot stage (Linkam Co., TH-600RMS).

X-ray diffraction (XRD) experiments were carried out with a RAD-rA diffractometer, Rigaku Denki Co. Ltd. Nickel-filtered CuK$_\alpha$ radiation was employed. XRD profiles were measured by a scintillation counter system with a 1.0 mm diameter pinhole collimator and 1 × 1° receiving slit using a step scanning method (0.05° steps every 4 s).

Table. Characteristics of the hompolymer, block copolymer, and copolymer.

				DSC^c		TGA		
Sample	M_n^{a}	M_w/M_n^{a}	**2**^{b} content/mol %	T_m/°C	ΔH/J g^{-1}	T_{d5}^{d}/°C	T_{d10}^{e}/°C	Layer spacing^f/nm
Homopolymer	10 890	1.61	100	119	11.8	356	373	2.68
Block copolymer	7303	1.60	60.58	108	10.5	339	362	2.99
Copolymer	8815	2.10	58.74	59	1.4	340	361	2.85

[a] Obtained from GPC using polystyrene standards in THF.
[b] Calculated from ^{1}H NMR spectra.
[c] Obtained from 2nd heating.
[d] Temperature of 5% weight of polymer decomposition.
[e] Temperature of 10% weight of polymer decomposition.
[f] Calculated from XRD data.

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Typical magnetic field processing was as follows. The samples were heated to their isotropic melt states, and then a magnetic field of 2.4 T was applied to the samples during cooling using Electromagnet TM-WV8615MRC-156 (Tamagawa Co.). The cooling rate was 1°C min^{-1}.

3. Results and discussion

Compound **2** was prepared in two steps as outlined in scheme 1. In the first step, **1** was prepared by reacting 6-bromo-1-hexanol with *p*-(*trans*-4-pentylcyclohexyl)-phenol in the presence of KOH in ethanol. Compound **2** was obtained by reacting **1** with acryloyl chloride in the presence of triethylamine in MEK at 0–5°C. The homopolymer, block copolymer and copolymer of **2** with styrene were synthesized as outlined in schemes 1 and 2. The polymers were characterized by FTIR and ^{1}H NMR. The FTIR spectra of the polymers show strong characteristic bands at about 1736 cm^{-1} due to ester C=O stretchings, around 1605 cm^{-1} due to aromatic C=C stretchings, and at about 1250 cm^{-1}, corresponding to aryl C–O stretching. ^{1}H NMR spectra of the polymers show a doublet at 7.2–6.6 ppm due to aromatic protons. The signals due to the cyclohexane $-CH_2-$, normal $-CH_2-$ and backbone $-CH_2-$ protons are coalesced and observed as a multiplets at 0.95–2.0 ppm.

Average molecular weight and thermal analysis data for the homopolymer and copolymers are given in the table. All the polymers are stable up to 300°C. The polymers were readily soluble in polar aprotic solvents such as

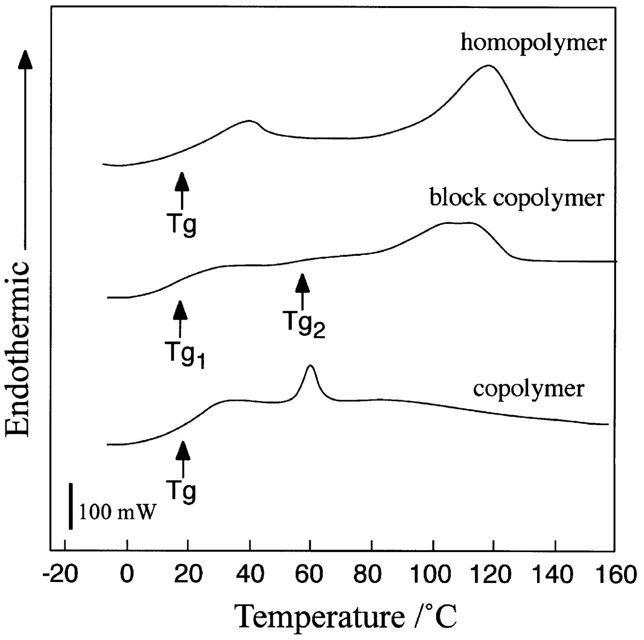

Figure 1. DSC thermograms of the homopolymer, block copolymer, and copolymer during heating.

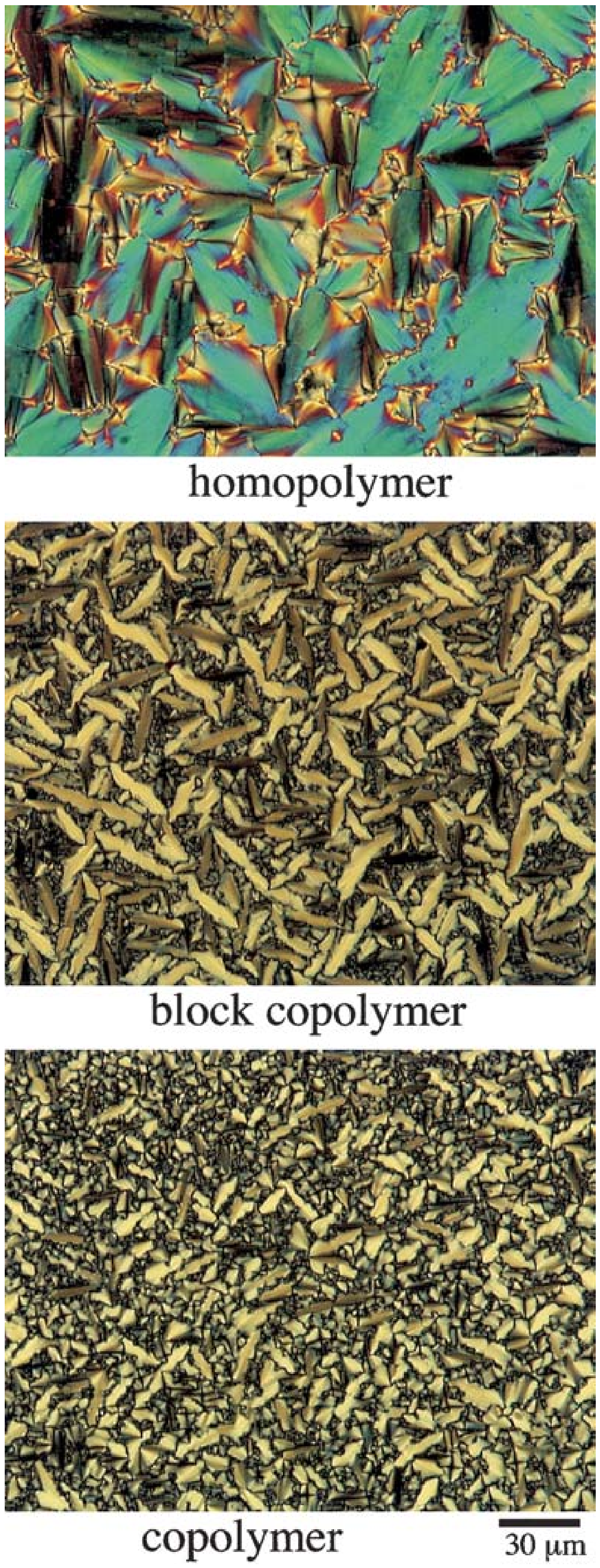

Figure 2. Polarizing optical micrographs of the homopolymer, block copolymer, and copolymer.

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dimethylformamide, dimethylacetamide and tetrahydrofuran, and in chlorinated solvents such as chloroform, 1,2-dichloroethane and dichloromethane.

DSC traces for the homopolymer, block copolymer and copolymer are shown in figure 1, and correspond to the second heating process. A single glass transition temperature (T_g) was observed in the homopolymer and copolymer at about 20°C. In the block copolymer, two T_g points were observed. The first T_g can be assigned to liquid crystalline polymer blocks at about 20°C, and the second T_g could be assigned to polystyrene block at about 60°C. The separation of the T_gs in the block copolymer can only be explained by a phase separation of the two different blocks [21]. The melting temperature (T_m) was decreased in the block copolymer and copolymer as compared with the homopolymer, however **2** content was about 60 mol % in the block copolymer and copolymer, as shown in the table. T_m and enthalpy change (ΔH) of the copolymer were lowered considerably, due to the nature of the addition of the two monomers in the polymer chain. Thus random monomer sequence disturbed the formation of ordered structure.

Figure 2 shows polarizing optical micrographs of the polymers during cooling at 25°C. A well defined focal-conic fan texture appeared in the homopolymer suggesting

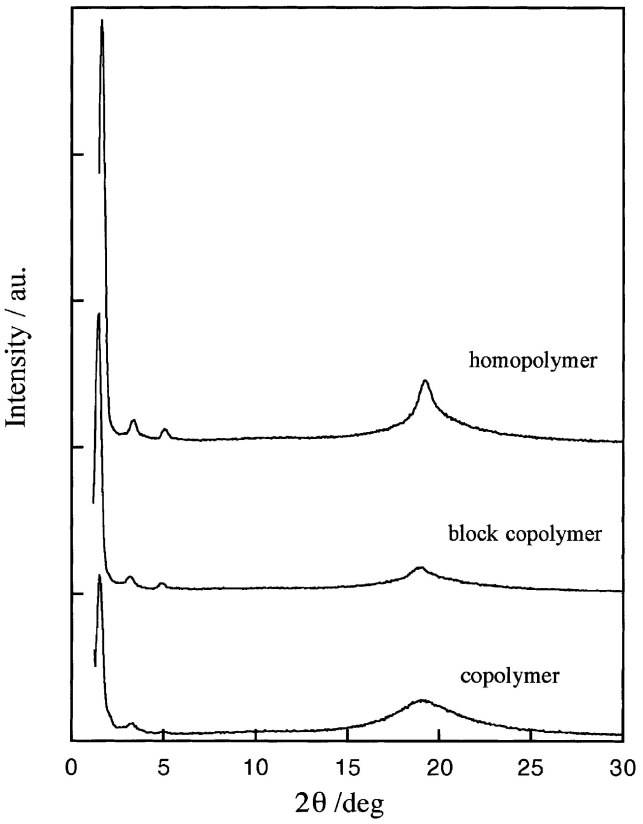

Figure 3. XRD traces measured at room temperature.

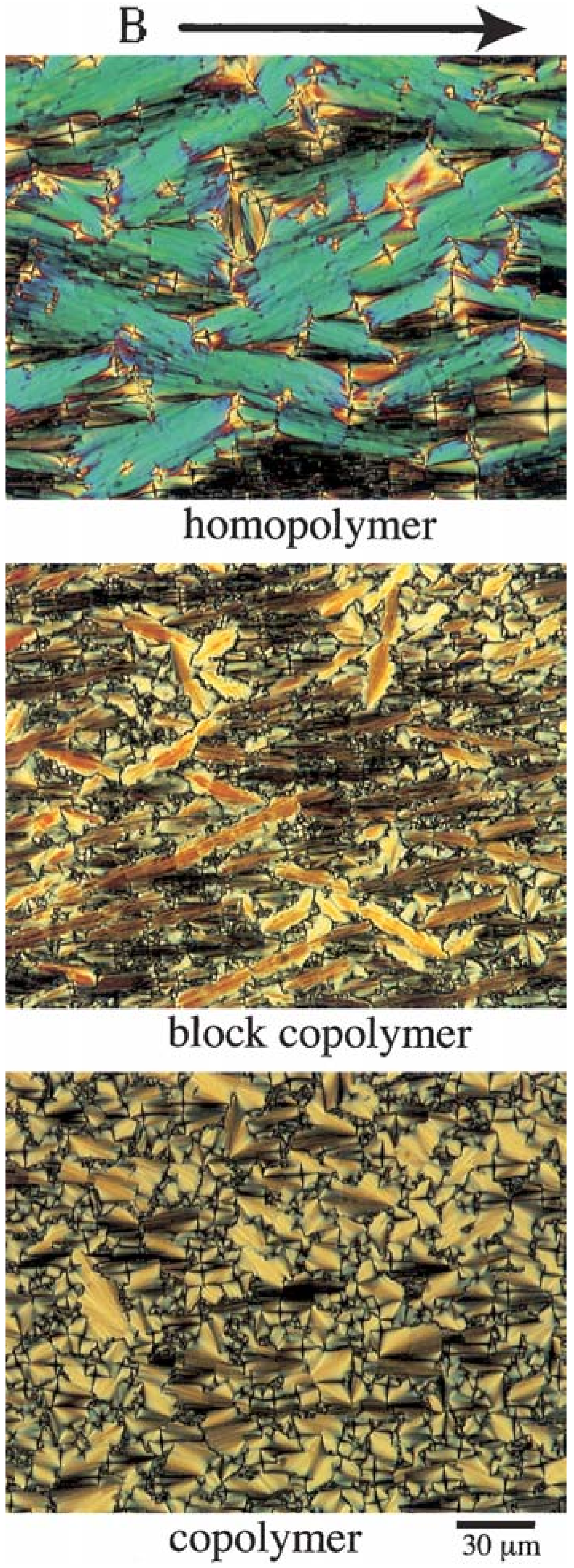

Figure 4. Polarizing optical micrographs of the homopolymer, block copolymer, and copolymer after magnetically forced alignment under a magnetic field of 2.4 T. The magnetic field was applied to the samples during cooling at 1°C min^{-1} from the melt.

that a smectic A (SmA) structure was formed. The block copolymer exhibited bâtonet texture, corresponding to SmA. The introduction of polystyrene decreased the SmA domain size. In the copolymer, on the other hand, a comparatively small fan texture was observed. This is due to random co-monomeric sequence of the copolymer.

XRD profiles of the homopolymer, block copolymer and copolymer are shown in figure 3. They showed comparatively sharp reflections around $2\theta = 2^\circ$, corresponding to the smectic layer structure. The values of the layer spacing were estimated at 2.6–3 nm, as shown in the table. Thus, SmA structure was formed in the copolymer as well as the homopolymer and block copolymer. In addition, 2nd and 3rd reflections were observed in the small angle area for the homopolymer and block copolymer, and diffused reflections were obtained for the copolymer.

In general, liquid crystalline materials exhibit macroscopic oriented structures under a high magnetic field [25], because the mesogenic groups have high anisotropic susceptibility. The different chemical structures among the above three samples may have an effect on the macroscopic textures formed in a magnetic field. A magnetic field of 2.4 T was applied to the samples during cooling from melt states. Figure 4 shows polarizing optical micrographs of the samples after magnetically forced alignment. The macroscopic oriented textures could be observed in all the samples. Oriented fan-like texture was formed in the homopolymer. The bâtonet textures were oriented parallel to the magnetic field direction in the block copolymer. In the copolymer, the small focal-conic fan textures were also aligned, and textures were larger than those before the magnetic field application. The domain size (long range order of layer structure) of the liquid crystalline phase increased under the magnetic field in all samples. The magneto-induced textures reflected the chemical structures of the samples. The behaviour of the magnetic orientation for the three samples are now under detailed investigation.

These findings suggest that the long range order of the smectic layer structure decreased in the order homopolymer > block copolymer > copolymer.

4. Conclusions

A homopolymer, block copolymer and copolymer have been prepared. We successfully prepared different optical textures in the SmA phase. The homopolymer exhibited a higher ordered SmA phase, as compared with the block copolymer and copolymer. The long range order of the SmA layer structure decreased in the order homopolymer > block copolymer > copolymer. It is possible to prepare a variety of fine texture using the copolymerization method.

References

[1] Hsu, C. S., 1997, *Prog. Polym. Sci.*, **22,** 829.

[2] Finkelmann, H., Happ, M., Portugal, M., and Ringsdorf, H., 1978, *Makromol. Chem.*, **179,** 2541.

[3] Shibaev, V. P., Kostromin, S. G., Plate, N. A., Ivanov, S. A., Vetrov, V. Y., and Yakovlev, I. A., 1983, *Polym. Commun.*, **24,** 364.

[4] Ringsdorf, H., and Schmidt, H. W., 1984, *Makromol. Chem.*, **185,** 1327.

[5] Shibaev, V. P., and Plate, N. A., 1984, *Adv. Polym. Sci.*, **60/61,** 173.

[6] Rehage, G., and Finkelmann, H., 1984, *Adv. Polym. Sci.*, **60/61,** 99.

[7] Simon, R., and Cole, H., 1984, *Mol. Cryst. Liq. Cryst. Lett.*, **102,** 43.

[8] Eich, M., and Wendroff, J., 1987, *Makromol. Chem. Rapid Commun.*, **102,** 43.

[9] Varshney, S. K., 1986, *JMS-Rev. Macromol. Chem. Phys.*, **C26,** 551.

[10] Ikeda, T., Iakura, H., Lee, C. H., Winnik, F. M., and Tazuke, S., 1988, *Macromolecules*, **21,** 3536.

[11] Shibaev, V., 1994, *Mol. Cryst. Liq. Cryst.*, **243,** 201.

[12] Akagi, K., and Shirakawa, H., 1996, *Macromol. Symp.*, **104,** 137.

[13] Hebert, M., Kant, R., and de Gennes, P. G., 1997, *J. Phys. I Fr.*, **7,** 909.

[14] De Gennes, P. G., Hebert, M., and Kant, R., 1997, *Macromol. Symp.*, **113,** 39.

[15] Adams, J., and Gronski, W., 1989, *Makromol. Chem. Rapid Commun.*, **10,** 553.

[16] Hefft, M., and Springer, J., 1990, *Makromol. Chem. Rapid Commun.*, **11,** 397.

[17] Pugh, C., and Kiste, A. L., 1997, *Prog. Polym. Sci.*, **22,** 601.

[18] Hefft, M., and Springer, J., 1990, *Makromol. Chem. Rapid Commun.*, **11,** 397.

[19] Kodaira, T., and Mori, K., 1990, *Makromol. Chem. Rapid Commun.*, **11,** 645; Kodaira, T., and Mori, K., 1992, *Makromol. Chem.*, **193,** 1331.

[20] Zaschke, B., Frank, W., Fischer, H., Schmatzler, K., and Arnold, M., 1991, *Polym. Bull. (Berlin),* **27,** 1.

[21] Arnold, M., Poser, S., Fischer, H., Frank, W., and Utschick, H., 1994, *Macromol. Rapid Commun.*, **15,** 487.

[22] Adams, J., Sanger, J., Tefehne, C., and Gronski, W., 1994, *Macromol. Rapid Commun.*, **15,** 879.

[23] Otsu, T., and Yoshida, M., 1982, *Makromol. Chem. Rapid Commun.*, **3,** 127.

[24] Turner, S. R., and Blevins, R. W., 1990, *Macromolecules*, **23,** 1856.

[25] Akagi, K., and Shirakawa, H., 1996, *Macromol. Symp.*, **104,** 137.

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