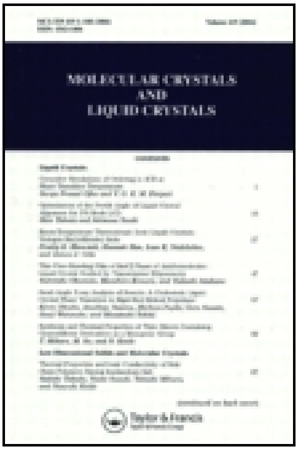

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Lee Soon Park [a] , Ki Ryong Ha [b] & Soon Nam Lee [a]

[a] Department of Polymer Science, Kyungpook National University, Taegu, 702-701, Korea

[b] Department of Chemical Engineering, Keimyung University, Taegu, 704-701, Korea

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Effect of Spacer Length on the Phase Transition of Polymer/LMWLC Composites

LEE SOON PARK[a], KI RYONG HA[b] and SOON NAM LEE[a]

[a]*Department of Polymer Science, Kyungpook National University,*
Taegu, 702-701, Korea;
[b]*Department of Chemical Engineering, Keimyung University,*
Taegu, 704-701, Korea

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Low molecular weight liquid crystals (LMWLCs), 4-[(4-bromoalkyloxy)-phenylazo]benzonitrile (AZO(*n*)) series were synthesized. Mesogenic monomers, 4-(4-propenoylalkyloxy)-4′-cyanobiphenyl (MCA) were synthesized and both homopolymer and copolymer with a methyl methacrylate (MMA) unit were prepared by free radical polymerization. Polymer/LMWLC composites (P/LCs) were prepared with LMWLC AZO(6) and AZO(8) and non-mesomorphic SCLCPs, PMCA(6)-3 and PMCA(8)-3, where (6) and (8) represent the number of methylene unit in the spacers of both LMWLC and SCLCP. It was observed that ΔT_g (defined as T_g of polymer-T_g of P/LC) was smaller and ΔT_{NI} (defined as T_{NI} of LMWLC-T_{NI} of P/LC) was larger, respectively in the case of P/LC samples with the same (6/6 and 8/8) spacer length.

Keywords: Polymer/LMWLC composite; side chain liquid crystalline polymer; phase transition; effect of spacer length; liquid crystal-polymer mixture

INTRODUCTION

Liquid crystalline polymers (LCPs) have characteristics of both polymers and liquid crystals. The electro-optical properties of LCP have become of interest recently. However, LCPs are more viscous than LCs in the mesomorphic state. Therefore, various types of polymer/LMWLC composites(P/LC) with increased mobility have been studied for potential application as large-area display and light-intensity controllable films [1–8]. For these types of applications it is important to understand the temperature-dependent phase separation and/or morphology of P/LC samples. Finkelmann's group studied phase separation of LCPs mixed with LMWLC of similar structures [9, 10]. W. Ahn *et al.* reported on the kinetics of phase separation in the polymer/LC blends [11]. Weiss's group reported on the various phase separation techniques of the P/LC system [12, 13]. In these systems, however, the effect of the spacer length of both LMWLC and polymer on the phase behavior was not studied in detail.

In this paper, cyanoazobenzene type LMWLCs with various spacer lengths were synthesized. These LMWLCs were blended with side chain liquid crystalline copolymers with varying spacer lengths and the effect of length of spacer on the miscibility and phase separation of resulting P/LC samples were studied.

EXPERIMENTAL

Materials

4-Cyano-4'-hydroxybiphenyl, 6-bromo-1-hexanol, 8-bromo-1-octanol, acryloyl chloride for the synthesis of mesogenic monomers were purchased from Aldrich Chemical Co. and used without further purification. 4-Cyanoaniline, 1,6-, 1,7-, 1,8-, 1,9- and 1,10-dibromoalkanes for the synthesis of low molecular weight liquid crystals were reagent grades from Aldrich Chemical Co.. Triethyl amine, potassium carbonate, calcium hydride, phenol and other solvents were also reagent grades.

Analysis

300MHz ^{1}H-NMR spectrometer (Bruker AM300) was used for the identification of mesogenic monomers and determination of composition of copolymers. Elemental(C, H, N) analysis of LMWLC and mesogenic monomer samples were conducted with a Carlo Elba (Model 1106) analyser. A mass spectrometer (Finnigan, Model MAT95Q) was used for the determination of M^+(m/e) at 70 eV with direct probe temperature of 50 ~ 250°C. The molecular weight of copolymers was determined by a Waters gel permeation chromatograph with a styragel HR 5E column and THF as eluent. Calibration was performed with the polystyrene standard samples.

Measurement

Thermal transition and liquid crystalline transition temperatures were measured with a differential scanning calorimeter (Perkin Elmer DSC-7).

Samples for DSC were about 10 mg and the heating or cooling speed of 10 °C/min was used in the range of −20°C to 140°C. The thermal transition temperature and texture of LMWLC and polymer/LMWLC composites were also observed with a polarized optical microscope (Zeiss Co.) equipped with Mettler's FP82 hot stage.

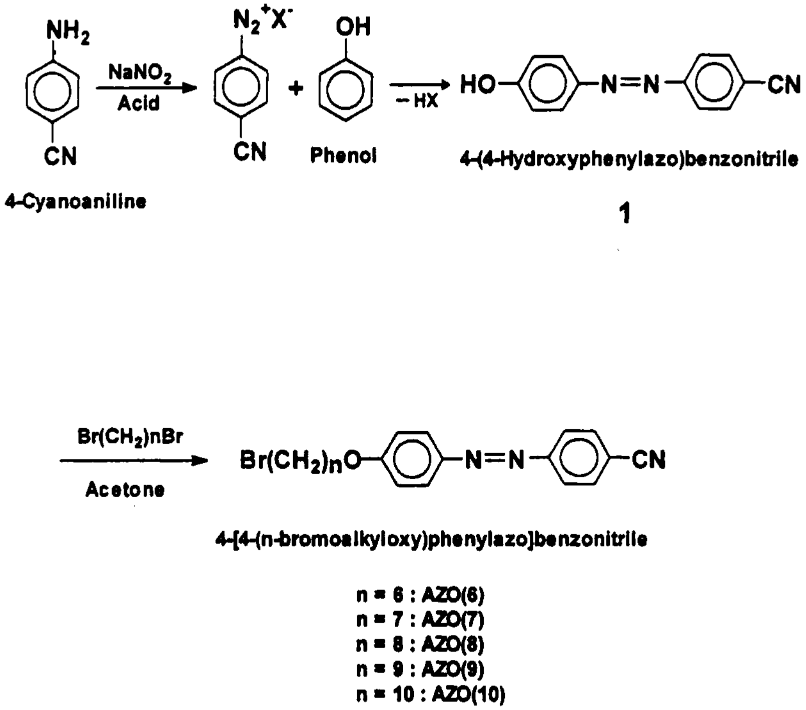
Fabrication of Polymer/LMWLC Composites(P/LCs)

Both the solvent-induced phase separation (SIPS) [14] and the thermally-induced phase separation (TIPS) [14] methods were used for the fabrication and characterization of P/LC samples. A mixture of polymer matrix and LMWLC was dissolved in CH_2Cl_2 at various weight ratios. After complete dissolution, the solvent was evaporated using a Petri dish. A small amount of polymer/LMWLC mixture was placed between two ITO glasses with a spacer (polyester film, thickness 10 μm). This P/LC sample was placed on the hot stage of a polarized optical microscope(POM). Slight pressing during the heating stage and then cooling to room temperature induced phase separation of P/LC samples. This procedure was repeated several times to observe the texture and thermal transition temperature of P/LC samples with the polarized optical microscope.

Synthesis of LMWLC

Synthetic routes to LMWLCs with azo linkage and ω-bromoalkyl tails are shown in Scheme 1 [15, 16]. 4-Cyanoaniline (8 g) was reacted with sodium nitrite (4.68 g) in the presence of an aqueous solution of hydrochloric acid (35 wt%, 27.32 g) as catalyst to give diazonium salt, while the temperature was controlled at about 0°C using an ice-bath. To this diazonium salt solution was added slowly an aqueous solution containing phenol (6.36 g) and sodium carbonate (6.56 g). A coupled product **1** was obtained as a yellow precipitate; yield = 81%, melting temp. = 202.9°C by DSC, $M^+(m/e) = 223.23$, elementary analysis data, C(69.95%), H(4.06%), N(18.82%), calculated, and C(69.83%), H(4.03%), N(19.25%), found.

An equimolar mixture of **1** and 1,6-dibromohexane was refluxed for 24 hr in an acetone solvent with a small amount of K_2CO_3. The reaction mixture was filtered while still hot to remove the KBr byproduct and then poured into an excess amount of distilled water. The precipitate was filtered and recrystallized in ethanol to give LMWLC, 4-[4-(6-bromohexyloxy)phenylazo]benzonitrile, AZO(6). Other azo-LC compounds, AZO(7) ~ (10), were obtained by a similar process from corresponding α,ω-dibromoalkanes.

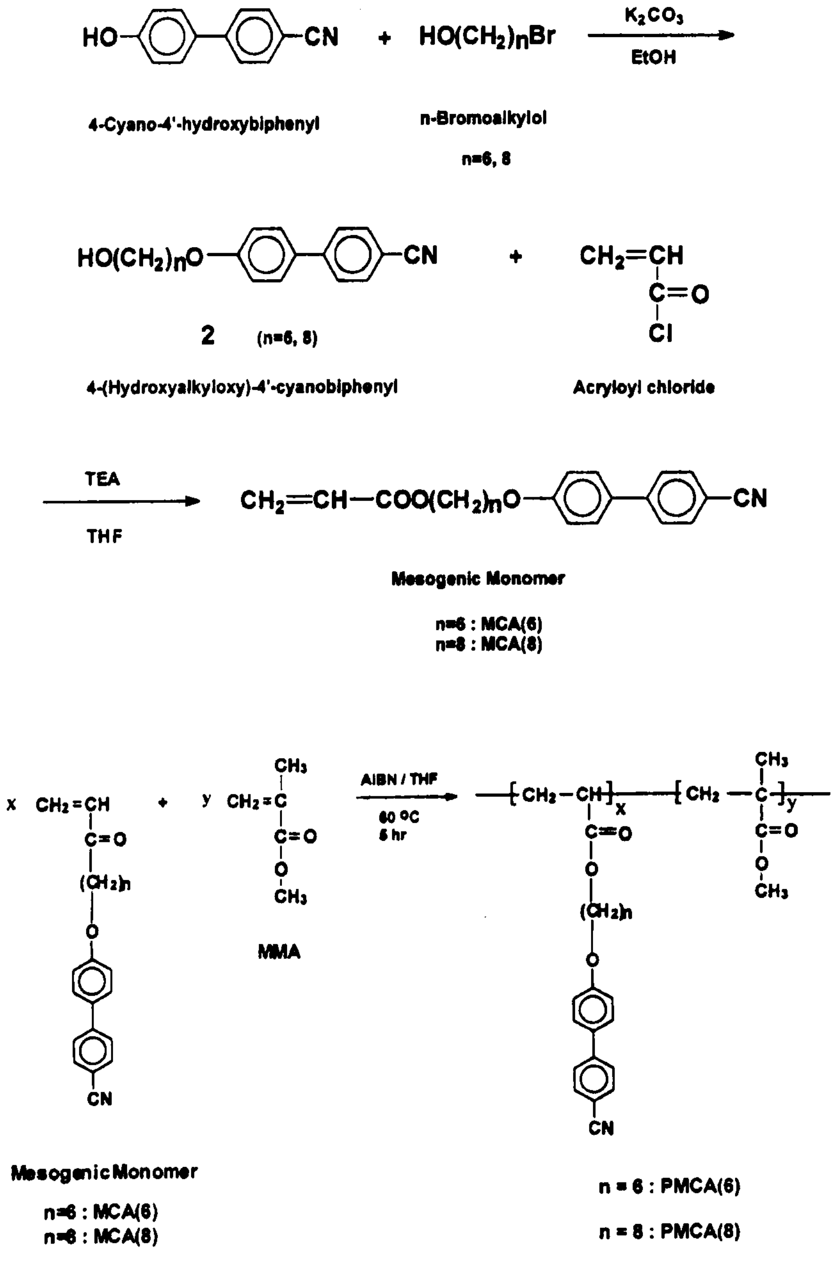


SCHEME 1 Synthesis of low molecular weight liquid crystals containing azo functional group.

Synthesis of Mesogenic Monomers and Polymers

In Scheme 2 are shown synthetic routes to mesogenic monomers containing the cyanobiphenyl mesomorphic group and the homopolymer and copolymers containing them [17, 18]. 4-Cyano-4'-hydroxybiphenyl (5.0 g) was dissolved in 90 mL of ethanol by heating. The mixture solution was refluxed for 2 hr with 5.0 g of K_2CO_3 and refluxed for 24 hr after adding 5.0 g of 6-bromo-1-hexanol. The hot mixture was filtered to remove the KBr by-product and the filtrate was poured into excess water. The precipitate was filtered, dried and recrystallized in benzene to give 4-(hydroxyhexyloxy)-4'-cyanobiphenyl(**2**); yield = 66%, melting temp. = 94–95°C, M^+(m/e) = 295.2.

The intermediate **2** (7.0 g) was dissolved in 90 mL THF. To this solution was added 3.8 g of triethylamine and then added slowly 3.2 g of acryloyl chloride dissolved in 70 mL of THF in an ice-water bath. After 24 hr reaction, the reaction mixture was filtered to remove triethylamine salt and the filtrate was evaporated to give crude 4-(4-propenoyloxyhexyloxy)-4'-



SCHEME 2 Synthesis of mesogenic monomers and copolymerization of mesogenic monomers and MMA.

cyanobiphenyl, MCA(6). This mesogenic monomer was recrystallized in methanol to give pure MCA(6); yield = 40%, melting temp. = 73.4°C, M^+(m/e) = 349.4. Another mesogenic monomer, MCA(8) was obtained through a similar procedure; yield = 50%, melting temp. = 76.1°C, M^+(m/e) = 377.5.

Mesogenic monomers were copolymerized with methyl methacrylate at various feed ratio. Polymerization was conducted at 15 wt% of monomers in a THF solvent at 60 C° with 2,2′-azobisisobutyronitrile (AIBN) as initiator. The copolymers were recovered by precipitating in methanol, washed and dried under vacuum.

RESULTS AND DISCUSSION

Identification and Properties of LMWLC

A typical ^{1}H-NMR spectrum of LMWLC, AZO(6) is shown in Figure 1; 0.6–1.2 ppm broad methylene(8), 2.8 ppm triplet —CH_2Br(2), 3.4 ppm triplet —CH_2—O—(2), and 7–8 ppm biphenyl hydrogens(8). FT-IR spectrum of AZO(6) exhibited peaks at 2222cm^{-1}(—CN), 1601cm^{-1}(phenyl ring), 2900 ~ 3100cm^{-1}(aromatic and aliphatic CH), and 1251cm^{-1}(C—O—C) as shown in Figure 2. A DSC thermogram and polarized optical microscopic observation of AZO(6) are shown in Figure 3. AZO(6) exhibited nematic texture and thermal transition temperatures were; $T_{KN} = 90.7$°C, $T_{NI} = 103 \cdot 0$°C. Both transition temperatures(T_{KN} and T_{NI}) of AZO series LMWLCs exhibited an even-odd effect with the ω-bromoalkyl chain length as shown in Figure 4.

Properties of Liquid Crystalline Copolymers

Mesogenic monomers, MCA(6) and (8) were polymerized by themselves and copolymerized with methyl methacrylate (MMA). The molecular weight and copolymer composition data are shown in Table I. The molecular weight of homopolymer was lower than that of a copolymer, indicating the steric hinderance between mesogenic groups. The composition of copolymer was determined by ^{1}H-NMR analysis. A ^{1}H-NMR spectrum of a typical copolymer, PMCA(6)-3 obtained from a feed ratio of MCA(6)/MMA = 66.7/33.3 is shown in Figure 5. The copolymer composition was calculated by eq. (1), where A is the peak area under 7–8 ppm due to biphenyl hydrogens and B is the area under about 3.6 ppm due to —OCH_3 hydrogens.

$$\frac{A/8}{A/8 + B/3} \times 100(\%) = \text{mol\% of MCA repeat until in copolymer} \qquad (1)$$

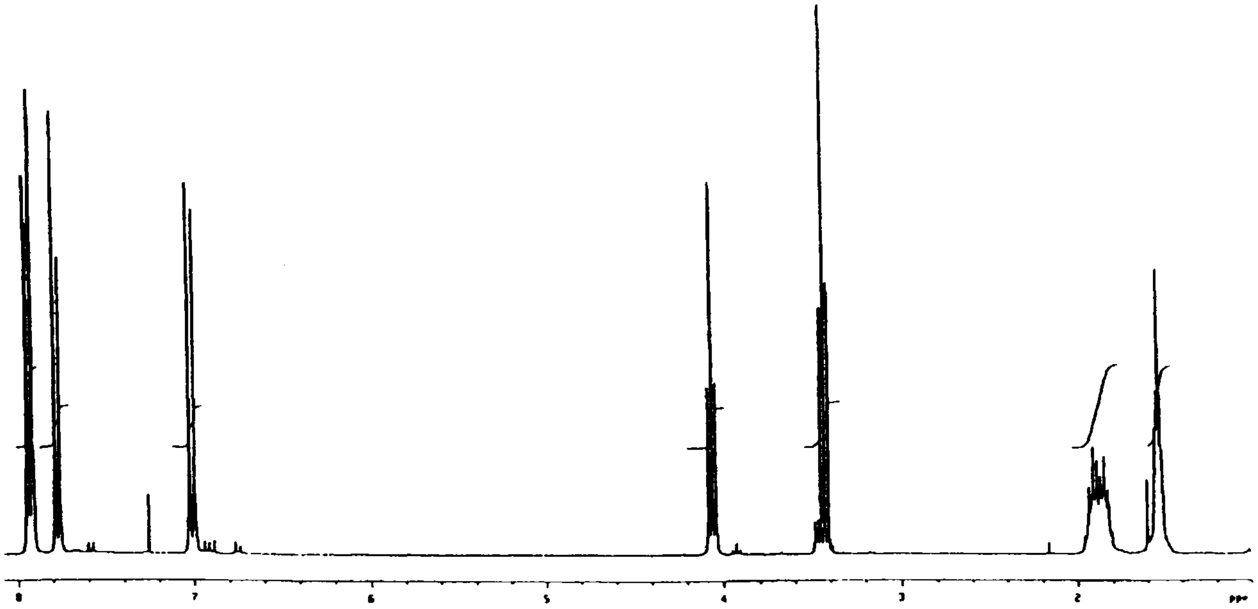


FIGURE 1 ^{1}H-NMR spectrum of AZO(6) in $CDCl_3$ solvent.

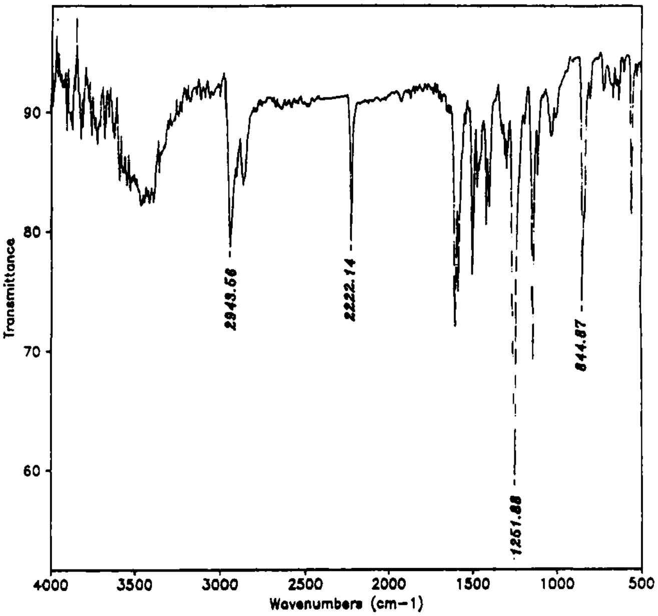


FIGURE 2 FT-IR spectrum of AZO(6) (4,000–500 cm^{-1} region).

Copolymers, PMCA(6), had a lower amount of MCA(6) repeat unit than that in the feed, while PMCA(8) copolymer showed nearly the same composition as that of monomer feed. This compositional change and increasing molecular weight of the copolymer with increasing MMA in the feed suggested that MCA(6) had a higher steric hinderance during polymerization than MCA(8) due to a shorter spacer.

The thermal transition behavior of the copolymer was investigated with both a DSC and polarized optical microscope. Homopolymer PMCA(6)-1 and PMCA(8)-1 exhibited T_{NI} at about the same temperature of 129°C. As the MMA unit in the copolymer increased, T_{NI} decreased and both copolymers lost LC property at about 26 mol% of MMA unit in the chain due to disruption of the mesomorphic order in the polymer backbone. The glass transition temperatures(T_gs) of PMCA(6)-1 and PMCA(8)-1 homopolymer were 27°C and 15°C, respectively, reflecting the plasticizing effects of a longer spacer unit. The T_gs of the copolymer increased steadily as the MMA unit in the copolymer increased. This was in correspondence with the higher T_g of PMMA than that either PMCA(6)-1 or PMCA(8)-1 homopolymer.

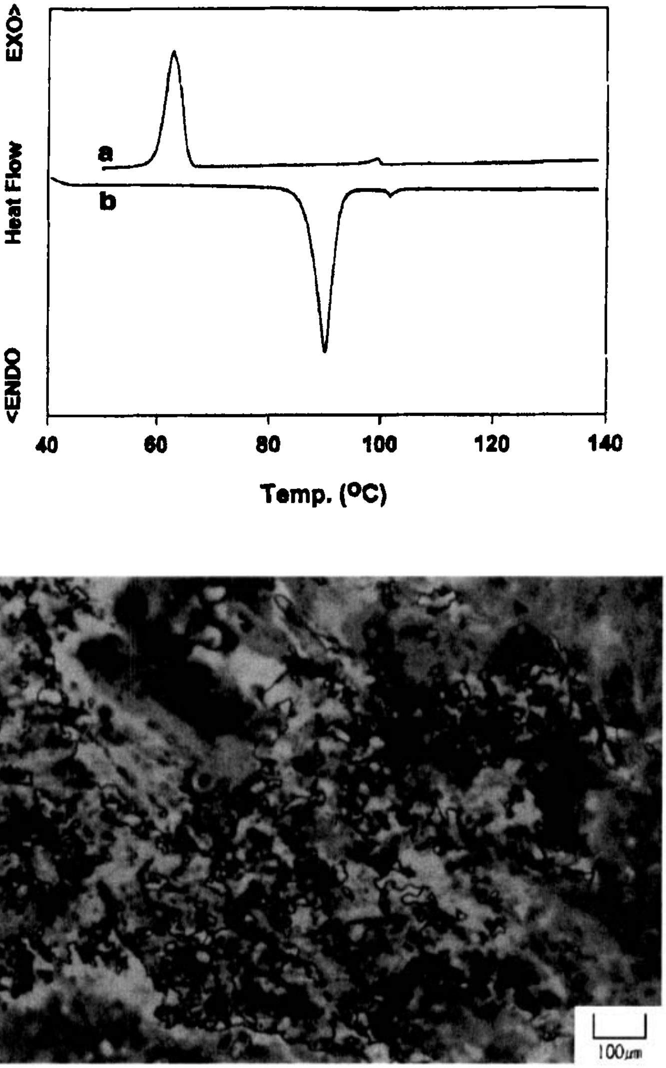


FIGURE 3 DSC thermogram and polarized optical microscope photograph of AZO(6) taken at 102.0°C. (See Color Plate I).

Properties of Polymer/LMWLC Composites

Both PMCA(6) and PMCA(8) copolymer lost their LC property as the content of the non-mesogenic unit(MMA) increased in the copolymer. It was observed in our previous experiment that these non-mesomorphic

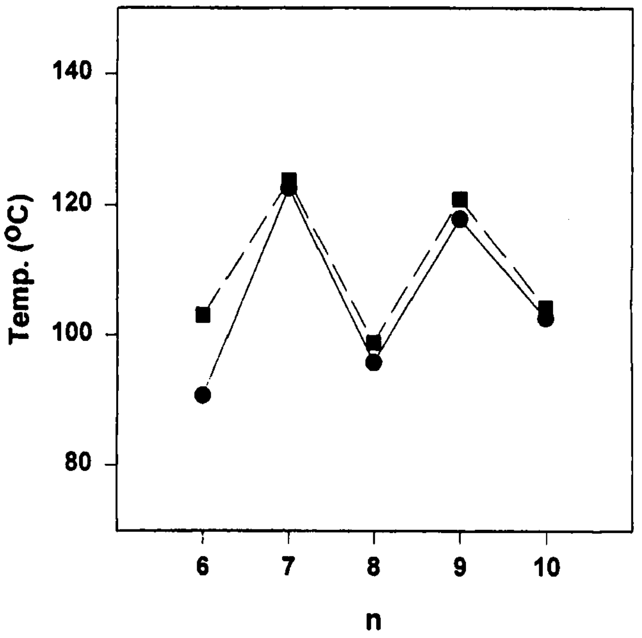


FIGURE 4 Effect of alkyl chain length *n* on the transition temperatures (●: T_{KN}, ■: T_{NI}) of LMWLC AZO(*n*) series.

TABLE I Molecular Weight, Molar Composition and T_g of Mesogenic Homopolymer and Copolymer Samples

Polymer No.	*Comonomer Feed MCA(6):MMA (mol%)*	*Copolymer Comp. MCA(6):MMA (mol%)*	*Mol. Wt.* $M_w \times 10^{-4}$	*Polydispersity* M_w/M_n	T_g (°C)	T_{iso} (°C)
PMCA(6)-1	100:0	100:0	1.02	1.51	27	129
PMCA(6)-2	80:20	74.2:25.8	1.50	1.63	36	92
PMCA(6)-3	66.7:33.3	52.5:47.5	2.57	1.82	39	–
PMCA(6)-4	50:50	33.7:66.3	3.59	1.94	46	–

Polymer No.	*Comonomer Feed MCA(8):MMA (mol%)*	*Copolymer Comp. MCA(8):MMA (mol%)*	*Mol. Wt.* $M_w \times 10^{-4}$	*Polydispersity* M_w/M_n	T_g (°C)	T_{iso} (°C)
PMCA(8)-1	100:0	100:0	0.77	1.46	15	129
PMCA(8)-2	80:20	73.9:26.1	1.31	1.60	17	86
PMCA(8)-3	66.7:33.3	62.7:37.3	1.57	1.70	22	–
PMCA(8)-4	50:50	42.9:57.1	2.70	2.50	31	–

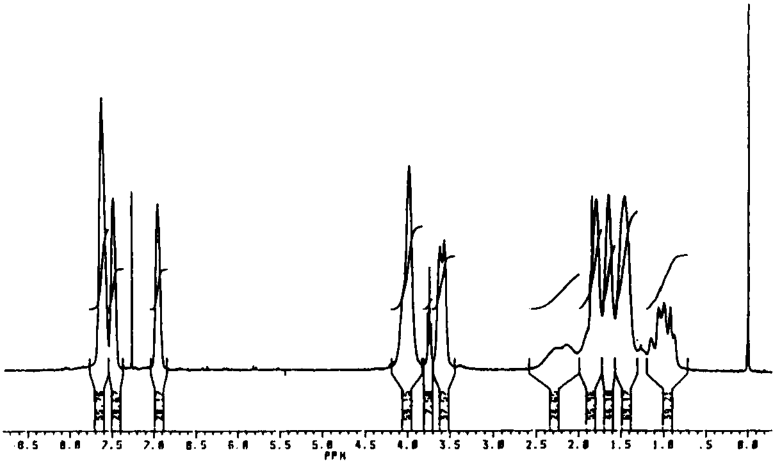


FIGURE 5 ^{1}H-NMR spectrum of PMCA(6)-3 co polymer in $CDCl_3$ solvent.

copolymers recovered the LC property when they were mixed with LMWLCs to give polymer/LMWLC composites (P/LCs) [19]. In this study P/LCs were made with non-mesomorphic PMCA(6)-3 and PMCA(8)-3 as polymer matrix and AZO(6) and AZO(8) as LMWLC to observe the effect of the spacer length on the LC property of PDLCs. The polymer/LMWLC ratio of P/LC samples was 40/60 by weight% and the thermal transition behavior was checked both by DSC and POM. The results are summerized in Table II. First, from the DSC analysis, T_g of PMCA(6)-3 copolymer itself was 39°C. This was decreased to 19°C for P/LC-2 sample with AZO(6) as LMWLC mixed and decreased further down to 9°C for P/LC-4 sample with AZO(8) as LMWLC mixed. The decrease of T_g of polymer matrix by blending with LMWLC is well known and explained by the plasticizing effect of LMWLC in the polymer matrix. In this experiment it was observed that ΔT_g (defined as T_g of the polymer-T_g of P/LC) was smaller in the P/LC-2 than in the P/LC-4 sample. This may be explained by the better packing of AZO(6) LMWLC into the void spacer region of PMCA(6)-3 created by the MMA repeat unit than AZO(8) due to similar size of the spacer length. Similar trend was also observed with PMCA(8)-3 as matrix polymer ($T_g = 22$°C by itself) as shown in P/LC-1 and P/LC-3 samples.

Secondly, as for the change of T_{NI}, LMWLC AZO(6) and AZO(8) had T_{NI} at 103.0°C and 99.0°C, respectively. By making P/LCs with copolymers, ΔT_{NI} (defined as T_{NI} of LMWLC-T_{NI} of P/LC) of AZO(6) decreased further in P/LC-2(with PMCA(6)-3 as matrix) than P/LC-1 (with PMCA(8)-3 as matrix).

TABLE II Phase Transition Temperatures of the Polymer/LMWLC Composite(P/LC) Samples Determined by DSC and Polarized Optical Microscope(POM)

P/LC Samples	*Polymer/LMWLC = 40/60 (wt%)*	T_g*(°C) of Polymer*	T_g*(°C) of P/LC*	ΔT_g^c *(°C)*	T_{KN}*(°C) (DSC)*	T_{NI}*(°C) (POM)*	ΔT_{NI}^d *(°C)*
P/LC-1	PMCA(8)-3/AZO(6)[a]	22	0	22	86.9	94.0	9.0
P/LC-2	PMCA(6)-3/AZO(6)	39	19	20	83.0	89.0	14.0
P/LC-3	PMCA(8)-3/AZO(8)[b]	22	2	20	82.3	93.2	5.8
P/LC-4	PMCA(6)-3/AZO(8)	39	9	30	84.5	94.9	4.1

a; AZO(6): $T_{KN} = 90.7°C$, $T_{NI} = 103.0°C$.

b; AZO(8): $T_{KN} = 95.8°C$, $T_{NI} = 99.0°C$.

c; $\Delta T_g = T_g(\text{polymer}) - T_g(\text{P/LC})$, T_g and T_{KN} by DSC.

d; $\Delta T_{NI} = T_{NI}(\text{AZO(n)}) - T_{NI}(\text{P/LC})$, T_{NI} by POM.

LMWLC AZO(8) exhibited a similar trend, i.e. $\Delta T_{NI} = 5.8$ with P/LC-3 and $\Delta T_{NI} = 4.1$ with P/LC-4. It has been reported that T_{NI} of LMWLC was lowered by blending with the polymer due to a restriction in the orientation of the mesogenic group. It is of interest to note that T_{NI} of both AZO(6) and AZO(8) LMWLCs were lowered further down in the polymer matrix with a similar spacer size. This may be due to the increased compatibility of LMWLC with the polymer matrix which has a similar spacer size.

CONCLUSION

Low molecular weight liquid crystals (LMWLCs), 4-[(4-bromoalkyloxy)phenylazo]benzonitrile (AZO(*n*)) series were synthesized and the even-odd effect depending on the length of the spacer was observed. Mesogenic monomers, 4-(4-propenoylalkyloxy)-4′-cyanobiphenyl (MCA) were synthesized and both homopolymer and copolymer with methyl methacrylate (MMA) units were prepared by free radical polymerization. These side chain liquid crystal polymers(SCLCPs) were found to lose LC property with about 26mol% of MMA units in the polymer chain. The polymer/LMWLC composites (P/LCs) were prepared with LMWLC, AZO(6) and AZO(8), and non-mesomorphic SCLCP, PMCA(6)-3 and PMCA(8)-3, where (6) and (8) represent the number of methylene units in the spacers of both LMWLC and SCLCP. It was observed that ΔT_g(defined as T_g of polymer-T_g of P/LC) was smaller and ΔT_{NI}(defined as T_{NI} of LMWLC-T_{NI} of P/LC) was larger, respectively in the case of P/LC samples with the same (6/6 and 8/8) spacer length.

Acknowledgment

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