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Phase behavior of liquid-crystalline copolymer/liquid crystal blends

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Abstract

Thermodynamic phase behavior was studied for blends between side-chain liquid-crystalline (SCLC) copolymers and a low molecular weight liquid crystal (LC). SCLC copolymers, Copoly$x$ having x mol fraction of a benzoic acid unit and $1 - x$ mol fraction of a cyanobiphenyl group in their side chain, were prepared by radical polymerization and mixed with a low molecular weight LC, 4-cyano-4′-*n*-hexyloxybiphenyl (6OCB). The phase diagram of the Copoly0.24/6OCB blend exhibited an upper critical solution temperature which was not observed for homopolymer systems. Employing SCLC copolymers having two different kinds of mesogens in polymer/low molecular weight LC blends enabled us to obtain the new type of phase diagram. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Liquid-crystalline copolymer/liquid-crystal blend; Phase diagram; Phase separation

1. Introduction

A large amount of work has been focused on polymer-dispersed liquid crystals (PDLCs) because of their potential use in electro-optic devices [1–11]. PDLCs are composed of microdroplets of a low molecular weight liquid crystal (LC) dispersed in a polymer matrix. One method of preparation of PDLCs is a thermally induced phase separation process. This technique is widely used with thermoplastic polymers such as polystyrene (PS) and poly(methyl methacrylate) (PMMA). For PDLCs prepared by this technique, only low molecular weight LCs in droplets are able to respond to an electric field — the polymer matrix has no function other than to maintain the shape and matching a refractive index to that of the LC. PS and PMMA are partially miscible with low molecular weight LC, therefore an upper critical solution temperature (UCST) phase separation is observed for the blends between them. The performance of PDLCs strongly depends on the morphology resulting from the UCST phase separation. Although many studies on the phase behavior and the morphology in general polymer/LC blends to elucidate the properties of PDLCs [12–18], have been reported, the mixtures between a functionalized polymer and a low molecular weight LC have seldom been examined except for the reports of Ringsdorf et al. [19] and Finkelmann et al. [20]. These authors prepared blends of side-chain liquid-crystalline (SCLC) polymers with low molecular weight LCs in order to investigate their miscibility behavior and briefly mentioned the morphology of their blends. Recently, Finkelmann and his co-workers have reported on the morphology of LC isotropic AB block copolymers in nematic solvents [21,22]. We consider that applying SCLC copolymers containing different types of mesogens to polymer/LC blend systems provides variety of phase behavior and morphology. If we could control the morphology of LC polymer/LC blends, we might expect to arrive not only at electro-optic thin films but also a whole new type of functional materials because both the polymer matrix and the low molecular weight LC can respond to external stimuli such as electric fields.

In this study, we examined the effect of composition and nature of the side chain of LC copolymers on the miscibility of the LC copolymers/low molecular weight LC blends. We synthesized the two homopolymers and the two copolymers differing in the side-chain composition, as shown in Fig. 1, and prepared the blends between the polymers and a low molecular weight LC, 6OCB. The thermodynamic phase behavior of the blends was studied by DSC and optical microscopy.

2. Experimental

2.1. Samples

Two monomers 6-(4-cyanobiphenyl-4′-yloxy)hexyl acrylate

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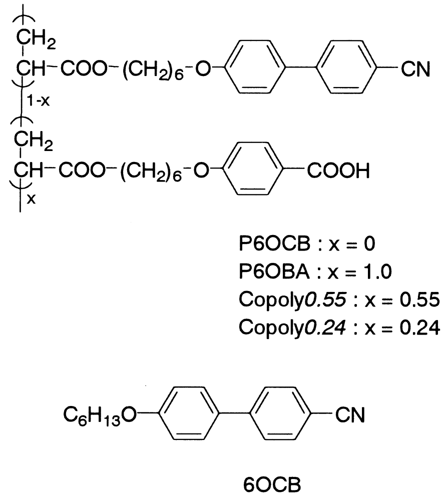

Fig. 1. Molecular structures of LC polymers and low molecular weight LC used in this study.

and 4-(6-acryloyloxyhexyl-1-oxyl)benzoic acid were synthesized according to the procedures described in Refs. [23–25]. Polymers were obtained by radical polymerization of the requisite amounts of monomers in dry DMF with AIBN at 70°C for 20 h. The resulting polymers were purified by repeated reprecipitation from DMF solutions by diethyl ether and dried in vacuum. Results of polymerization and properties of the polymers are summarized in Table 1. The compositions of the copolymers were determined by UV spectroscopy by measuring the optical density of the absorption band of the biphenyl group $\lambda = 297$ nm. Homopolymer P6OCB containing a cyanobiphenyl group as a mesogen exhibits a nematic phase. This is in agreement with the literature [23]. In contrast, homopolymer P6OBA having a benzoic acid unit in its side chain shows a smectic phase in the wide temperature range. This result indicates that the benzoic acid group in the side chain of P6OBA forms a dimer through hydrogen bonds and serves as a mesogenic group [24–27]. The copolymer consisting of x mol fraction of a benzoic acid and $1 - x$ mol fraction of a cyanobiphenyl is designated as Copoly*x*. Copoly0.55 shows a smectic phase while Copoly0.24 exhibits a nematic phase. The isotropization temperatures of the copolymers are higher than the calculated values based on their compositions. This observation might be attributed to the interaction between the two different kinds of mesogenic groups [27–30]. Low molecular weight LC 6OCB was synthesized by etherification from 4-hydroxy-4′-cyanobiphenyl and 1-bromohexane. 6OCB shows a nematic phase between 58 and 77°C.

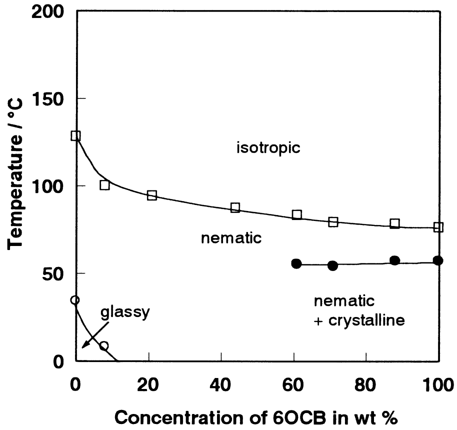

Fig. 2. Phase diagram of the binary P6OCB/6OCB blend.

2.2. Preparation of binary blends

The requisite amounts of the polymers and 6OCB were dissolved in THF (or DMF in the case of P6OBA) and the solutions were evaporated under reduced pressure. The residual solids were dried in vacuum for 24 h. All measurements were carried out on freshly melted materials.

2.3. Characterization

Phase transition temperatures were determined using Seiko Instruments Inc. DSC 120. A heating rate of 5°C/min was used for the measurements. A polarizing microscope (Olympus BH2) equipped with a Mettler FP82HT hot stage was used to observe the liquid-crystalline textures and the phase separation behavior of the samples. UV spectroscopy was performed on a Shimadzu UV 2500PC spectrophotometer. Molecular weights of the resulting polymers except for P6OBA were obtained with Waters Alliance

Table 1
Results of polymerization and properties of the polymers (radical polymerization in DMF solution using 1 mol% AIBN as an initiator at 70°C for 20 h)

Polymer	Proportion of benzoic acid		Polymer yield (%)	M_n[a] × 10^4	M_w[a] × 10^4	Phase transition temperature[b] (°C)				
	In feed	In copolymer[c]								
P6OCB	0.0	0.0	85	2.00	7.54	g	34	N	128	I
P6OBA	1.0	1.0	85	–[d]	–[d]	g	90	S	178	I
Copoly0.55	0.50	0.55	83	3.35	15.9	g	47	S	180	I
Copoly0.24	0.20	0.24	82	2.18	12.6	g	34	N	140	I

[a] Determined by GPC using THF as an elulent and PS standards.

[b] Determined by the DSC measurement at a scanning rate of 5°C /min. g: glassy; N: nematic; S: smectic; I: isotropic.

[c] Determined by UV spectroscopy.

[d] P6OBA was insoluble in THF.

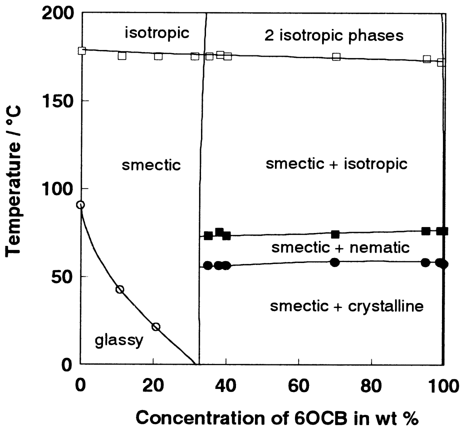

Fig. 3. Phase diagram of the binary P6OBA/6OCB blend.

HPLC Systems (Waters Co.) using THF as an eluent and standard PS as the reference. The homopolymer P6OBA was insoluble in THF. However, the phase transition behavior of P6OBA suggests that a molecular weight of P6OBA is sufficient to discuss in this study [24–27].

3. Results and discussion

There are a lot of reports on the phase behavior of homopolymer/low molecular weight LC blends. In this study, we also have examined blends of SCLC homopolymers and a low molecular weight LC before we investigate SCLC copolymer systems. The phase diagram of P6OCB and 6OCB was prepared from the results of DSC measurements and optical microscopy. As shown in Fig. 2, homogeneous nematic and isotropic phases can be observed for the whole concentration range of 6OCB. The isotropization temperature (T_i) of the blends decreases with the increase of 6OCB concentration. The glass transition temperature (T_g) of P6OCB is also lowered by the addition of 6OCB. The low molecular weight LC, 6OCB is found to act as a plasticizer for the blends. Electrorheological properties of an analogous SCLC homopolymer/low molecular weight LC blend was studied by our group [31]. The viscosity of this blend was appropriate to deal with under an electric field [31]. As can be seen in Fig. 2, when the 6OCB concentration exceeds 60 wt%, endothermic peaks are detected for the blends by DSC at about 57°C. This result suggests that crystallization of 6OCB occurs in the blends. A similar phase diagram was reported in the blend of a low molecular weight LC and a liquid-crystalline polyacrylate both having a cyanophenyl group as a mesogen [20]. The complete miscibility between P6OCB and 6OCB was confirmed in this study, which results from the identity of the mesogen and the suitability of the length of the alkyl groups.

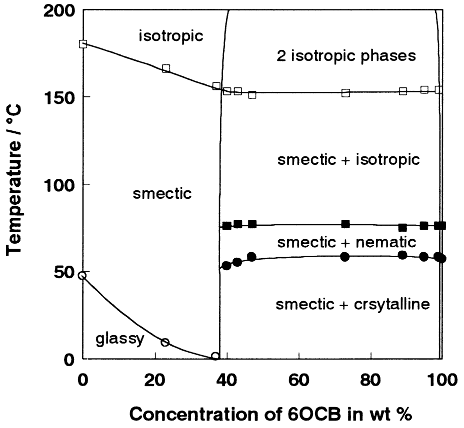

Fig. 4. Phase diagram of the binary Copoly0.55/6OCB blend.

Fig. 3 shows a phase diagram for P6OBA/6OCB blends. The acrylate polymer P6OBA was reported by Kato et al. [24–27]. They used P6OBA in order to obtain homogeneous LC complexes by stoichiometric formation of intermolecular hydrogen bond between a carboxylic acid of P6OBA and a pyridyl group of a low molecular weight component [24–27]. In this study, the basicity of the cyano group is too weak to form a hydrogen bond with a benzoic acid. In the P6OBA/6OCB blend, a benzoic acid unit of P6OBA preferentially forms a dimer. When the concentration of 6OCB is lower than 35 wt%, the blends show homogeneous smectic and isotropic phases as shown in Fig. 3. T_g significantly decreases with the increase of 6OCB concentration while no remarkable decrease is seen for T_i. When the concentration of 6OCB is 35 wt% or higher, two domains are clearly observed for the blends under an optical microscope. Even in the isotropic state these domains remain. As the temperature decreases, one domain shows a smectic phase below about 175°C, while the other exhibits a nematic phase below about 74°C and subsequently crystallizes at ca. 57°C. These results indicate that two domains correspond to a P6OBA-rich phase containing 35 wt% of 6OCB and a 6OCB-single phase, respectively. This type of miscibility behavior was widely observed for other polymer/low molecular weight LC blends [32]. The P6OBA/6OCB blend is essentially immiscible although P6OBA can be plasticized by 6OCB in the low concentration range.

We have expected that we can obtain a different type of phase diagram which shows intermediate nature between P6OCB/6OCB and P6OBA/6OCB blends if we employ SCLC copolymers having both cyanobiphenyl and benzoic acid groups. The phase diagram for the blends of Copoly0.55 and 6OCB is depicted in Fig. 4. Copoly0.55 is a random copolymer having 45 mol% of a cyanobiphenyl group and 55 mol% of a benzoic acid group in its side chain. Similar SCLC copolymers were employed by Zhao et al. [33] and Shibaev et al. [34]. Zhao and his co-workers prepared interpenetrating networks by providing a hydrogen bond between benzoic acids of the copolymer. Shibaev et al., obtained homogeneous SCLC complexes through the formation of a hydrogen bond between a carboxylic acid of the copolymer and a pyridyl unit of a low molecular weight compound. Unfortunately, the phase diagram for

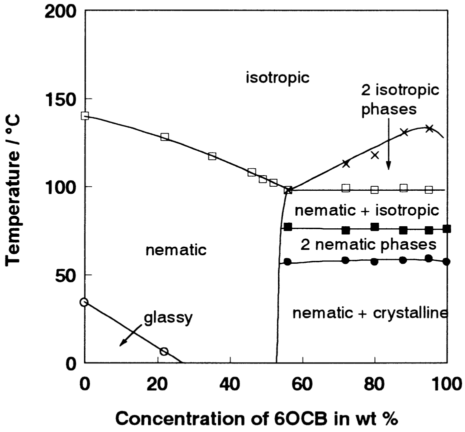

Fig. 5. Phase diagram of the binary Copoly0.24/6OCB blend.

the blend of Copoly0.55 and 6OCB is similar to that of the P6OBA/6OCB blend. Copoly0.55 can be molecularly mixed with 6OCB in the concentration less than 40 wt% and this homogeneous blend shows a smectic phase. T_i of P6OBA was slightly lowered by the addition of 6OCB whereas T_i of Copoly0.55 linearly decreases from 185 to 153°C as the concentration of 6OCB increases up to 40 wt%. Once the concentration of 6OCB exceeds 40 wt%, the blends separate into two domains, namely, a polymer-rich phase and a 6OCB-single phase, and T_i of the polymer-rich phase stays constant at ca. 153°C. The physical properties of Copoly0.55 are found to be predominantly affected not by a cyanobiphenyl group but rather by the benzoic acid unit.

Next, we have prepared another SCLC copolymer, Copoly0.24, which has a lower mole fraction of benzoic acid group than Copoly0.55. Fig. 5 illustrates the phase diagram for the blend of Copoly0.24 and 6OCB. Copoly0.24 consists of 76 mol% of a cyanobiphenyl and 24 mol% of a benzoic acid mesogen. This random copolymer is molecularly mixed with 6OCB in the concentration range less than 56 wt%. The T_i of Copoly0.24 continuously decreases from 145 to 100°C as the concentration of 6OCB increases up to 56 wt%. The T_g of Copoly0.24 is also lowered by the addition of 6OCB. As can be seen in the phase diagram, when the concentration of 6OCB is 56 wt% or larger, the blend shows a specific thermodynamic behavior, which is quite different from that of the other blends stated in this study. The blend containing more than 56 wt% of 6OCB shows a homogeneous isotropic phase at an elevated temperature. As the temperature decreases, however, the homogeneous blends begin to divide into two isotropic phases. It was found that the blend between Copoly0.24 and 6OCB exhibits UCST type phase separation. This phase separation temperature is so-called the cloud point (T_c). Because no peak associated with the phase separation could be detected by DSC, we determined it as the point at which two phases began to appear in the blend under an optical microscope on cooling. The peak of UCST line lies too close to the 100 wt% of 6OCB. The result allows us to make the following assumption. The two isotropic phases correspond to a Copoly0.24-rich phase and a 6OCB-rich phase consisting of almost 100 wt% of 6OCB, respectively. On lowering the temperature the polymer-rich phase in the isotropic state excludes 6OCB until its concentration decreases to 56 wt%, and subsequently changes to a nematic phase at about 98°C. For LC homopolymer/low molecular LC blends, UCST was briefly mentioned by Finkelmann et al. [20]. They used the identical SCLC homopolymer and varied only kinds of low molecular LCs in their blends. In our study, adjustment of the composition of LC copolymer could generate UCST phase separation for LC copolymer/low molecular weight LC blends.

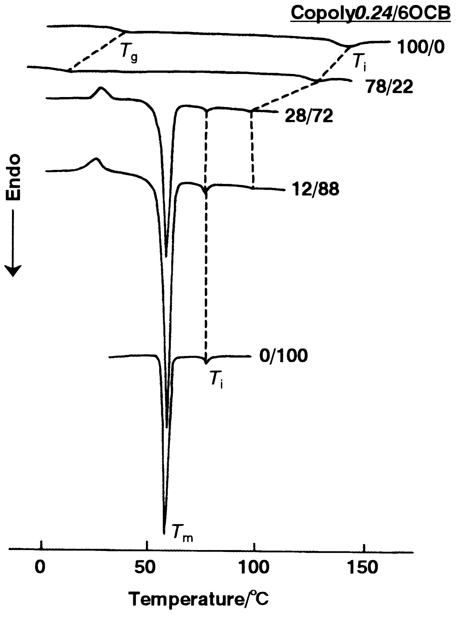

Fig. 6. DSC thermograms of the binary Copoly0.24/6OCB blends.

DSC thermograms of pure Copoly0.24, 6OCB, and Copoly0.24/6OCB blends with different compositions are shown in Fig. 6. In the DSC curve of the pure Copoly0.24, a base line shift associated with glass transition and a broad endothermic peak corresponding to isotropization appears at 34 and 140°C, respectively. No phase transition of the pure components is observed, and T_g and T_i shift to 6 and 128°C, respectively, in the DSC curve of Copoly0.24/6OCB (78/22) blend. This confirms that Copoly0.24 can be molecularly mixed with 6OCB in the low concentration range. In the DSC curves of Copoly0.24/6OCB (28/72) and Copoly0.24/6OCB (12/88) blends, large sharp peaks of melting and smaller peaks of clearing are observed at almost the same temperatures as those of pure 6OCB. In addition, isotropization peaks in the polymer-rich region appear at ca. 98°C. The two domains, that is, polymer-rich and 6OCB-single domains exhibit individual phase transition behavior. These two domains become one homogeneous phase on heating above T_i of polymer-rich phase. However, no peak

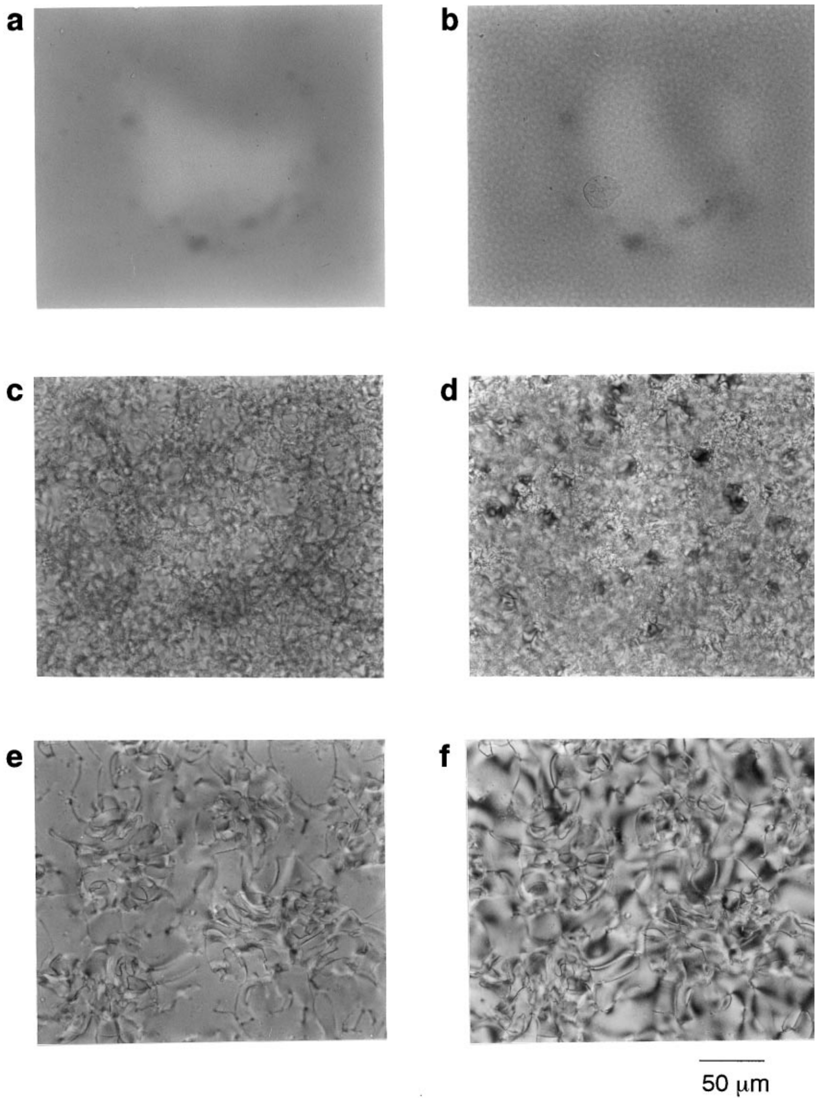

Fig. 7. Optical photomicrographs of the binary Copoly0.24/6OCB (20/80) blend taken at: (a) 140°C without a cross polarizer; (b) 110°C without a cross polarizer; (c) 93°C without a cross polarizer; (d) 93°C with a cross polarizer; (e) 74°C without a cross polarizer; (f) 74°C with a cross polarizer.

due to molecularly mixing was detected by the DSC measurement.

Since the Copoly0.24/6OCB blend shows UCST phase separation, a specific morphology can be observed for the blend by optical microscopy. Photomicrographs of the Copoly0.24/6OCB (20/80) blend taken at various temperatures on cooling are shown in Fig. 7. A homogeneous isotropic phase is observed at 140°C (Fig. 7a). As shown in Fig. 7b, phase separation has taken place by 115°C. Microdroplets of isotropic 6OCB are dispersed in the isotropic matrix of the Copoly0.24-rich phase. According to the literature [15–18], there is a possibility of spinodal decomposition in the early stage of the phase separation. We are now trying to confirm this in our systems. Once the Copoly0.24-rich phase transforms to a liquid-crystalline phase, the two domains agglomerate and become larger. Fig. 7c is a photomicrograph taken at 93°C without a cross polarizer. Copoly0.24-rich phase still forms networks and isotropic 6OCB domains with a diameter of around 20 μm are surrounded by these. When observed with a cross polarizer, Copoly0.24-rich phase is found to exhibit birefringence as shown in Fig. 7d. The coalescence proceeds both with the elapse of time and on lowering the temperature, which might be due to the surface tension and the significant reduction of viscosity resulted from transformation into LC phase. As can be seen in Fig. 7e taken at 74°C without a cross polarizer, Copoly0.24-rich phase was no longer a network but formed domains with a diameter of ca. 80 μm in the continuous phase of 6OCB. Both two regions show a schlieren texture characteristic of a nematic phase under a cross polarizer (Fig. 7f).

4. Conclusion

The SCLC homopolymer, P6OCB having a cyanobiphenyl moiety as a mesogen, was completely miscible with the low molecular weight LC, 6OCB. In contrast, P6OBA containing a benzoic acid group was not miscible but plasticized with 6OCB in the low concentration range. The SCLC copolymer, Copoly0.55 consisting of 55 mol% of a benzoic acid and 45 mol% of a cyanobiphenyl, was also immiscible but plasticized with 6OCB. Interestingly Copoly0.24 having a lower mol fraction of benzoic acid group than Copoly0.55 was partially miscible with 6OCB and the Copoly0.24/6OCB blend exhibited an UCST phase separation. When the concentration of 6OCB is 56 wt% or higher in the Copoly0.24/6OCB blend, a homogeneous isotropic phase divided into two domains and each domain subsequently transformed into a liquid-crystalline phase at an individual transition point on lowering the temperature. In this study, we demonstrated that the miscibility between SCLC copolymers having two different types of mesogens and a low molecular weight LC could be controlled by varying the side-chain composition of the copolymers. The specific morphology resulting from the UCST decomposition in LC polymers/low molecular weight LCs is expected to afford new types of functional materials.

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