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Thermoplastic polymer-dispersed liquid crystals prepared from solvent-induced phase separation with predictions using solubility parameters

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The optical effects of liquid crystals can be realized when the mesogens are dispersed in a supporting and stabilizing polymer phase. Thermoplastics were chosen for their structural reversibility and ease of fabrication of polymer-dispersed liquid crystals (PDLCs) from solution via solvent-induced phase separation (SIPS). The component match and tuning in PDLCs was achieved in a common solvent through predictions of solubility parameters. The PDLCs were first prepared using SIPS and were then exposed to thermal treatments on a hot stage polarizing microscope or in a differential scanning calorimeter. At elevated temperatures the polymer and mesogen may become miscible, while upon cooling thermally induced phase separation (TIPS) should occur, preferably above the isotropic–nematic transition temperature. The nematic phase existed within disperse phase droplets that were stabilized and supported by the matrix polymer. The temperature range of the nematic phase was extended in the PDLC configuration. The droplet size was important for liquid crystalline optical behaviour. Polymer–mesogen interactions, identified through solubility parameters, were important in ensuring sufficient but not coarse phase separation.

1 Introduction

Polymer-dispersed liquid crystals (PDLCs) are a relatively new class of materials that hold promise for many applications ranging from switchable windows to projection displays [1–7]. This is because they offer a number of potential advantages over the well-established nematic devices (twisted and super-twisted) as well as over a number of other competitors (e.g. ferroelectric or emissive). PDLCs require no polarizers that absorb more than half of the transmitted light. As a result, they efficiently increase brightness, minimize heat-control problems and reduce the power and weight. Furthermore, PDLCs require no alignment layers or stringent thickness control, which would greatly simplify the processing of larger-size displays. There have been several approaches used to prepare PDLCs, including polymerization-induced phase separation (PIPS), thermally induced phase separation (TIPS) and solvent-induced phase separation (SIPS) [1, 2, 6, 8, 9]. The formation of PDLCs is closely associated with phases, phase separation or phase transformation. A fundamental understanding of phase-related issues is essentially the first step for designing and tailoring the structures of PDLCs in order to gain electro-optical properties or optimization of device performance [1, 10, 11].

In the SIPS process, solvents can be used to solubilize a liquid crystal (LC) and a thermoplastic polymer in order to create a single phase. As the solvent is evaporated, the LC phase separates as droplets in a polymer matrix. The droplet size can be tuned by controlling the rate of solvent evaporation. However, in practice it is not easy to gain the desired droplet size using SIPS. As the polymers used in SIPS processes are thermoplastic in most cases, it is possible to reset the droplet size of a SIPS film by a subsequent TIPS process. Usually, the PDLC film is heated to a temperature at which the LC molecules are dissolved throughout the polymer matrix. The LC phase can separate from the polymer matrix upon cooling. The LC droplet size would be better controlled by the cooling rate of TIPS. As can be seen, two steps are involved in the preparation of PDLCs with a controlled LC droplet size. Alternatively, the LC droplet size could be controlled using a one-step approach, where the desired LC droplets with fine sizes form directly from phase separation of an initial uniform LC–polymer solution.

Apparently, the thermodynamics of mixing for two kinds of components plays an important role in the understanding of phases and phase separation occurring in the preparation of PDLCs. The free energy of mixing has a form involving a combinatorial entropy and an

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energy of mixing [12]. The key quantity is an interaction parameter between LCs and the polymer that, in particular, would be a starting point in selecting a suitable polymer for a required mesogen [13, 14]. The solubility parameter (δ), proposed by Hildebrand (see [15, 16]), provides an objective and quantitative predictor of PDLC combinations. This means that the solubility of a given mesogen in a given polymer is favoured if the solubility parameters of polymer and mesogen are equal. The solubility parameter is defined as the square root of cohesive energy density (E_{coh}):

$$\delta = (E_{\mathrm{coh}})^{1/2} = (\Delta E_{\mathrm{V}}/V)^{1/2} \quad \left(\mathrm{J}^{1/2}\cdot\mathrm{cm}^{-3/2}\right) \tag{1}$$

$$\Delta E_{\mathrm{V}} = \Delta U_{\mathrm{vap}} = \Delta H_{\mathrm{vap}} - RT \quad \left(\mathrm{J}\cdot\mathrm{mol}^{-1}\right). \tag{2}$$

Where, ΔE_{V} is the latent energy of vaporization, V is the molar volume of the liquid involved, ΔU_{vap} is the latent heat of vaporization, R is the universal gas constant and T is temperature (in Kelvin). There are two main methods to calculate solubility parameters: the method of Hoftyzer and Van Krevelen, and the method of Hoy. Both of these methods are used for comparison in this paper. The results of the two methods in estimating the solubility parameter and its components are of the same order in accuracy (10%) [16]. The most reliable method for estimation is to apply both methods, and use an average result.

The aim of this research is to apply solubility parameters to the choice of materials to make PDLC films with controlled phase separation, suitable dispersed phase droplet size and stable phase structure. The PDLCs are characterized using differential scanning calorimetry (DSC) and hot-stage polarized optical microscopy (POM) to study the thermal and optical properties of PDLC films. The melting endotherm was expected to be sufficiently isolated from the other thermal transitions to extend the method described by Smith and co-workers [17–20] to an analysis of the melting transition.

2 Experimental details

2.1 *Materials*

All chemicals used in the present work were purchased from Sigma–Aldrich, Australia. The three mesogens were 4-(decyloxy)benzoic acid, 4,4′-azoxyanisole and trans-4-methoxycinnamic acid. Their structures are presented in figure 1. The purity of the materials was 98%. The polymers were poly(2-hydroxyethyl methacrylate) (PHEMA; M_{w}=20,000 g mol^{-1}), poly(methyl methacrylate) (PMMA; M_{w}=996,000 g mol^{-1}), poly(-vinyl chloride) (PVC; M_{w}=43,000 g mol^{-1}). Chloroform ($CHCl_3$), N,N-dimethylformamide (DMF) and tetrahydrofuran (THF) were used without further purification.

2.2 *Preparation of the PDLC films*

The PDLC films were prepared following a combination of SIPS and TIPS. In general, a selected polymer and a mesogen were dissolved in a common solvent at room temperature. Each solution was stirred for about

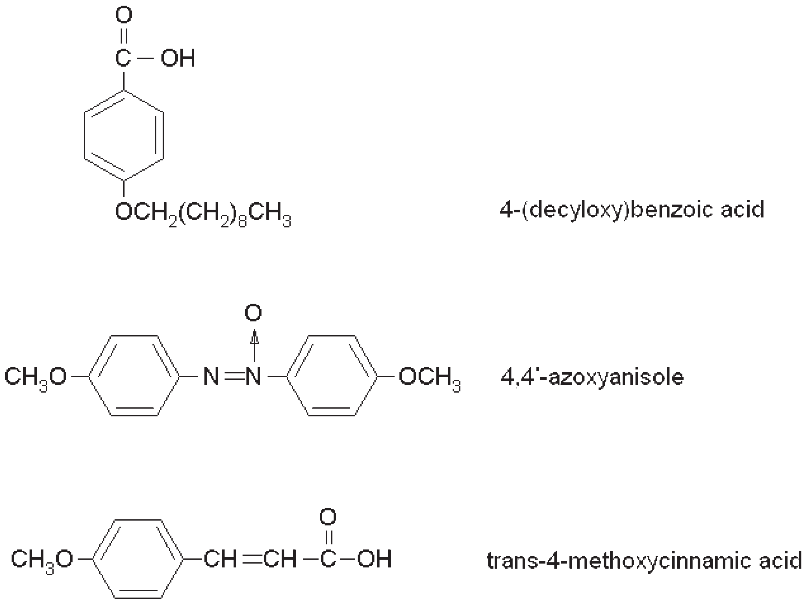


Figure 1. Structures of the mesogens.

5 min. A small quantity was then cast on a carefully cleaned glass substrate. The PDLC films were formed by a slow evaporation of the solvent (over 24 h). The films were then dried under vacuum, which allows complete evaporation of the solvent. A glass cover was placed over the PDLC film and the dry film was pressed.

2.3 *Measurements*

DSC measurements were performed using a Perkin-Elmer Pyris 1 instrument. The sensor was purged with nitrogen at a rate of 20 ml min^{-1}. The PDLCs were first heated at a rate of 40°C min^{-1}, then cooled and subsequently heated at a rate of 5°C min^{-1}, to allow phase separation and the formation of ordered liquid crystalline regions, from room temperature to 10°C above the transition temperature leading to the isotropic phase. The PDLCs were held for 3 min in both the isotropic and the crystalline states. Transition temperatures were recorded systematically during the cooling program and the second heating program.

A Nikon Labophot 2 optical microscope equipped with a Mettler FP-82 hot stage and Mettler FP90 temperature programmer was used to explore the thermal transitions and morphologies. PDLC films were first heated at a rate of 10°C min^{-1} to 140°C (for 4,4′-azoxyanisole dispersion) or higher (150°C for 4-(decyloxy)benzoic acid dispersion; 200°C for trans-4-methoxycinnamic acid dispersion) depending on the different components, to ensure that a homogenous isotropic state has been reached. PDLC films were cooled from above isotropic temperature to room temperature at a cooling rate of 2°C min^{-1}. Texture images were captured during the cooling process.

3. Results and discussion

The solubility parameters of the materials were calculated by the method of Hoftyzer and Van Krevelen and the method of Hoy; moreover, the final results were determined by taking the average value of these two methods because the results of the two algorithmic methods for estimation of the solubility parameter and its components are of the same order of accuracy (10%) [16]. The results for mesogens, polymers and solvents are presented in Tables 1 and 2, respectively. Suitable polymers and solvents were chosen for the required LCs, depending on the smallest difference in solubility parameter. LC–polymer pairs with small solubility parameter difference are expected to be miscible before solvent evaporation and immiscible after solvent evaporation and temperature decrease to form a PDLC film.

When the concentrations of LCs were lower in the PDLCs, no discrete domains were observed in the PDLCs with the decrease of temperature, because LCs were completely miscible in the polymer matrix; therefore, no phase separation occurred. Figure 2(a) shows that some tiny batonnets could be observed and no droplets were formed at 108°C in the 25 wt% 4-(decyloxy)benzoic acid dispersed in PHEMA. As the LC concentration increases, the density and size of the domains increases. However, when the LC concentration was greater than 70 wt% and two-phase mixture was continuous with LC phase and polymer phase, respectively, the LC phase became continuous instead of forming spherical droplets. Small polymer beads that have aggregated wind through the LC phase creating a co-continuous two-phase morphology, which is presented in figure 2(b). Large individual pockets of 4-(decyloxy)benzoic acid existed in the 75 wt% PDLC in the nematic phase and the dark area corresponds to the polymer matrix. The PDLCs with about 50 wt% LCs were synthesized in this project in order to create suitable LC droplets morphologies.

Figure 3 shows the thermograph for PHEMA dispersed in 4-(decyloxy)benzoic acid prepared in $CHCl_3$ solvent. The concentration of mesogen was 54 wt%. The pure 4-(decyloxy)benzoic acid showed two mesophases, smectic (S) and nematic (N), in different temperature ranges. When this PDLC was cooled from the isotropic (I) phase, the I–N peak appeared at about 133°C. As can be seen from figure 3(a), the Schlieren texture of the N phase appeared and covered the whole field of view. This texture persisted until the temperature reached 119°C at which point the N phase changed to

Table 1. The solubility parameters of the mesogens (J$^{1/2}$ cm$^{-3/2}$).

	Hoftyzer and Van Krevelen				Hoy			
LCs	δ_t	δ_d	δ_p	δ_h	δ_t	δ_d	δ_p	δ_h
4-(decyloxy)benzoic acid	19.5	18.1	2.2	7.0	19.3	15.0	7.1	9.8
4,4′-azoxyanisole	23.2	20.3	5.0	10.1	19.9	13.7	7.0	12.6
Trans-4-methoxycinnamic acid	23.4	20.7	4.4	9.9	22.8	13.3	11.9	14.1

Table 2. Average solubility parameter for mesogens, polymers and solvents ($J^{1/2}\,cm^{-3/2}$).

Mesogen/polymer/solvent	δ_t	δ_d	δ_p	δ_h
4-(decyloxy)benzoic acid	19.4 (0.1)	16.6 (0.2)	4.7 (3.6)	8.4 (2.0)
4,4′-azoxyanisole	21.6 (0.9)	17.0 (2.2)	6.0 (3.2)	11.4 (4.2)
Trans-4-methoxycinnamic acid	23.1 (0)	17.0 (1.8)	8.2 (2.2)	12.0 (3.4)
PHEMA	19.5	16.4	8.3	6.4
PVC	22.5	19.2	9.2	7.2
PMMA	23.1	18.8	10.2	8.6
$CHCl_3$	18.9	17.8	3.1	5.7
THF	19.5	16.8	5.7	8.0
DMF	24.9	17.4	13.7	11.3

The data in parentheses shows the difference of parameter in absolute value between the mesogen and its matching polymer.

Table 3. Thermal properties of materials, the LC solubility limit, *A*, and the fraction of liquid crystals, α, separated from the polymer matrix in the PDLCs.

Materials		T_m (°C)	T_{NI} (°C)	ΔH_{NI} ($J\,g^{-1}$)	A	α
4-(decyloxy)benzoic acid	Pure LC	96.3	141.2	5.08	43	0.36
	PDLC	96.1	133.6	0.98		
4,4′-azoxyanisole	Pure LC	119.1	133.7	1.99	42	0.28
	PDLC	117.9	129.0	0.27		
Trans-4-methoxycinnamic acid	Pure LC	172.8	188.5	11.76	49	0.27
	PDLC	173.0	188.3	1.81		

an S phase. A different texture from the N phase was observed at 108°C, as shown in figure 3(b). The S phase appeared in a lower temperature range than the N phase, which is attributed to the more ordered molecules of the S phase, because a more ordered mesophase lies closer to the crystalline phase. As shown in figure 4(a), the molecular axes of the N molecules are aligned parallel to a preferred direction and the centres of gravity are distributed at random as in an ordinary liquid. All smectic LCs have a layered structure as shown in figure 4(b). The centres of gravity of the elongated molecules are arranged in equidistant planes and the long axes of the S molecules are parallel to a preferred direction that may be normal to the planes (S_A) or tilted by an angle (S_C). The PDLC presents two different crystalline structures that are confirmed by both the DSC curves and the morphologies observed by POM below the melting temperature (T_m=96°C). The change between the two different crystalline structures occurred at about 85°C (figures 3(c) and (d)).

Figure 5 presents the thermal and optical properties of PVC dispersed 4,4′-azoxyanisole prepared in the THF solvent. The concentration of LCs is about 50 wt%. The droplets only show the N phase between 129°C and 120°C. The evolution of droplets generated by cooling is discussed later. The micrograph in

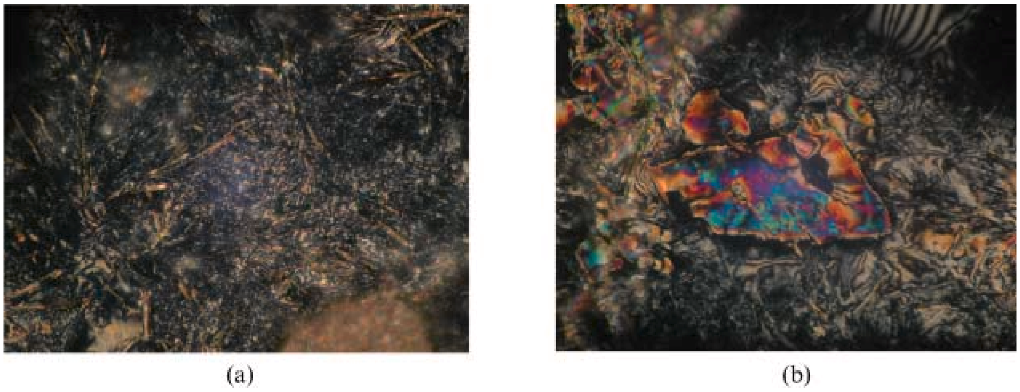

(a) (b)

Figure 2. (a) The morphology of 25 wt% 4-(decyloxy)benzoic acid dispersed in PHEMA at 108°C. (b) The two-phase morphology of 75 wt% 4-(decyloxy)benzoic acid PDLC at 125°C.

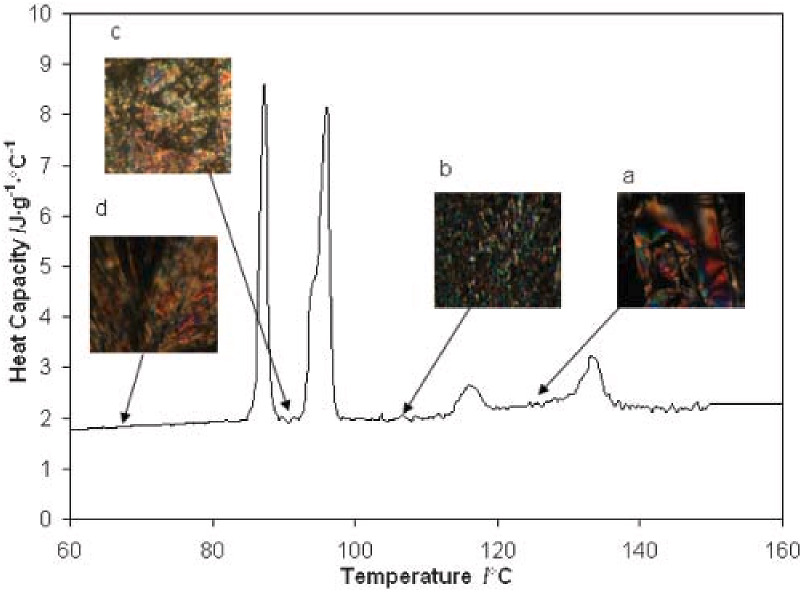


Figure 3. DSC thermogram and POM micrographs of PHEMA dispersed 4-(decyloxy) benzoic acid during cooling: (a) 126°C; (b) 108°C; (c) 91°C; and (d) 70°C.

figure 5(a) was taken at 122°C, showing the N droplets. After continuing cooling, the fan-shaped focal conic texture of the liquid-crystalline phase, shown in figure 4(b), was observed.

Figure 6 presents the DSC curve and the textures of PMMA dispersed trans-4-methoxycinnamic acid prepared in DMF solvent. The concentration of mesogen is 57 wt%. The N phase of droplets was observed in the temperature range from 175°C to 190°C, as shown in figure 6(a). The needle-like crystalline phase (figure 6(b)) appeared below 170°C. The appearance of the first generation of tiny droplets of 4,4′-azoxyanisole was observed at 130.1°C when cooling from the isotropic phase. At 129.8°C (figure 7(a)), the initial droplets had significantly grown and a new generation of smaller particles was observed (the dark region corresponds to PVC and the isotropic 4,4′-azoxyanisole phase). At 129.5°C (figure 7(b)), an agglomeration of the large droplets of nematic domains was observed (initiation of phase inversion). Older particles continued their growth and new particles appeared. When the temperature reached 129.1°C, the coalescence of the oldest droplets had significantly advanced (figure 7(c)). At 128.6 °C (figure 7(d)), phase inversion was evidenced by the appearance of a continuous nematic phase leaving dispersed domains of the isotropic solution. As the temperature decreased further (figures 7(e) and (f)), new generations of nematic particles appeared, covering the whole sample.

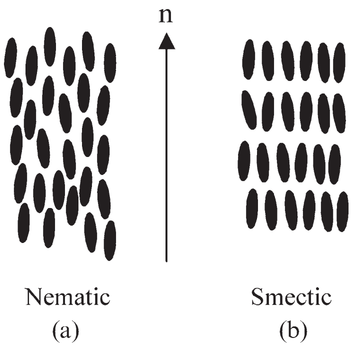


Figure 4. The structures of the N and S phases.

Smith and co-workers [17–20, 22–24] have shown that the LC solubility limit, A, in the polymer matrix may be related to the ratio of the nematic isotropic enthalpy of the matrix, $\Delta H_{\mathrm{NI}}(X)$, to that of the pure LC, ΔH_{NI} (LC), using

$$\frac{\Delta H_{\mathrm{NI}}(X)}{\Delta H_{\mathrm{NI}}(LC)} = \frac{X-A}{1-A} \tag{22}$$

where X is the weight fraction liquid crystal in the sample. So the fraction α of LCs contained within the droplets is given by (as opposed to LCs dissolved in the polymer):

$$\alpha = \begin{cases} \frac{(X-A)}{X(1-A)} & X \geq A \quad (23) \\ 0 & X < A \quad (24) \end{cases}$$

Three assumptions are made in the derivation of these equations: (i) the LC dissolved in the polymer matrix did not contribute to the nematic–isotropic enthalpy

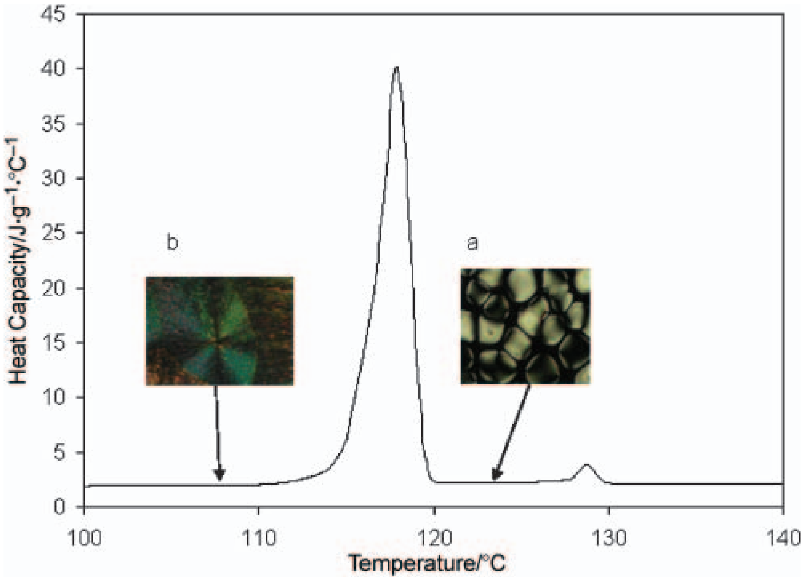


Figure 5. DSC thermogram and POM micrograph of PVC dispersed 4,4′-azoxyanisole during cooling: (a) 124°C; and (b) 108°C.

and the phase-separated LC was contained wholly within droplets; (ii) the amount of LC a given mass of the polymer matrix can dissolved is constant for $X \geqslant A$; (iii) the presence of polymer in the LC droplets did not affect ΔH_{NI} (see [19]). As shown in Table 3, for the polymer–LC systems, the clearing temperature showed only a weak dependence on composition.

Note that the values of A determined from the data shown in Table 3 were slightly higher than the value reported in the literature [25]. However, these values are much higher than the typical values ranging from 10 to 20 measured for a thermally cured system [18, 19]. Table 3 shows the dependence of α on composition. The maximum value of α was 0.36 and observed for the 54 wt% 4-(decyloxy)benzoic acid mixture. The α values of 4,4′-azoxyanisole dispersion and trans-4-methoxycinnamic acid dispersion were 0.28 and 0.27, respectively. The smallest difference in polar solubility

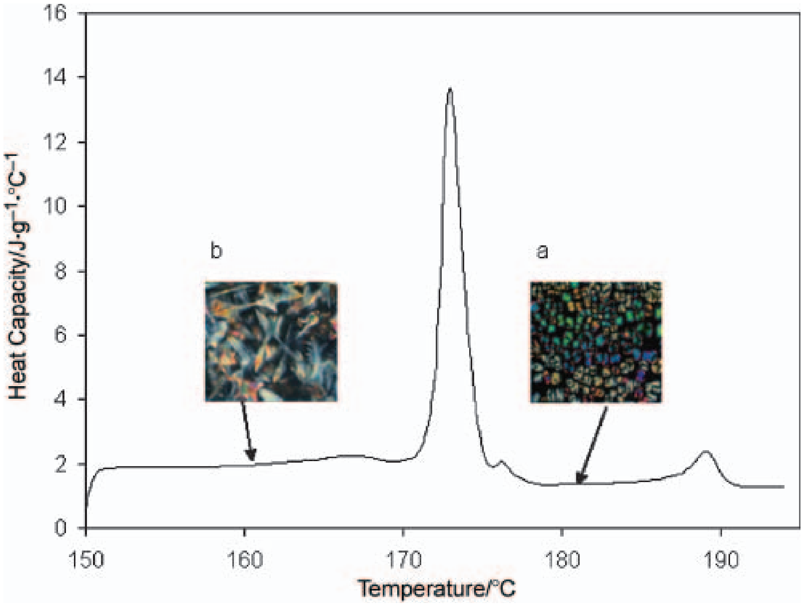
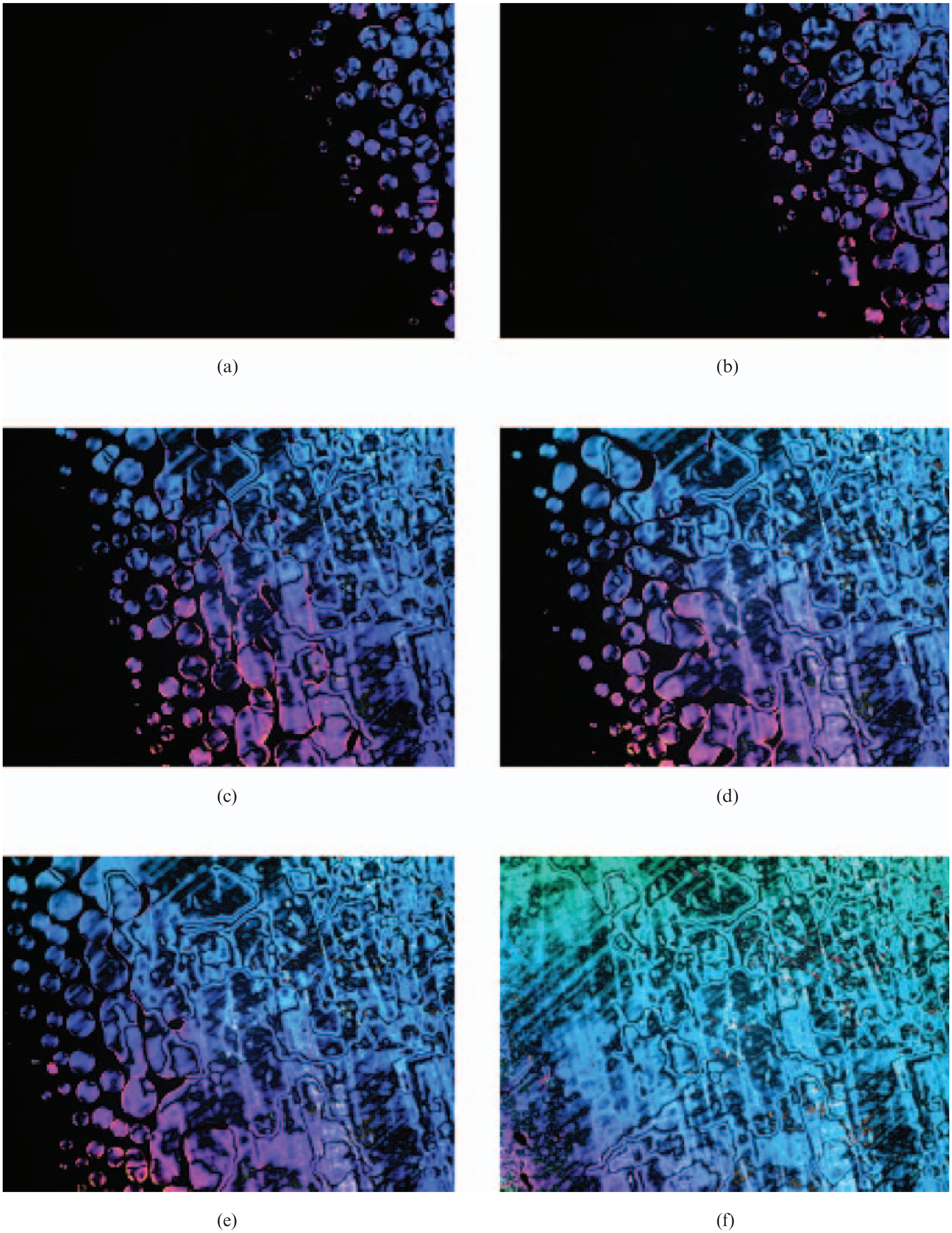


Figure 6. DSC thermogram and POM micrograph of PMMA dispersed trans-4-methoxycinnamic acid during cooling: (a) 180°C; and (b) 157°C.



(a) (b) (c) (d) (e) (f)

Figure 7. Evolution of morphologies generated by cooling PVC dispersed 4,4′-azoxyanisole with 50 wt% 4,4′-azoyxanisole at 2°C min^{-1}, observed by POM: (a) 129.8°C; (b) 129.5°C; (c) 129.1°C; (d) 128.6°C; (e) 127.9°C; (f) 127.5°C.

component between the trans-4-methoxycinnamic acid and the PMMA caused the highest solubility limit (49) in the PMMA matrix and the smallest LC fraction.

The solubility parameter was used to match the polymers and the given LCs and to choose the suitable solvents to dissolve the LC–polymer compositions to create a single phase. The other phase transition enthalpies, ΔH_{CN} or ΔH_{SN}, had been expected to be used to determine more reliable estimates of A and α. This expectation was not realized, however, because the endotherms, particularly for lower concentration LC mixtures for which complete miscibility between the polymer matrix and LC was observed, were not sufficiently isolated from other endotherms to allow ΔH_{CN} or ΔH_{SN} to be determined accurately.

Both the melting temperature and the clearing temperature of the PDLC systems were slightly lower than that of pure LCs owing to the dispersion of microdroplets and the effects of the polymers.

4. Conclusions

The difference in solubility parameter between the mesogen and polymer has been a useful parameter for predicting good dispersion. It provides a convenient approach to obtain the most uniform LC dispersion in a polymer matrix. Improving LC dispersion by selecting different polymers and solvents has been proposed for use in the design of PDLC films and controlling the morphology of mesogen droplets in PDLCs. The degree of phase separation in different PDLC systems using the melting, S–N phase transition and clearing enthalpies associated with the LC component has been investigated. Unfortunately, the melting enthalpy was not suited to this task because complex sequences of solid transitions prevented its accurate determination. Different mesophases are expected to be obtained in PDLC films when LCs exhibit different mesophases between the melting temperature and isotropization temperature.

The total solubility parameter has been considered when matching the polymer–LC solvent pair. However, the polar component of the solubility parameter is most important in predicting the solubility limit in a polymer matrix and the LC fraction in the droplets, while the other components, dispersive and hydrogen bonding, were not critical.

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