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PHASE TRANSITION STUDIES BY THERMAL AND THERMOOPTICAL ANALYSIS OF LIQUID CRYSTALS INSERTED INTO A POLYMERIC MATRIX

M. Mucha and *M. Kryszewski*

POLYMER INSTITUTE, TECHNICAL UNIVERSITY, 90–362 ŁÓDZ, POLAND

Phase transitions of nematic and cholesteric liquid crystals (LC), either pure or inserted into a polymeric matrix, were investigated by using DSC and thermooptical analysis (TOA) techniques. The morphological structures of these LC, their stabilities in polymer film and their phase transitions were found to depend on the LC concentration and its distribution in the polymeric matrix. The polymer affects the LC ordering, leading to a decrease of the mesophase range.

Liquid crystals (LC) display many important features: the anisotropy of optical, dielectric and magnetic properties, a relatively low viscosity and facile deformation and orientation. The insertion of LC into transparent polymers or their microencapsulation leads to the preparation of various materials which can be used for many practical purposes [1–4]. The aim of this study was to investigate the morphological structures and phase transitions of two typical LC inserted into a cross-linked polymer matrix.

Experimental

Samples: Films 50 μm thick were prepared in the following way. Photopolymerizing synthetic resin (Polimal 194, obtained on the basis of unsaturated esters with styrene monomer) was blended mechanically with LC in appropriate concentrations: 1, 2, 4, 7 and 10 wt. % (samples 1–5). Sandwiches of the mixture were irradiated with UV light for several minutes. Photopolymerization yielded thin solid films with inserted LC. The procedure was applied for the insertion of two types of LC: a) *p*-butyloxyphenyl *p*-pentyloxybenzoate, and b) cholesteryl nonanoate.

Methods: The phase transitions of these LC were studied with a 990 du Pont (DSC) differential scanning calorimeter and a home-made thermooptical analyzer (TOA). The heating rate was 10 deg min^{-1} in DSC and 7 deg min^{-1} in TOA. The morphological structures of the prepared films were analyzed by using a polarizing optical microscope with crossed nicols.

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Results and discussions

Nematic LC inserted into a polymeric matrix

Figure 1 presents DSC curves obtained for pure LC in heating and cooling processes. During heating (I) two endothermic heat effects are observed, for the two phase transitions occurring at temperatures T_1 and T_2. At $T_1 = 68°$ the transition form the solid (crystalline) to the mesomorphic-nematic phase takes place and at $T_2 = 83°$ the transition from the nematic to the isotropic phase occurs. During cooling (II) from the isotropic phase exothermic effects are found at $T_2 = 80°$ and $T_1 = 48°$. In the case of nematic LC, the mesomorphic phase is easily supercooled, this explaining the strong difference in T_1 and T'_1. The enthalpy and entropy changes at the two transitions are different,

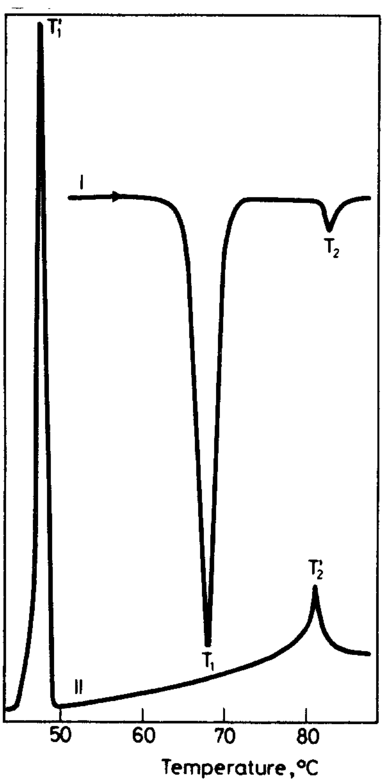

Fig. 1 DSC curves of pure nematic LC: I heating, II cooling. T_1, T_2 – transition temperatures from solid to nematic and from nematic to isotropic phase respectively.

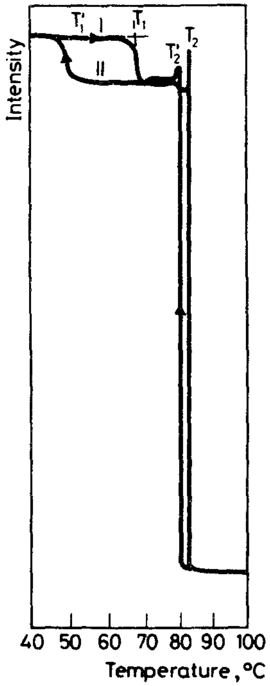

Fig. 2 TOA curve obtained on heating (I) and cooling (II) of pure nematic LC.

and much higher at T_1. Figure 2 presents TOA curves of the same LC obtained in heating (I) and cooling (II) processes. The phase transition temperatures T_1 and T_2 are taken at the beginning of the sharp light intensity decrease. The optical effect is more intense at T_2 than at T_1, in contrast with the thermal (DSC) effect. The DSC and TOA methods are therefore complementary. Figure 3 presents DSC heating curves of samples 1–5. The peak height of the phase transition from the solid to the nematic phase at T_1 = 67° depends on the LC concentration in the polymeric matrix. The phase transition from the nematic to the isotropic phase is only weakly marked. Its temperature T_2 is clearly lower than that for pure LC. Figure 4 presents TOA curves of samples 2, 3, 5 and 6. Curve 6 depicts the behaviour of sample 1 after aging, during which LC diffuses from the matrix and precipitates on the sample surface. LC exists in the form of small microcrystalline structures. For samples 2–5, T_1 is 67–70° and T_2 is 78°. This value is about 5 deg lower than that for pure LC. This decrease results from a considerable influence of the polymeric matrix on the LC ordering and the kinetics of

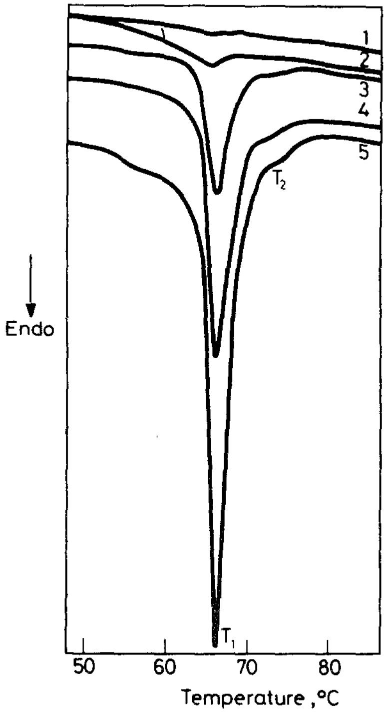

Fig. 3 DSC curves of nematic LC inserted in polymeric matrix LC concentrations: 1 (1), 2 (2), 4 (3), 7 (4), 10 wt.% (5)

its phase transition phenomena. The samples with low LC concentration are less stable. A very high dispersion of the LC leads to the possibility of its migration out of the cross-linked polymeric matrix and its crystallization on the film surfaces, especially during heating or annealing processes. If the LC particles are large enough, their diffusion from the matrix is not possible, as observed for samples 4 and 5, which revealed a stable morphological structure. The optical micrographs (which are not presented here) clearly support the conclusion concerning the dependence of the morphology of LC on its concentration in the polymeric matrix.

Generation of the heterophase structures results from phase separation of the two components during the photopolymerization process of the matrix. The phase separation has a different nature, being dependent on the state of the mixture and the LC concentration [5–6]. In the low range of LC concentrations, the phase separation is generated by the activated nature of the nucleation and growth mechanism of the crystallizing LC component. At

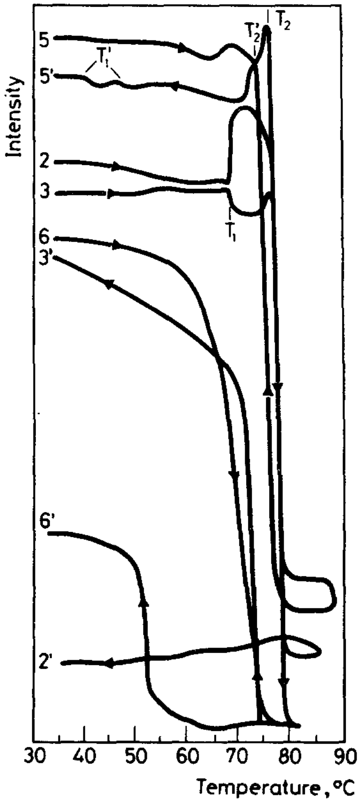

Fig. 4 TOA curves obtained on heating and cooling of nematic LC inserted in polymeric matrix (samples 2–6).

concentrations of LC higher than 7%, the phase separation has a kinetic nature, and it leads to a biphasic structure with a certain connectivity of the LC phase in the polymeric matrix.

Cholesteric LC inserted into a polymeric matrix

Figures 5 and 6 present DSC and TOA curves of pure cholesteric LC. The DSC curve (I) shows a broad endothermic peak with maximum at 72°, which includes all the thermal effects of the phase transitions: solid-smectic-cholesteric and cholesteric-isotropic. The TOA curve reveals three transition temperatures, however, at $T_1 = 55°$, $T_2 = 68°$ and $T_3 = 73°$. For

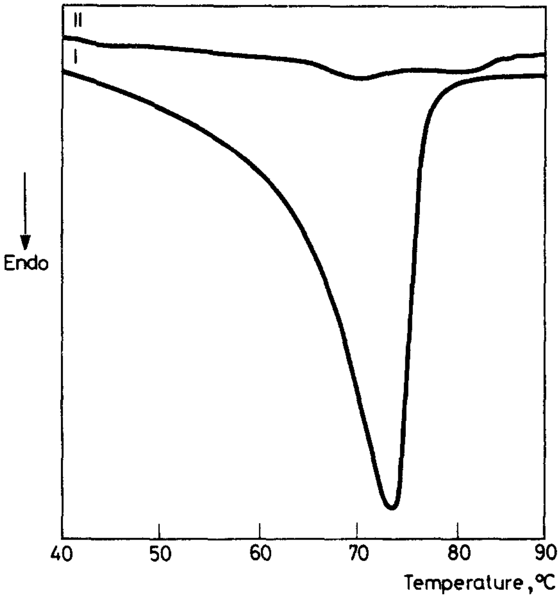

Fig. 5 DSC curves of cholesteric LC; I – pure LC II – 10% LC inserted in polymeric matrix.

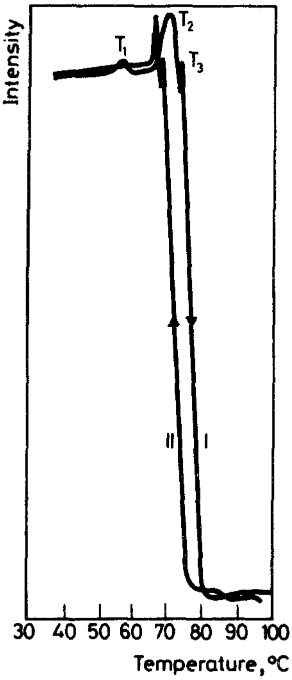

Fig. 6 TOA curves of pure cholesteric LC obtained on heating (I) and cooling (II) processes. T_1, T_2, T_3 – transition temperatures: from solid to smectic phase T_2 – from smectic to cholesteric phase and T_3 – from cholesteric to isotropic phase.

cholesteric LC inserted into the polymeric matrix (DSC curve II. Fig. 5), only a small minimum is observed, but TOA (Fig. 7) clearly reveals a transition at 67°, which is lower than that observed for pure cholesteric LC. Two other transitions (T_1 and T_2) are very close, and thus separation is difficult. Micrographs of the pure cholesteric LC and of their dispersions at different concentrations in the polymeric matrix are characteristic of different morphological structures, similarly to nematic structures in polymeric matrices.

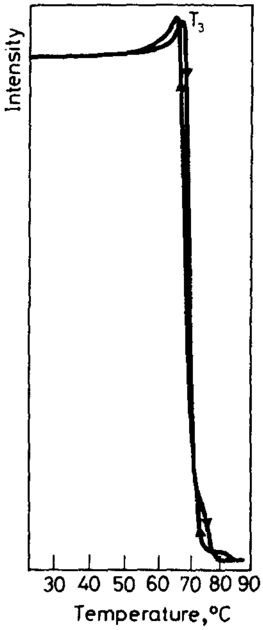

Fig. 7 TOA curves of 10 wt.% cholesteric LC inserted in polymeric matrix.

Conclusions

The morphological structures and stabilities of heterogeneous systems of LC inserted into a cross-linked polymer matrix depend on the concentration and distribution of the LC. To avoid the effect of migration of the LC from the polymeric matrix. sufficiently large aggregates of LC are required. In this case the morphological structure of the LC is reproducible in the succeeding stages of the heating and cooling processes. The polymer matrix affects the ordering and causes a decrease of the range of mesophases of LC. Analogous phenomena have been observed for other systems [7–9], and have been explained on the basis of the thermodynamics of solution of some LC substances blended with low and high-molecular compounds. The hysteresis phenomena of the optical and thermal properties of LC inserted into a polymeric matrix can be explained in terms of specific interactions at the LC/polymer interface. This effect was shown to be dependent on the concentration and distribution of the LC in the polymeric medium.

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Zusammenfassung – Phasenumwandlungen nematischer und cholesterinischer Flüssigkristalle (LC), in reiner Form oder in einer Polymermatrix dispergiert, wurden durch DSC und thermooptische Analyse (TOA) untersucht. Die morphologische Struktur, ihre Stabilität im Polymerenfilm, und die Phasenumwandlungen hängen von der Konzentration und Verteilung des LC in der Polymermatrix ab. Die Polymermatrix beeinträchtigt die Ordnung im LC, was zu einer Verkleinerung des kristallin-flüssigen Bereichs führt.

РЕЗЮМЕ — С помощью ДСК и термооптического анализа исследованы фазовые переходы нематик — холестерик жидких кристаллов, как в чистом состоянии, так и в полимерной матрице. Морфологическая структура жидких кристаллов, стабильность их в полимерной пленке и фазовые переходы зависят от концентрации и распределения жидкого кристалла в полимерной матрице. Полимер затрагивает порядок жидкого кристалла, приводя к уменьшению мезофазы.