THERMAL INDUCED PHASE SEPARATION OF E7/PMMA PDLC SYSTEM

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Abstract

The phase behaviour of thermoplastic polymer-dispersed liquid crystal system is studied with particular emphasis on the various transitions that occur within the system. The extent of plasticization of the polymer(polymethyl methacrylate) by the low molecular weight liquid crystal(E7) along with the several transitions of the LC(Liquid Crystal) are determined by modulated DSC. Optical microscopy was used to construct the temperature versus composition phase diagram. Our study indicates the existence of a limiting temperature of 40°C around which the PMMA matrix turns glassy irrespective of the initial composition within the phase separated region, suggesting the intersection of the glass transition curve with the coexistence curve. A slight depression of the N–I(Nematic to Isotropic) transition of the LC is observed with increasing composition of PMMA whereas the S–M(Smectic to Nematic) transition and the T_g (Glass transition temperature) of the LC remain unaffected. The one phase mixture remains isotropic until phase separation at a lower temperature where the LC rich domains become nematic. The growth of LC rich domains is studied as a function of temperature and time.

Keywords: thermoplastic, liquid crystal, T_g

Introduction

Polymer-dispersed liquid crystal films(*PDLC*) have been the subject of recent studies because of potential for electro-optical applications including displays and optical shutters [1–3] PDLCs are micron-sized droplets of liquid crystal dispersed in a polymer matrix. The refractive index mismatch between the droplets and the matrix renders the film opaque in the OFF state. Application of electric field causes the *LC*(Liquid Crystal) molecules to orient within the droplets and if the ordinary refractive index of the *LC* matches that of the matrix, the film becomes transparent.

The dispersion of the *LC* within the matrix is achieved by phase separation processes which are brought about by polymerization, solvent evaporation or a thermal quench depending upon the materials used [1–6]. Understanding and control of the phase separation phenomenon is extremely important because the

electro-optical properties are dependent on the shape, size and distribution of the *LC* droplets. Kim *et al.* [7] reported the phase separation in liquid crystal epoxy mixtures. Hirai *et al.* [8] studied the mixture of *LC* and UV(Ultra Violet) curable vinyl acrylate compounds. Extensive calorimetric studies of UV curable PDLCs have been carried out by Smith *et al.* [4–6, 9, 10]. Kyu *et al.* [11] dealt with the dynamical aspects of thermal quench induced phase separation of thermoplastic PDLCs but have not probed in detail the various transitions in the mixture. Several authors [12–21] have reported the theoretical and experimental results on the phase behaviour of the polymer–*LC* blends.

The focus of this study is the thermal-induced phase separation of E7/PMMA system, particularly the several transitions that occur within the system. The plasticization of the polymer by the liquid crystal and the influence of the polymer on the *N–I*(Nematic to Isotropic), *S–N*(Smectic to Nematic) and T_g(Glass transition temperature) of the liquid crystal are investigated by modulated DSC. In modulated DSC, sinusoidal oscillation(temperature modulation) is superimposed onto the conventional linear temperature ramp or timed isothermal period. Deconvolution of the resultant heat flow, a signal similar to the conventional DSC is separated into a reversing and nonreversing component and results in better sensitivity, resolution and ease of interpretation. Light microscopy with cross polarizers was used to construct the phase separation curve as well as verify the results obtained from DSC. The interference of the phase separation with the glass transition of the polymer and the transitions of *LC* is examined.

Experimental

The low molecular weight liquid crystal used in the studies was E7, an eutectic liquid crystal mixture consisting of four types of cyano-biphenyls. E7 is manufactured by BDH Chemical Co. Ltd, Poole, England and distributed by EM Industries Inc., Hawthorne, NY. Poly(methyl methacrylate) of molecular weight 12 000 g/mole was purchased from Aldrich Chemical Co. The materials were used as received.

Samples for optical studies were prepared by the combination of solvent induced phase separation and thermal induced phase separation techniques. Desired amounts of E7 and PMMA were weighed out and the mixture dissolved in the appropriate amount of chloroform, usually in the ratio of 1:9 of mixture and solvent. The solutions were cast onto glass slides and solvent was allowed to evaporate in air for an hour and then placed in a vacuum oven maintained at 80°C for about 24 h to remove any solvent that may be remaining in the system. The material was sandwiched between two glass slides and 25 μ mylar spacers were used to maintain constant thickness.

Samples for the DSC studies were prepared in the same manner described above. The solutions with compositions ranging form 0 to 100% *LC* in 5% increments were directly weighed out into the DSC pans, left in the air for an

hour and then placed in the vacuum oven maintained at 80°C for 24 h to get rid of the residual solvent. The initial concentration of the solution was calculated so as to have about 10 mg of the material left in the pan after the evaporation of the solvent. Then the pans were hermetically sealed and used in the analysis.

A Mettler FP84HT/FP80HT thermal microscopy cell was used to control the cooling and heating rates. For quenching experiments two such devices were used, one maintained at 80°C and the other maintained at the desired quench temperature. These were used in conjunction with a Spectra-Tech Inc. IRμS infrared microscope and a Zeiss standard 25 microscope, the former equipped with a frame grabber and the latter with a video recorder. The cross-polarized mode was used to observe the N–I transition.

A TA instruments' Thermal Analyst 2910 DSC module with TA 2000 controller unit and accessories was used to run MDSC^{TM}. Base line calibration of the cell was done by running the empty cell through the operating range (−100 to 120°C). Temperature calibration and cell constant calibration were done by heating an Indium sample through its transition temperature. These files were analyzed with the calibration program of the instrument. Temperature modulation amplitude and period are the important parameters which determine the sensitivity of the readings. A modulation amplitude of ±1.5°C and a period of 40 seconds was used in all the experiments except in those with samples of less than 40% LC which required greater sensitivity to detect the transitions. In these experiments an amplitude of ±2°C and a period of 60 seconds was used. The experiments were run under nitrogen atmosphere and an underlying linear ramp of 5 deg·min^{-1}. Only the reversible component of the heat flow is used to obtain the data.

Results

The temperature versus composition phase diagram obtained from optical microscopy is shown in Fig. 1. Samples were continuously cooled from 80°C to room temperature at a rate of 0.2 deg·min^{-1}. The first observation of droplets was taken as a temperature point on the phase separation curve. Several regions of the sample were taken into consideration and the values averaged to take into account any minor concentration fluctuations. The curve shows upper-critical-solution-temperature *(UCST)* behavior. No phase separation is seen in samples with less than 40% of LC composition.

A sample MDSC thermogram of 85% E7 content is shown in Fig. 2. It shows the curve for the total heat flow, reversible heat flow and the nonreversible heat flow. The peaks in nonreversible heat flow are associated with endothermic volume relaxations. The reversible heat flow clearly indicates the T_g of E7, T_g of PMMA and the *N–I* transition of the E7. A faint signal of the *S–N* transition is seen at around −10°C. Ahn *et al.* [12] reported that the changes in

heat flow during phase separation are too small to be detected whereas Smith [10] reported the contrary. The temperature of mixing was not observed in the thermograms of the present system.

Several reversible components of the thermograms are shown in Fig. 3, predominantly demonstrating the changes in the T_g of the polymer and the N–I transition temperature of the LC. The N–I transition temperature decreases with increasing PMMA composition. The N–I transition curve seems to follow the phase separation curve (Fig. 1) with the crirical temperature nearly equal to that of the N–I transition of pure E7. Cross polarized microscopy (Fig. 4) re-
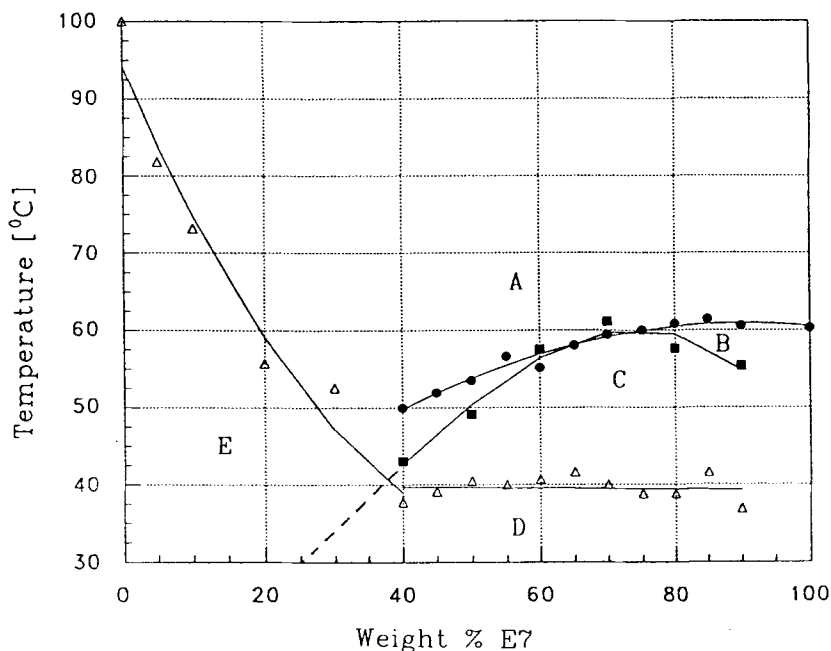

Fig. 1 Phase diagram of the E7/PMMA system depicting the T_g of PMMA, phase separation curve and the N–I transition of the LC. (A) isotropic single phase state, (B) PMMA/nematic E7 single phase state, (C) PMMA/nematic E7 two-phase state, (D) Glassy PMMA/glassy E7 two-phase state, (E) Glassy single phase state

veals that the droplets are nematic immediately after phase separation, indicating that the I–N transition may be taking place before the phase separation. Data from MDSC confirms this observation.

Another issue in the thermally induced phase separation of LC/polymers is the existence of the polymer glass transition. A steep drop in the glass transition temperature of the polymer is observed with an increasing concentration of the LC. The LC essentially acts as a plasticizer bringing down the T_g of the pure PMMA at 100 to 40°C at a LC composition of 40%. We were able to detect the glass transition temperatures within the phase separated region as shown in
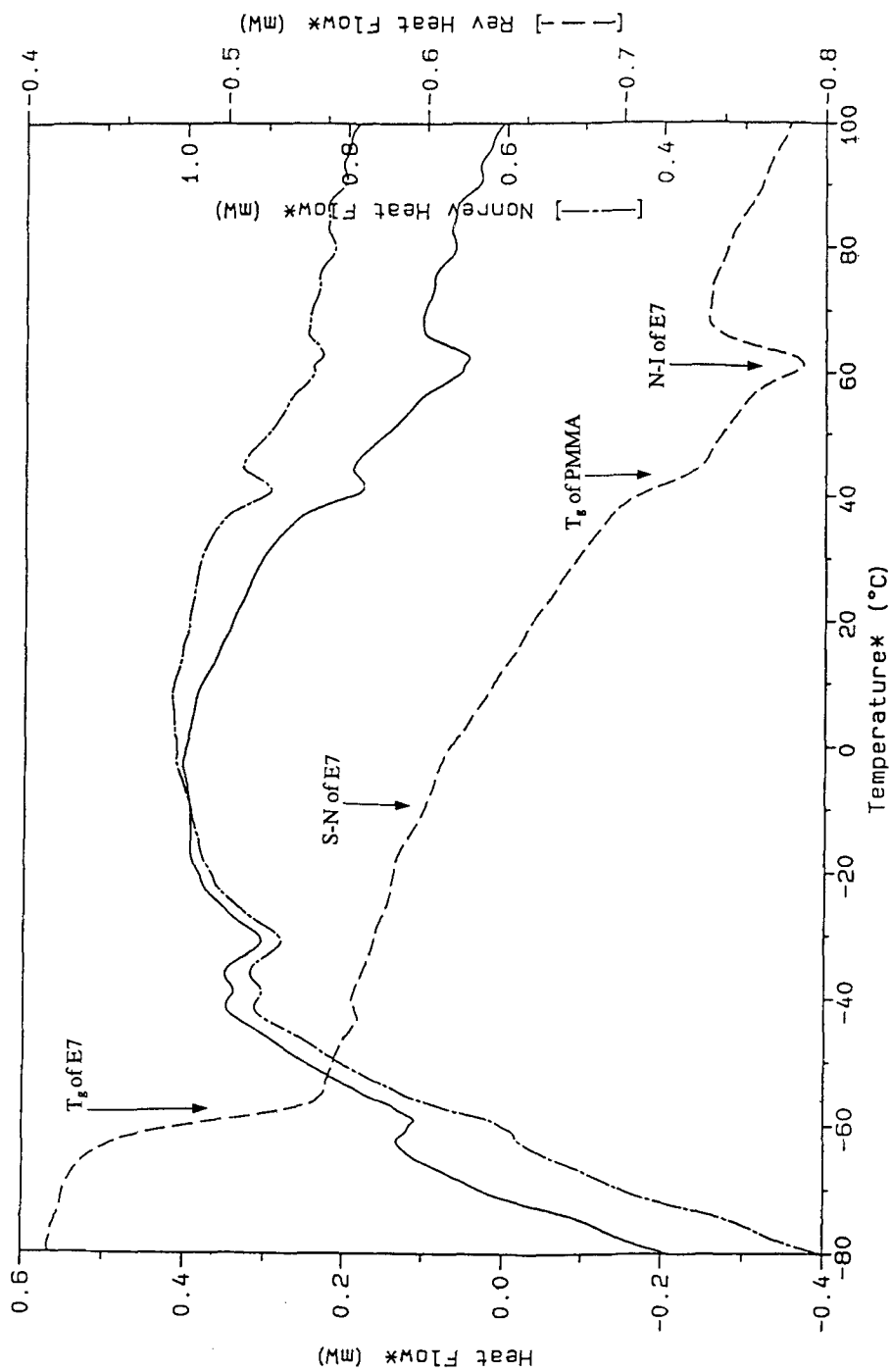
Fig. 2 A typical DSC curve of a PDLC. The figure shows the total heat flow (solid line), reversible heat flow (dashed line) and nonreversible heat flow (dash-dot line) for a mixture of 85% E7 with 15% PMMA
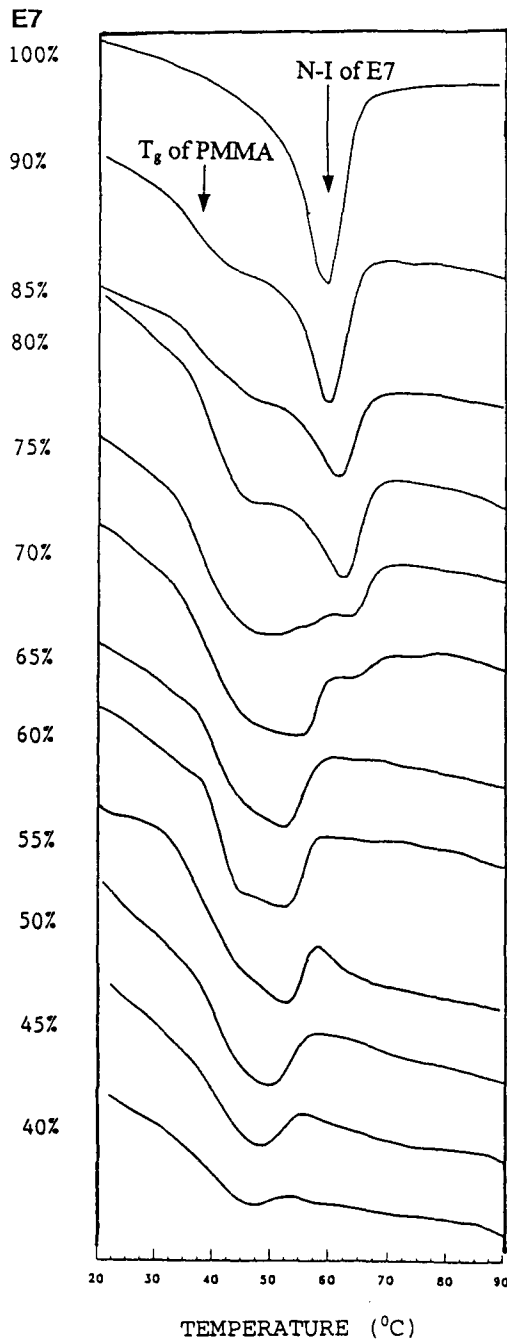
Fig. 3 Reversible DSC curves of mixtures of several concentrations of E7 from 40% to 100%. Both the T_g of PMMA and the $I-N$ transition of LC are seen in these plots

Fig. 1. The T_g remains constant at about 40°C within the phase separated region. The interplay between the glass transition curve, the phase separation curve and the $N–I$ curve is discussed in the next section.

Optical microscopy sheds some light on the glassy state of the polymer matrix. Two samples, one of 70% E7 and the other of 80% E7 were cooled from 70°C to room temperature at a rate of 0.2 deg·min^{-1}. This slow rate was chosen to allow sufficient time for the LC to separate at each temperature. Also the larger sizes of the phase in the optical micrographs enable us to observe them more closely. The 70% E7 sample phase separates at 60.7°C and the 80% sample at 56°C. A number of droplets nucleate and the growth is a result of coalescence and continuous separation of the LC from the matrix with decreasing temperature. Optical micrographs (Figs 6, 7) show the darkening background due to the hardening of the matrix. The droplet size is fairly uniform. The droplet diameter is plotted as a function of temperature as shown in Fig. 8. An average diameter of five droplets is used. The size remains constant after 40°C in both the cases indicating hindrance to the growth of droplets.

E7 has a wide nematic range and is suitable for PDLC applications. It exhibits a nematic-smectic transition at –10°C. The samples from 40 to 100% E7 showed a faint signal of this transition. Below 40%, there are no droplets and hence this signal is not observed. This transition remains unaffected with increasing composition of PMMA, essentially remaining constant at –10°C.

The phase diagram of the PMMA/E7 is shown in Figs 1, 5. The filled squares represent the phase separation curve, unfilled squares the T_g of E7 and the filled circles in Fig. 2 indicate the $N–I$ transition whereas those in Fig. 5 indicate $S–N$ transition. These transitions divide the phase diagram into several regions where the LC and the polymer coexist in different phases.

Formation of monodisperse droplets is desirable from the application point of view. Several thermal processes are evaluated. A sample of 90% E7 is quenched from 90 to 53°C, just below its observed phase separation temperature and the resulting structure is recorded. Numerous droplets appear and grow with time as shown in Fig. 9. The evolution of structure of an 80% E7 sample that is quenched from 90 to 50°C in shown in Fig. 10. The process differs from the previous one and is discussed in the next section.

Discussion

The phase separation curve shown in Fig. 1 can be considered as the coexistence curve or the binodal since the cooling rates are slow. The distinction between the spinodal and binodal is difficult to observe by using only optical microscopy because of the limitations in both length and times scales. Even in deeper quenches one can see the formation of numerous droplets which will eventually coalesce to form larger domains depending upon the composition and the quench temperature. Kyu et al. [11] report similar observations. Phase separation is not observed in samples with less than 40% of LC composition indicating that the E7 is dissolved or molecularly mixed in PMMA.
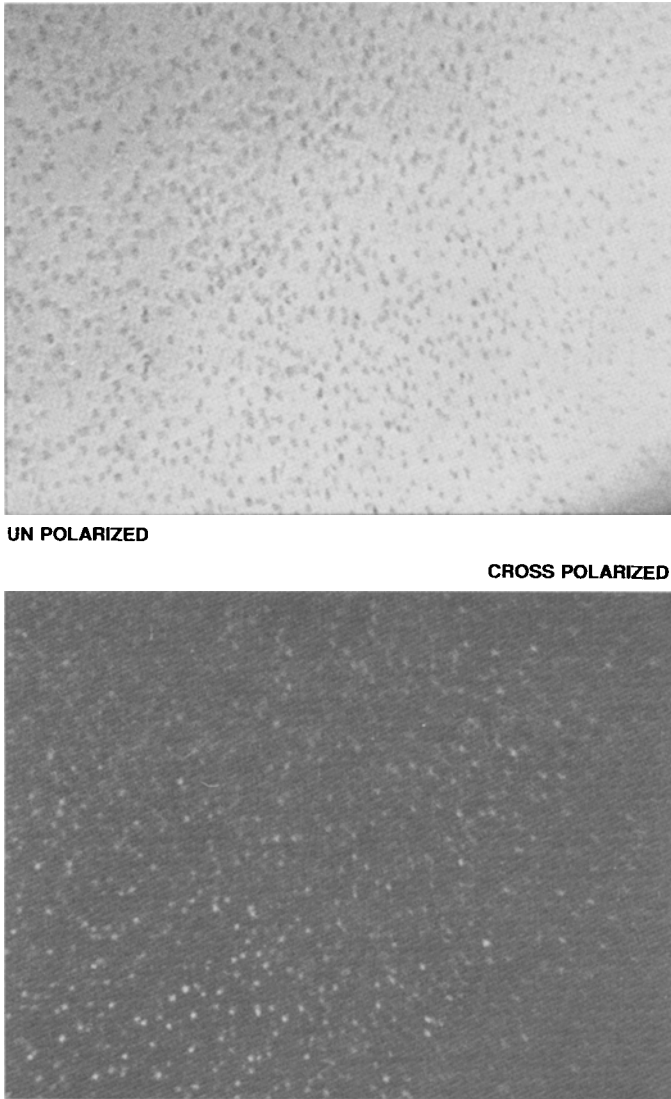
UN POLARIZED

CROSS POLARIZED

Fig. 4 E7:PMMA::70:30 sample shown right after phase separation indicates nematic droplets

The decrease of *N–I* transition temperature with increasing PMMA composition is to be expected since the interference of the polymer chains with the *LC* molecules increases with increasing concentration of polymer. But at the same time since the polymer chains do not dissolve in the nematics, phase separation is induced. So when the mixture is brought to a lower temperature, unlike a conventional system of polymeric chains in an isotropic solvent, these two processes of *N–I* transition and phase separation take place in a coupled fashion. If

the phase separation occurs prior to the I–N transition, it may induce the I–N transition in the liquid crystal regions which in turn may accelerate the phase separation. Also, the I–N transition curve follows the phase separation curve (Fig. 1) with the critical temperature nearly equal to that of the I–N transition of pure E7. The other factor to be taken into account is the reproducibility of optical measurements. Until the droplets are about 1 to 2 µ, they are not detectable. So the actual phase separation curve may be slightly above the one shown. In such a situation there might exist a narrow region of liquid–liquid phase separation near the critical composition. In other words there is liquid–liquid phase separation leading to the formation of droplets rich in LC. This LC behaves like bulk LC with little interference from the polymer and so assumes the nematic configuration revealing itself under crossed polars. Model calculations and experimental evidence by Kyu *et al.* [13] indicate that the liquid–liquid phase separation region falls within a small temperature gap.

The glass transition curve as shown in Fig. 1 complicates the phase separation curve. Thus a mixture of 35% LC when quenched from 70 to 30°C encounters the glass transition curve before the phase separation curve. The polymer hardens before the LC can separate and thus the LC is trapped and remains molecularly mixed. So the phase separation is kinetically prohibited at short times although the thermodynamic driving forces for the phase separation exist. When a mixture of 40% LC is cooled, it meets the phase separation curve first
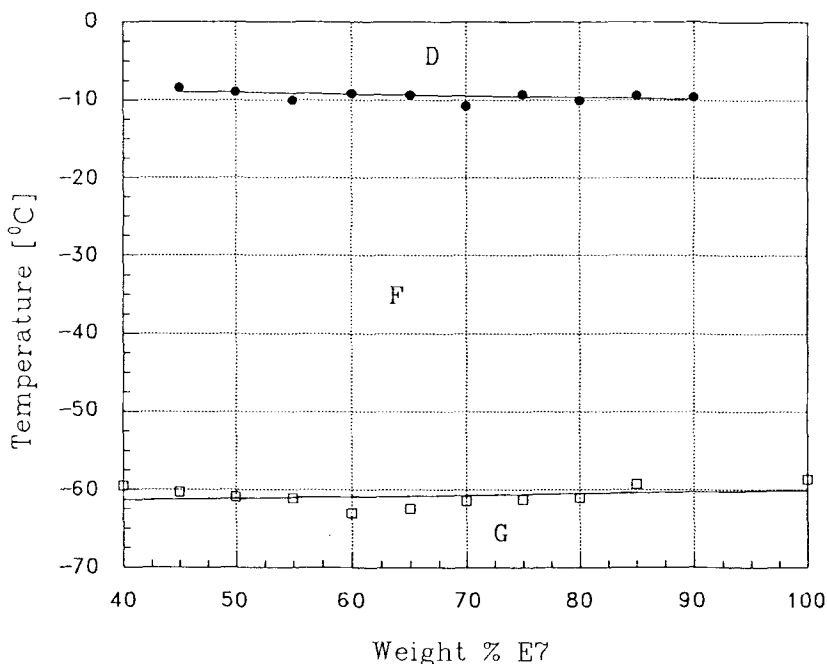

Fig. 5 A supplement to Fig. 1 showing the S–N and the T_g of E7. (F) Glassy PMMA/crystalline E7 two phase state, (G) Glassy PMMA/glassy E7 two phase state

60.7°C

54.2°C

52.5°C
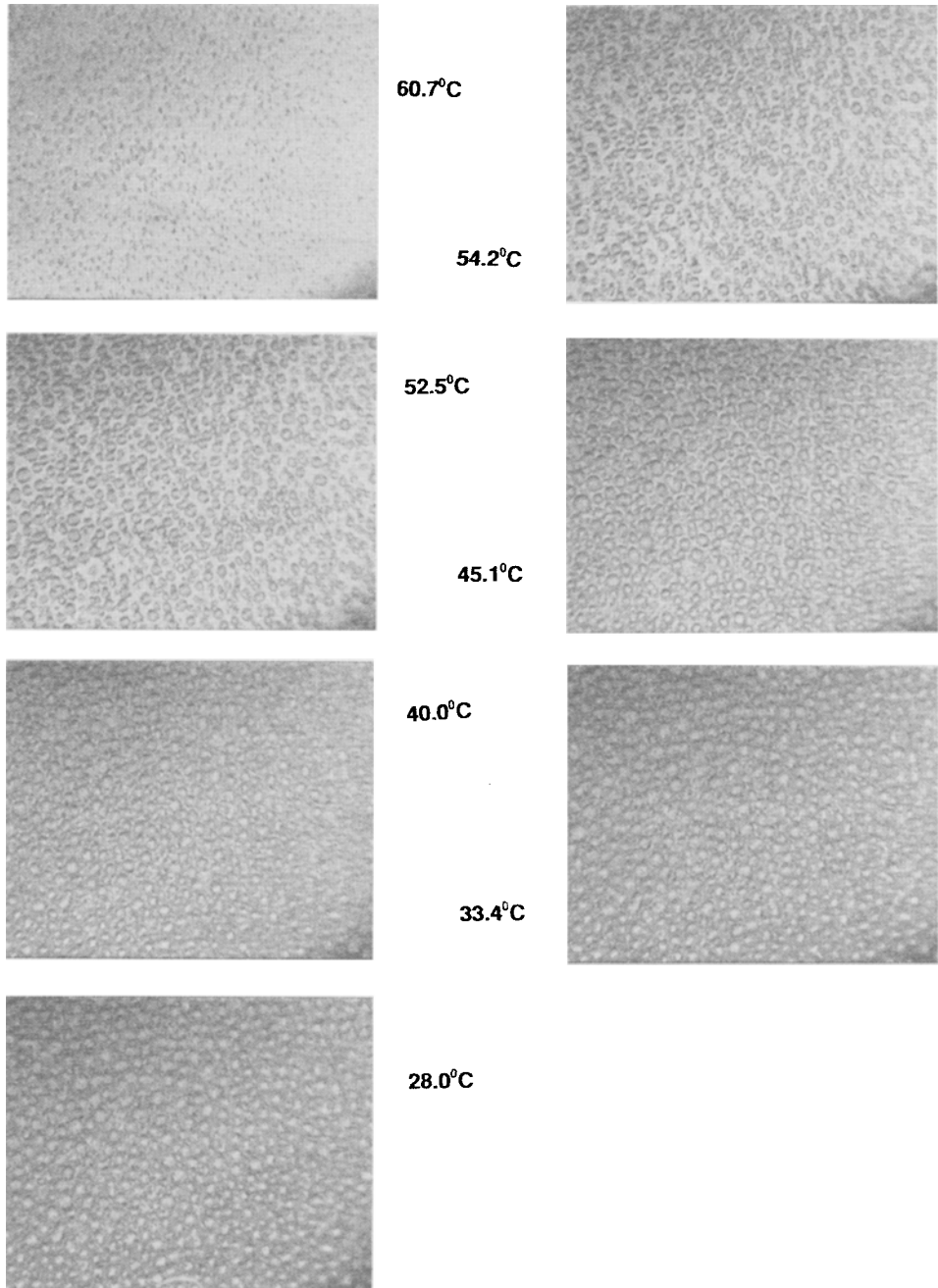
45.1°C

40.0°C

33.4°C

28.0°C

Fig. 6 E7:PMMA::70:30 cooled at a rate of 0.2 deg·min⁻¹

and so the LC separates out as droplets which are then trapped in the polymer-rich glassy environment without coalescence. Hence the temperature at which the polymer hardens is essential in controlling the droplet size.

Figure 1 shows that the T_g of the PMMA remains constant within the phase separated region at about 40°C. The explanation directly follows from the characteristics of phase separation of binary systems. When the mixture is cooled, it separates into two phases, LC rich phase and a polymer rich phase. The composition of each phase is determined by the tie lines at that particular temperature and the amount of LC dissolved in the matrix determines the extent of plasticization. So when a mixture of 70% E7 is cooled from 70 to 50°C, the polymer matrix has about 50% LC by weight and the expected T_g at that composition would be about 30°C (obtained by extrapolating the curve from 0 to 40% E7). So the droplets can grow by coalescence and Ostwald ripening at that temperature. When this system is gradually cooled to lower temperatures, lesser LC remains in the matrix resulting in less plasticization and eventually the temperature to which the mixture is cooled matches that of the T_g of the polymer at that composition and the polymer hardens. So regardless of the initial composition of the mixture, in thermal induce phase separation the droplets are trapped at a particular temperature. This temperature in case of a PMMA/E7 system is 40°C and the amount of E7 trapped within the matrix is approximately 40%. This phenomenon is verified by optical microscopy. Figures 6, 7 show that the growth of the droplets ceases at around 40°C indicating that the polymer matrix turns glassy.

The smectic-nematic transition temperature of LC is –10°C that remains unaffected with increasing composition of PMMA. At this temperature the LC rich phase must contain some polymer as determined by the phase diagram. Once again following the reasoning given above the amount of polymer within this phase is the same for all initial compositions. So this polymer in principle should affect the transition but this is not the case because the polymer amount is very small and also the exclusion of polymer coils from the LC domains to the interface is conceived. Theoretical and experimental work of other authors [14–19] lends support to this interpretation. Similarly the T_g of the LC is unaffected and remains at –60°C.

Figure 9 exhibits the nucleation and growth regime. The droplets appear in the sample of 90% E7 that is quenched from 90 to 53°C and grow with time by coalescence and Ostwald ripening. Initially due to local concentration variations part of the sample reacts to the sudden drop in temperature and rest follows soon after. The droplets are fairly uniform but the matrix cannot be hardened at this temperature and subsequent cooling or quenching results in the matrix behaving like a mixture by it self brings about the formation of several droplets. Figure 10 shows the evolution of structure of a 80% E7 sample that is quenched from 90 to 50°C. This deeper quench might be expected to result in a spinodal structure of interconnected domains, but the process is similar to the nucleation and growth described above, keeping in mind the time of observa-
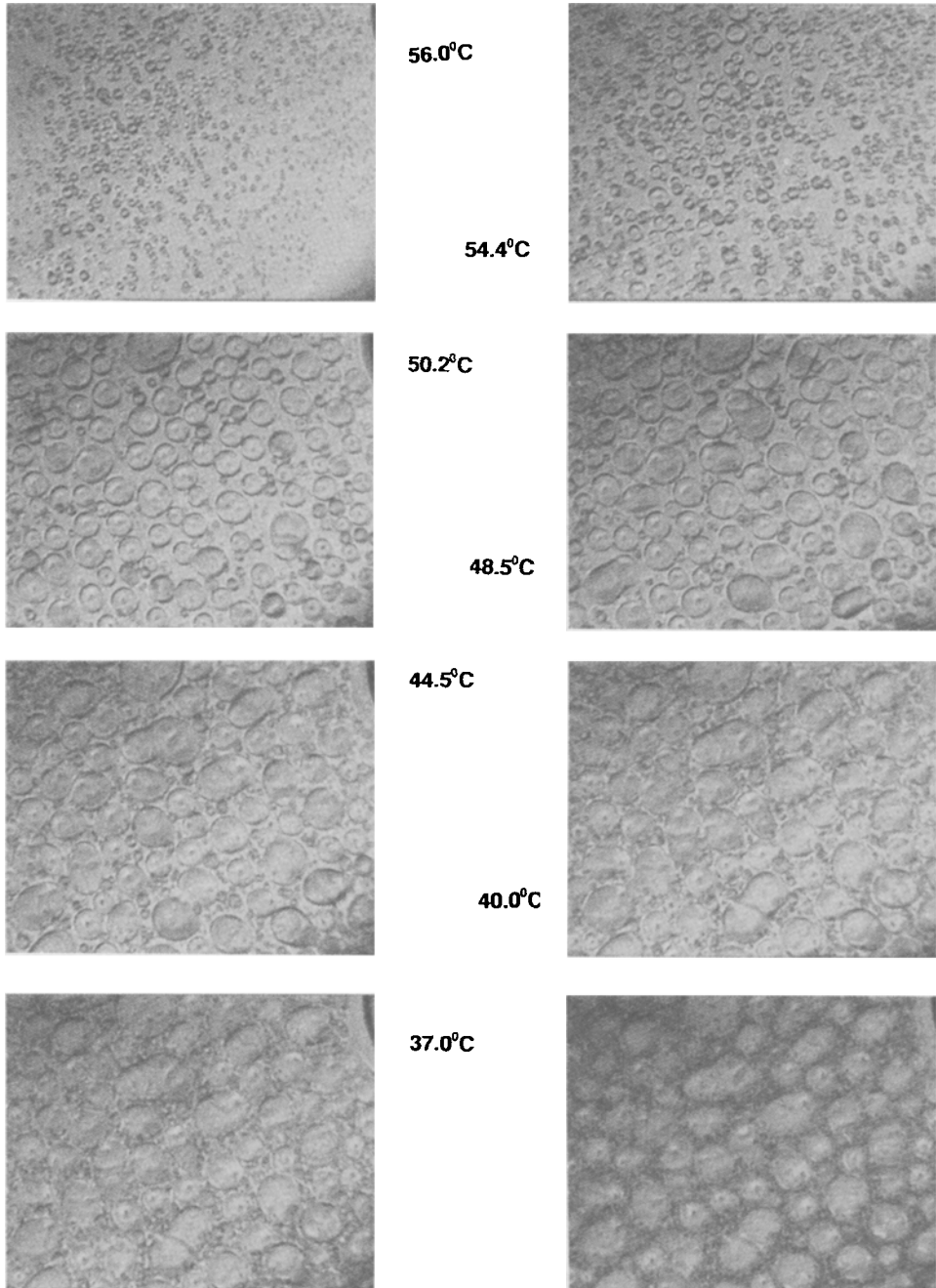
56.0°C

54.4°C

50.2°C

48.5°C

44.5°C

40.0°C

37.0°C

Fig. 7 E7:PMMA::80:20 cooled at a rate of 0.2 deg·min^{-1}
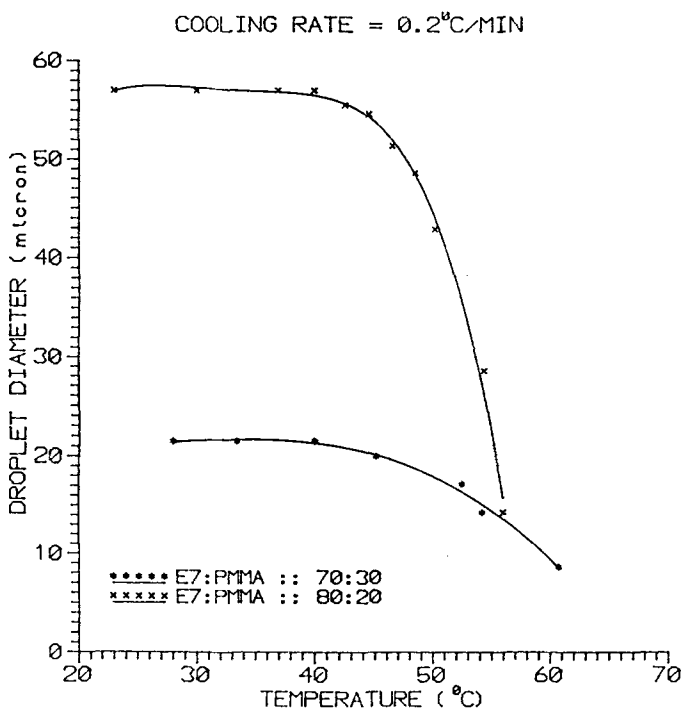
COOLING RATE = 0.2°C/MIN

Fig. 8 Droplet diameter from the micrographs of Figs 6, 7 is plotted as a function of temperature

tion. The droplet diameters grow with time as coalescence and ripening occur. The only way to assure uniform sized droplets is to form them and simultaneously harden the matrix. Either the system can be continuously cooled as shown in Figs 6, 7 till the system crosses 40°C or it can be quenched close to 40°C and then very slowly cooled past that temperature to obtain a uniform distribution of droplets.

Conclusions

The phase behavior of a low molecular weight liquid crystal E7 and PMMA system was studied by Modulated DSC and optical microscopy. A phase diagram was constructed from the observations. The intersection of the glass transition curve with the phase separation curve limits the phase separation to mixtures with greater than 40% E7. This also determines the amount of E7 that remains in the PMMA matrix at 40% and the temperature of hardening at 40°C, for all the compositions of the mixture that can phase separate. This result was verified by light microscopy. The *I–N* transition of the E7 takes place in the *LC* rich domains exhibiting nematic droplets as soon as the system phase separates. The *I–N* transition decreases with increasing PMMA content. The S–N transi-
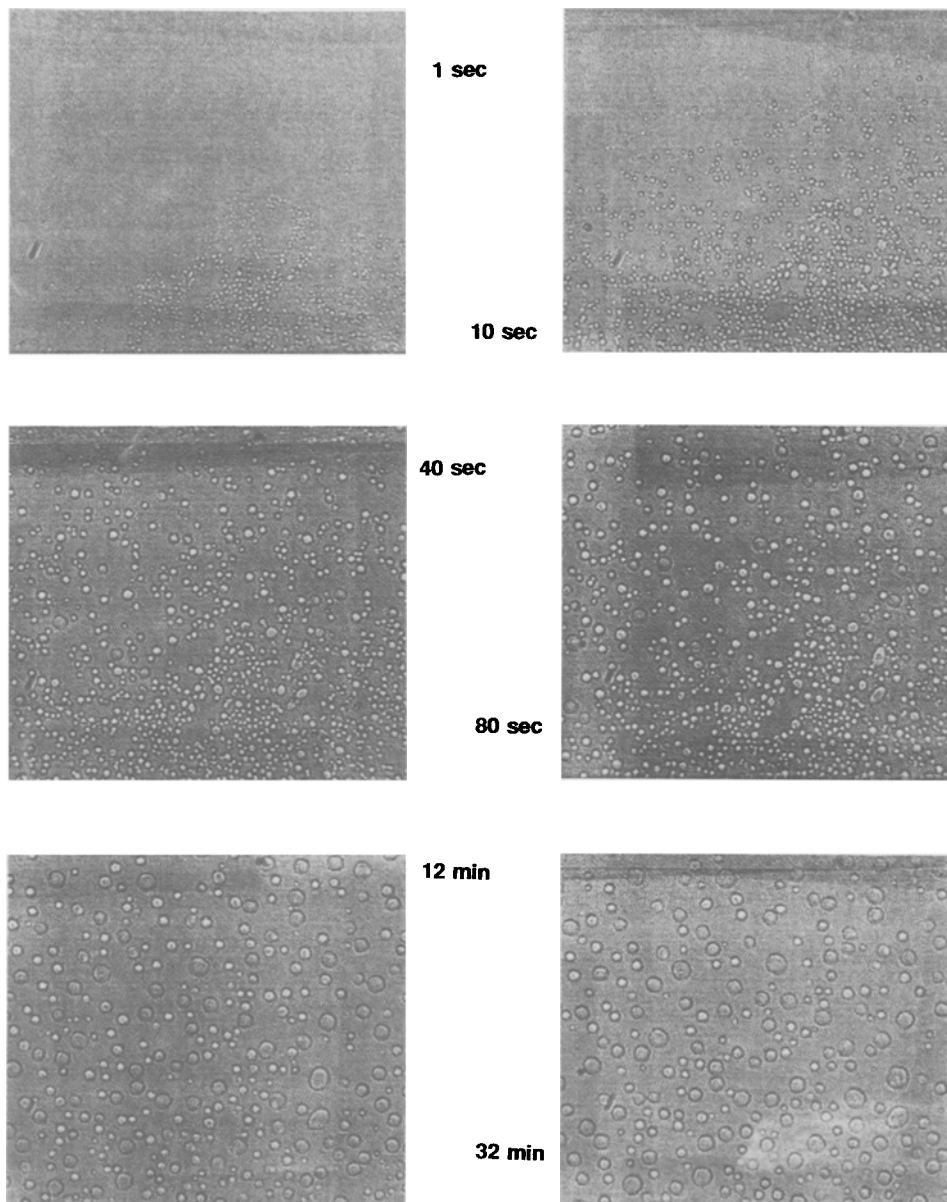
Fig. 9 Mechanism of nucleation and growth illustrated by a sample of 90% E7 quenched from 90 to 53°C

tion and the T_g of the LC rich phase are not affected indicating that the polymer coils are driven to the boundary of the droplets. The size and distribution of droplets is dependent upon the composition of the mixture, the temperature and the mode of cooling such as gradual cooling, quenching or a combination of
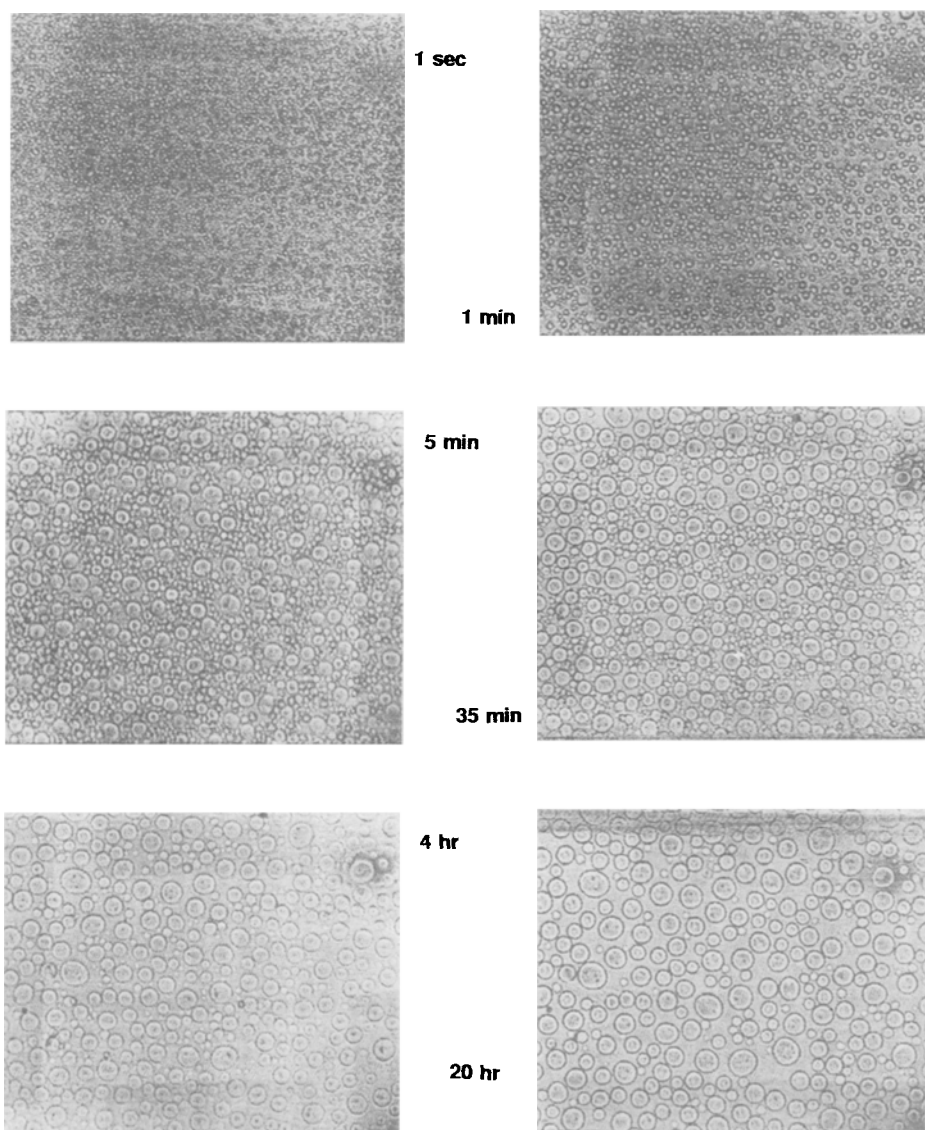
Fig. 10 Growth of the droplets through coalescence and Ostwald ripening is depicted by a sample of 80% E7 quenched from 90 to 50°C

both. Examples of the growth of the droplets as a function of time and temperature are given. It is concluded that the phase transitions in general and the glass transition of the polymer in particular play a very crucial role in the final morphology of any PDLC formed by thermal induced phase separation and one such system E7/PMMA has been thoroughly dealt with to understand this process.

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Zusammenfassung — Das Phasenverhalten des Systemes thermoplastisches Polymer–disperses Flüssigkeitskristall wurde mit besonderer Rücksicht auf die in diesem System vorkommenden Umwandlungen untersucht. Mittels modifizierter DSC wurde das Ausmaß der Plastifizierung des Polymers (Polymethylmethacrylat) durch das niedermolekulare Flüssigkeitskristall(E7) bei verschiedenen Umwandlungen des LC(Liquid Crystal) ermittelt. Am besten konnte die Mikroskopie zur Erstellung des Temperatur-Zusammensetzung-Phasendiagrammes eingesetzt werden. Unsere Untersuchung beweist die Existenz einer Grenztemperatur von 40°C, bei der die PMMA-Matrix ungeachtet der Ausgangszusammensetzung innerhalb der phasenabgegrenzten Region in den Glaszustand übergeht, was auf einen Schnittpunkt der Glasumwandlungskurve mit der Koexistenzkurve hinweist. Mit zunehmendem PMMA-Gehalt wird eine leichte Depression der $N–I$(nematisch zu isotropisch) Umwandlung des LC beobachtet, wobei die $S–M$(smektisch zu nematisch) Umwandlung und die Glasumwandlungstemperatur T_g des LC unverändert bleiben. Bis zur Phasentrennung bei niedrigerer Temperatur bleibt das Einphasengemisch isotropisch, wobei die LC-reichen Bereiche nematisch werden. Der Zuwachs LC-reicher Bereiche wurde in Abhängigkeit von Temperatur und Zeit untersucht.