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Effect of molar mass of an epoxy oligomer on the phase separation in epoxy based polymer dispersed liquid crystals

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Polymer dispersed liquid crystals based on epoxy–amine crosslinked matrices and a nematic liquid crystal, E7, have been studied over the course of polymerisation, *i.e.* as a function of the polymerisation conversion. The influence of epoxy oligomer molar mass on the initial temperature–concentration and the temperature–conversion phase diagrams has been investigated.

An increase of the epoxy oligomer molar mass greatly reduces the initial liquid crystal solubility and brings the cloud points to earlier polymerisation conversions, which have been quantified. Thus the phase separation is markedly enhanced.

The temperature–conversion phase diagrams have been characterised at two isothermal polymerisation temperatures for one liquid crystal composition (50 wt.%). These diagrams (isotropic–nematic and nematic–isotropic transition temperatures) are shown to obey master curves when the epoxy molar mass is varied.

Finally, the size of the liquid crystal droplets is shown to decrease when the epoxy molar mass increases. This effect is mainly due to the viscosity increase resulting from the oligomer mass increase. Viscosity measurements were made at intervals during polymerisation.

Microcomposites obtained from the phase separation of low molar mass liquid crystal molecules in a polymer matrix combine the fluidity and anisotropy of mesophases and the characteristics of polymers (mechanical properties, film formation *etc.*). Polymer dispersed liquid crystals (PDLCs) are one type exhibiting a closed cell structure where the liquid crystal is dispersed as fluid droplets. The properties of these heterogeneous materials are dependent on their morphologies. Therefore the control of morphology during the formation process of PDLCs is of the utmost importance. Three main formation processes[1] are currently found in the literature [solvent induced phase separation (SIPS), thermal induced phase separation (TIPS) and polymerisation induced phase separation (PIPS)]. This paper deals with the latter process, where a nematic liquid crystal (LC) is separated during the polycondensation of the diepoxy and diamine oligomers. The diamine is an α,ω-amino poly(propylene-oxide) (Jeffamine D400), while the diepoxy species, the diglycidyl ether of bisphenol A (DGEBA), has two different molar masses.

The effects of an increase in molar mass of one component on the isotropic polymer–polymer phase diagrams are well known.[2] However, in the case of PDLC, few authors have studied this. In fact, one of the first reported phase diagrams, concerning PDLC, prepared by PIPS by Hirai and Niyama,[3] dealt with monomer–oligomer/LC phase diagrams where either the oligomer/monomer ratio or the monomer molar mass was varied. The monomers were monoacrylates of different molar masses, while the oligomer was a urethane–acrylate oligomer of number average molar mass 2000 g mol^{-1}. These authors showed that, as either the molar mass of the monomer or the oligomer concentration increases, the phase separation area extends and the binodal line in particular moves into higher temperature regions. On the other hand, the molar mass dependence of the oligomer does not contribute much to phase separation. The authors explained that the monomer contributes to both terms of the free energy, *i.e.* enthalpic and entropic, while the oligomer contributes only to the enthalpic term. Other PDLC composites based on poly(methyl methacrylate) and prepared by the SIPS process have been studied by Kim[4] and Ono.[5] Both the authors reported a decrease in size of the dispersed particles upon increasing the average molar mass of PMMA. According to Kim this is a consequence of an increased solution viscosity, which hinders the growth of the particles. A theoretical and experimental approach has also been reported by Kyu *et al.*,[6] who concluded that the critical temperature T_c moves to pure LC limits with an increase in the molar mass of PMMA. The increase in temperature is of the order of 2–3 °C. In addition, the pure nematic region becomes narrower.

In previous papers[7–8] we investigated the effect of the polymerisation temperature, cure cycles and gelation on the morphology. It was shown that an epoxy (low molar mass DGEBA)–amine/LC system remained homogeneous throughout the reaction at 100 °C, a temperature higher than the T_{N-I} of the pure LC. However it could separate into two phases only when cooling the reaction mixture from the reaction temperature to room temperature (TIPS). At a temperature lower than the T_{N-I} of the pure LC (*e.g.* 30 °C), an isotropic + nematic phase separation was obtained at the reaction temperature (PIPS). Furthermore, when the TIPS is operative, T_{N-I} is shown to be independent of the gelation, while in the case of PIPS we observe an increase of T_{N-I} beyond gel point. This jump of T_{N-I} was suggested to be due to the appearance of elastic properties and thus a contribution of the matrix elastic term to the overall free energy of mixing. The morphologies were found to be strongly dependent on the thermal cycles selected.

Now we present the dependence of phase separation and morphology on the molar masses of the initial epoxy oligomer, *i.e.* we will compare two DGEBA species with average constitutional repeating units equal to $\bar{n} = 0.03$ or 0.49. The same diamine will be used in a stoichiometric amount. The polymerisation temperatures and the LC concentration will also be kept the same.

Experimental

A detailed description of the reactants, the LC (E7 nematic mixture from Merck) and the preparation of samples is given in refs. 7 and 8. The abbreviations DGEBA0.03 and

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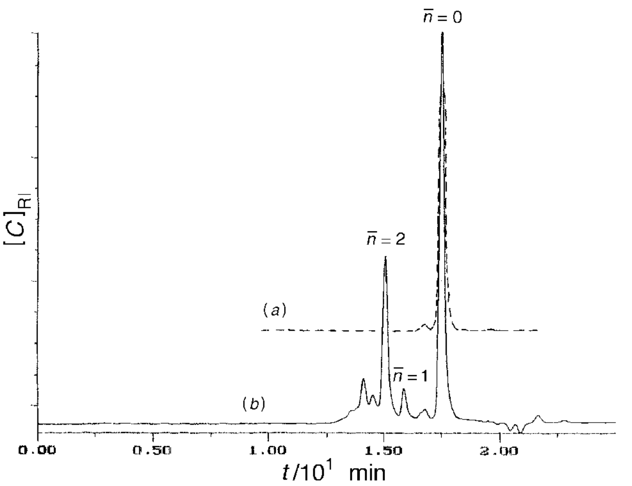

Fig. 1 Size exclusion chromatograms of the epoxy oligomers as a stoichiometric mixture with D400: (*a*) DGEBA0.03 and (*b*) DGEBA0.49

DGEBA0.49 will be used for the two diepoxy monomers (0.03 and 0.49 refer to the average constitutional repeating unit $\bar{n}$).[7] Their number average molar masses are respectively 348.5 and 479 g mol^{-1}. The diamine D400 has a number average molar mass of 400 g mol^{-1}. Fig. 1 shows size exclusion chromatograms of the epoxy–amine stoichiometric mixtures. On both chromatograms, the diamine D400 is neither detected by UV spectroscopy nor by refractometry. The DGEBA0.49 oligomer contains epoxy i-mers with three main different degrees of polymerisation. It is therefore a polydisperse oligomer, while DGEBA0.03 is nearly monodisperse and contains mainly the oligomer $\bar{n}=0$.

Temperature–concentration phase diagrams, before polymerisation, were constructed in the following way: mixtures with different LC concentrations were prepared (LC percentages are given in wt.% of the total PDLC mixture), then a drop of the initial mixture was confined between two glass plates and mounted on a hot plate under a polarized optical microscope (POM) (Leica laborlux 12POLS equipped with a Mettler FP82 hot plate). The sample was heated rapidly to 100 °C (homogeneous state) and then cooled at 1 K min^{-1} until tiny nematic droplets are observed. This temperature was taken as the $T_{\mathrm{I-N}}=T_{\mathrm{cp}}$ temperature (CP = cloud point).

Temperature–conversion phase diagrams, in the course of polymerisation, were drawn for only one epoxy–amine/LC mixture (50/50 wt.%), which was cured isothermally at either 30 or 100 °C. The mixture was reacted in both DSC pans and between glass plates (POM).

In the calorimetric measurements (DSC Mettler 3000), a series of samples was cured to different stages of reaction and each system was analysed ($T_{\mathrm{I-N}}$, $T_{\mathrm{N-I}}$, T_{g}). Cooling scans were performed at 5 K min^{-1} and the $T_{\mathrm{I-N}}$ was read at the onset of the exothermic peak. Heating scans were performed at 10 K min^{-1} and the $T_{\mathrm{N-I}}$ was read at the maximum of the endothermic peak.

For the isothermal cure at 30 °C, phase separation was characterized (POM) by the appearance of nematic droplets at a conversion x_{cp}.[7–8] The same sample was observed using POM at 30 °C during the rest of the polymerisation.

For the cure at 100 °C, several samples were prepared and reacted, under POM, to different extents of reaction (x_{100}). Then each sample was cooled at 1 K min^{-1} to induce phase separation and to measure the I–N transition temperatures as a function of the conversion reached at 100 °C.[7,8]

The changes in the viscosity of the two reactive diepoxy–diamine systems (DGEBA0.03–D400 and DGEBA0.49–D400), in stoichiometric ratios, were followed upon curing by a mechanical dynamic analyser (Rheometrics RDAII) at an isothermal temperature of 60 °C. The reactive mixture was confined between parallel plates in order to apply an angular periodic deformation.[9,10] The plate diameter was 40 mm and the sample thickness close to 2 mm. In the measurements, the shear rates varied from 1 to 100 rad s^{-1} with an angular deformation of 10%. The dynamic mechanical measurements give access to the complex dynamic shear modulus (G', G'') and also to the complex dynamic viscosity.[9] The real part of the complex dynamic viscosity is currently named η' ($\eta'=G''/\omega$, where G'' is the loss shear modulus at an angular frequency ω). In fact, in the frequency sweep mode, measurements were recorded at different times of reaction, and at each frequency the reaction was maintained during the measurement time. However, the reaction rate is sufficiently slow as to consider that the change in modulus during testing is negligible. Therefore the frequency sweeps were made on the same sample over the course of reaction, at several stages of reaction.

Results and Discussion

Effect of increase in molar mass of prepolymer DGEBA on the pure epoxy systems (without LC)

The non-reacted mixtures of the DGEBA oligomers with the diamino poly(propylene oxide) showed the initial glass transition tempratures $T_{\mathrm{g0}}{}^{0.03}=-51$ and $T_{\mathrm{g0}}{}^{0.49}=-29$ °C, respectively. After a 3 h cure at 100 °C the polymers were checked for any residual heat of reaction by DSC. The final values are $T_{\mathrm{g}\infty}{}^{0.03}=39$ and $T_{\mathrm{g}\infty}{}^{0.49}=49$ °C.

The gel point was determined experimentally as described previously;[7] an average value of $x_{\mathrm{gel}}=0.565\pm0.015$ was obtained, which agrees fairly well with the theoretical value of 0.577.[11]

Effect of increase in molar mass of prepolymer DGEBA on the phase diagrams in oligomer/LC mixtures before polycondensation

The initial temperature–composition phase diagrams before any reaction (considered as pseudo-binary diagrams between the diepoxy–diamine monomers and the LC) are shown in Fig. 2 and 3. Two kinds of curves are plotted: (i) the isotropic–nematic transition temperatures ($T_{\mathrm{I-N}}$) of DGEBA–D400/LC mixtures corresponding to the appearance of separated nematic droplets on cooling from a homogeneous isotropic phase and (ii) the glass transition temperatures of the DGEBA–D400/LC mixtures.

The $T_{\mathrm{I-N}}$ values were obtained by two techniques, namely POM and DSC, with 1 and 5 K min^{-1} cooling rates,

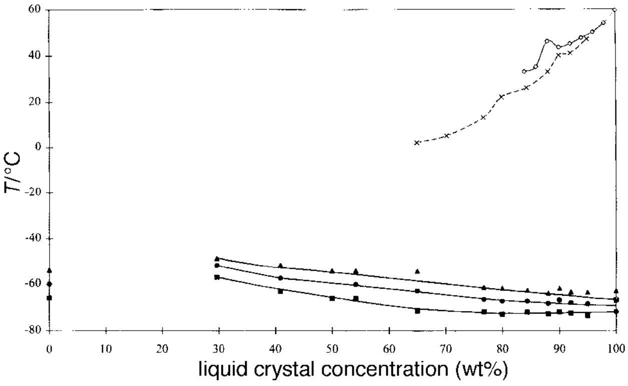

Fig. 2 Initial phase diagrams for DGEBA0.03–D400/E7 system: (×) $T_{\mathrm{I-N}}$ values, measured by DSC, on cooling at 5 K min^{-1}, (◇) $T_{\mathrm{I-N}}$ values, measured by POM, on cooling at 1 K min^{-1}, (▲) T_{g} onset, measured by DSC, on cooling at 5 K min^{1}, (●) T_{g} mid-point, measured by DSC, on cooling at 5 K min^{-1}, and (■) T_{g} end, measured by DSC, on cooling at 5 K min^{-1}

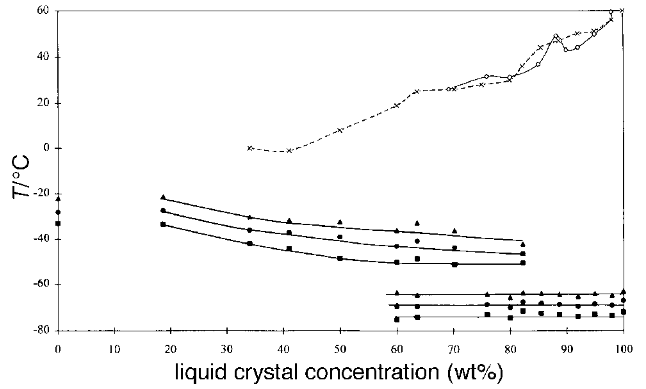

Fig. 3 Initial phase diagrams for DGEBA0.49–D400/E7 system: (×) T_{I-N} values, measured by DSC, on cooling at 5 K min^{-1}, (◇) T_{I-N} values, measured by POM, on cooling at 1 K min^{-1}, (▲) T_g onset, measured by DSC, on cooling at 5 K min^{1}, (●) T_g mid-point, measured by DSC, on cooling at 5 K min^{-1}, and (■) T_g end, measured by DSC, on cooling at 5 K min^{-1}

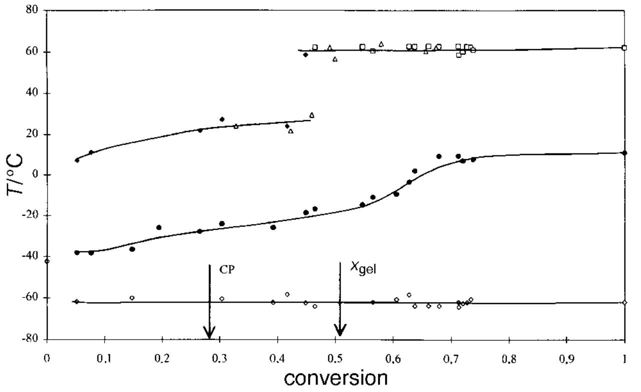

Fig. 4 Transition temperatures as a function of reaction conversion (measured by DSC on a heating ramp, 10 K min^{-1}, after cooling to -100 °C) for the DGEBA0.49–D400/E7 (50 wt.%) system, cured at 30 °C: (◇) $T_g(\beta)$, (●) $T_g(\alpha)$ and (◆, □, △) T_{N-I}

respectively. Cooling scans were preferred over heating scans, thus T_{I-N} curves are considered as cloud point curves. The T_{I-N} values increase with LC content because the temperature at which the order parameter reaches a critical value of 0.44, according to the Maier–Saupe theory, increases with the LC content.[12] The temperature at which the nematic interactions appear (giving a nematic phase) increases with LC content. However, the minimum amount of LC required to demix the system is quite different for the two epoxy monomers: 65 wt.% of LC for DGEBA0.03 and only 35 wt.% of LC for DGEBA0.49 (DSC measured values). This means that oligomer/LC mixtures whose LC contents are less than 65 or 35 wt.%, respectively, will not exhibit any LC phase and no demixing will take place on cooling until the vitrification of a single homogeneous isotropic phase occurs. In other words, in these LC concentration ranges, the DSC cooling scans of the corresponding mixtures exhibit a single T_g and no isotropic–nematic transition. Therefore, 65 and 35 wt.% represent the solubility limits of the LC molecules in the initial DGEBA0.03–D400 and DGEBA0.49–D400 monomers. So an increase in epoxy oligomer molar mass decreases the LC initial miscibility by a considerable amount.

Fig. 2 and 3 also show the decrease in T_g with the LC content. The T_g of the pure LC is -63 °C. According to the Fox equation,[13] the introduction of LCs in epoxy–amine monomers lowers the T_g of the mixture, and the calculated T_g of a 65 wt.% LC mixture in DGEBA0.03–D400 is -59 °C whereas that of a 35 wt.% LC mixture in DGEBA0.49–D400 is -42 °C. Both values agree well with the measured ones of -62 and -36 °C (mid points). This is consistent with the presence of a single homogeneous phase at these concentrations.

Effect of increase in molar mass of prepolymer DGEBA on the phase separation during an isothermal cure at 30 or 100 °C of a 50 wt.% LC blend

As described in the introduction and experimental sections, phase separation is obtained isothermally at 30 °C (PIPS) or on cooling partially reacted samples from the reaction temperature, 100 °C (TIPS). The conversion which is used in the following section is that attained at the reaction temperature.

Firstly, we consider that the epoxy–amine monomers reacted isothermally at 30 °C in the presence of 50 wt.% LC. With both epoxy oligomers, phase separation takes place during cure at 30 °C in the form of birefringent points which are detected under POM. The cloud point conversions where the nematic particles are detected are $x_{cp}=0.45$ for DGEBA0.03-based PDLC and $x_{cp}=0.28$ for DGEBA0.49-based PDLC. This difference is a direct consequence of the decrease in miscibility as a result of the increase in $\overline{Mn}$ of DGEBA0.49.

In parallel with optical microscopic observations, the T_{N-I} and T_g temperatures were followed by DSC by increasing the reaction conversion for the DGEBA0.49-based PDLC cured at 30 °C (Fig. 4). It is clear that two T_g and one T_{N-I} are present as early as a reaction conversion of 0.05, in contrast to the DGEBA0.03 PDLC,[8] which required a conversion of 0.3. But in exactly the same way as for DGEBA0.03, there is a jump of T_{N-I} values close to conversions of $x=0.45$ (DGEBA0.49) and $x=0.55$ (DGEBA0.03). In the DGEBA0.03 system, the T_{N-I} jump was attributed to the role of elasticity in the mixing energy;[8] however, in the DGEBA0.49 system the increase in T_{N-I} occurs before gelation is attained. So, in this case, the effect of gelation is overruled and this phenomenon is only an effect of cooling in the DSC. Indeed, the DSC measurements are carried out on a heating ramp after cooling to -100 °C, so the cooling will certainly have contributed to phase separation. To prove this we measured the T_{N-I} values of the glass slide samples on the hot plate under POM (Fig. 5). It can be seen that, without any previous cooling, a smooth increase of T_{N-I} as a function of conversion is observed.

Subsequently, the DGEBA0.49–amine monomers were reacted at 100 °C in the presence of 50 wt.% LC. At this temperature, the system remains homogeneous throughout the reaction (DSC, POM) and its behaviour is quite similar to PDLCs based on DGEBA0.03. Phase separation is only

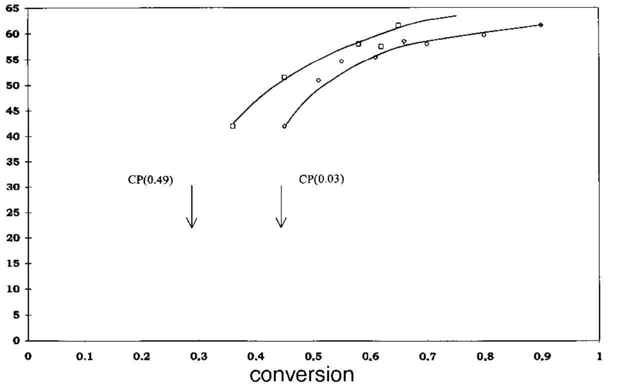

Fig. 5 N–I transition temperatures (measured by POM) as a function of conversion for two DGEBA–D400/E7 (50 wt.%) PDLC systems, cured at 30 °C: (□) DGEBA0.03–D400/E7 and (◇) DGEBA0.49–D400/E7

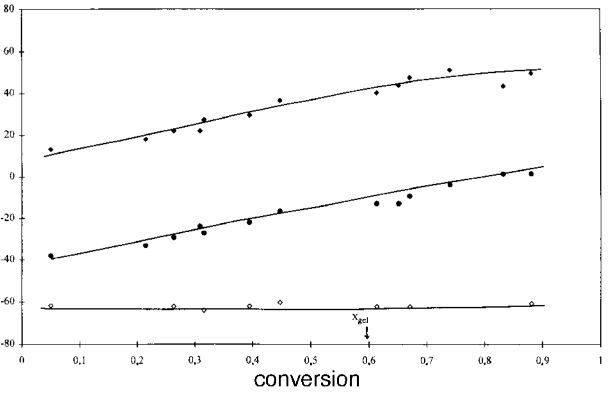

Fig. 6 Transition temperatures as a function of reaction conversion (measured by DSC on a heating ramp, 10 K min^{-1}, after cooling to -100 °C) for the DGEBA0.49–D400/E7 (50 wt.%) system, cured at 100 °C: (◇) $T_g(\beta)$, (●) $T_g(\alpha)$ and (◆) $T_{N\text{–}I}$

obtained on cooling the reacting system at different conversions.

Fig. 6 presents the evolution of different transition temperatures (DSC measurements on a heating ramp after cooling to -100 °C). Comparing Fig. 4 and 6 one can see that the 30 °C cure provides higher transition temperatures (T_g, $T_{N\text{–}I}$) than the 100 °C cure, which reflects a better phase separation at lower temperatures. This is again mainly the result of the lower miscibility of DGEBA0.49 in terms of entropic contribution.

In order to check this hypothesis, the number average molar mass of the epoxy–amine i-mers can be calculated using Makosco–Miller theory,[14] without deriving the molar mass distribution function [eqn. (1)],

$$\overline{Mn}=\frac{2M_{\mathrm{D400}}+4M_{\mathrm{DGEBA}}}{2+4(1-2x)} \qquad (1)$$

where $M_{\mathrm{D400}}=400$ g mol^{-1}, $M_{\mathrm{DGEBA0.03}}=348.5$ g mol^{-1}, $M_{\mathrm{DGEBA0.49}}=479$ g mol^{-1} and x is the epoxy conversion.

At $x=0.05$, we calculate $\overline{Mn}=485$ g mol^{-1} for DGEBA0.49–D400, and at $x=0.20$[8] $\overline{Mn}_2=498$ g mol^{-1} for DGEBA0.03–D400. These conversions are those where phase separation is first detected by DSC. One can note that the number average molar masses of the epoxy–amine i-mers are comparable, showing only the effects of entropy.

Correlation and 'master curves' of $T_{N\text{–}I}$–conversion curves

We measured $T_{N\text{–}I}$ and/or $T_{I\text{–}N}$ of two 50 wt.% LC systems differing by the DGEBA molar mass and the reaction temperature. These measurements provided us with several $T_{N\text{–}I}$ and $T_{I\text{–}N}$ conversion evolutions, namely $T_{N\text{–}I}=f(x)$ for DGEBA0.03–D400/LC (50 wt.%), or DGEBA0.49–D400/LC (50 wt.%) at $T_i=30$ or $T_i=100$ °C for either DSC or POM measurements. We attempted a correlation of these curves by plotting master curves. Can the $T_{I\text{–}N,\,N\text{–}I}$ curves, obtained with different molar masses, be superimposed by applying a conversion-shift factor, $a(T)$ for a given temperature? Such a correlation would help predict the conversion dependence of the transition temperatures when one uses different oligomer molar masses. The final purpose is to plot transition temperature–conversion dependences on a unique curve. The approach is similar to the time–temperature superposition of the viscoelastic behaviour of amorphous polymers.[15]

The reference curve being that of DGEBA0.49, Fig. 7 shows that the $T_{I\text{–}N,\,N\text{–}I}$ (POM) curves can be accurately superimposed by applying a conversion shift factor of $a(30\,°\mathrm{C})=0.09$. We checked that the same shift factor can be applied to superimpose the $T_{N\text{–}I}$ (DSC) curves at 30 °C. At 100 °C, a shift factor of $a(100\,°\mathrm{C})=0.23$ (Fig. 8) is calculated to superimpose the $T_{N\text{–}I}$ (DSC) curves.

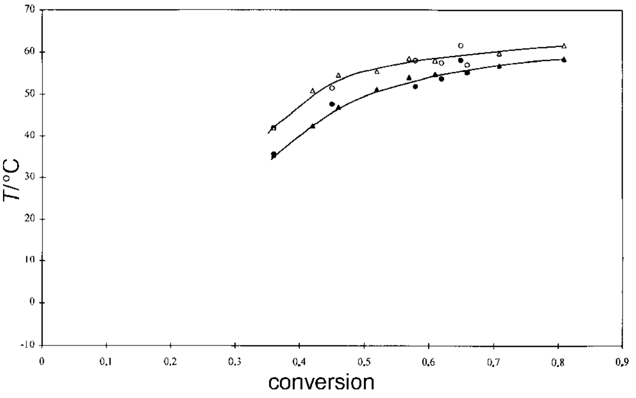

Fig. 7 Master curves of the systems cured at 30 °C; shift factor equal to 0.09; reference curve is DGEBA0.49. (○) $T_{N\text{–}I}$ (POM measured) DGEBA0.49–D400/E7, (△) $T_{N\text{–}I}$ (POM measured) DGEBA0.03–D400/E7, (●) $T_{I\text{–}N}$ (POM measured) DGEBA0.49–D400/E7, (▲) $T_{I\text{–}N}$ (POM measured) DGEBA0.03–D400/E7.

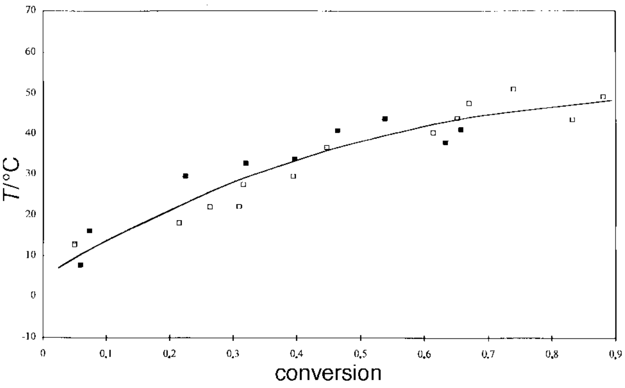

Fig. 8 Master curves of the systems cured at 100 °C; shift factor equal to 0.23; reference curve is DGEBA0.49. A line is drawn to guide the eye. (□) $T_{N\text{–}I}$ (DSC measured) DGEBA0.49–D400/E7 and (■) $T_{N\text{–}I}$ (DSC measured) DGEBA0.03–D400/E7

Therefore it has been shown that master curves can be constructed on which the conversion evolution of the nematic–isotropic or isotropic–nematic temperatures of PDLCs based on different molar masses can be superimposed. The shift factors can be determined experimentally both from DSC or POM measurements.

Effect of increase in molar mass of prepolymer DGEBA on the morphology of a 50 wt.% LC composite cured at 30 °C

Fig. 9 shows the evolution of the LC droplet diameter as a function of the reduced conversion $x-x_{\mathrm{cp}}$. It appears that the diameters obtained with the higher epoxy oligomer are smaller than those obtained with the lower epoxy oligomer. This diameter evolution results from the influence of both miscibility and viscosity.[8,16,17] We performed measurements of viscosity over the course of polymerisation of the two neat systems at 60 °C. Experiments at 30 °C would be very slow, while at 100 °C the systems are too fluid, but assuming a single activation energy, viscosity can be compared at 60 °C. At this temperature, we found that before the gel point (where only viscous behaviour is present), the dynamic viscosity of the DGEBA0.49–D400 reactive system is ten times higher than that of the DGEBA0.03–D400 system at any conversion (Fig. 10). Thus, if the two PDLC systems are compared at the same conversion after the cloud point (x–x_{cp} is fixed), the real epoxy conversion is smaller with the high molar mass DGEBA, but the diameter is smaller. This means that the main effect that accounts for the particle size is the viscosity of the reaction medium.

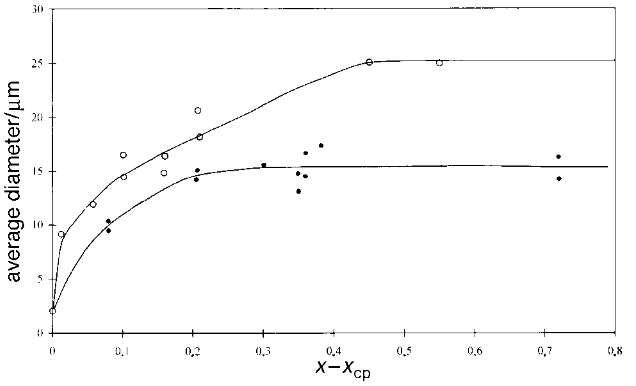

Fig. 9 Evolution of liquid crystal droplet average diameter as a function of 'reduced' conversion ($x-x_{cp}$) at 30 °C: (○) DGEBA0.03–D400/E7 and (●) DGEBA0.49–D400/E7.

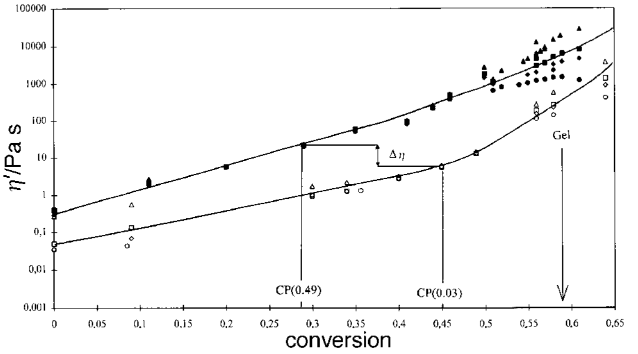

Fig. 10 Real part of dynamic viscosity η' ($\log_{10}$ plot) as a function of conversion at 60 °C. Various angular frequencies were used. DGEBA0.49–D400: (▲) 1, (■) 10, (◆) 25, (●) 100 rad s^{-1}. DGEBA0.03–D400: (△) 1, (□) 10, (◇) 25, (○) 100 rad s^{-1}.

Conclusion

Two epoxy monomers (DGEBA0.03 and DGEBA0.49) differing by their molar mass were compared in an epoxy–amine based PDLC. In this study the amine was kept the same. Firstly, before polymerisation, pseudo-binary temperature–composition phase diagrams between the epoxy–amine monomers and a LC (nematic E7) show that the solubility limit of the LC is considerably reduced when the epoxy monomer molar mass is increased from $M_{\mathrm{DGEBA0.03}}=348.5$ to $M_{\mathrm{DGEBA0.49}}=479$ g mol^{-1}. Then, a 50 wt.% LC mixture was chosen and the effect of the epoxy molar mass was characterized over the course of polymerisation. In our PDLC systems, we illustrate the influence of molar mass using two parameters: the thermodynamic stability of the reacting mixture (illustrated by temperature–conversion phase diagrams obtained by both DSC or POM) and the viscosity of the reaction medium at the cloud point. For the same isothermal cure (30 or 100 °C), the cloud point conversion is lowered with increasing epoxy molar mass and the phase separation is enhanced. The decrease in miscibility resulting from a decrease in entropy is the major parameter that affects phase separation during polycondensation. Furthermore, the temperature–conversion diagrams (isotropic–nematic and nematic–isotropic transition temperatures) are shown to obey master curves when the epoxy molar mass is varied. On the other hand, the viscosity of the reaction medium at the cloud point is the parameter that affects the morphology evolution and the final size of the LC droplets.

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