Characterization of a novel blend consisting of a liquid crystalline polymer and a photopolymerized crosslinked acrylic matrix

John J. Fitzgerald and John M. Noonan*
Research Laboratories, Eastman Kodak Company, Rochester, NY 14650-2109, USA

and Heinrich Kapitza and Rudolf Zentel
Institut fur Organische Chemie, J.-J. Becher Weg 18–20, D-6500 Mainz, Germany
(Received 28 May 1990; accepted 21 July 1990)

A blend of a novel soluble main chain liquid crystalline (LC) copolymer with a low molecular weight photopolymerizable trifunctional acrylate was formed. X-ray diffraction studies revealed that the structure of the mesophase was disrupted upon addition of the monomeric acrylates. However, once the blend was exposed to ultraviolet radiation and post-cured, a densely crosslinked semi-interpenetrating network of the second kind (semi-IPN-II) was formed, and the original structure of the mesophase was restored. The unique feature of this crosslinked blend is that the LC copolymer can undergo transitions from its LC to isotropic phase in the presence of the densely crosslinked acrylate matrix. In addition, this blend has mechanical integrity at temperatures well above the LC to isotropic transition region.

(Keywords: liquid crystalline polymers; photopolymerization; semi-IPNs; blends)

INTRODUCTION

Thermotropic liquid crystalline (LC) polymers have been the subject of a vast number of studies in the last 10 years. The unique physical and mechanical properties that LC polymers exhibit result from the incorporation of rod-like mesogens into the main chain or side chain of a macromolecule[1]. Liquid crystalline polymers exhibit these unique properties because of the spontaneous self-organization of the mesogenic groups in the polymer matrix. Many structural variations involving the mesogen unit, and the flexible spacer unit have been studied, and have resulted in processible LC polymers, which exhibit unique properties in the direction of orientation[2–4].

Recently, there has been considerable interest generated in crosslinked LC polymers. These crosslinked polymers have been used to investigate the orientational tendencies of both the mesogenic groups and the polymer chains and their interactions. Crosslinked polymers that have been prepared via non-photochemical reactions[5,6] usually exhibit a very low degree of crosslinking. Only a very few examples have been reported of densely crosslinked LC polymers. In these studies, the LC polymers were functionalized with reactive groups that underwent either a photochemically induced polymerization[7] or dimerization[8,9]. In a recent report by Broer *et al.*[10], a densely crosslinked LC polymer was obtained by the photoinitiation of the bulk polymerization of a mesomorphic diacrylate. Unlike previous studies, the crosslinks between the main chains contain the mesogenic groups. However, because of the high degree of crosslinking, the orientation generated upon crosslinking was irreversible.

An approach to obtaining a densely crosslinked network, yet retaining the possibility of orientating the LC polymer would be through polymer blending. Recently Weiss *et al.*[11] reviewed the status of blends of low and high molecular weight liquid crystals with either amorphous or LC polymers. The studies dealing with blends of low molecular mass liquid crystals and LC polymers have typically been concerned with the thermodynamic and phase behaviour of these systems. Of particular note to this study is the work of Ringsdorf *et al.*[12] who have shown that the miscibility of high and low molecular weight liquid crystals can be enhanced if the mesogenic units are similar.

There have also been a few investigations that have considered polymer–polymer blends in which at least one component is LC. Seurin *et al.*[13] blended polyethylene glycol with a thermotropic cholesteric cellulose. The polyethylene glycol was found to be miscible with the cholesteric LC at low molecular weight, but as the molecular weight of the amorphous polymer increased, the system became immiscible. In another recent report[14], a LC polymer was blended with a thermoplastic polymer that generated a phase-separated polymer blend. In this case, a significant improvement in the melt viscosity was realized, however, certain mechanical properties of the blend were adversely affected because of the incompatibility.

One possible method used to control the homogeneity, and therefore the compatibility of polymer blends is by the formation of an interpenetrating polymer network (IPN)[15–19]. We attempted to form an IPN by blending a LC main chain polymer with a photopolymerizable multifunctional acrylate. While a number of different types of IPNs have been distinguished by Sperling[15], this particular blend is designated as a semi-IPN of the second

---

* To whom correspondence should be addressed

0032-3861/91/122244–08
© 1991 Butterworth-Heinemann Ltd.

kind (semi-IPN-II) since the multifunctional acrylate is crosslinked in the presence of the linear polymer.

Even though the LC polymer's mechanical properties are highly anisotropic, because of the highly crosslinked acrylate matrix, this blend would be expected to show good mechanical properties in more than one direction. Further, photocrosslinking could allow a 'locking in' of different orientations and phase structures, since the photocrosslinking reaction could be performed within different LC phases by modulating the temperature. This phenomenon opens up the possibility of preparing specially designed materials that might be useful in the electronic industry where dielectric materials are needed that exhibit not only imaging capabilities, but low dielectric constants and low thermal expansion coefficients[20].

This paper describes the selection and the synthesis of a glassy soluble main chain LC polymer. The thermal and dynamic mechanical properties of the semi-IPN-II formed from the photopolymerization of the trifunctional acrylate in the presence of the LC copolymer are described. Also the effects of crosslinking on the LC phase, as well as the dynamic mechanical properties of the final semi-IPN-II, are presented.

EXPERIMENTAL

Synthesis of tris(2-acryloyloxyethyl)-1,2,4-benzene tricarboxylate

Dichloromethane (68 g) and 2-hydroxyethylacrylate (8.6 g) were added to a 300 ml round-bottom flask equipped with a stirrer, condenser, thermometer and addition funnel. The flask and contents were cooled to 0–10°C and nitrogen was bubbled through for 20 min. Triethylamine (7.85 g) was then added to the flask and a solution of 6.54 g of 1,2,4-benzenetricarbonyl chloride dissolved in 21 g of dichloromethane was slowly added. The reaction was stirred well for 4 h and allowed to come to room temperature. The precipitated triethylamine hydrochloride was filtered off, and the dichloromethane solution was washed four times with 100 ml of distilled water. The dichloromethane solution was dried over magnesium sulphate, filtered and the dichloromethane was distilled off. A light yellow viscous liquid was obtained. The yield of the triacrylate was 86%. Elemental analysis using infra-red (i.r.) and ^1H nuclear magnetic resonance (n.m.r.) spectroscopy confirmed the structure shown in *Figure 1*.

Synthesis of 1,4-bis-(2-hydroxyethyloxy)benzene

1,4-Bis-(2-hydroxyethyloxy)benzene was synthesized by etherification of hydroquinone. Hydroquinone (55.05 g, 0.05 mol) and a trace amount of KI were dissolved in ~500 ml of absolute ethanol in a nitrogen atmosphere. A sodium ethanolate solution [28.75 g (1.25 mol) of sodium in 500 ml of ethanol] was first added to the reaction flask followed by the addition of 100.7 g (1.25 mol) of 2-chloroethanol, which was added slowly (a white precipitate formed). After refluxing (N_2) the mixture for 5 h, it was poured into 1500 ml of ice and water. The solid residue was washed first with aqueous NaOH (~2 N) and then with water. Column chromatography (silica gel with ethyl acetate:acetone 1:1) and recrystallization from ethyl acetate gave white crystals (m.p. 102–103°C, yield 40%).

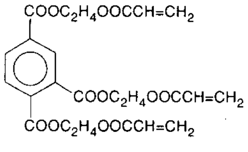

Figure 1 Trifunctional acrylate

Synthesis of 4,4'-bis(6-hydroxyhexyloxy) biphenyl

4,4'-Bis(6-hydroxyhexyloxy) biphenyl[21] was synthesized by etherification of 4,4'-dihydroxybiphenyl. 4,4'-Dihydroxybiphenyl (31.99 g, 0.17 mol) and a trace amount of KI were dissolved in a mixture of 28 g of KOH, 100 ml of ethanol and some water. Under reflux the 6-chlorohexanol was added slowly (white precipitate). After 4 h of refluxing, the mixture was poured into 1 litre of cold aqueous NaOH (~2 N). The solid precipitate was washed with aqueous NaOH, water and recrystallized from ethanol (m.p. 162°C, yield 82%).

General synthesis of polyesters

The polyesters were synthesized by the standard high-temperature melt-condensation procedure. A polymerization flask was charged with the appropriate diols and diesters. The flask was capped with a Vigreux condenser which was fitted with a nitrogen inlet tube. Gas was flushed through the system. The flask was immersed in a 200°C salt bath to a level just below the stoppered side arm. When the chemical mixture became a homogeneous melt, one drop of tetraisopropyl *o*-titanate was added as a catalyst. The volatiles were distilled at 200°C at atmospheric pressure for 2 h. The condenser and inlet tube were replaced with a stainless steel stirrer attached to be vacuum tight. The pressure was reduced to 6.7 Pa, the temperature was raised to 230°C and the polymer stirred at 200 rev min^{-1}. The torque applied by the melt to the stirrer was measured. When the torque was high enough to indicate sufficient polymerization, the stirring and vacuum were stopped and the polymerization flask removed from the bath as quickly as possible. The polymerizations were run stoichiometrically, and the polymers were characterized by inherent viscosity, ^1H and ^{13}C n.m.r. The viscosities were determined using a Ubbelohde capillary viscometer. Measurements were made at 25°C and at a concentration of 0.5 g dl^{-1} in chloroform. The LC phases of the polymers were studied by differential scanning calorimetry (d.s.c.), polarizing microscopy and wide angle X-ray diffraction.

The blend that formed consisted of a LC main chain polymer, the crosslinkable trifunctional monomer, tris (2-acryloyloxyethyl) 1,2,4-benzene tricarboxylate and a free radical inhibitor (4,4'-thiobis(2-methyl-6-t-butylphenol). In addition, a very efficient photoinitiator system[22,23], which consisted of an activator, ethyl *p*-dimethylaminobenzoate, and a sensitizer, 3-(4-cyanobenzoyl)-5-di-n-propoxycoumarin, was added to initiate the photopolymerization of the trifunctional acrylate.

The samples were knife coated from a 25 to 40 wt% solids solution of dichloromethane onto a suitable support $\sim 30 \times 10^{-5}$ m wet thickness. The coatings were dried for 5 min at 20°C, then for 10 min at 55°C, to obtain a 5×10^{-5}–5.6×10^{-5} m dry coating. A thin Mylar® cover sheet was laminated to the surface once the samples were dried. The samples were irradiated for 5 min

(800 mJ cm^{-2}) with a Colight model M218 ultraviolet (u.v.) source. The samples were held at room temperature for 15 min, and then separated from the Mylar® cover sheet. Post-curing of the samples was accomplished by placing the sample in an air oven at either 160 or 200°C for various periods of time.

Microscope. The microscope investigations were performed with a Nikon Optiphot microscope at a magnification of ×320, and a Mettler hot stage. The samples were investigated using cross-polarizers at room temperature and at elevated temperatures.

Dynamic mechanical spectroscopy. Dynamic mechanical measurements were performed using the Rheometrics RSA-II. The dynamic mechanical data were normally taken between −50°C and 200°C at a driving frequency of 10 Hz. The heating rate during the experiments was ~2°C min^{-1}. The experimental data are presented as the dynamic tensile storage modulus (E') and dissipation factor (tan δ) plotted as a function of temperature.

Differential scanning calorimetry. A Perkin-Elmer DSC-4 that was attached to a data station was used to measure the thermal transition temperatures of the polymers. The measurements were carried out under a nitrogen atmosphere, and the heating rate was typically 10°C min^{-1}.

X-ray apparatus. Flat plate camera: all data were collected using a Stanton type camera with wide-angle data collected at a sample-to-film distance of 5 cm and a 2 h exposure time. The small angle data were collected at a sample-to-film distance of 32 cm and an exposure time of 24–65 h depending on sample thickness. For both exposures, nickel-filtered Cu Kα radiation was used with a power setting of 35 kV and 30 mA, the scatter chamber was evacuated to 1.33×10^{-2} Pa and the diffractometer data were collected on X-ray film.

Diffractometer. All diffractometer data were collected using a Rigaku Ru-300 rotating anode system equipped with a Bragg-Brentano diffractometer. Cu Kα radiation operated at a power setting of 50 kV and 280 mA was used with a diffracted beam graphite monochromator tuned to Cu Kα radiation, and a scintillation detector.

RESULTS AND DISCUSSION

In order to achieve a sufficiently soluble main chain LC polymer a 'semiflexible' instead of a 'rigid-rod' polymer was selected. In order to suppress the crystallization, the use of lateral substituents was desirable[24,25]. Therefore, substituted polymalonates[21,26] of the structure shown in *Figure 2* were selected.

Differential scanning calorimetry indicates that polymer **1**, which was prepared by a melt polycondensation reaction, has two LC phases (*Table 1*, *Figure 3*). The LC phases were identified by polarizing microscopy and by X-ray diffraction (*Figure 4*). X-ray diffraction studies of drawn fibres (*Figure 5*) exhibited two reflections that are

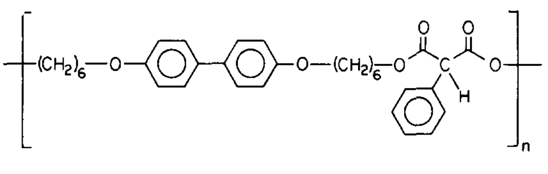

Figure 2 Liquid crystal polymer **1**

Table 1 Characterization of polymers

Polymer	Molecular weight[a]	Phase transition (°C)[b]
1	61 000	S_B 86 n 103
2	15 200	g 42 i
3	34 600	g 25 LC 70 i

[a] Determined by g.p.c. in THF, polystyrene equivalent weight
[b] Abbreviations: S_B, smectic B; n, normal nematic phase; g, glassy phase; LC, nematic phase with a well developed lateral packing; i, isotropic phase

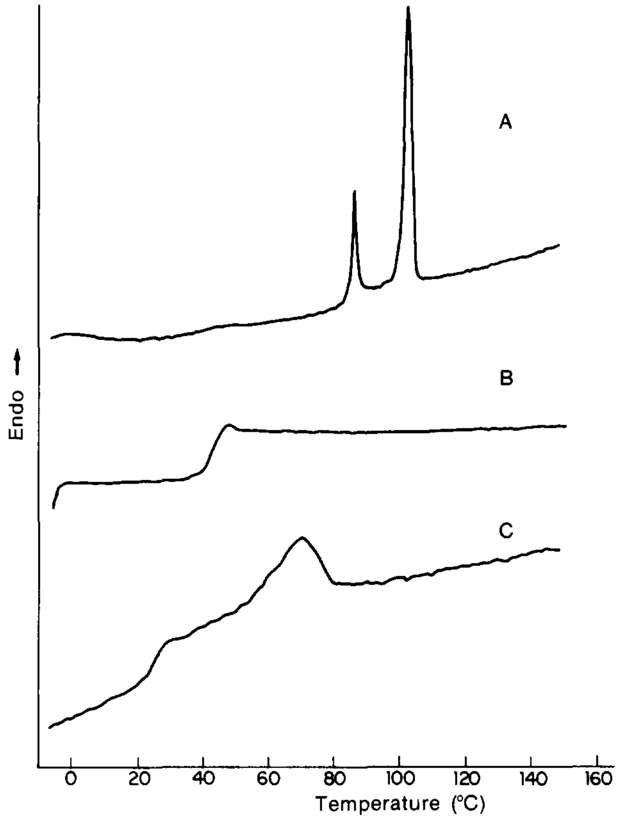

Figure 3 Differential scanning calorimetry results of (A) LC polymer **1**, (B) amorphous polymer **2** and (C) LC copolymer **3**

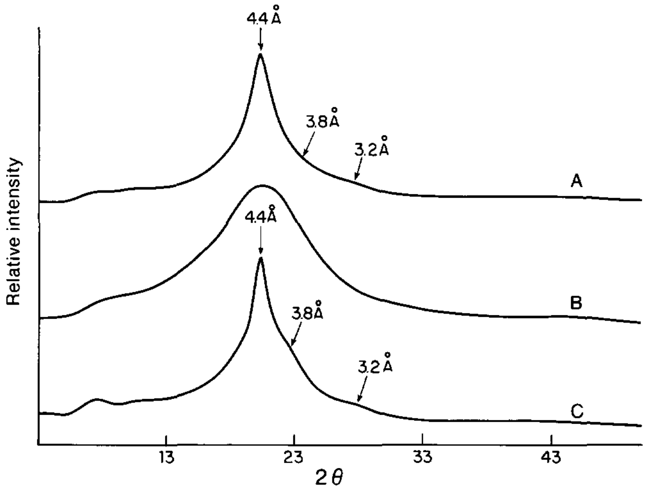

Figure 4 X-ray diffraction pattern of (A) LC polymer **1**, (B) amorphous polymer **2** and (C) LC copolymer **3**. Note the small angle reflection of polymer **1** is not shown here

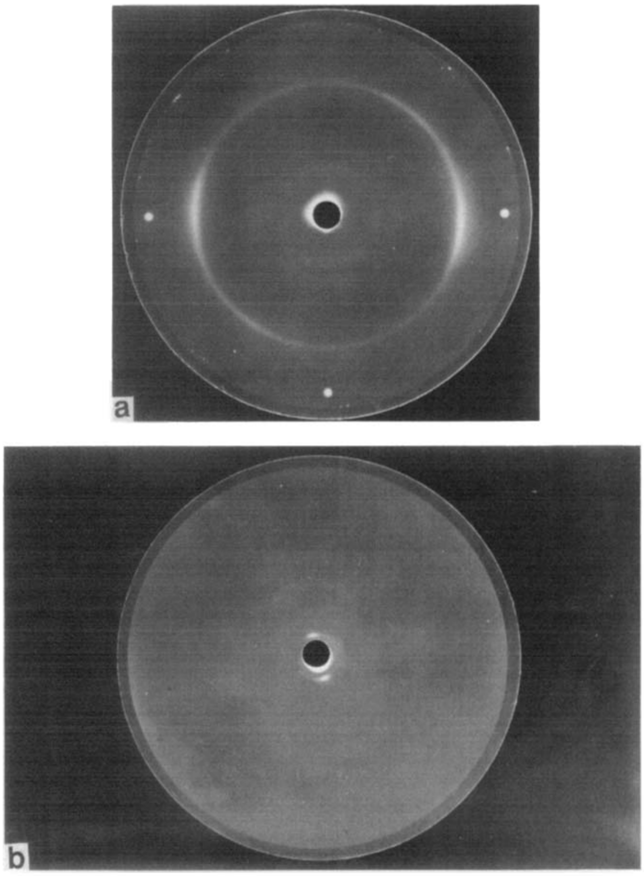

Figure 5 X-ray diffraction patterns of drawn fibres. Sample-to-film distance (a) 10 and (b) 15 cm. (Fibre axis is vertical)

oriented at right angles to each other. The low temperature mesophase was identified as being smectic B since it exhibits a sharp small angle reflection at 35.5 Å (layer spacing) and another sharp reflection at 4.4 Å (lateral packing). Two additional halos that were much less intense were also observed at $d = 3.8$ and 3.2 Å.

The high-temperature phase is believed to be nematic, since no small angle reflections were observed. Furthermore, wide-angle X-ray diffraction patterns exhibited only a broad halo, and the analysis of the sample under the polarizing microscope exhibited a texture that is commonly observed for nematic structures.

Polymer **2**, which is shown in *Figure 6*, is completely amorphous, presumably because the aspect ratio associated with the hydroquinone diol alone is much too small to act as mesogen. Differential scanning calorimetry results (*Figure 3*) indicate that the material exhibits a glass transition temperature (T_g) at 42°C, and the wide-angle X-ray diffraction results (*Figure 4B*) show only a broad amorphous halo, typical of amorphous polymers.

In order to prevent the arrangement of the mesogens into smectic layers (homopolymer **1**) and to favour a nematic phase, copolymer **3**, which is shown in *Figure 7* was prepared. Both ^1H and ^{13}C n.m.r. analysis indicated that the diols were incorporated randomly along the backbone of the polymer. This copolymer forms a viscous LC phase, and the texture under polarizing microscopy could not be identified. X-ray diffraction measurements (*Figure 4C*) show one sharp wide angle reflection at $d = 4.4 \pm 0.1$ Å, and two broadened reflections corresponding to $d = 3.8$ and 3.2 Å as in polymer **1**, but no small angle reflection. Therefore, it is not possible for this polymer to be smectic. However, the results also suggest that the LC phase formed is not the typical nematic phase found in low molar mass liquid crystals[27], because the lateral packing is too well developed.

This phase is best described as a nematic phase, in which the lateral packing of the mesogens is unchanged compared to the smectic B phase of polymer **1**, but the arrangement of the mesogens in layers is lost. A similar, if not the same, phase has been observed for different 'rigid-rod' polymers[28,29].

Dynamic mechanical properties

Crosslinked triacrylate. The dynamic mechanical properties of the homopolymerized trifunctional acrylate and the linear LC copolyester **3** are shown in *Figure 8*. The homopolymerized trifunctional acrylate was first exposed to u.v. irradiation for 4 min at 35°C, and subsequently post-cured for 2 h at 200°C. The tan δ curve shows the presence of a major damping peak centred at 120°C that is associated with the T_g of this crosslinked polymer. The presence of this peak also coincides with the decrease in E'. However, because of the high degree of crosslinking,

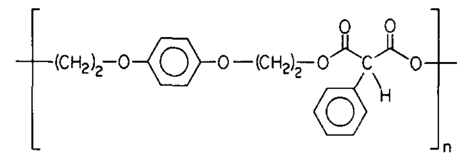

Figure 6 Amorphous polymer 2

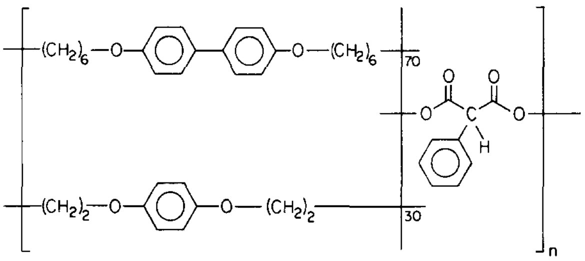

Figure 7 Liquid crystalline copolymer 3

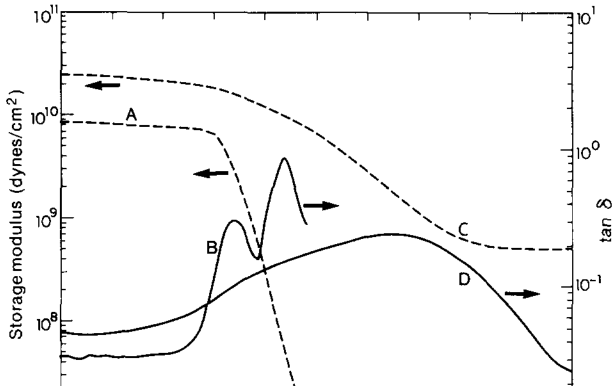

Figure 8 Dynamic mechanical properties of the LC copolymer: (A) storage modulus *versus* temperature; (B) tan δ *versus* temperature. Also, dynamic mechanical properties of the trifunctional acrylate that was photopolymerized and subsequently post-cured for 2 h at 200°C; (C) storage modulus *versus* temperature; (D) tan δ *versus* temperature

E' decreases to a value that is essentially constant until the decomposition temperature of the polymer.

Liquid crystalline copolyester. The LC polyester exhibits a peak in tan δ at 32°C, which is associated with the T_g of the LC copolyester. The T_g is slightly higher than the T_g observed by d.s.c. (24°C), but this is a manifestation of the frequency dependence of this transition. The dynamic mechanical analysis (d.m.a.) exhibits another major damping peak at 68°C [as does the d.s.c. at 70°C (*Figure 3*)] which is attributed to the LC to isotropic transition. The fact that the sample has mechanical integrity in its nematic phase is believed to be due, in part, to the lateral packing of the mesogens, which results in a very viscous nematic phase. Above this nematic to isotropic transition temperature, the linear LC copolyester chains are able to freely translate, and the material enters into a viscous flow regime.

Non-crosslinked blend. When the LC polymer is blended with the multifunctional acrylate monomers (50/50 LC copolymer/trifunctional acrylate), two T_gs were observed at -34 and -10°C by d.s.c. (*Figure 9a*). This result suggests that the monomeric acrylate and the LC copolymer are partially miscible. This results in a depression of the T_g of the LC phase of the LC polymer and an increase in the T_g of the monomeric acrylate.

X-ray diffraction studies indicate that the original LC mesophase has been disrupted due to the presence of the monomeric trifunctional acrylate. X-ray studies (*Figure 10a*) show that five new reflections are present, their d-spacings are at 15.6 (very strong), 8.00 (medium), 4.99 (strong), 2.92 (weak) and 2.50 Å (weak). Three amorphous bands are also observed in the diffraction pattern. Differential scanning calorimetry results indicate that the phase transition of this new phase is depressed by 8–10°C compared to the LC to isotropic transition of the LC copolymer. The d.s.c. results (*Figure 9a*) also suggest that since the breadth of this LC to isotropic transition is slightly narrower, this phase is more homogeneous than the original mesophase in the copolymer.

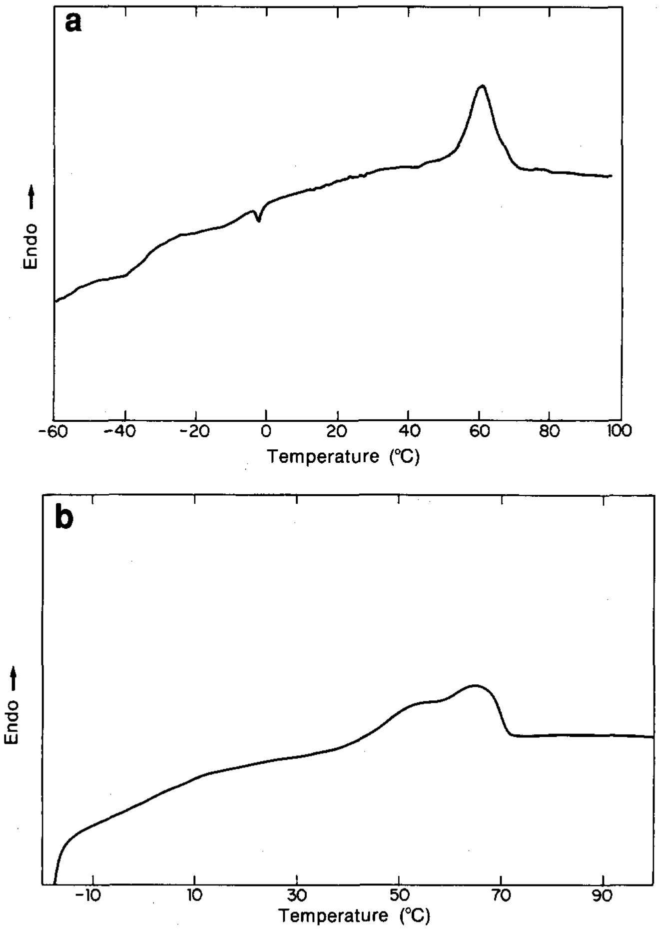

Figure 9 Differential scanning calorimetry of 50/50 blend of the LC copolymer and the trifunctional acrylate (a) before photopolymerization (the small peak is an instrument artifact) and (b) after photopolymerization

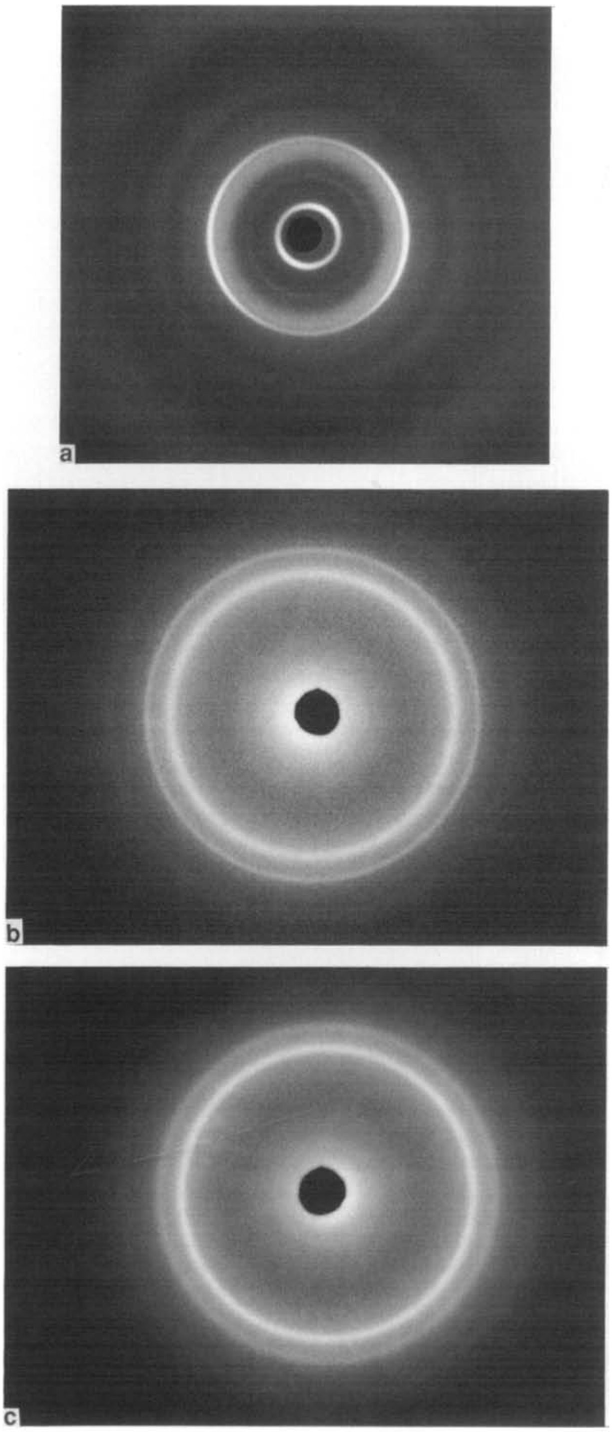

Figure 10 X-diffraction patterns of the 50/50 blend of the LC copolymer and the trifunctional acrylate (a) before photopolymerization, (b) after 5 min photopolymerization, and (c) after 5 min photopolymerization and post-baking at 200°C for 2 h

These data indicate that the low molecular weight monomeric trifunctional acrylate and the LC copolymer interact in the ansiotropic phase of the LC copolymer, and these interactions change the structure within the mesophase. This results in the formation of a new phase whose phase transition occurs at a lower temperature (60°C) than the original LC copolymer (70°C). The optical microscope provides further evidence that a mesophase is still present in the 'as coated film' since a small amount of birefringence is detected.

Photopolymerized crosslinked blends. Ultraviolet exposure of the 'as coated films' results in the photopolymerization of the trifunctional acrylate, and a three-dimensional network begins to form. However, because of the vitrification of the film, a substantial amount of trifunctional acrylate remains unreacted after the initial photopolymerization[30–32]. Further, gel permeation chromatography (g.p.c.) studies of the soluble fraction shows that the monomeric trifunctional acrylate is present along with the high molecular weight LC copolymer. The dynamic mechanical data shows (*Figures 11* and *12*) that after photopolymerization the T_g of the LC copolymer has increased to nearly 29°C. One would expect that as the molecular weight of the acrylate increases during the photopolymerization, and in the absence of any specific interactions between the trifunctional acrylate and LC copolymer, that demixing and phase separation would result. However, because of the presence of the monomeric acrylates, and unreacted acrylate chain ends, which are part of the crosslinked matrix, both the d.m.a. and d.s.c. data indicate that the T_g for the LC copolymer is broader in the blend than for the homopolymer and is slightly depressed. The results also indicate that the LC to isotropic transition is broad, which is expected for a multicomponent system. It is believed that remaining low molecular weight acrylates are still diluting the anisotropic interactions. However, X-ray diffraction studies (*Figure 10b*) show a return to the presence of three wide angle reflections at $d = 4.4$ (very sharp with a halo), 3.81 (very sharp) and 3.21 Å (weak and broad), which are identical to the original LC copolymer. This result suggests that the original mesophase has been restored after the initial photopolymerization, and the low molecular weight acrylates that remain have less effect on the orientation of the mesophase. As shown in *Figure 12*, a second higher temperature transition (80°C), which was also quite broad, was detected by d.m.a. Previous studies have shown that the photopolymerized acrylates exhibit their T_g in this region[30].

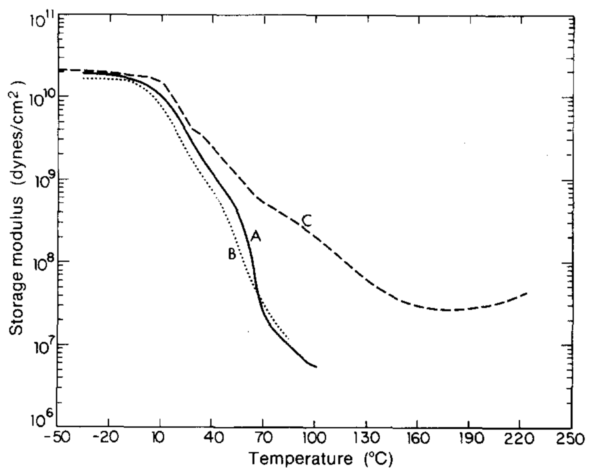

Figure 11 Storage modulus *versus* temperature behaviour for the 50/50 blend of the LC copolymer and the trifunctional acrylate after (A) photopolymerization, (B) photopolymerization and heating to 120°C, and (C) photopolymerization and post-baking at 200°C for 2 h

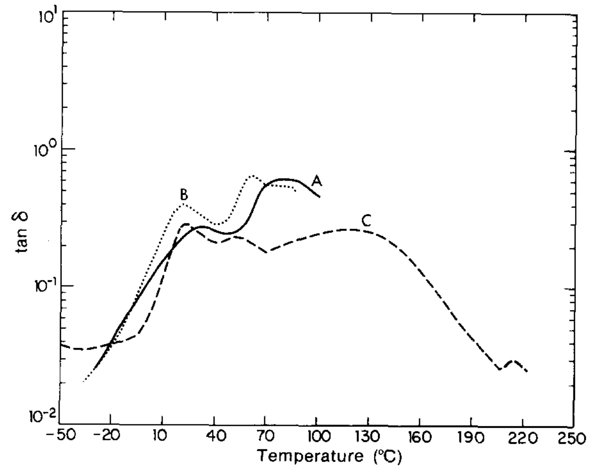

Figure 12 Dissipation factor (tan δ) *versus* temperature behaviour for the 50/50 blend of the LC copolymer and the trifunctional acrylate after (A) photopolymerization, (B) photopolymerization and heating to 120°C, and (C) photopolymerization and post-baking at 200°C for 2 h

Photopolymerized crosslinked and heat-cured blends. A sample that had been photopolymerized was heated to 120°C and then cooled slowly to room temperature. The dynamic mechanical data for this sample indicates that the peak associated with the T_g of the LC copolymer is sharper, and the peak associated with the LC to isotropic transition is also sharper than the blend that had only been irradiated. Presumably, as the temperature was increased the mobility in the film increased which allowed the acrylates to react further. In addition, for the first time since being coated, the film was heated in the region where the LC copolymer exhibits its isotropic phase. The LC to isotropic transition temperature seen in these films is similar to the pure LC copolymer, and the results suggest that the LC copolymer and the trifunctional acrylate matrix are more completely phase separated than in the non-radiated samples.

A morphological model, that appears consistent with the data, evolved from the following experiment. In this study, the sample was first irradiated for 5 min and then heated to 160°C for 1 h. This was followed by heating to 110°C on the hot stage and holding for 10 min, slowly cooling to 50°C and holding for 2 h, and finally cooling to room temperature. In *Figure 13*, a dark region is observed surrounding a highly birefringent area. The results suggest that the LC copolymer appears to be present in domains that are surrounded by an amorphous crosslinked acrylate phase. It is possible to increase the temperature to above the LC to isotropic transition and the birefringence disappears. Upon cooling the birefringent areas reappear in the same locations. This indicates that while the LC copolymer is able to exhibit some mobility and can undergo reversible anisotropic to isotropic transitions, the crosslinked acrylate matrix provides the necessary mechanical integrity to prevent viscous flow at temperatures well above the LC to isotropic transition. X-ray analysis once again indicates

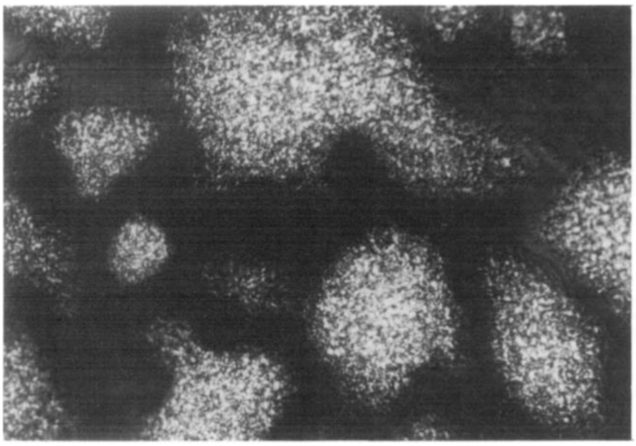

Figure 13 Photomicrograph of the 50/50 blend of the LC copolymer and trifunctional acrylate

Figure 14 Photomicrograph of the 80/20 blend of the LC copolymer and trifunctional acrylate

that the mesophase that exists in this phase-separated sample is similar to the original mesophase present in the LC copolymer since the three wide-angle reflections were observed at identical *d*-spacing and intensities.

Another sample was then photopolymerized and subsequently post-cured at 200°C for 2 h. The dynamic mechanical data (*Figures 11* and *12*) indicate that the acrylates and LC polymer are phase separated. The T_g of the LC copolymer is observed to decrease by 8–10°C to 22°C (by d.m.a.) for both this sample and the sample heated to 120°C. Although we have not fully investigated this phenomenon the reduction in the T_g may be due to unreacted acrylates or oligomers, which are dissolved within the LC phase and can act as a plasticizer. Since these oligomers are not mesogenic, their presence would also explain the decrease in the LC to isotropic phase transition temperature.

Dynamic mechanical analysis indicates that a broad peak that has been identified as the T_g of the acrylates is centred at ~120°C. Further, E' exhibits an extended rubbery plateau, which is consistent with the formation of a continuous crosslinked acrylate phase.

The dynamic mechanical data also indicate that the LC to isotropic transition is depressed to ~55°C from its initial value of 68°C. Interestingly, even though the LC to isotropic transition has been depressed, the X-ray analysis indicates that the structure of the LC polymer is retained during the post-curing regime since similar *d*-spacings are obtained for the cured sample as for the original copolymer.

This unique phase behaviour was not observed for a blend of 80% LC copolymer and 20% trifunctional acrylate. In this case, the blend was treated in a similar fashion as the 50/50 blend described above. However, the photomicrograph (*Figure 14*) does not indicate that there is any gross phase separation, in fact a relatively homogeneous LC texture was observed.

CONCLUSIONS

Two novel LC polymers have been prepared. While the homopolymer was smectic, the smectic arrangement has been disrupted in the copolymer due to the statistical incorporation of repeating units of a different length. It was demonstrated that by blending this soluble main chain LC copolymer the T_g of the LC copolymer was plasticized, and the monomeric acrylates disrupt the orientational order of the mesophase of the LC copolymer. Once photopolymerized, a semi-IPN-II was formed, and an increase in the glass transition of the blend was observed. Further, X-ray analysis indicates that the structure of the original LC phase of the copolymer was restored by this process. The sample can be post-cured above the isotropic transition temperature of the LC copolymer to further increase the extent of reaction of the acrylates, and after cooling the LC copolymer still retains the original structure of the LC mesophase. Clearly, the most interesting feature about these blends was the creation of a highly crosslinked matrix in which an LC copolymer was embedded. The LC polymer can reproducibly undergo transitions from its LC to isotropic phase, and in addition, the blend has mechanical integrity above the LC to isotropic phase transition.

ACKNOWLEDGEMENTS

The authors would like to sincerely thank Thomas Blanton of the Advanced X-ray Scattering Laboratory for his X-ray diffraction work. Further, we would like to thank John Chambers for his technical assistance.

REFERENCES

1 Kreuder, W. and Ringsdorf, H. *Makromol. Chem., Rapid Commun.* 1983, **4**, 807; Ringsdorf, H., Schlarb, B. and Venxzmer, J. *Angew. Chem. Int. Edn. Engl.* 1987, **27**, 113

2 Platé, N. A. and Shibaev, V. P. in 'Advances in Polymer Science' (Eds M. Gordon and N. A. Platé), Vol. 60/61, Springer, Berlin, 1984, p. 173

3 Blumstein, A., Asrar, J. and Blumstein, R. B. in 'Liquid Crystals and Ordered Fluids' (Eds. A. C. Griffin and J. F. Johnson), Vol. 4, Plenum Press, New York, 1984, p. 311

4 Ober, C., Jin, J.-I. and Lenz, R. W. in 'Advances in Polymer Science' (Eds. M. Gordon and N. A. Platé), Vol. 59, Springer, Berlin, 1984, p. 103

5 Gleim, W. and Finkelmann, H. in 'Side Chain Liquid Crystal Polymers' (Ed. C. B. McArdle), Blackie and Son, Glasgow, 1989, p. 287

6 Zentel, R. *Angew. Chem. Int. Edn. Engl. Adv. Mater.* 1989, **28**, 1407

7 Bhadani, S. N. and Gray, D. G. *Mol. Cryst. Liq. Cryst.* (*Lett.*) 1984, **102**, 255

8 Noonan, J. M. and Caccamo, A. F. US Patent 4696990, 1987; Noonan, J. M. and Caccamo, A. F. *Polym. Prepr.* 1989, **30** (2), 501

9 Haddleton, D. M., Creed, D., Griffin, A. C., Hoyle, C. E. and Venkataram, C. K. *Makromol. Chem., Rapid Commun.* 1989, **10**, 391

10 Broer, D. J., Boven, J., Mol, G. N. and Challa, G. *Makromol. Chem.* 1989, **190**, 2255

11 Weiss, R. A., Huh, W. and Nicolais, L. *Polym. Eng. Sci.* 1987, **27**, 684

12 Ringsdorf, H., Schmidt, H.-W. and Schneller, A. *Makromol. Chem., Rapid Commun.* 1982, **3**, 745

13 Seurin, M. J., Gilli, J. M., Ten Bosch, A. and Sixou, P. *Polymer* 1984, **25**, 1073

14 Cogswell, F. N., Griffin, B. P. and Rose, J. B. US Patent 4443083

15 Sperling, L. H. 'Interpenetrating Polymer Networks and Related Materials', Plenum Press, New York, 1981; Sperling, L. H. *Modern Plastic Int.* 1981, **11** (10), 68

16 Hourston, D. J. and McCluskey, J. A. *J. Appl. Polym. Sci.* 1986, **31**, 645

17 Lipko, J. D., George, H. F., Thomas, D. A., Hargest, S. C. and Sperling, J. H. *J. Appl. Polym. Sci.* 1979, **23**, 2739

18 Widmaier, J. M. and Sperling, L. H. *J. Appl. Polym. Sci.* 1982, **27**, 3513

19 Hourston, D. J. and Zia, Y. *J. Appl. Polym. Sci.* 1983, **28**, 3849

20 Sroog, C. E., Endrey, A. L., Abramo, S. V., Berr, C. E., Edwards, W. M. and Oliver, K. *J. Polym. Sci. A-1* 1965, **3**, 1373

21 Reck, B. and Ringsdorf, H. *Makromol. Chem., Rapid Commun.* 1985, **6**, 291

22 Specht, D. P., Matric, P. A. and Farid, S. *Tetrahedron* 1982, **38** (9), 1203

23 Williams, J. R., Specht, D. P. and Farid, S. *Polym. Eng. Sci.* 1983, **23** (18), 1022

24 Blumstein, A., Vilasagar, S., Ponrathnam, S., Clough, S. B. and Blumstein, R. B. *J. Polym. Sci., Polym. Phys. Edn* 1982, **20**, 877

25 Dicke, M. R. and Lenz, R. W. *J. Polym. Sci., Polym. Chem. Edn* 1983, **21**, 2581

26 Zentel, R. and Reckert, G. *Makromol. Chem.* 1986, **187**, 1915

27 Gray, G. W. and Goodby, J. W. G. 'Smectic Liquid Crystals', Leonard Hill, London, 1984

28 Lieser, G. *J. Polym. Sci., Polym. Phys. Edn* 1983, **21**, 1611

29 Schwartz, G. and Kricheldorf, H. R. *Macromol. Chem., Rapid Commun.* 1988, **9**, 717

30 Fitzgerald, J. J. and Landry, C. J. T. *J. Appl. Polym. Sci.* 1990, **40**, 1727

31 Kloosterboar, J. G., van de Hei, G. M. M., Gossink, R. G. and Dortant, G. C. M. *Polym. Commun.* 1984, **25**, 322

32 Kloosterboar, J. G., Lijten, G. F. C. M. and Greidanus, F. J. A. M. *Polym. Commun.* 1987, **28**, 2