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Liquid crystal elastomers
Interaction between the network and smectic ordering

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Side chain liquid crystal polymers which exhibited a smectic phase were cross-linked, both in the smectic phase and in the isotropic phase. In general, the stability of the phase of the sample at cross-linking is enhanced by this procedure. This stabilization reflects the elastic energy required to distort the polymer chain from its equilibrium conformation at the phase transition. In the case of the smectic phase, the relatively high magnitudes for the shifts in phase transition temperatures support neutron scattering data, that shows that the polymer backbone is highly constrained by the layer-like arrangement of the mesogenic units. Materials cross-linked in the isotropic phase also produce a smectic phase on cooling, although there is some destabilization of this phase, as the isotropic phase is enhanced.

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1. Introduction

Liquid crystal elastomers are composite materials which incorporate the anisotropic behaviour of low molecular weight liquid crystals with the unique properties of rubber-like elasticity [1–3]. Such materials are interesting not only for the scope which they offer for providing materials with unusual properties, but also because their behaviour offers a considerable challenge to the theoretical scientist [4]. In this latter respect, it is of particular interest to understand the way in which the polymer chain, with its entropically driven desire for random configurations, can be reconciled with the driving force towards alignment of the mesogenic side groups [5]. This account describes our continuing investigations into the nature of the coupling between mesogenic units and the polymer backbone in liquid crystal polymer systems [6–8].

We recently described the effect of cross-linking conditions on the phase behaviour of a nematic liquid crystal polymer system [6]. It was found that cross-linking in the nematic phase resulted in an increase in the stability of this phase; similarly, cross-linking in the isotropic state was found to enhance the stability of this state, i.e. the nematic–isotropic transition temperature decreased. These results were found to be in excellent agreement, both qualitatively and quantitatively with the theoretical predictions of Warner [5, 9]. Thus, it would appear that coupling between the mesogenic units and the polymer backbone results in a preferred conformational arrangement of the latter in the liquid crystal phase, i.e. localized ordering of the side groups results in a corresponding ordering of the polymer chain. Such alignment may bring the polymer chains either broadly parallel or broadly perpendicular with locally aligned mesogenic units, depending, in particular, upon the nature of the coupling chain connecting the two units [7, 8]. Introduction of cross-linking into the polymer in this state enhances the stability of the phase, since transition to the isotropic phase

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requires that both the mesogenic units and the polymer backbone take up random orientations; for the backbone, this can only be achieved at the expense of the elastic energy required to distort the network from its initial cross-linked state.

In this contribution we have extended our studies of coupling phenomena in liquid crystal elastomers [6–8] to an investigation of the influence of a smectic phase on the polymer backbone. It was of particular interest to determine if the additional dimension of order present in this phase type, with the associated stacking of polymer chains between the layers [10, 11], would result in a more marked influence of cross-linking conditions on the phase behaviour.

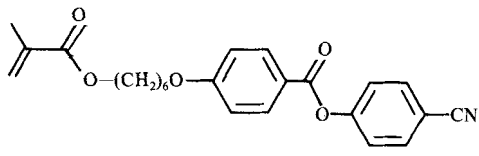
2. Experimental

The phase behaviour of the polymers and elastomers studied here were measured using both polarizing microscopy and differential scanning calorimetry. Microscopy was performed using a Carl-Zeiss Jenalab polarizing microscope equipped with a temperature controlled hot stage (Linkam TH601). The clearing temperature, i.e. the temperature at which the anisotropic liquid crystal state is replaced by the isotropic state, was determined from the thermo-optic response of the material under the polarizing microscope, using a photodiode coupled to a microcomputer system. Typically, a heating rate of $1°C\,min^{-1}$ was employed. These phase transition measurements were complemented by those obtained from differential scanning calorimetry (Perkin–Elmer DSC-2) using a scan rate of $10°C\,min^{-1}$. Wide angle X-ray scattering (WAXS) was conducted on moulded polymer films and solution cast elastomer films to confirm the nature of the phases.

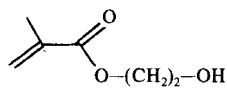
Molecular weights of polymers were obtained by gel permeation chromatography (GPC). The data were obtained using solutions in THF with either a UV or refractive index detector, and calibrated using polystyrene standards.

The modulus data for the elastomers were obtained from stress–strain curves evaluated in the isotropic phase, using a Microscope Tensile Tester from Rosand Precision Ltd., interfaced with a microcomputer system. The apparatus was fitted with a small hot air oven which allowed controlled temperatures in the range $20–200 \pm 1°C$. Infra-red spectroscopy of films was performed using a Nicolet FT–IR spectrometer.

3. Materials



[I]



[II]

Mesogenic monomers were based on the cyanophenyl benzoate methacrylate monomer [I]. This material was chosen because it has a well-characterized smectic phase [10]. In order to provide potential sites for cross-linking, the material was copolymerized with varying proportions of 2-hydroxyethyl methacrylate [II]. Monomer [I] was synthesized using established procedures [12]; hydroxyethyl acrylate was

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purchased and purified by distillation under reduced pressure prior to use. Polymerization was performed under reduced pressure using deoxygenated chlorobenzene solutions (10 per cent *w/v*) for 16 h at 55°C using AIBN (1 mol %) as initiator. After polymerization the materials were purified by repeated precipitation into cold methanol (twice) and then into cold diethyl ether. ^{1}H NMR revealed that the composition of the copolymer was as expected on the basis of the concentration of the two monomers in the initial polymerization mixture. The compositions of the copolymers used in this study, together with their phase behaviour are listed in table 1. As inspection shows, increasing non-mesogenic content of the polymer results in a decrease in the clearing point (i.e. the temperature at which the material goes isotropic). This is entirely consistent with observations on other liquid crystals systems [13, 14].

Cross-linking was introduced via the thermal reaction of either hexyl or dodecyl diisocyanates [6, 15] with the pendent hydroxl units provided by the hydroxyethyl methacrylate units on adjacent chains (see figure 1). The copolymer and a calculated amount of the cross-linking mixture were dissolved in a minimum amount of dry dichloromethane. The solution was then cast on a polyimide sheet and the solvent allowed to evaporate at room temperature. The films were then placed in a hot air oven preset to the required cross-linking temperature (unless otherwise stated for samples cross-linked in the smectic phase, $T_{XL} = 75$°C; for those cross-linked in the nematic phase, $T_{XL} = 121$°C).

Selected samples of the polymer were removed from the oven at different time intervals during the cross-linking reaction and examined under the polarizing microscope. A steady shifted value of the clearing temperature consistent with the completion of the cross-linking reaction was typically obtained after 40 h when the cross-linking was performed at a temperature in the isotropic state of the starting polymer. This is similar to the reaction time for the acrylate polymers in both the isotropic and nematic states [6]. The rate of cross-linking for the methacrylate material in the smectic state was much slower, the reaction typically taking 200 h before a steady shifted value of the clearing temperature was obtained. Consequently, all samples were cross-linked for 250 h.

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4. Results

4.1. *Uncross-linked materials*

Figure 2 shows the DSC trace obtained from the homopolymer of monomer [I], and is typical of those observed for both the uncross-linked copolymer samples and for

Table 1. The compositions of the copolymers used together with their phase behaviour.

Polymer	Copolymer content I	Copolymer content II	T_g/°C‡	T_{SN}/°C‡	T_C/°C‡	M_n	M_w
0	1·00	0·00	40·2	107·3	113·1	$1·3 \times 10^5$	$2·5 \times 10^5$
1	0·94	0·06	40·5	96·1	103·6	$1·1 \times 10^5$	$1·9 \times 10^5$
2	0·90	0·10	41·7	90·6	98·8	$1·3 \times 10^5$	$5·1 \times 10^5$
3	0·75	0·25	49·5	—	97·1	$9·4 \times 10^4$	$1·4 \times 10^5$
4	0·60	0·40	50·8	—	93·3	$7·6 \times 10^4$	$1·2 \times 10^5$

† Composition determined by NMR (see text).
‡ Obtained from DSC measurements; all values subject to uncertainties of *c.* ±2°C.

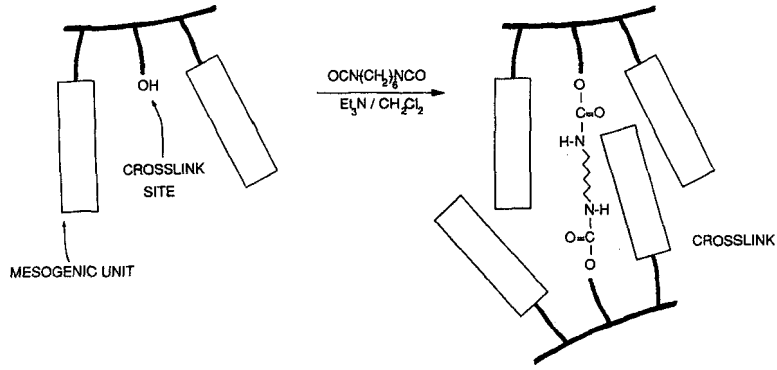

Figure 1. The cross-linking reaction.

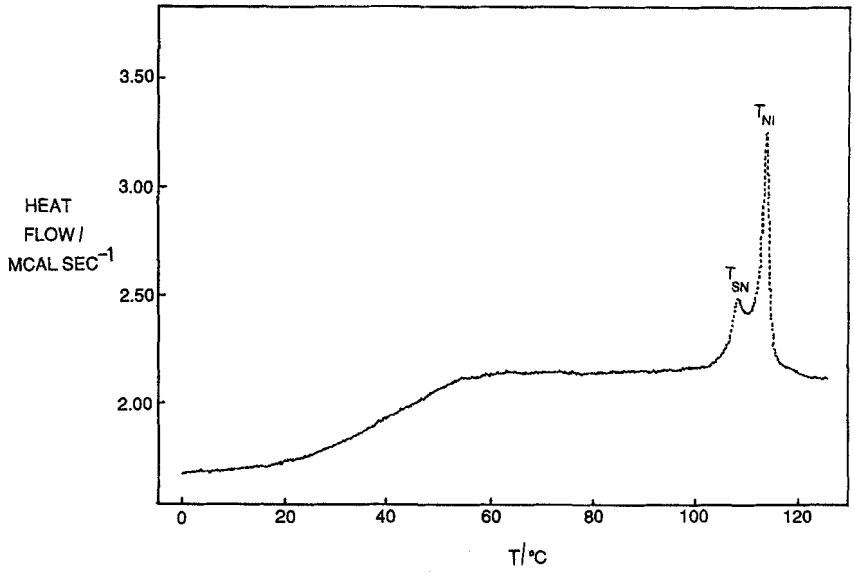

Figure 2. Typical DSC trace observed for the methacrylate based liquid crystal polymer systems studied in these investigations; the region at about 100°C has been expanded to show the presence of the two transitions observed.

the cross-linked material. These data, together with optical microscopy and X-ray scattering, show the similarity between the phase behaviour of the copolymers and that of the homopolymer (see table 1). In particular, the materials exhibit both a smectic phase over a relatively broad temperature range, and a nematic phase over a rather narrow temperature range. As observed for similar acrylate systems, considerable fractions of the non-mesogenic monomer can be added without completely disrupting the liquid crystal phase [13, 14]. At low proportions of hydroxyethyl methacrylate, the gap between the smectic–nematic and nematic–isotropic transitions increased with increasing non-mesogenic content. However, at high proportions hydroxyethyl methacrylate, only a single transition could be detected.

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Table 2. The cross-link densities determined using modulus measurements from a liquid crystal polymer cross-linked with hexyl di-isocyanate hexane.

Starting polymer	Elastomer	Cross-link agent added†	Phase of parent polymer at cross-linking temperature‡	Cross-link sites reacted (as % of total repeat units)	% Cross-link density§	% Cross-link efficiency‖
2	2(a)	2	S	1·7	0·29±0·04	15
	2(b)	2	I	1·3	0·38±0·05	19
	2(c)	5	S	4·3	0·99±0·20	20
	2(d)	5	I	3·8	0·89±0·23	18
	2(e)	7	S	6·3	1·41±0·29	20
	2(f)	11	S	9·9	2·05±0·35	20
	2(g)	11	I	9·9	2·76±0·34	26

†Hexyl di-isocyanate calculated as a function of the repeat unit.
‡S = smectic; I = isotropic.
§Network points as a function of the repeat unit.
‖Measured cross-link density as a function of that expected on the basis of complete reaction of the di-isocyanate.

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4.2. *Degree of cross-linking*

Table 2 shows the cross-link densities, determined using modulus measurements [16], from a liquid crystal polymer cross-linked with hexyl di-isocyanate in both the smectic and the isotropic phase. IR spectroscopy revealed the presence of large amounts of unreacted hydroxyl groups in the materials consistent with the low efficiency of cross-linking indicated in table 2. As inspection of the table shows, there is some greater level of efficiency for the materials cross-linked in the isotropic phase over those cross-linked in the mesophase. We can relate this difference to either the reduced temperature of cross-linking, or the lack of spatially available sites for cross-linking in the smectic phase. In similar experiments in which the longer molecular unit, dodecyl di-isocyanate, was used as a cross-linking agent, cross-link efficiencies increased from 15 to 55 per cent for materials held in the smectic phase, and from 21 to 61 per cent in the isotropic phase. The increased efficiency of this longer cross-linking agent suggests that spacial considerations are indeed important in the cross-linking process.

4.3. *Phase behaviour*

Figure 3 shows a plot of clearing temperature against the cross-link density for samples cross-linked with hexyl di-isocyanate hexane in the smectic or isotropic phase. Two points are immediately apparent; firstly, for materials cross-linked in the smectic phase, the phase transition increases with increasing cross-link density, while for the polymer samples cross-linked in the isotropic phase a decline in the clearing point is apparent. Secondly, for materials containing *c.* 2·5 per cent cross-linking there is a temperature difference of almost 15°C between the corresponding samples. Although a precise comparison with the nematic polymers studied in [6] is not possible due to insufficient knowledge of the cross-link density of the nematic polymer, the differences are considerably smaller, of the order of 5°C. In addition, for the smectic phase the stabilization of the liquid crystal phase is of the order of 10°C, compared to *c.* 1°C for the nematic case.

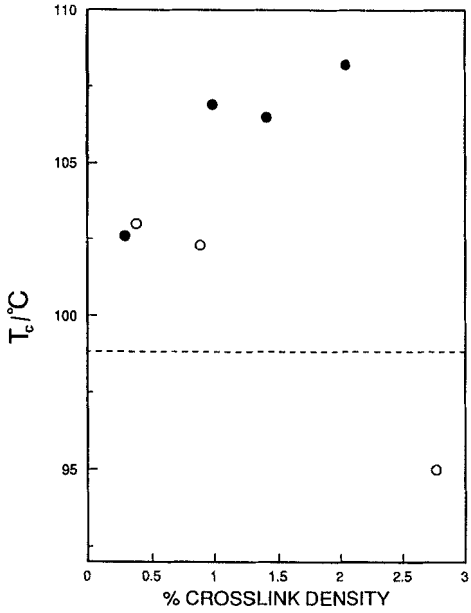

Figure 3. Plot of the clearing temperature versus cross-link for samples cross-linked with hexyl di-isocyanate (●) in the smectic phase, and (○) in the isotropic phase.

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Table 3. The phase transition data obtained from an analysis of the DSC traces for selected materials.

Sample	Phase of parent polymer at cross-linking†	T_g/°C‡	T_{SN}/°C‡	T_C/°C‡	ΔH/kJ mol^{-1}§
2	Uncrossed-linked	41·7	90·6	98·8	3·4
2(b)	I	43·0	100·5	103·2	—
2(c)	S	43·5	100·0	106·9	1·6
2(f)	S	44·8	103·2	108·2	1·4
2(g)	I	45·2	—	95·0	0·3

†I = isotropic; S = smectic.
‡Obtained from DSC measurements, all values subject to uncertainties of *c.* ±2°C.
§Measured by comparison with an indium standard.

A more careful consideration of the data shown in figure 3, clearly shows there are a number of additional considerations to be taken into account before a detailed analysis of the data can be given. In particular, the phase behaviour for these materials is relatively complicated and consideration of both the nematic and the smectic phases must be brought into our argument. Table 3 shows the phase transition data obtained from an analysis of the DSC traces for selected materials and includes both the smectic–nematic and nematic–isotropic transition temperatures where these data could be extracted from the DSC curves. For samples cross-linked in the smectic phase the marked increase in the smectic–nematic transition temperature was accompanied by a

smaller increase in the nematic–isotropic transition temperature; the net result is that the nematic phase interval contracts. Thus, while in general the smectic phase is stabilized in these samples, the nematic phase is less stabilized by cross-linking; for one sample, where a relatively high level of cross-linking was present, no nematic phase could be detected.

In addition to the temperature data, table 3 includes representative data for the enthalpy change on transition from mesophase to isotropic melt. Of particular note is the low value obtained for materials cross-linked in the isotropic phase. We suggest that this reflects serious perturbations to the smectic phase caused by cross-linking. However, it is likely that there are not only thermodynamic, but also kinetic considerations to be taken into account when studying these phenomena (see also [6]). We suggest that it is kinetic influences which give rise to the apparent stabilization of the mesophase relative to the uncross-linked material for samples cross-linked in the isotropic phase at low cross-link densities. In particular, there may be regions of the polymer which retain some of the conformational features of the smectic phase, even when cross-linked in the isotropic phase. Thus, the slow relaxation to the equilibrium isotropic structure is inhibited by the onset of cross-linking. The relatively slow rate for cross-linking in the smectic phase prevents any reverse effect. Further investigations of this phenomenon are currently being undertaken.

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5. Discussion

The data presented here provide clear evidence that cross-linking a liquid crystal polymer in the smectic phase has a marked effect on the phase transition behaviour. In particular, the stabilization of the smectic phase induced by cross-linking in this phase is considerably greater than the stabilization previously observed for a nematic polymer cross-linked in the nematic phase [6]. In both cases the stabilization represents the extent to which distortion of the network occurs on transition from the anisotropic liquid-crystalline state to the isotropic state. The methacrylate polymer discussed in this work and the acrylate polymer discussed in [6] have both been the subject of neutron scattering studies [17, 18]. For a magnetically aligned sample of a methacrylate based on monomer [I], Pépy *et al.* [17] measured a radius of gyration perpendicular to the field direction $R_\perp$ of 27 Å, while that parallel to the field direction $R_\parallel$ was found to be 21 Å, although some variation with temperature was noted. for the acrylate monomer discussed in [6], neutron scattering experiments on a magnetically aligned sample [18] give $R_\perp$ as 18·5 Å, and $R_\parallel$ as 21 Å. (For the methacrylate polymer the backbone aligns perpendicular to the mesogenic units; for the acrylate, parallel alignment is observed.) Though measurements of this type may be influenced by a number of parameters, such as the molecular weight of the polymer, it is the temperature variation of the data which provides the most serious obstacle to a direct comparison of the values obtained. However, it is clear from [17] that the temperature variations are only marked at temperatures close to the phase transition; the radius of gyration data listed above refer to samples aligned at temperatures considerably below the phase transition, i.e. conditions similar to those at which the cross-linking experiments described both here and in [6] were performed. Thus, the values of $R_\perp$ and $R_\parallel$ may be used to measure the deformation of the molecule in terms of a macroscopic strain λ [18]; for the smectic polymer, λ is found to be 1·23, while for the nematic acrylate, λ is 1·09. In addition Finkelmann [19] has reported the stress-induced stabilization of a nematic phase, and the values of the temperature shifts, *c.* 2·5°*C* for a strain of *c.* 1·5, are broadly in line with the shifts for the nematic polymer of [6], which

arise from the internal distortions of the polymer chain (*c.* 1°C for a 10 per cent strain). This is in marked contrast to the smectic phase shifts reported here which are *c.* 7°C for a 10 per cent strain.

Samples cross-linked in the isotropic phase also showed a smectic phase, although in some cases there was a clear reduction in the stability of the phase. Interestingly, DSC experiments suggest reduced ordering in this phase, and the data presented here suggest that, at least in part, smectic ordering in these systems may result from non-equilibrium conformations of the polymer chain at the time of cross-linking. We are currently evaluating alternative cross-linking routes to evaluate the importance of such kinetic effects.

6. Conclusion

It has been seen that cross-linking liquid crystal polymers in the smectic phase results in a considerable enhancement of the stability of that phase. This stabilization, as manifested by shifts in phase transition temperatures, is considerably greater than that previously observed for a nematic polymer system. The results indicate that the additional dimensionality in the ordering for a smectic phase results in far greater constraints on the conformational ordering of the polymer backbone.

We have already reported, for a nematic phase, how cross-linking an ordered sample may produce a reversible, temperature controlled memory [20]; the significance of the enhanced constraints for a smectic phase in terms of effects has yet to be evaluated.

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