ELSEVIER

Liquid crystal elastomers: controlled crosslinking in the liquid crystal phase

F. J. Davis* and G. R. Mitchell
Polymer Science Centre, University of Reading, Whiteknights, Reading RG6 2AD, UK
(Received May 1991; revised 28 June 1995)

A method of chemically crosslinking side-chain liquid crystal polymers at carefully controlled temperatures and with variable crosslinking densities in the bulk phase is described. The nematic–isotropic phase transition temperatures of the resulting liquid crystal elastomers are found to show a marked dependence on the history of the sample. In particular, crosslinking a polymer in the nematic phase results in an elastomer in which the nematic phase shows an enhanced stability. The results are compared with theoretical expectations, and related to the coupling between the mesogenic units and the polymer backbone. Copyright © 1996 Elsevier Science Ltd.

(Keywords: liquid crystal polymer; liquid crystal elastomer; phase transitions)

INTRODUCTION

The incorporation of mesogenic units as side chains in polymeric systems is an area that has attracted considerable attention in recent years[1,2]. The resultant side-chain liquid crystal polymers are of interest to a broad range of scientific disciplines, from synthetic organic chemistry, through polymer chemistry and polymer physics, to theoretical physics and engineering. In addition, there has been no shortage of industrial interest in such materials, since any unusual properties for such materials might offer considerable scope for technological exploitation.

One particular property of liquid crystal polymers, not exhibited by their low-molecular-weight analogues, is the possibility of forming elastomers[3]. The introduction of intermolecular crosslinks into liquid crystal polymers clearly offers enhanced scope for the observation of unique properties. For example, studies have shown that in the isotropic phase such materials display mechanical behaviour typical of conventional rubber-like elasticity[4], but in the liquid crystal phase more complex mechanical behaviour is observed, reflecting the coupled response of the mesogenic side groups to an applied stress[5,6].

This contribution is concerned with the phase behaviour of liquid crystal elastomers. In particular, we have synthesized some liquid crystal polymers containing a small proportion of a non-mesogenic comonomer with terminal hydroxyl groups, to act as reactive sites for crosslinking[4,7]. The introduction of a suitable reactive difunctional unit, particularly a di-isocyanate, is found to be an effective method of crosslinking such polymers. By a small modification to this conventional 'curing' procedure, we have been able to crosslink these novel polymers in the bulk at carefully controlled temperatures. This enables materials to be crosslinked either in the ordered liquid crystal phase or in the isotropic state.

We describe here experiments to determine the way in which the crosslinking history influences the nature of the resultant elastomer; in particular, to correlate the phase transitions observed with expectation on the basis of the theory of Warner et al.[8]. This theory, building on the original suggestions of de Gennes[9], suggests that crosslinking a polymer in the nematic phase should stabilize that phase, with a resultant increase in the nematic–isotropic transition temperature; conversely, for materials crosslinked in the isotropic phase the liquid crystal phase is destabilized. A similar but less detailed proposal has been made by Brand[10].

EXPERIMENTAL

Liquid crystal polymers were prepared by copolymerization of the cyanobenzoate monomer [I] with different proportions of hydroxyethyl acrylate (HEA) [II]: one sample contained 6% HEA, the other 20% HEA. Polymerization was performed in chlorobenzene solution at 55°C using 1 mol% azobisisobutyronitrile as initiator[4]. The materials were purified by repeated precipitation into diethyl ether and dried in vacuum at 50°C for 24 h. Nuclear magnetic resonance spectra of the resulting materials showed the proportion of the two comonomers in the final product was as expected on the basis of their relative concentrations in the initial polymerization solution. Gel permeation chromatography data revealed the 6% HEA polymer to have a number-average degree of polymerization of c. 220, and a weight-average degree of polymerization of c. 680 monomer units; the 20% polymer (which was used to provide the data shown in *Figure 2*) had a number-average degree of polymerization of 150 and a weight-average value of 1300. All other materials were commercially available and purified prior to use.

Crosslinking on small (~ 30 mg) samples was performed by adding a known volume of a solution of di-isocyanatohexane and triethylamine in dichloromethane

---

$$CH_2=CH-C\underset{O-(CH_2)_6-O}{\overset{O}{\parallel}}$$

[I]

$$CH_2=CH-C\underset{O-(CH_2)_2-OH}{\overset{O}{\parallel}}$$

[II]
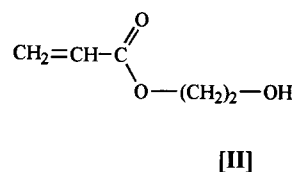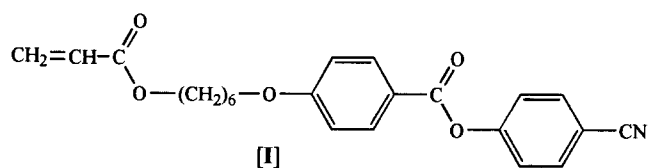
to a solution of the polymer at room temperature. For samples nominally crosslinked 4% (of the acrylate units in the chain), a polymer containing $\sim 6 \, mol\%$ hydroxyl units was used, together with an isocyanate solution such that the final mixture contained $4 \, mol\%$ of the cross-linking agent and 1% of triethylamine catalyst. This ensured a slight excess of the crosslinking units in comparison to the available hydroxyl units. For samples where higher levels of crosslinking were required, a polymer containing $\sim 20\%$ HEA was used to provide the additional reactive moieties required, and the isocyanate solution concentration was adjusted accordingly. The solutions thus obtained were carefully dropped onto pieces of polyimide film, and the volatile solvent evaporated at room temperature under reduced pressure. The polymer films were held at a specified constant temperature for $\sim 100 \, h$, after which time the cross-linking reaction appeared to be complete (see below). Some of the crosslinking experiments were performed in the thermal stage of a polarizing microscope, which facilitated monitoring of the phase of the reacting materials.

The levels of crosslink density were evaluated through swelling experiments using toluene at room temperature and by infra-red (i.r.) spectroscopy using a Nicolet FTIR spectrometer. For this latter method the degree of reaction was determined as a function of the intensity of the signal at $3300 \, cm^{-1}$, due to unreacted OH; the measurements were calibrated using specially prepared samples of the liquid crystal polymer system containing differing quantities of HEA. In addition, the mechanical moduli of slightly larger samples were measured in the isotropic phase, using a microscale tensile testing apparatus; the experimental details of such measurements have been described previously[6]. Phase transition data were determined by monitoring the intensity of light through a sample placed between crossed polarizers in an optical microscope equipped with a thermal stage, photodiode and associated recording electronics. A heating rate of $2°C \, min^{-1}$ was used throughout.

RESULTS

All of the uncrosslinked copolymers prepared exhibited a reversible phase transition between the nematic and isotropic phases, the precise temperature of the transition being dependent upon the composition[4].

Liquid crystal elastomer samples were prepared in which both the temperature of crosslinking and the crosslink density were varied. A series of samples with

approximately constant crosslinking density was prepared by crosslinking the copolymer containing $4 \, mol\%$ of hydroxyl sites at selected temperatures between 60 and 150°C. A second series of samples, designed to monitor the effect of variations in crosslink density, was prepared using the copolymer containing $20 \, mol\%$ of hydroxyl sites with increasing proportions of di-isocyanatohexane from 3 to 15%. At the higher concentrations the crosslinking units were present nominally (see later) in a considerable excess. For each level of crosslink density two samples were prepared, with one such sample crosslinked at 108°C in the nematic phase, the second at 135°C in the isotropic phase.

All of the crosslinked liquid crystal materials in these two series of samples displayed textures in the optical microscope which corresponded to a nematic phase, although there was no large-scale alignment. On heating, all samples, even those with nominal high crosslink densities, showed a reversible phase transition from a liquid crystal to the isotropic phase. For selected samples, X-ray scattering measurements on aligned samples confirmed the nature of this phase. Additional experiments with extremely high isocyanate concentrations indicated that it was possible to lock in the nematic texture through high levels of crosslinking, as had been reported previously[11-13]. The lightly crosslinked samples that are the subject of the current study showed retention of their initial shape in the isotropic phase and were found to deform reversibly when compressed.

All the samples studied were insoluble in the various organic solvents which dissolved the uncrosslinked systems (for example, toluene and dichloromethane), but were found to swell, as would be expected for a crosslinked polymer. Assessment of the level of this swelling was limited by the relatively small samples examined. However, all of the samples nominally $4 \, mol\%$ crosslinked showed swelling levels of $\sim 100\%$; although no evaluation of the sol content in these small samples was possible. This indicates that the level of cross-linking is similar despite the differing crosslinking temperatures. A similar conclusion was drawn from the i.r. analysis. These two methods, while providing some indication that the level of crosslinking is relatively unaffected by the reaction temperature, provide limited quantitative evidence regarding the level of crosslinking present in the samples. As a consequence, two larger samples were prepared to allow mechanical testing. From the moduli values obtained from these samples[6], the crosslink densities (expressed in terms of percentage of backbone acrylate units) were calculated to be $1.4 \pm 0.3\%$ for a sample crosslinked in the nematic phase and $1.6 \pm 0.3\%$ for a sample crosslinked in the isotropic phase (i.e. a crosslinking efficiency of $c. \, 25\%$). Thus, clearly while there may be some systematic errors involved in the procedures described here, they are relatively small.
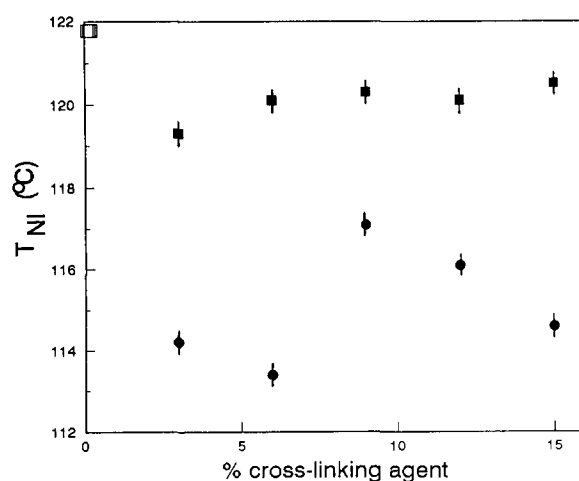
The clearing points of the samples were determined from thermo-optic curves, which monitor the intensity of light passing through to the microscope eyepiece. A sudden drop in the intensity observed from these curves reflects the diminution of light intensity from the sample placed between crosspolarizers, as a result of heating from the liquid crystal to isotropic phase. In all cases the mid point of the drop in intensity was taken as an indication of the nematic–isotropic transition temperature.
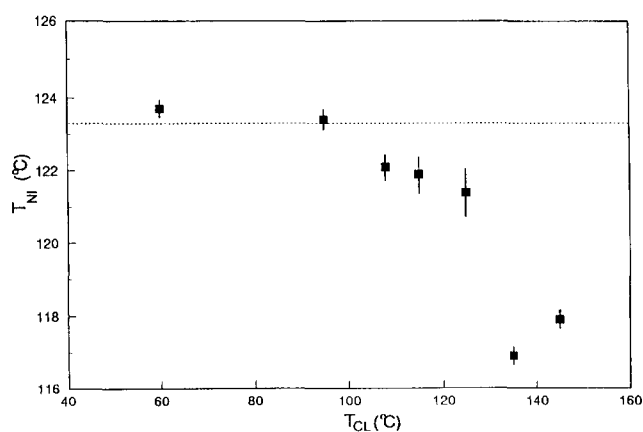
Figure 1 Plot of the observed nematic–isotropic transition temperature for a range of samples crosslinked at different temperatures under identical conditions. The dotted line corresponds to the nematic–isotropic transition temperature of the uncrosslinked copolymer (errors bars represent uncertainty in nematic–isotropic transition temperatures)

Figure 2 Plot showing the effect on the subsequent nematic–isotropic transition temperature of increasing the concentration of crosslinking agent for a series of liquid crystal elastomers prepared (a) in the nematic phase at 108°C (■), (b) in the isotropic phase at 135°C (●). The point marked □ is the transition temperature for the uncrosslinked copolymer containing 20% HEA and with a number-average degree of polymerization of 150 (error bars represent uncertainty in nematic–isotropic transition temperature)

As a second approach to monitor the rate of the crosslinking process, the variation in the transition temperature of partially crosslinked elastomers was monitored as a function of reaction time. For samples crosslinked in both the nematic phase and the isotropic phase, it was found that little variation in the transition temperature was observed over the first 2 to 3 h, but that a significant variation in T_{NI} was observed over the following $\sim$ 20 h. After 48 to 72 h the nematic–isotropic transition temperature reached a constant value. Thus, to a first approximation, the kinetics of the crosslinking reaction appears not to show a significant temperature dependence, at least within the 30°C range considered here. As a consequence, it was possible by allowing sufficient time ($\sim$ 100 h) to prepare samples with similar crosslinking densities although the crosslinking temperatures were varied. Such a conclusion is consistent with the observations made by swelling, i.r. spectroscopy, and from modulus measurements. Thus, it would appear that any conformational ordering or viscosity effects arising from the different phases in which the crosslinking was performed do not significantly affect the crosslinking process if sufficient time is allowed for the reaction to reach completion.

The nematic–isotropic transition temperatures of materials crosslinked at different temperatures, but with similar crosslink densities, are shown in *Figure 1*. It is clear that the phase transition temperatures are highly dependent on the temperature at which the crosslinking occurred. Liquid crystal elastomers prepared at temperatures greater than $\sim$ 125°C, corresponding to crosslinking in the isotropic phase, show a marked decrease in the observed T_{NI} values. Such behaviour might well be expected, since the crosslinking agent incorporated will act simply as a solute in a process similar to the well-known freezing point depression for crystalline solids. This is reflected in the transition temperature variation for series of copolymers containing non-mesogenic units[14–16]. However in addition, as the theory of Warner *et al.* suggests[8], this depression of T_{NI} for the elastomers may also reflect interactions between the mesogenic units and the polymer network. In contrast to the materials crosslinked in the isotropic phase, elasto-
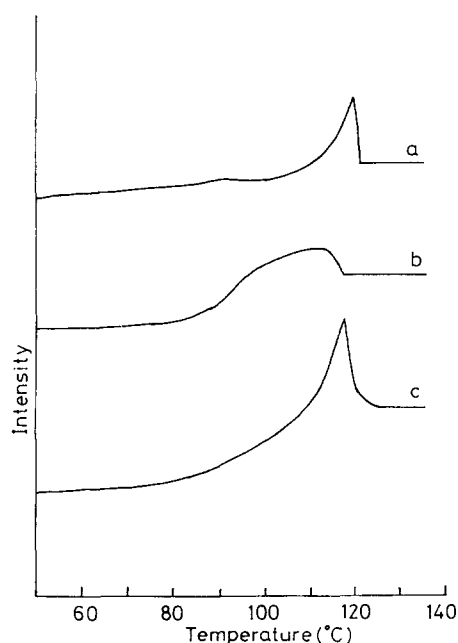
mers prepared in the nematic phase exhibit only a slight decrease in T_{NI} as shown in *Figure 1*. Indeed, for materials crosslinked at the lower temperatures, a slight increase in the phase transition temperature to a value higher than observed for the precursor mixture is recorded. The relative enhancement of the nematic phase for elastomers prepared in the ordered liquid crystal phase is a prediction of the theory developed by Warner *et al.*

The data in *Figure 2* show the phase transitions observed for a liquid crystal polymer crosslinked with differing concentrations of the di-isocyanate. The increasing levels of crosslink density should lead to enhancements of the effects displayed in *Figure 1*. In other words, increasing the level of crosslinking in the isotropic phase should result in an increased depression of the nematic–isotropic phase transition temperature. Similarly, the materials crosslinked in the nematic phase should show increasing stability of the liquid phase with increasing crosslink density. However, if the observations described in *Figure 1* were simply a manifestation of poor chemical kinetics, resulting in ineffective crosslinking, then with higher di-isocyanate concentrations the sample crosslinked in the nematic phase should show reductions in T_{NI} comparable with those observed for samples lightly crosslinked in the isotropic phase. From *Figure 2* this is clearly not the case: all the samples crosslinked in the nematic phase showed a higher nematic–isotropic transition temperature than those crosslinked in the isotropic phase. It must be concluded, therefore, that the data of *Figures 1* and *2* illustrate that the crosslinking history of the sample has a significant effect on its nematic–isotropic transition temperature. The greater depression at low crosslinking levels in the isotropic phase may be attributed to the high probability of intramolecular crosslinking due to the high proportion (20 mol%) of potential reaction sites. This is less significant for samples crosslinked in the nematic phase due to the more ordered arrangement of the polymer chains. Despite this probable

inhomogeneity, the basic conclusion from *Figure 2* remains.

Figure 1 shows a marked variation in the transition temperatures of elastomers prepared at different temperatures. It is of particular significance to determine whether the step in the transition temperature occurs for a crosslinking temperature equivalent to the T_{NI} of the uncrosslinked precursor mixture. To be completely sure, all of these crosslinking preparations were performed in the optical microscope to facilitate constant monitoring of the sample's phase. It was found that a sample crosslinked at 125°C (i.e. just above the phase transition temperature) exhibited a significant increase in T_{NI} over those crosslinked at 5–10°C above the clearing point. This seems to indicate that the influence of the nematic phase extends, at least in part, to the isotropic phase, and as such is consistent with other observations on the behaviour of side-chain liquid crystal elastomers[17]. In other words, the transition from destabilization to stabilization of the nematic phase occurs when crosslinking is performed at a temperature just above the T_{NI} of the initial polymer. Such pretransitional effects are not dissimilar to those found in low-molecular-mass liquid crystals[18].

It is clear that the nematic–isotropic phase transition for each of the elastomers studied was reversible. However, perhaps not surprisingly there were significant time-dependent effects which serve to reinforce the observations of the phase behaviour described above. Samples of liquid crystal elastomers that had been crosslinked in the nematic phase only showed constant values for the transition temperature if sufficient time for equilibration in the nematic phase was allowed. This may be seen most clearly by examining (*Figure 3*) a sample held for a prolonged period in the isotropic

phase (i.e. for periods greater than $\sim 20\,\mathrm{min}$). Subsequent cooling and reheating to determine the phase transition revealed a significant decrease in the apparent transition temperature. In fact, the nematic–isotropic transition temperature had been reduced to a value more typical of material crosslinked in the isotropic phase. However, on holding in the nematic phase the measured value for the nematic–isotropic transition increased slowly, gradually returning to its original value as shown in *Figure 3*. In contrast, for materials crosslinked in the isotropic phase, holding in the nematic phase had little effect on the transition temperature or the appearance of the thermo-optic curves.

DISCUSSION

Phase transition temperatures

From the results detailed above, it is clear that the phase behaviour of a liquid crystal elastomer shows a marked dependence upon the history of preparation of the sample. There are two phenomena, namely a kinetic effect and an equilibrium or thermodynamic effect. We shall discuss the kinetic phenomenon later, for it is the latter contribution to the observed behaviour that is the main concern of this account. These measurements were initiated as a direct result of the proposals of Warner et al.[8,19]. Such theoretical studies are particularly concerned with the effect of nematic ordering in side-chain liquid crystal polymers on the conformational arrangement of the polymer backbone. It is apparent that, if there is some coupling between the polymer backbone and the mesogenic side groups, there are two essentially competing effects: the nematic ordering is in direct conflict with the entropy-driven desire for the polymer to take up random conformations. As a consequence, ordering in the nematic phase, albeit on a local rather than a global scale, results in the imposition of some ordering within the backbone conformations. Such effects have been observed by small-angle neutron scattering[20,21] and in particular in the polymer which is the subject of this study[22].

The theory described by Warner et al.[8,19] suggests how this coupling might affect the phase behaviour of liquid crystal elastomers. In particular, crosslinking introduces network points that are chemically immobile. Thus, although there is some flexibility in the chain between network points, the introduction of such fixed points imposes additional stability on those conformations present at the time of crosslinking. Since the nematic phase (assuming some degree of coupling) imposes a degree of orientation on the polymer backbone, the result of crosslinking in the nematic phase is to stabilize this phase and therefore increase the nematic–isotropic transition temperature. In the isotropic phase, the effect of crosslinking is to stabilize the random polymer conformations typical of the isotropic phase. Thus, to achieve the conformational arrangements required for nematic ordering, the elastomer must be distorted, and the elastic energy of the modulus must be overcome. The nematic phase is thus reduced in stability. It might be expected that the imposition of network points in the isotropic phase would inhibit liquid crystalline ordering.

Figure 3 Thermo-optic curves showing the effect of sample treatment on the phase behaviour: (a) behaviour of a polymer crosslinked at 108°C, heated directly from the nematic phase; (b) the behaviour observed from the same sample following prolonged heating ($\sim 12\,\mathrm{h}$) in the isotropic phase; (c) the same sample after annealing in the nematic phase for several days
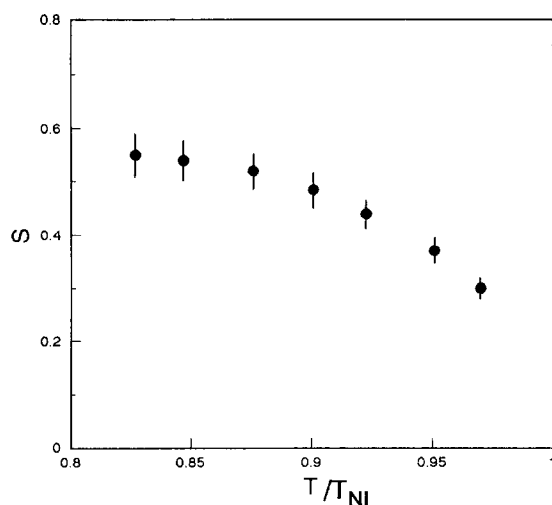
Figure 4 A plot of the order parameter for the liquid crystal copolymer used as base materials for the elastomers described here (i.e. the sample containing 6% HEA), as a function of temperature relative to the nematic–isotropic transiton temperature

Figure 5 Plot of the reciprocal of the experimental nematic–isotropic transition temperature *versus* the square of the order parameter (error bars represent uncertainty arising from the nematic–isotropic transition temperature given in *Figure 1*). The dotted line represents a linear fit to the data in accord with the theories of Warner *et al.* from ref. 8

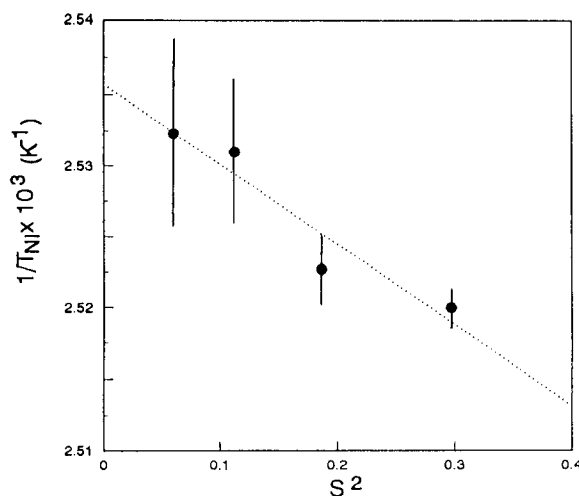However, at sufficiently low levels of crosslinking this evidently is not the case.

The phase behaviour exhibited by the series of liquid crystal elastomer samples in this contribution can be seen to fit well with the broad thrust of such theoretical models of ordering in comb-like liquid crystal polymers[19]. However, it is also of interest to consider a more quantitative assessment of the experimental data. According to Warner *et al.*, the nematic–isotropic transition temperature (T_{NI}) is given by[8]:

$$T_{NI} = T_0 + N_x k_B \frac{D}{A} T(S_x^2 - \tfrac{1}{2} S_0^2) \qquad (1)$$

where T_0 is the nematic–isotropic transition temperature for the uncrosslinked sample, S_x is the order parameter at crosslinking of the crosslinked liquid crystal polymer, S_0 is the order parameter at transition of the uncrosslinked liquid crystal polymer, and N_x is related to the number density of strands N_s and the crosslink functionality ϕ by:

$$N_x = N_s \left(1 - \frac{2}{\phi}\right) \qquad (2)$$

We have reported elsewhere the order parameter for this side-chain liquid crystal polymer as a function of temperature by utilizing X-ray scattering and infra-red dichroism methods[15,23]. *Figure 4* shows the recorded order parameter S as a function of the temperature for the uncrosslinked copolymer. However, these data relate to the order of the mesogenic side groups, rather than the polymer backbone. Small-angle neutron scattering studies show that the backbone orientation is $\sim 10\%$ of the side-chain units[22]. Mean field model calculations show that over the restricted temperature range in this study, there is a reasonably constant proportionality between the order parameters of the two components[24,25]. Thus, using the order parameter of the side groups as a measure of the backbone ordering, it is possible to determine the fit of our experimental data to the theoretical expectation and thereby estimate the values for the coefficients in equation (1). The approach we have chosen is a graphical one. Reorganisation of

equation (1) gives:

$$\frac{1}{T_{NI}} = \frac{1}{T_0} \left[1 - N_s k_B \frac{D}{A} \left(S_x^2 - \frac{1}{2} S_0^2\right)\right] \qquad (3)$$

A plot of $1/T_{NI}$ *versus* the square of the order parameter is shown in *Figure 5*. Within the confines of experimental accuracy, the data are consistent with the form suggested by Warner's theory. Equation (1) suggests that T_{NI} will increase with the crosslink density. *Figure 2* shows such trends, as does a series of photochemically crosslinked liquid crystal polymers[26]. All these data support the concept that crosslinking in either the nematic or the isotropic phase places constraints on the system that are related to the level of orientational ordering at the time of crosslinking and on the density of those constraints. That is the qualitative prediction of Warner *et al.*[8].

In order to understand what equation (1) represents, it is perhaps instructive to consider a simplified form of the free energy change at the clearing point. At transition the free energy change for the uncrosslinked material is given by:

$$\Delta G = 0 = \Delta H - T_0 \Delta S \qquad (4)$$

For the crosslinked case there is an additional term to be considered, namely the energy required to distort the network ΔF. This term represents the energy required to transform the network configuration in the nematic phase to that of the isotropic phase. If the system was crosslinked in the nematic phase then this is a positive contribution, whereas for an elastomer prepared in the isotropic phase this transition will be favourable and hence of opposite sense. In essence the force could be a macroscopic strain, but in this particular study it represents an internal strain generated by the nematic ordering. Introduction of this term gives:

$$\Delta G = 0 = \Delta H + \Delta F - T_{NI} \Delta S \qquad (5)$$

ΔF is a function of the modulus of the network multiplied by the extension or contraction in the x, y and z directions from an isotropic random coil imposed

by the formation of the nematic phase. Combining equations (4) and (5) and assuming the enthalpy change is unaffected by the crosslinking gives:

$$T_{NI} = T_0 + \frac{\Delta F}{\Delta S} \qquad (6)$$

Thus, as inspection of equation (6) shows, the variation of the nematic–isotropic transition temperature with crosslinking is directly related to the three-dimensional distortion of the network required at the phase transition. Such a distortion only results from the coupling between the polymer chain configuration and the nematic ordering. Hence any variations in the nematic–isotropic transition temperature are a direct measure of that coupling. Such coupling may arise through the nematic mean field imposed on the polymer chain by the mesogenic side groups. This effect has been shown to be smaller than that arising from the geometric conse-quences of the stereochemistry of the coupling chain[27,28]. Clearly materials with more direct coupling through a shorter or stiffer coupling chain, and those with highly anisotropic chain configurations in the liquid crystal phase, will exhibit more marked variation in T_{NI} upon crosslinking than displayed in this study, and this possibility is currently being investigated.

Reversibility of the phase transition

It was noted earlier that for samples crosslinked in the nematic phase, prolonged holding in the isotropic phase reduced the nematic–isotropic phase transition tempera-ture if it was remeasured directly. It is clear from this firstly that considerable care must be taken to ensure that any phase transition data are obtained from samples held in equilibrium. Secondly, the effect highlights the slow relaxation of the polymer network and in doing so demonstrates again the role of the chain configuration in determining the nematic–isotropic phase transition. It would seem reasonable to accept that, on heating to the isotropic phase for short periods, the polymer network is not fully relaxed on a large scale. However, on prolonged holding in the isotropic phase complete randomization occurs, and when the polymer is cooled to the nematic phase the low mobility of the polymer backbone prevents the immediate re-formation of the more stable con-formations that were present at crosslinking. Clearly, if an attempt is made to measure the nematic–isotropic phase transition immediately, the apparent T_{NI} will be depressed from a true equilibrium value. If sufficient time is given to reach equilibrium, then the original T_{NI} is obtained. This implies that if very slow heating rates were used, some enhancement of nematic–isotropic transition temperatures would be observed. However, from these and other experiments, it is anticipated that unreason-ably slow rates would be required for any significant variations. The reverse case, namely the greater stabili-zation of materials crosslinked in the isotropic phase by holding in the nematic phase, does not occur to the same extent, presumably because the network elasticity restricts the polymer in the nematic phase. It is interesting to note that a similar effect has been observed for elastomers prepared by copolymerization with a difunctional monomer[4,29]. A typical example is shown in *Figure 6*. Extension of the above argument to these samples would suggest that in the highly concentrated solutions present during their formation, a nematic
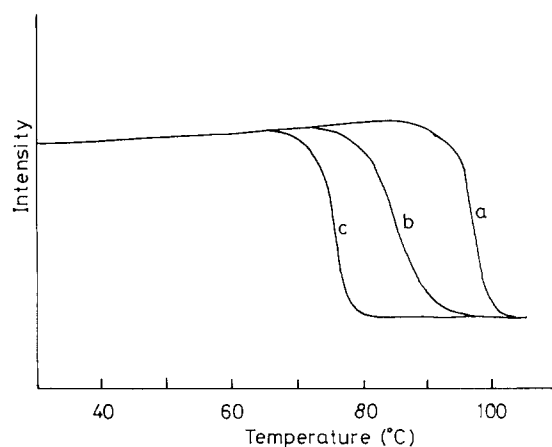
Figure 6 Influence of the thermal history on the nematic–isotropic transition temperature for a liquid crystal elastomer sample prepared by copolymerization of a mesogenic monomer with a difunctional comonomer. Curve (a) shows the phase transition for the as-prepared elastomer, (b) shows the cooling curve obtained for the sample after leaving for ~ 15 min in the isotropic phase. Curve (c) shows a similar trace for a sample left for 1 h in the isotropic phase. On prolonged heating of sample (c) in the nematic phase, the curve (a) was regained

phase might be present. Such consequences of the slow large relaxation of the polymer chain have been observed for both side-chain liquid crystal polymers in connection with electro-optic measurements[16] and in main-chain liquid crystal polymers[30].

CONCLUSIONS

The phase behaviour of liquid crystal elastomers has been found to show a marked dependence on their thermal history. In particular, there is a significant stabilization of the nematic phase through an increase in the nematic–isotropic phase transition temperatures for samples which had been crosslinked in the nematic phase. In a similar way, crosslinking in the isotropic phase appears to enhance the isotropic phase over the nematic phase. These variations in nematic–isotropic transition temperature are a direct result of the coupling between the orientational ordering of the mesogenic side chains and the polymer chain trajectory. The results obtained are compatible with the theoretical predictions of Warner *et al.*[8].

ACKNOWLEDGEMENTS

REFERENCES

1   Plate, N. A., Friedzon, Ya. S. and Shibaev, V. P. *Pure Appl. Chem.* 1985, **57**, 1715
2   Finkelmann, H. in 'Polymer Liquid Crystals' (Eds A. Ciferri, W. R. Krigbaum and R. B. Meyer), Academic Press, New York, 1982
3   Zentel, R. *Angew. Chem. Int. Ed. Engl. Adv. Mater.* 1990, **28**, 1407
4   Davis, F. J., Gilbert, A., Mann, J. and Mitchell, G. R. *J. Polym. Sci., A* 1990, **28**, 1455

5   Hammerschmidt, K. and Finkelmann, H. *Makromol. Chem.* 1989, **190**, 1089
6   Mitchell, G. R., Davis, F. J. and Ashman, A. S. *Polymer* 1987, **28**, 639
7   Zentel, R. and Reckert, G. *Makromol. Chem.* 1987, **187**, 1915
8   Warner, M., Gelling, K. P. and Vilgis, T. A. *J. Chem. Phys.* 1988, **88**, 4008
9   De Gennes, P. G. *Compt. Rend. Acad. Sci. (Paris)* 1975, **B281**, 101
10   Brand, H. *Makromol. Chem., Rapid Commun.* 1989, **10**, 57
11   Strzelecki, L. and Liebert, L. *Bull. Soc. Chim. Fr.* 1973, **597**, 605
12   Liebert, L. and Strzelecki, L. *Compt. Rend. Acad. Sci. (Paris)* 1973, **C276**, 647
13   Broer, D. J., Mol, G. N. and Challa, G. *Makromol. Chem.* 1991, **192**, 59
14   Hirai, A., Davis, F. J. and Mitchell, G. R. *New Polym. Mater.* 1990, **1**, 251
15   Al Ammar, K. PhD Thesis, University of Reading, 1991
16   Whale, E. A., Davis, F. J. and Mitchell, G. R. *J. Mater. Chem.* submitted
17   Schatzle, J., Kaufold, W. and Finkelmann, H. *Makromol. Chem.* 1989, **190**, 3269
18   Vertogen, G. and de Jeu, W. 'Thermotropic Liquid Crystals: Fundamentals', Springer, Berlin, 1988
19   Warner, M. in 'Side-Chain Liquid Crystal Polymers' (Ed. C. B. McArdle), Blackie, New York, 1989
20   Kirste, R. G. and Ohm, H. G. *Makromol. Chem., Rapid Commun.* 1985, **6**, 179
21   Keller, P., Carvalho, B., Cooton, J. P., Lambert, M., Moussa, F. and Pepy, G. *J. Phys. Paris Lett.* 1985, **46**, 1065
22   Mitchell, G. R., Davis, F. J., Guo, W. and Cywinski, R. *Polymer* 1991, **32**, 1347
23   Legge, C. H., Davis, F. J. and Mitchell, G. R. *J. Phys. II (France)* 1991, **1**, 1253
24   Guo, W., Davis, F. J. and Mitchell, G. R. *Polymer* 1994, **35**, 2952
25   Guo, W., Davis, F. J. and Mitchell, G. R. *Polymer* 1994, **35**, 2952
26   Legge, C. H. PhD Thesis, University of Reading, 1992
27   Guo, W., Davis, F. J. and Mitchell, G. R. *Polym. Commun.* 1991, **32**, 268
28   Mitchell, G. R., Coulter, M., Davis, F. J. and Guo, W. *J. Phys. II (France)* 1992, **2**, 1121
29   Davis, F. J., Gilbert, A., Mann, J. and Mitchell, G. R. *J. Chem. Soc., Chem. Commun.* 1986, 1333
30   Ungar, G., Keller, A. and Percec, V. in 'Liquid Crystalline Polymers' (Eds R. A. Weiss and C. K. Ober), ACS Symposium Series 435, American Chemical Society, Washington, DC, p. 308, 1990