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Molecular Switching in Liquid Crystal Elastomers†

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The synthesis is described of some liquid crystal polymers containing various degrees of cross linking units. Such materials show properties over and above those observed either from low molecular weight liquid crystals, or from conventional rubbers. Thus, though these compounds show simple rubber like elasticity in the isotropic phase, on cooling to the liquid crystal region, more complex behavior is observed, an example being the high levels of orientation produced at relatively low strain. Such materials also show unusual properties in that, when swollen with a low molecular weight liquid crystal, they undergo macroscopic shape changes in the presence of applied electric fields, in addition to the more usual electro-optic effects.

INTRODUCTION

A wide variety of polymeric liquid crystal systems has now been produced.[1] For those uncross-linked materials in which the mesogenic units are linked by semi-flexible spacer chains, the liquid crystal properties approach those displayed by low molar mass compounds. In contrast, liquid crystal elastomers offer the possibility of unique phenomena through the combination of a macromolecular network with mesogenic moieties.[2,3,4,5] The addition of a three dimensional network to a liquid crystal system may result in particular and specific interactions of the mesogenic units with that network, a possibility not available in low molar mass liquid crystals.

This contribution is concerned with liquid crystal elastomers, formed from side chain liquid crystal polymers, and their properties. In particular, the role of the various components within the molecular composites is evaluated through changing chemical configurations:—the length of the coupling chain in the side chain unit, the level of cross linking, and the type of cross-linking. This account describes two of the properties observed from these materials, namely, the effect of an applied stress on these compounds, and in particular on the orientation of the mesogenic

†Presented at the International Conference on Liquid Crystal Polymers, Bordeaux, France, July 1987.

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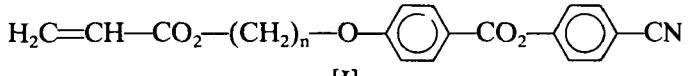
groups relative to the polymer backbone, and the behavior of such elastomers in the presence of an applied electric field.

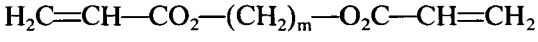
MATERIALS

Cross-linked liquid crystal elastomers were prepared by copolymerization of the mesogenic monomer [I] (where n = 2 or 6) with the diacrylate [II] (where m = 2 or 10).[6,7] Polymerization was undertaken at 55°C in chlorobenzene as solvent using 1% AIBN as an initiator. The elastomers were collected, washed several times to extract any unreacted momomers, and dried in vacuum at 50°C for 48 hours.

N.m.r. studies, infrared spectroscopy, and elemental analysis confirmed that the proportion each of monomer [I] and [II] in the final product was as expected on the basis of their relative concentrations in the initial feedstock. In addition, the rate of uptake of each monomer was found to remain unchanged as the polymerization progressed, indicating that it occurs randomly. However, the diacrylate concentration does not give a direct measure of the number of active cross-link points, since branching, loose ends and intrachain loops readily form.



[I]



[II]

Figure 1 shows the phase transition temperatures observed (using Differential Scanning Calorimetry and a heating rate of 10°C/min) for a range of samples cross-

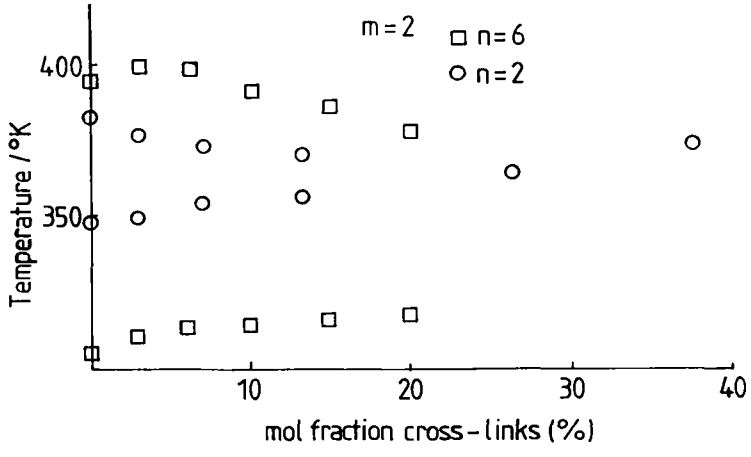


FIGURE 1. Observed nematic–isotropic and glass transition data (using Differential Scanning Calorimetry and a heating rate of 10°C/min) for side chain liquid crystal polymers containing a range of diacrylate concentrations.

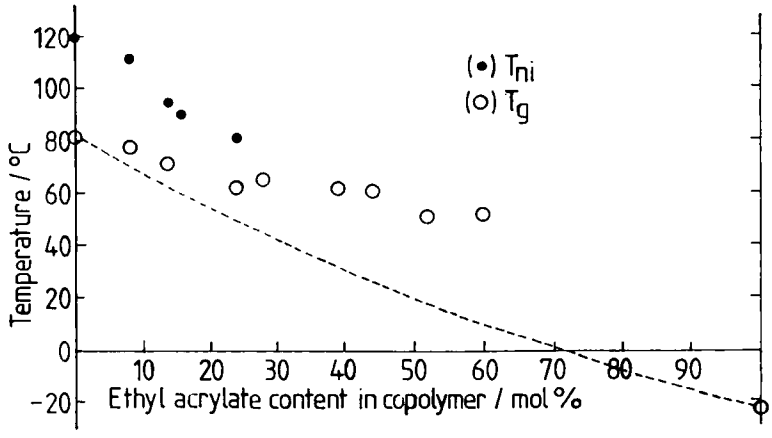


FIGURE 2. Observed nematic–isotropic and glass transition data (using Differential Scanning Calorimetry and a heating rate of 10°C/min) for a side chain liquid crystal copolymer of $n = 2$ mesogenic monomer with varying mol% of ethyl acrylate monomer. The dotted line represents the expected variation of Tg for an ideal random copolymer.

linked with ethylene glycol diacrylate. All samples show two transitions; at low temperatures there is a glass transition, and at higher temperatures a further change, which (from additional data utilizing X-Ray Diffraction and Optical Microscopy) corresponds to a reversible nematic–isotropic phase transition. Of particular interest are, firstly, the wider range of the liquid crystal region for the $n = 6$ compared to the $n = 2$ type polymer, which is consistent with expectations.[8] Secondly, the nematic–isotropic phase transition is depressed as the (nominal) cross-link density increases. As inspection of Figure 2 shows, a similar depression is observed when monoacrylate (in this case ethyl acrylate) units are introduced into the polymer chain. Finally, and probably most significantly, increasing the proportion of diacrylate in the polymer raises the glass transition temperature (Tg), while for the monoacrylate, Tg is decreased. Both these trends can be readily explained in terms of the effects that the introduction of the respective groups have on the polymer backbone; the diacrylate forms cross-links which restrict the mobility of the polymer chain, whilst addition of the monoacrylate improves mobility through increasing the flexibility of the macromolecular backbone. However, it should be noted that the increase in Tg with cross-linking is rather lower than might have been expected, with, for example, the observation of a liquid crystal phase for samples containing up to 20% diacrylate units. Thus it is clear that the concentration of the latter cannot be directly converted into active cross-links, as already mentioned.

Most of the samples studied here showed the properties which would be expected from an elastomer in the isotropic phase; that is, they are readily distorted by an applied stress and, on release of the force, return to their original shape. The initial modulus of an elastomer may be related to the molecular weight between cross-link points.[9]† These modulus values, equivalent to a Youngs Modulus, were meas-

†For example $G = RT\rho/M_s$; where M_s is the number average molecular weight of the chain section between cross-link points. ρ is the bulk density, T the temperature and R the gas constant.

TABLE I

Observed Isotropic Moduli for some Liquid Crystal Elastomers (T = 120°C)

n	m	% cross link	Observed moduli (Nm^{-2})	Calculated moduli (Nm^{-2})
2	2	6.9	8.4×10^4	6.7×10^5
2	2	10.0	1.8×10^5	9.7×10^5
2	2	13.7	3.9×10^5	1.3×10^6
2	2	26.4	7.4×10^5	2.4×10^6
6	2	10.0	[a]	9.7×10^6
6	2	15.0	1.2×10^4	1.5×10^6
6	2	20.0	5.0×10^4	1.9×10^6
6	10	10.0	1.3×10^4	9.7×10^5

[a]No elastomeric properties observed in the isotropic melt.

ured from the intitial slopes of stress-strain curves obtained using a miniature tensometer operating under constant strain conditions with a strain rate of $10^{-2}s^{-1}$. The experimentally determined values, together with those calculated for the appropriate level of cross-linking, assuming all diacrylate units are involved in active cross-links, are listed in Table I. As inspection shows, the values are all lower than might be expected, suggesting either that the diacrylate reacts to form loops with the same polymer chain, or that it reacts only partly to leave unreacted alkenic groups as side chains. For materials with longer mesogen-backbone coupling chains it is this latter explanation which appears the more likely. A substantially higher modulus was observed for the $n = 6$ elastomer with the $m = 10$ cross-link unit, compared to that with the $m = 2$ cross-link unit. It would appear that there is steric inhibition of reaction at the second acrylate site by the bulky mesogenic groups. The longer coupling chain in the $m = 10$ cross-linking unit relieves this steric inhibition and a higher number of active cross-link units results.

MECHANICALLY INDUCED MOLECULAR SWITCHING

The effect of an applied stress on these elastomers in the liquid crystal phase was markedly different to the observed behavior in the isotropic phase (Figures 3, 4 and 5). On initial extension, relatively large stress levels were built up and the initial modulus appeared to increase as the temperature decreased (Figure 3). As Figure 4 shows, this behavior is in contrast to the behavior in the isotropic phase. Above the nematic–isotropic transition, the modulus increases in the expected manner as a result of the entropically driven elasticity. However, below this transition, the apparent modulus increases rapidly as the temperature is reduced. On further extension (> *ca.* 10%), the increase in stress with strain is somewhat smaller. On subsequent holding of the sample at constant strain, the stress level decreased rather rapidly. As can be seen from Figure 5, this speed of stress relaxation showed a strong temperature dependence, which it is reasonable to associate with the variation in viscosity.

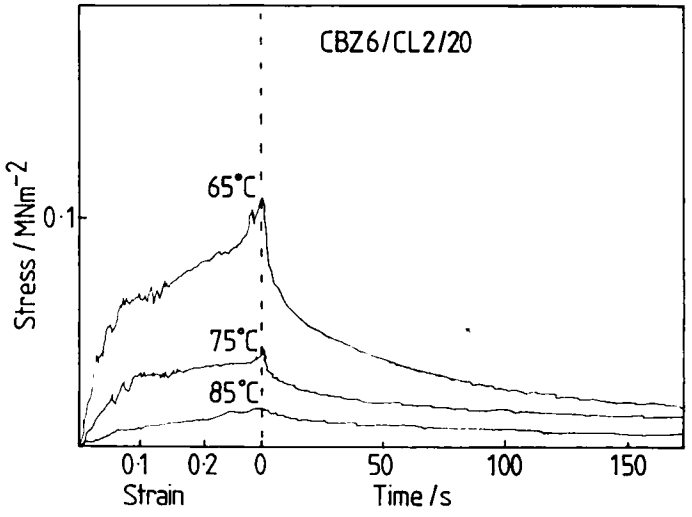


FIGURE 3. Observed stress/strain behavior for a liquid crystal elastomer (in this case $n = 6$, $m = 2$, 20 mol% diacrylate concentration). The sample was held at an extension of 1.3 and the stress monitored as a function of time.

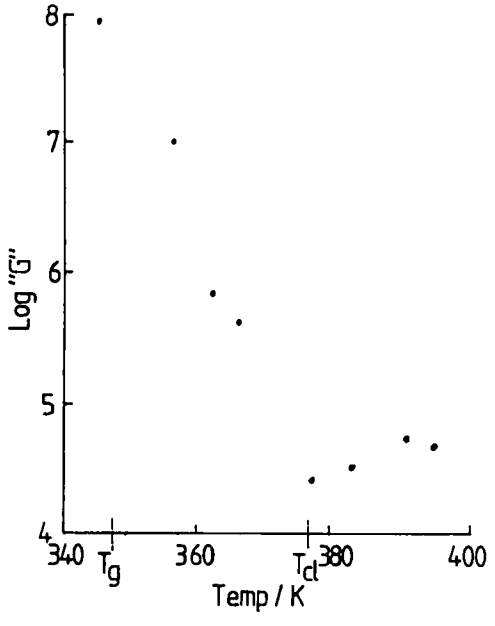


FIGURE 4. The logarithm of the initial modulus of a liquid crystal elastomer (in this case $n = 2$, $m = 2$, 2.8 mol% diacrylate concentration) as a function of temperature. The modulus was obtained from the slope of the stress-strain curve (for example, Figure 3) for strains < 0.1.

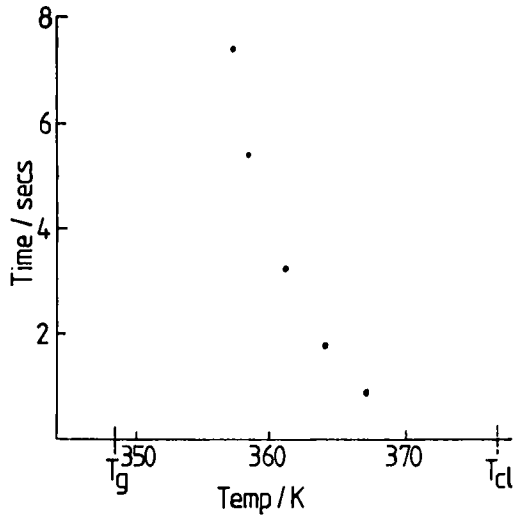


FIGURE 5. Temperature dependence for the time taken to reach 50% of the total decay in stress in a liquid crystal elastomer (in this case $n = 2$, $m = 2$, 2.8 mol% diacrylate concentration) after an initial strain of 0.3 (see Figure 3). The sample was extended by a strain of 0.3 and immediately held constant at that strain while the decay in stress was monitored as a function of time.

It is clear from the above observations that the presence of the liquid crystal phase strongly influences the behavior of these elastomers. By analogy, with magnetic and electric fields, it might be expected that introduction of stress fields might result in preferential alignment of the liquid crystal directors. The direction of this orientation should depend to a large extent on the way the liquid crystal elastomer interacts with the stress field and the polymer chain. For example, with weak coupling between the mesogenic units and their polymer backbones, such orientation could result in the mesogenic groups lying parallel to the draw direction; however, with considerably stronger coupling such orientation may not be possible, and extension of the polymer could result in the side chain aligning at right angles to the stress field in a 'bottle brush' type structure.

Preliminary experiments were undertaken with a miniature tensile tester, mounted in an optical microscope between crossed polars and additional wave plates, in which the birefringence was monitored as the samples were stretched. In the isotropic phase a gradual change in the level of birefringence was noted, with a preferential alignment parallel to the direction of the applied stress. In the liquid crystal phase however, while once again alignment appeared to occur parallel to the stress direction, relatively low extensions ($< 5\%$) produced changes of many orders in the birefringence (although sample thickness was kept to a minimum). Clearly, much higher levels of preferential orientation are produced in the liquid crystal phase, and the orientation lies parallel to the stress direction. Unfortunately, such large changes proved difficult to quantify using optical techniques; consequently the alternative technique of x-ray scattering was utilized.

Wide-angle x-ray scattering measurements were undertaken *ex situ* on samples stretched under the appropriate conditions and then cooled rapidly with a cold air

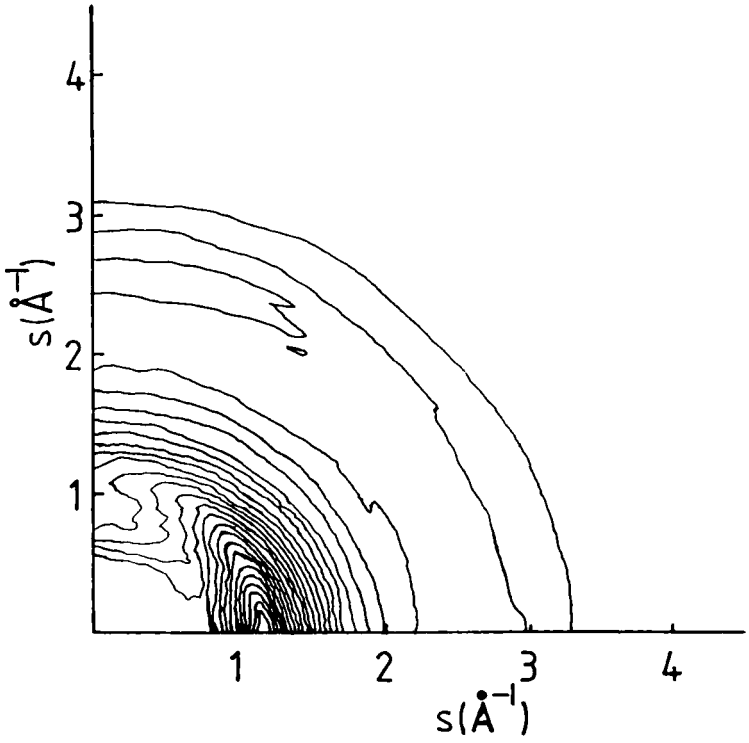


FIGURE 6. X-Ray scattering pattern obtained from an elastomer (n = 6, m = 2, 20 mol% diacrylate concentration) stretched to an extension of 1.2 in the liquid crystal phase (60°C).

jet into the glassy state. Figure 6 shows a typical scattering pattern obtained for an elastomer (in this case a cross-linked n = 6 type polymer, though similar data were obtained for the n = 2 systems). The important feature is the equatorial arcing at $s \sim 1.3 Å^{-1}$(†) showing considerable alignment of the mesogenic groups parallel with the stress direction. Both the n = 2 and the n = 6 type polymers showed no evidence of alignment perpendicular to the draw direction even for a sample stretched *ca.* 1000%, where considerable straightening of the polymer chain might be expected. A quantitative measure of the orientation was obtained from the parameter $\langle P_2 \rangle$,‡[6] and Figures 7 and 8 show examples of the variation measured as a function of extension ratio and temperature respectively. Of particular interest is the observation that the orientation reaches its maximum value at relatively low extensions typically <0.5. A similar behavior is observed for both the n = 2 and n = 6 type polymers. These orientation *versus* strain curves were obtained for samples of both the n = 2 and n = 6 type elastomers held at the same temperature, namely 80°C. Under these circumstances the samples of the n = 6 elastomers were further removed from the glass transition. As may be seen from Figure 4, the initial modulus, and hence initial stress levels reached are strongly temperature depend-

†$s = (4\pi/\lambda)\mathrm{Sin}\theta$, where 2θ is the scattering angle and λ the wavelength of X-radiation employed.

‡Where $\langle P_2 \rangle = (3\cos^2\alpha - 1)/2$, α being the angle between the molecular axis and the extension direction.

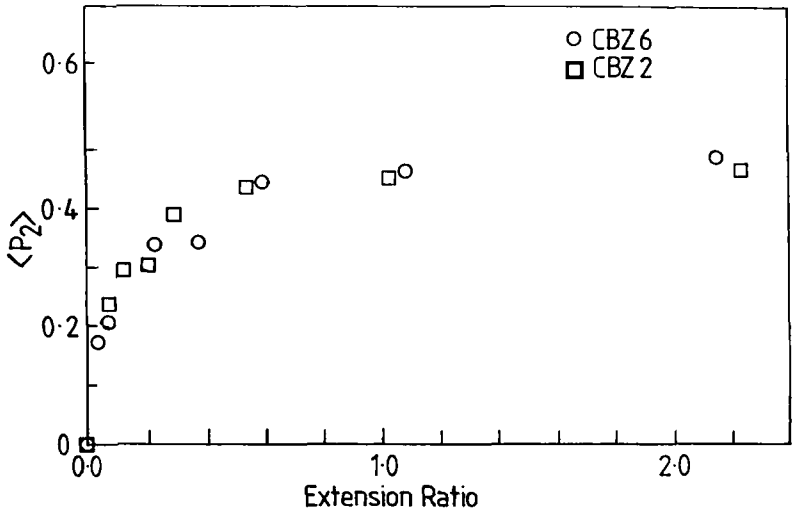


FIGURE 7. Orientation parameters of two elastomers of comparable moduli (n = 2, m = 2, 2.8 mol% diacrylate concentration and n = 6, m = 2, 20 mol% diacrylate concentration) as a function of extension ratio. The samples were deformed at 80°C, and held at the indicated extension ratio until steady state conditions were obtained.

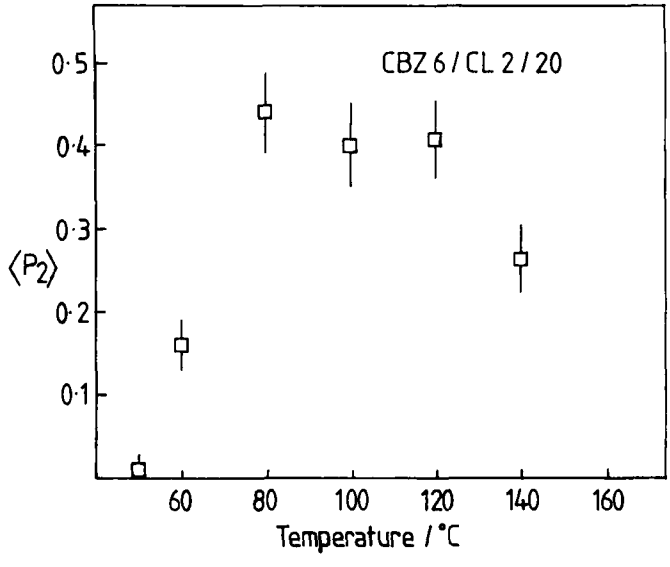


FIGURE 8. Variation of orientation parameter as a function of temperature for a sample (n = 6, m = 2, 20 mol% diacrylate concentration) extended 50%. The samples extended at 55°C and 60°C did not reach steady state conditions due to the high viscosity of the sample (see text).

ent. Consequently, the $n = 6$ type materials were exposed to much lower initial stress fields than were the $n = 2$ type. The similarity of the orientation levels reached for two types of material for the same strain values indicates that it is the strain on the network rather than the stress levels which dictate the behavior. For samples of the $n = 6$ type elastomer stretched 50% at different temperatures (Figure 8), significant degrees of orientation were observed over a wide temperature range, independent of the stress levels reached during the stretching of the sample, though here additional complications arising from cooling and slow alignment of the sample must also be taken into account, and will be discussed elsewhere.[10] Samples stretched in the liquid crystal phase at temperatures $< 80°C$ show low levels of orientation, which may be related to the high viscosity of the medium and hence slow rate of alignment of the liquid crystal directors. Samples stretched in the isotropic phase and rapidly cooled to room temperature also show low levels of orientation. However, if these samples are slowly cooled into the liquid crystal phase while a mechanical stress is applied, they develop a level of orientation similar to that seen for samples stretched initially in the liquid crystal phase.

From the above observations, it would appear that the behavior of these liquid crystal elastomers reflects both kinetic and thermodynamic considerations. Extending the samples, in all cases, resulted in alignment of the mesogenic units parallel to the draw direction; of itself, this suggests that the side chains prefer to lie parallel to the chain rather than perpendicular. This result might not have been expected on the basis of certain neutron scattering experiments.[10,11] These neutron scattering experiments were performed on materials with uncrosslinked methacrylate backbones and with similar side-chains (though without the cyano-group) aligned in a magnetic field. They indicated that the side-chains prefer to lie perpendicular to the backbones. Should this normally be the case for the materials studied here, it would appear that the stress field induces a parallel alignment of the liquid crystal directors, in competition with the effects of the polymer network. This alignment is energetically favored, but may only occur with some reorganization of the polymer backbone. It may be this latter effect which is responsible for the high initial stress levels, particularly for the $n = 2$ elastomers.

ELECTRICALLY INDUCED MOLECULAR SWITCHING

A cross-linked liquid crystal polymer (with $n = 6$ and 10% $m = 10$ diacrylate) was microtomed to 8 μm and heated in an electro-optic cell to 130°C with a low molecular weight liquid crystal (in this case the B.D.H. cyanobiphenyl M18 was used). Both low molecular weight and polymeric species were in the isotropic phase. The cell consisted of two plates of conducting glass with an ~25 μm spacing to ensure space for swelling. Under these conditions, the elastomer swelled to *ca.* twice its original area, as viewed down a polarizing microscope. On applying a suitable electric field to the cell, it was found that a marked reduction in the cross-sectional area of the elastomer sample occurred. No information is yet available on the third dimension (*i.e.*, parallel to the viewing direction). This contraction

effect was reversible and temperature dependent. Under optimum conditions, contractions as large as 20% were observed (Figure 9) and switching speeds less than a second generally obtained. These observations confirm the initial findings of Zentel.[4]

From Figure 10 it can be seen that the measured threshold voltage for this contraction effect decreases with increasing temperature. This threshold voltage must be dependent on the elasticity of the sample. From entropy considerations, the elastic modulus of a classical polymer network increases with increasing temperature. The curvature elastic constant of a liquid crystalline phase, on the other hand, decreases with increasing temperature. It would therefore be reasonable to suggest that, in this shape change, the liquid crystalline curvature elasticity dominates over that from the polymer network. This is not necessarily surprising, since swelling an elastomer has the effect of reducing its network elastic modulus. In addition, the increased proportion of mesogenic components in the system may make for a more strongly correlated mesophase and so increase the relevant component of the curvature elasticity tensor.

A possible explanation of the shape change may be the realignment of anisotropic polymer envelope. Prior to the application of an electric field, the mesogenic side chains will have local areas of anisotropic alignment. The polymer backbone, preferring to lie perpendicular or parallel to these groups should show similar localized anisotropy, as seen in the neutron scattering experiments[10,11] mentioned earlier, though in the bulk, the net effect is to produce an averaged "isotropic" polymer

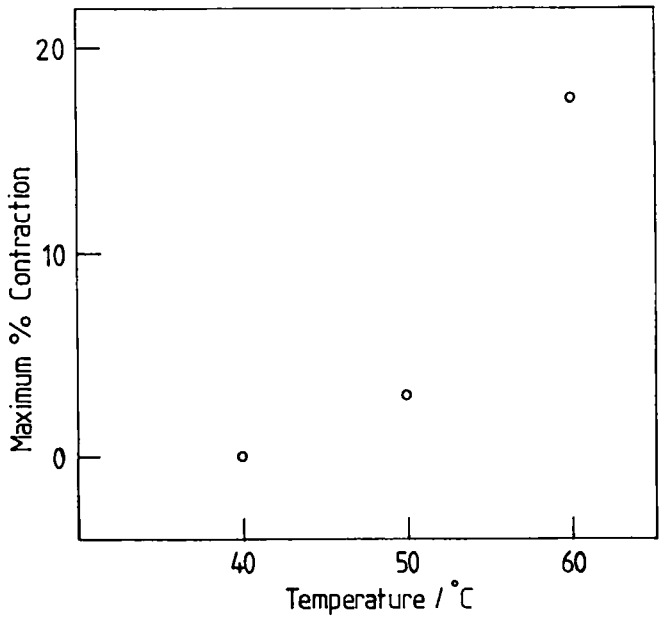


FIGURE 9. Maximum possible % linear contraction of a swollen liquid crystal elastomer (n = 6, m = 10, 10 mol% diacrylate concentration in B.D.H. cyanobiphenyl M18) in an electric field as a function of temperature.

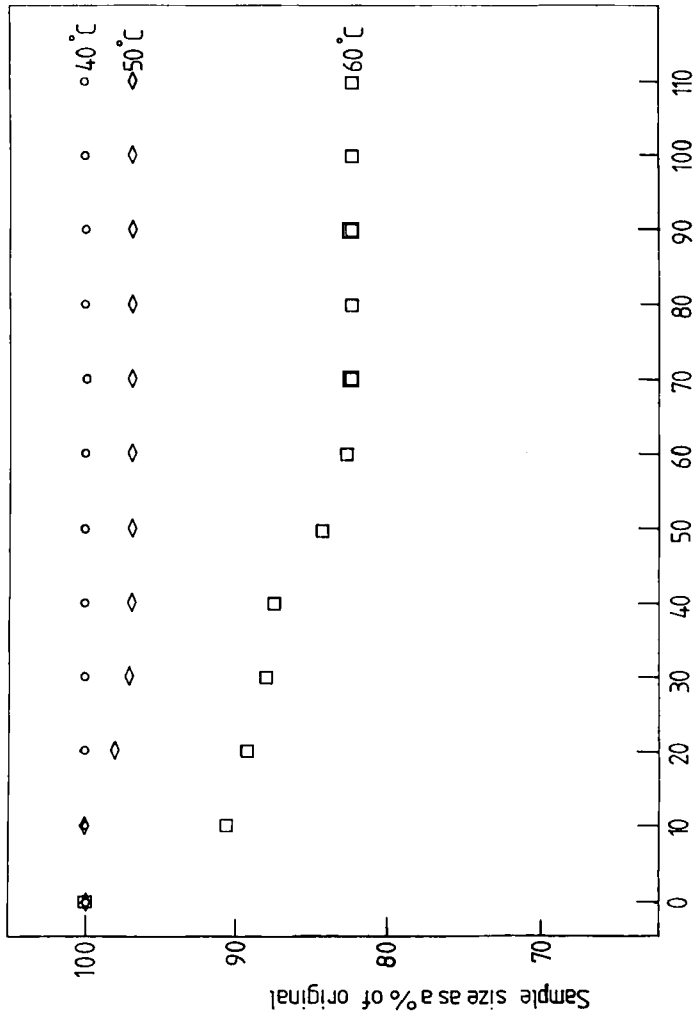


FIGURE 10. Observed % of linear contraction of a swollen liquid crystal elastomer (n = 6, m = 10, 10 mol% diacrylate concentration in B.D.H. cyanobiphenyl M18) as a function of applied voltage over a range of temperatures. (Electro-optic cell spacing of 25 μm).

envelope. On application of the electric field, these anisotropic envelopes will align and result in an overall shape change. Experiments on unswollen elastomers, where realignment in electric fields proves to be difficult, suggest that such a mechanism may perhaps take considerably longer than the effects observed here. However, the swellant will "lubricate" the motion of the backbone. This might be sufficient to allow the reorganization of the backbone envelopes involved.

An alternative explanation of the shape changes would be to consider the re-orientation of anisotropic liquid crystal "domains." It is quite likely that there are relatively few "domains" in any given sample, although there is no reason to assume that they are anisotropic in shape. However, the connectivity of the mesogenic units to the polymer network may inhibit their required translational motion when re-orientating in the electric field. This could produce anisotropic distortions in the domains.

The threshold voltages measured here may not be true static thresholds. That is to say, switching may have been taking place, but so slowly that it was not detected, and thus the thresholds observed are a function of viscosity. Since viscosity decreases with increase in temperature, this might well be an explanation. However, samples were left for substantial periods with electric fields still applied without any additional dimensional changes being observed.

SUMMARY

It has been shown that relatively large amounts of a non-mesogenic group may be introduced into a liquid crystal polymer without completely destroying the liquid crystal phase, although this may create large changes in the properties of the system. Introduction of cross-links produces a polymer network, which behaves as a conventional elastomer in the isotropic phase. In the liquid crystal phase, when a stress field is applied, the behavior is dominated by the aligning of the mesophase directors. That this orientation occurs such that the side chains lie parallel to the extension direction suggests there is a low level of coupling between the mesogenic group and the polymer backbone. However, it is clear that the coupling has a marked effect on the mechanical behavior of the polymer in the liquid crystal phase.

The presence of an elastomeric network also has a marked impact on the electro-optic properties of these materials. When the effect of the network is suppressed by swelling with a low molecular weight liquid crystal, remarkable shape changes are seen upon applying an electric field. The origin of the latter effect and the interaction between the network and the liquid crystal structure is still unclear.

Acknowledgments

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