Coupling between mesogenic units and polymer backbone in side-chain liquid crystal polymers and elastomers

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The levels of alignment of the mesogenic units and of the polymer backbone trajectory for polyacrylate based nematic side-chain liquid crystal polymers and elastomers were evaluated by using wide angle X-ray and small angle neutron scattering procedures. The X-ray scattering measurements show that substantial levels of preferred orientation of the mesogenic units may be introduced through magnetic fields for uncrosslinked polymers and through mechanical extension for liquid crystal elastomers. Small angle neutron scattering measurements show that for highly aligned samples an anisotropic polymer backbone trajectory is observed in which the envelope is slightly extended by ≈10% in the direction parallel to the axis of alignment of the mesogenic units. The sense of this coupling differs from that recorded for other uncrosslinked side-chain liquid crystal polymers. Possible mechanisms to account for this anisotropy and its relationship to the properties of liquid crystal elastomers are discussed. The observed deformation behaviour of the liquid crystal elastomer is non-affine and this appears to confirm the dominating influence of the liquid crystal order of the side chains on the mechanical properties of these novel networks.

(Keywords: side-chain liquid crystal polymers; coupling; mesogenic units; polymer backbone; elastomers)

INTRODUCTION

Side-chain liquid crystal polymers contain three basic types of molecular unit. These are the polymer backbone, the mesogenic or liquid crystal forming unit, which is often rod or lath like, and a coupling chain joining the mesogenic unit to the polymer chain. A wide variety of such types of materials have been synthesized and studied[1,2]. Fundamental to understanding these complex materials is a quantitative knowledge of the interactions between the three components, namely the backbone, the coupling chain and the mesogenic unit. Although early studies discussed the possibility of a decoupling between the mesogenic unit and the flexible spacer, this is clearly not the case since many of the observed properties and phenomena may be related to the nature of the coupling. Warner and co-workers[3–5] have postulated that a variety of types of nematic phase can exist, dependent upon the nature of the sign of the coupling between the side chain and the polymer backbone. For example the side chain may have a preference for parallel or perpendicular coupling to the polymer chain as shown schematically in *Figure 1*. For smectic phases the density wave defining the layered structure of the mesogenic units also acts to confine the polymer chain. Experimental results from small angle neutron scattering[6–12] confirm these expectations that the polymer chain will lie preferentially perpendicular to the mesogenic unit in the smectic phase. These small angle neutron scattering studies of side-chain liquid crystal polymers show that a similar coupling, albeit much reduced in anisotropy, exists in the nematic phase. However, in all the cases considered the materials exhibited a nematic phase above the smectic phase.

This study is concerned with extending neutron scattering measurements of the polymer chain configuration to an acrylate based side-chain system which displays only a nematic liquid crystal phase. Extensive studies of liquid crystal elastomers prepared from the same polymer have also been made[13–16]. These liquid crystal elastomers are prepared from side-chain liquid crystal polymers by introducing moderate levels of chemical crosslinking[17–19] (*Figure 2*). Such crosslinking has the effect of attenuating the interactions between the mesogenic units and the polymer backbone chains, and various striking phenomena, such as electrically induced shape changes[20,21], mechanical and electrical molecular switching[20,22,23], memory effects[14] and variations in phase behaviour[16,24], are thought to arise directly from these interactions. The focus of the current study is to examine directly the shape and dimensions of the polymer chain trajectory in this type of elastomer as a function of temperature and strain by exploiting the power of small angle neutron scattering through labelling of the polymer backbone with deuterium. Comparison is made with the equivalent uncrosslinked liquid crystal copolymers.

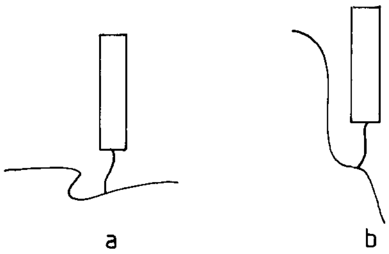

Figure 1 Schematic representation of the different modes of coupling between the mesogenic unit and the polymer backbone in a side-chain liquid crystal polymer: (a) parallel; (b) perpendicular configuration

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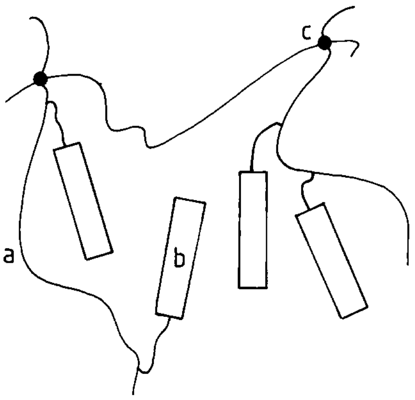
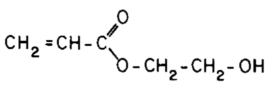


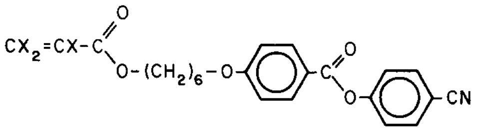
Figure 2 Basic molecular components of a liquid crystal elastomer: (a) polymer backbone; (b) mesogenic side-chain; (c) crosslink point

MATERIALS

The measurement of chain configuration by small angle neutron scattering requires a mixture of similar side-chain polymers with hydrogenated and deuterated backbones. The basic polymer used in these studies was a copolymer formed from hydroxyethylacrylate (I) and an acrylate based cyano phenyl benzoate (II):



$CH_2{=}CH{-}C({=}O){-}O{-}CH_2{-}CH_2{-}OH$ (I)



(II)

where X = H or D. The hydroxy groups provide functionality for introducing chemical crosslinking after polymerization. The acrylate monomer II with X = H was prepared by established routes[25]. The labelled version of that monomer was prepared similarly but deuterated acrylic acid was used when adding the polymerizable group. The deuterated acrylic acid was synthesized from d_1 methyl propiolate (prepared from the protonated form by exchange of the acidic proton in D_2O/OD^-) by deuteration with D_2 using Lindlars Catalyst and subsequent hydrolysis[26]. Hydroxyethylacrylate was obtained from Aldrich and distilled under reduced pressure before use. The polymers were prepared as 10% solutions in chlorobenzene at 55°C using 2% AIBN as initiator. The feedstock for polymerization was (1) a mixture of 90 mol% of II (X = H) and 10 mol% of I, and (2) 90 mol% of II (X = D) and 10 mol% of I. The copolymers were purified by repeated precipitation. The molecular weight distributions of these copolymers were measured by gel permeation chromatography (g.p.c.) (RAPRA Ltd) using THF as the solvent and polystyrene standards. The parameters obtained are shown in *Table 1*.

Liquid crystal elastomers were prepared from a concentrated solution of the copolymer(s) in toluene (≈25% w/v) containing 4% equivalent of monomer repeat units of 1,6 diisocyanatohexane and a small amount of triethylamine (≈1%). A quantity of this solution was added to a specially prepared 'Kapton' mould and the solvent was evaporated at room temperature under the draught of a fume hood. The resultant film, ≈0.3 mm thick, was crosslinked by heating at 130°C for 48 h. Optical microscopy on similar samples shows that during the crosslinking the sample was in the isotropic phase. Infrared spectroscopy and other measurements show the level of effective crosslinking to be ≈1% (Reference 13). To obtain a maximum scattered intensity, labelled samples for the neutron scattering experiments were prepared by mixing equal quantities of the deuterated and undeuterated copolymers. Crosslinked systems were prepared from such mixtures. The detected neutron intensity is that scattered by the polymer backbone since that is the only part deuterated.

EXPERIMENTAL

The phase type and phase transitions of the samples prepared were evaluated by using a polarizing microscope (Carl Zeiss JENALAB) equipped with a Linkam variable temperature stage and a photodiode/microcomputer system to record the variation of transmitted light with temperature.

To observe both the order parameter of the mesogenic units by X-ray scattering and the order parameter of the polymer backbone by neutron scattering it is necessary to prepare monodomain samples. Such monodomain samples of the uncrosslinked copolymers were obtained by alignment in an electromagnet equipped with a variable temperature stage. An uncrosslinked sample was sandwiched between two sheets of 'Kapton' and heated at 107°C for 2 h. The sample was then cooled quickly into the glassy state to preserve the macroscopic orientation induced by the magnetic field. The magnetic field was uniform throughout the sample area at 0.6 T. The orientation was preserved by rapidly cooling into the glassy state. The relaxation rate for this polymer may be measured in hours and, therefore, we can safely assume that the static component of the structure in the glassy sample is that of the mobile liquid crystal phase. It was not possible to produce significant levels of macroscopic orientation in the crosslinked samples through the use of a magnetic field.

A miniature tensometer equipped with an oven and load cell was used for deforming samples of the liquid crystal elastomer for both X-ray and neutron scattering[15]. For the X-ray scattering measurements the following procedure was adopted. Samples of size 5–7 × 15 mm^2 in area for deformation were cut from larger sheets while the sample was in the isotropic phase. The samples were extended at a strain rate of ≈0.09 s^{-1} at 60°C. Each sample was held at the required extension ratio before being cooled quickly in the glassy state to preserve the orientation. An attached computer system allowed the load to be displayed as a function of time

Table 1 Molecular weight distributions

	Copolymer, 90% II, 10% I	
Parameter	X = H	X = D
M_n	4.70×10^4	6.59×10^4
P_n	134	188
M_w	6.55×10^4	10.5×10^4
P_w	187	300
M_w/M_n	1.4	1.6
M_z	8.52×10^4	14.6×10^4

and strain, and these parameters were recorded in addition to monitoring the temperature.

X-ray scattering measurements were made using a computer controlled symmetrical transmission three-circle diffractometer equipped with incident beam monochromator and pinhole collimation. CuKα radiation was used for the experiments, which provided a scattering vector range $0.2 \leqslant s \leqslant 6.2$ Å^{-1} (Reference 27), where $s = 4\pi \sin\theta/\lambda$, the scattering angle is 2θ and λ is the incident wavelength. Data was recorded as a function of s in steps of 0.05 Å^{-1}* and as a function of the angle between the symmetry axis of the sample and the normal to the plane containing the incident and scattered beams α from 0 to 90° in steps of 9°. The scattered X-ray intensity data were used to obtain the orientation order parameter for the mesogenic groups $\langle P_2\rangle^m$, where $\langle P_2\rangle^m = \langle 3\cos^2\alpha - 1\rangle/2$, using the procedures described elsewhere[27-29].

The neutron scattering measurements were made at the Institut Laue-Langevin in Grenoble, France using the D17 small angle scattering spectrometer. This is equipped with an area detector enabling the anisotropy in the scattering pattern to be recorded directly. A sample to detector distance of 2.8 m was used, and the incident neutron wavelength was selected at 12.1 Å. These parameters gave a useful scattering vector range of 6×10^{-3} to 68×10^{-3} Å^{-1}. The liquid crystal elastomers were deformed *in situ* using the tensometer system described above. A microscope cover slip glass was used as the window material for the oven in these neutron scattering measurements. Not only was this ideal in giving little or no small angle scattering, but also it provided the opportunity to monitor the samples optically at elevated temperatures. The force on the sample and its temperature were recorded by using a personal computer system. The scattering data were processed by standard procedures[30]. The data was analysed by using the Guinier approximation[31] over the scattering vector range 0.02–0.06 Å^{-1}. The radius of gyration was obtained from a least squares linear fit to a plot of $\ln I(s)$ *versus* s^2 over that scattering vector range. To obtain an estimate of the level of anisotropy in the chain trajectory the following procedure was used. For the anisotropic scattering patterns a composite $I(s)$ function was prepared for segments of width 22.5° centred around $\alpha = 0$ and 90°. Since the level of anisotropy expected was low, such an approximation introduces insignificant geometric errors, but has the advantage of considerably improving the statistics of the intensity data. For each of these sections a radius of gyration $R_g^{\parallel}$ or $R_g^{\perp}$ is obtained. These and the isotropic radius of gyration obtained in this way R_g' do not take account of the differences between the molecular weight distributions of the labelled and unlabelled chains. The apparent and true radii of gyration are related by the expression given by Boué *et al.*[32]:

$$R_g'^2 = R_g^2\left[1 + \frac{\phi_D\Delta_z}{1 + (1-\phi_d)\Delta_w}\right]$$

$$N_{zH} = N_{zD}(1 + \Delta_z)$$

$$N_{wH} = N_{wD}(1 + \Delta_w)$$

where ϕ_d is the volume fraction of the deuterated or labelled chains and N_z and N_w are z and w averages of the polymerization index. Evaluation of this correction for the mixture used in this study gives a factor of $\approx 10\%$, i.e. about twice the uncertainty in the measured values of R_g. Of course, this correction applies to all measurements of the radius of gyration and this correction does not influence the level of anisotropy derived.

RESULTS

Optical microscopy confirmed, as expected, that these copolymers form only nematic liquid crystal phases, as is the case for the homopolymer of II[25]. In fact, similar copolymers prepared from II and ethylacrylate show nematic phases over the composition range of 0–55 mol% of ethylacrylate[33,34]. The isotropic transition temperature of the hydrogenated copolymers prepared in this study was ≈ 120°C; that for the mixture used for the neutron scattering 107°C. The isotropic–nematic transition of the crosslinked copolymers is similar to that of the uncrosslinked copolymer although, as is reported elsewhere[16,35], the nature of the crosslinks and the temperature of crosslinking has a significant effect on the temperature of the isotropic–nematic transition. *Figure 3* shows the X-ray scattering recorded for a sample of the uncrosslinked copolymer after alignment in a magnetic field of 0.6 T for 2 h at a temperature just below the nematic–isotropic transition and being cooled to the glassy state. The scattering pattern indicates a high level of alignment of the mesogenic groups. The fact that the scattering at $s \approx 1.4$ Å^{-1}, which arises principally from correlations between the mesogenic units, is most intense in the direction normal to the magnetic field indicates that the mesogenic units are aligned preferentially parallel to that field, as is expected. Analysis of the data gives an orientation parameter $\langle P_2\rangle^m$ of 0.51. This is very similar to that obtained by infrared dichroism for a copolymer of II with 10% ethylacrylate[33].

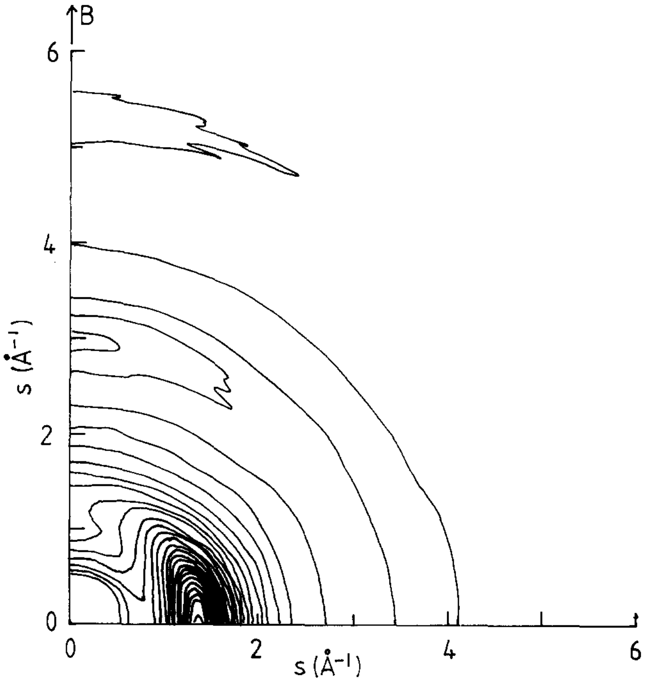


Figure 3 X-ray scattering data $I(s, \alpha)$ recorded for a copolymer of 90 mol% of II and 10 mol% of I after alignment in a 0.6 T magnetic field for 48 h. The X-ray scattering measurements were made on a glassy sample at room temperature. The magnetic field direction is vertical

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* 1 Å = 10^{-1} nm

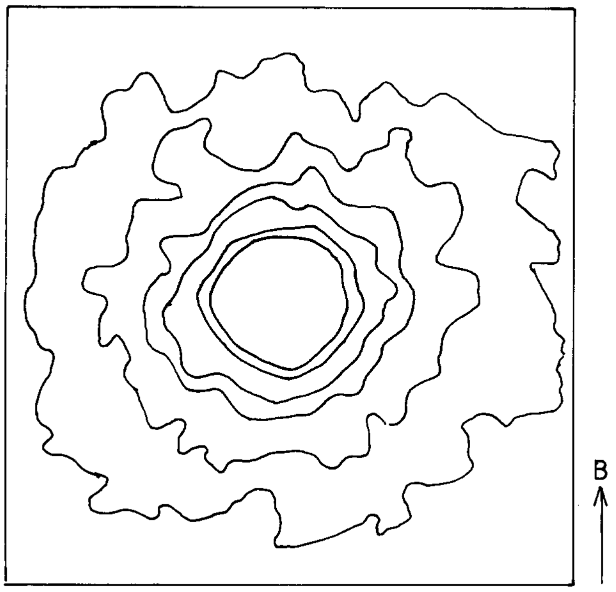

Figure 4 Measured small angle neutron scattering pattern for the glassy sample examined in *Figure 3*. Contours are drawn at equal intervals on an arbitrary intensity scale. The x and y extents of the data shown correspond to $s \approx 0.07$ Å^{-1}

Figure 4 shows the small angle neutron scattering pattern recorded for the copolymer sample aligned in a magnetic field for which the X-ray scattering data is displayed in *Figure 3*. Although the scattered intensities are relatively low, due to the small contrast available with acrylate based systems, the scattering pattern is clearly anisotropic. The small angle scattering envelope is slightly extended in the direction normal to the axis along which the magnetic field had been applied. Analysis of the scattering in the range 0.02–0.06 Å^{-1} gives the radius of gyration parallel to B as 21 Å (± 1 Å) and the radius of gyration perpendicular to B as 18.5 Å (± 1 Å). This level of anisotropy is small and is only just above the resolution of the experiment. However, it is clear that the orientation parameter for the polymer backbone $\langle P_2 \rangle^B$ is positive since its configuration is slightly more extended in the direction parallel to the axis of alignment of the mesogenic groups.

Figure 5 shows the orientation parameter $\langle P_2 \rangle^m$ measured from X-ray scattering data for a sample of a liquid crystal elastomer extended at 60°C in the nematic phase as a function of the extension ratio. The positive sign of the measured orientation parameter indicates that the mesogenic units are aligned preferentially parallel to the extension axis. The sign and the rapid development of the global orientation with strain is similar to that observed for liquid crystal elastomers prepared from II by a direct copolymerization route[13,20]. The X-ray scattering patterns of the deformed elastomers were essentially the same as that observed for the uncrosslinked copolymer, shown in *Figure 3*. The alignment developed in liquid crystal elastomers may be eliminated by heating the sample into the isotropic phase.

Small angle neutron scattering measurements were made on samples of liquid crystal elastomers as a function of temperature and of strain. The radius of gyration for an undeformed and hence unaligned sample of a liquid crystal sample showed a slight contraction of $\approx 10\%$ on heating through the liquid crystal phase until the isotropic phase was reached. The small angle neutron scattering from a liquid crystal elastomer sample held at a temperature of 60°C subjected to increasing mechanical extensions showed no discernible anisotropy up to an extension ratio of 1.2. The scattering pattern for the sample with an extension ratio of 1.5 is shown in *Figure 6b*; for comparison, the data recorded for the same sample before extension (i.e. $\lambda = 1$) is shown in *Figure 6a*. The

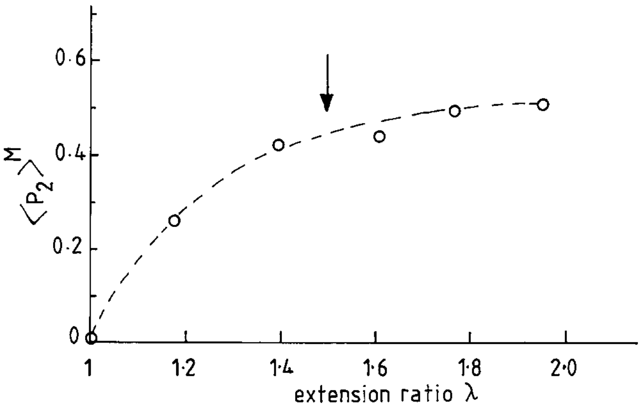

Figure 5 Orientation parameter $\langle P_2 \rangle^m$ obtained from X-ray scattering data for a sample of a liquid crystal elastomer extended at 60°C as a function of applied mechanical extension. The liquid crystal elastomer was formed from a copolymer of 90 mol% of II and 10 mol% of I with 4 mol% potential crosslinking. Orientation measurements were made at room temperature on glassy samples. The arrow indicates the equivalent sample conditions for obtaining the small angle scattering data shown in *Figure 6b*

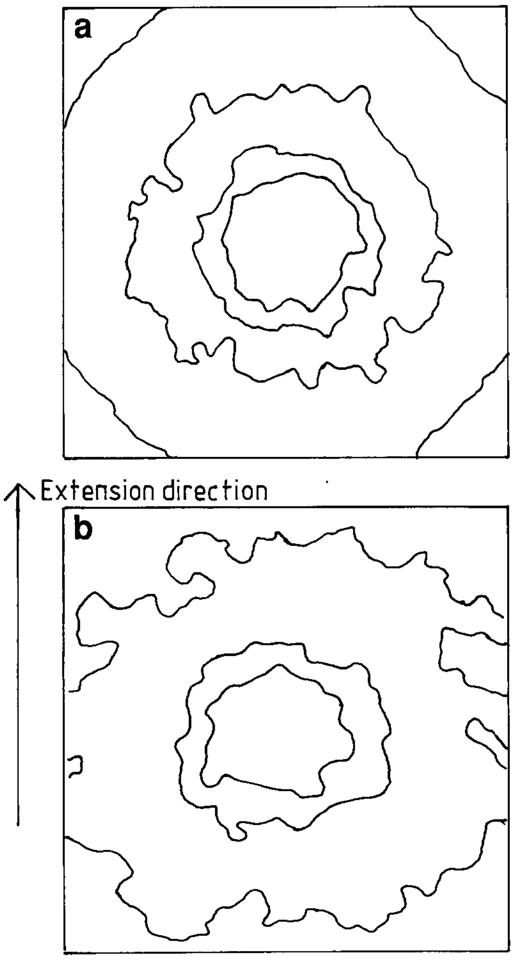

Figure 6 Measured small angle neutron scattering pattern for a liquid crystal elastomer sample: (a) unextended at 60°C; (b) extended to an extension ratio $\lambda = 1.5$ at a temperature of 60°C. Contours are drawn at equal intervals on an arbitrary intensity scale. The x and y extents of the data shown correspond to $s \approx 0.07$ Å^{-1}

scattering from the extended sample is anisotropic, with scattering envelope extended normal to the stretching direction. Analysis of this data using the approach described above gives a radius of gyration parallel to the extension axis of 22 Å (± 1 Å) and a radius of gyration perpendicular to the extension axis of 20 Å (± 1 Å). The sign of the anisotropy of the polymer chain configuration is again positive and the level is similar to that observed for the uncrosslinked copolymer aligned in a magnetic field. If we treat the scattering as isotropic the averaged radius of gyration increases from 21 Å (± 1 Å) by $\approx 10\%$ as the strain is increased from 1 to 1.5.

DISCUSSION

The small angle neutron scattering data show that the polymer chain configuration for both crosslinked and uncrosslinked copolymers is slightly anisotropic. The level of anisotropy is broadly similar to that observed in neutron scattering studies of other nematic forming liquid crystal polymers based on both methacrylates[6–9] and acrylates[10]. However, the sense of the anisotropy is opposite to that seen in other materials. In the polyacrylates studied here the polymer chain aligns preferentially parallel to the mesogenic units (*Figure 1b*). This type of arrangement was labelled N_{III} by Warner[3].

The nature of the relative dispositions of the backbone and the mesogenic unit are controlled by the strengths of the interactions between the mesogenic units, between the polymer backbones, and between the mesogenic units and the polymer backbone. The latter term may be resolved into two components. One component favours parallel alignment between the mesogenic units and the polymer chains simply because of the nematic field. The second component is related to the nature of the coupling chain. If the coupling chain is rigid it may force the mesogenic unit to lie perpendicular to the polymer chain. Quantitative details of these different interactions are of course unknown.

We note that all other small angle neutron scattering measurements to date have found that the coupling between the molecular components in uncrosslinked liquid crystal polymers favours a perpendicular arrangement. However, all these previous examples show a smectic phase on cooling from the nematic phase. Clearly the smectic phase demands a perpendicular configuration; any smectic-like short range ordering in the nematic phase would propagate such tendencies into the nematic phase. Also, all but two of these materials were based on methacrylate backbones. It is well established that the steric crowding of the substituents of such methacrylate chains leads to unequal skeletal bond angles, and hence local curvature of the chain segments[36,37]. Such curvature would clearly depress the tendency for a parallel alignment of mesogenic unit and parallel chain. In this study no smectic phase is observed. The polymer backbone, an acrylate, is flexible and there is no tendency to form curved chain segments. This type of parallel alignment was found in a small angle X-ray scattering study of a siloxane based system in which the polymer was dissolved in a nematic liquid crystal solvent of low molar mass[38]. Conflicting evidence for the same parallel alignment comes from a nuclear magnetic resonance study[39] on a similar material to that used in neutron scattering measurements, in which a perpendicular alignment was deduced[10]. That polymer also showed a smectic phase.

The sense of the anisotropy of the polymer chain may be inferred by the direction of alignment of the mesogenic units in a liquid crystal elastomer upon extension if we assume the observations are made in near equilibrium conditions. Finklemann and co-workers have observed both perpendicular and parallel arrangements of the mesogenic units with respect to the extension direction for liquid crystal elastomers with coupling chains of different lengths[40]. In the materials studied here we observed a parallel configuration as indicated by the data in *Figure 5*, and this is obviously consistent with small angle scattering observations. Extension of similar liquid crystal elastomers to extension ratios of ≈ 10 (Reference 13) does not reveal any tendency of a perpendicular type configuration. However, in a previous study of the mechanically induced molecular switching in liquid crystal elastomers formed from mesogenic units with a coupling chain of two alkyl units, a similar parallel arrangement of the side chains with respect to the extension direction was observed[20,22]. Shortening the coupling spacer is expected to enhance the probability of the perpendicular configuration as the hinge aspect of the coupling interactions begin to dominate. Detailed analysis of the X-ray scattering from the $n=2$ type elastomer reveals a high concentration of *gauche* isomers in the coupling chain[27], the presence of which is necessary for a parallel correlation between the mesogenic units and the polymer backbones.

Figure 5 shows that, at a strain of 1.5, the alignment of the mesogenic units or liquid crystal directors is almost complete. At this strain the small angle neutron scattering data show the anisotropy of the polymer chain trajectory to be that observed for a monodomain sample of the uncrosslinked copolymer. The theory of the deformation of non-crystalline networks has been the subject of intensive study and many models have been developed. Central to these models is the manner in which the macroscopic externally applied strain is transferred to the molecular level. In the simplest models (which are not usually applied to rubber networks) all vectors transform affinely. In other words, the vector $r_{ij} = (x_{ij}, y_{ij}, z_{ij})$ between two chain segments i and j, for example, is transformed to $r^*_{ij} = (\lambda^{-1/2}x_{ij}, \lambda^{-1/2}y_{ij}, \lambda z_{ij})$, in which the z axis is the direction of extension. For the affine model the ratio $R_0^\lambda = R_g^\lambda / R_g^{\lambda=1}$ is equal to the macroscopic strain λ. Clearly the data of *Figure 6* does not represent a level of anisotropy commensurate with a ratio $R_0^\lambda = 1.5$. A more reasonable approach for a polymer network is one in which the vectors between the junction or crosslink points deform affinely[41] and this leads to a ratio $R_0^\lambda = [(1+\lambda^2)/2]^{1/2}$, which for the data shown in *Figure 4* corresponds to 1.27. Again the predicted anisotropy is substantially higher than that observed. The fact that the junction points do not deform affinely in the case of mechanical deformation may be of some importance in the development of models of the nematic–isotropic transition in liquid crystal elastomers[35].

It is not surprising that such a simplistic model fails in the description of the deformation of a liquid crystal elastomer system. Affine deformation of the junction points in a liquid crystal elastomer would imply that they act independently of the surrounding matrix of reorganizing mesogenic side chains. In fact we know that there is cooperative interaction between the network chains and the mesogenic groups, since relatively small deformations are required to give complete alignment of the liquid crystal directors. The deformation of a phantom network allows for fluctuations of the positions of the junction points which are independent of the applied macroscopic strain[42]. These fluctuations allow the energy of the network to be minimized and of course in a liquid crystal elastomer system we anticipate large additional energies arising from the interactions of the liquid crystal directors. The effect of such fluctuations is to reduce the rate of orientation of the network with strain. The value of R_0^λ depends upon the functionality of the crosslink points. For example, for tri-functional crosslinking $R_0^\lambda = [(5 + \lambda^2)/6]^{1/2}$, giving a value of 1.1 for $\lambda = 1.5$. In other words, allowing for deviations from affine deformation of the junction points results in a lower level of anisotropy and this is the case for the liquid crystal elastomer studied here. Only a small bias in the anisotropy of the polymer backbone through deformation is required to result in reorientation of the liquid crystal directors from a polydomain to a monodomain structure. At the point of complete alignment we would expect the anisotropy of the polymer backbone in the deformed elastomer to parallel that of the uncrosslinked monodomain liquid crystal polymer sample (*Figure 4*) and this is the case. In other words, alignment of the polymer backbone configuration through mechanical extension of the network results in a coupled alignment of the side chains. The first stage of this results in a monodomain structure and this accounts for the rapid change and saturation in the value of $\langle P_2 \rangle^{\mathrm{m}}$ as a function of strain, as observed in *Figure 3*. Further extension can only result in a higher level of orientation of the polymer chains and this will couple through the nematic field with the level of alignment of the mesogenic units. However, considerable extension is probably required for this effect to be significant. In the current experiments, deformation ratios greater than 1.5 were not possible, but future experiments will allow larger levels of strain to be explored.

We have previously reported on the intriguing electrically induced macroscopic shape changes that are observed in swollen samples of liquid crystal polymers[20,21]. These observations, in common with parallel experiments described by Zentel[43], show an extension of the sample along the axis of the applied electric field. One explanation for such shape changes is that reorientation of the liquid crystal directors by the electric field from a polydomain to a monodomain texture parallel to the electric field (for these materials $\Delta\varepsilon > 0$) results in coupled reorientation of the backbone chains. Since the latter are crosslinked together with anisotropic trajectories, a macroscopic shape change occurs. Although it is possible to construct an alternative model to account for this effect on the basis of macroscopic dielectric phenomena[21], it is interesting to note that the sign of the shape change is in accord with the anisotropy of the chain trajectory found from the small-angle neutron scattering. However, the size of the electrically induced shape change, up to 20%, far exceeds the anisotropy of the chain envelope found in these studies by small angle neutron scattering.

CONCLUSIONS

The neutron scattering measurements show that, for a polyacrylate based copolymer system, the coupling between the mesogenic side chain and the polymer backbone results in positive order parameters for both components, i.e. the two molecular units prefer to lie in parallel configuration. Substantial levels of global orientation of the mesogenic side chains may be introduced in liquid crystal elastomers prepared by a two stage process, through small mechanical extensions. For such extensions the deformation of the polymer network is far from being affine. This is attributed to the dominating influence of the mesogenic side chains in the deformation behaviour. The sense of the coupling between the backbone and the side chains in the elastomer is similar to that observed in the uncrosslinked liquid crystal copolymer.

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