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Liquid crystalline elastomers: the relationship between macroscopic behaviour and the level of backbone anisotropy

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Abstract

Nematic monodomain liquid crystalline elastomers have been prepared through in situ cross-linking of an acrylate based side-chain liquid crystalline polymer in a magnetic field. At the nematic–isotropic transition, the sample is found to undergo an anisotropic shape change. There is found to be an increase in dimensions perpendicular — and a decrease parallel — to the director, this is consistent with alignment of the polymer backbone parallel to the direction of mesogen alignment in the nematic state. From a quantitative investigation of this behaviour, we estimate the level of backbone anisotropy for the elastomer. As second measure of the backbone anisotropy, the monodomain sample was physically extended. We have investigated, in particular, the situation where a monodomain sample is deformed with the angle between the director and the extension direction approaching 90°. The behaviour on extension of these acrylate samples is related to alternative theoretical interpretations and the backbone anisotropy determined. Comparison of the chain anisotropy derived from these two approaches and the value obtained from previous small-angle neutron scattering measurements on deuterium labelled mixtures of the same polymer shows that some level of chain anisotropy is retained in the isotropic or more strictly weakly paranematic state of the elastomer. The origin and implications of this behaviour are discussed. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Elastomers; Macroscopic behaviour; Anisotropy

1. Introduction

The potential for liquid crystalline elastomers to exhibit unusual properties was first suggested by de Gennes [1,2], some years before such materials were prepared in the laboratory. Subsequently, such elastomers have been prepared [3], and their resultant properties investigated [4,5]. In general, the elastomers most frequently studied have been those based on side-chain liquid crystalline polymers, rather than the main chain systems considered originally by de Gennes; this is a consequence of rather more thermally accessible liquid crystalline phases for side-chain liquid crystalline polymers. Such materials have received considerable attention from a theoretical point of view by Warner [6–9] amongst others [10]. The main feature of the theoretical models proposed by Warner and his colleagues lies in the possibility of coupling between the orientational order of the mesogenic units and the (entropically driven) conformation of the polymer backbone; thus, order of the side-groups will be accompanied by some level of orientational order in the polymer backbone as indicated in Fig. 1. Evidence for this coupling can be found in the range of novel behaviours shown by liquid crystalline elastomers, examples of which include stress-induced orientation (of the mesogenic side-groups) [11], shifts in phase transition temperatures [12,13], and memory effects [14–16]. All of these properties and others can be considered to be manifestations of coupling between the polymer chain and side-groups; the network acting to allow the observation of such effects by restricting the relative motion of polymer chains.

The possibility of introducing a permanent, but reversible global alignment to a sample by cross-linking an aligned (monodomain) polymer sample provides scope for studying anisotropic properties within the bulk material since it allows properties to be monitored without the masking effects of polydomains [5]. Two approaches have been successfully employed to prepare such elastomers: the first approach, developed in this laboratory, involves cross-linking an acrylate polymer pre-aligned in a magnetic field [14]. Such samples are found to show complete recovery of their global orientation on cooling to the nematic phase from the isotropic phase, i.e. the samples retain a memory of their global macroscopic orientation at the time of cross-linking.

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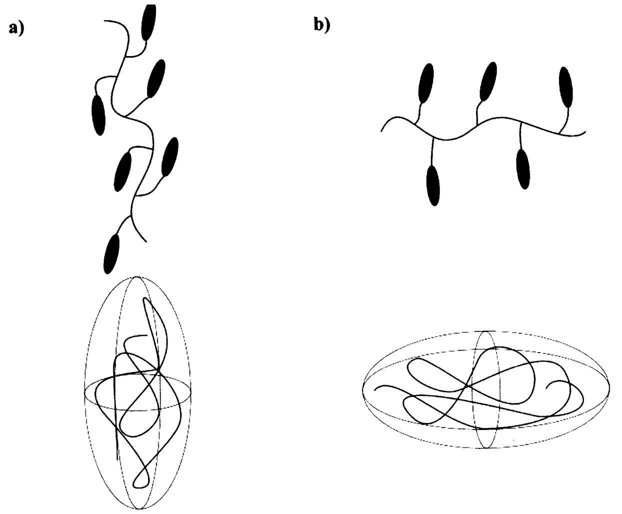


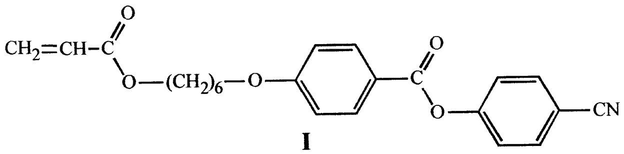
Fig. 1. Coupling in a side-chain liquid crystalline polymer (a) for parallel coupling the mesogenic side-chains align in the same direction as the polymer backbone; in (b) where coupling is perpendicular, the polymer chain trajectory is extended at right angles to the mesogenic ordering direction. The coupling is due, at least in part, to conformational preferences in the coupling chain.

The second method due to Finkelmann and his co-workers [15] involves lightly cross-linking a siloxane liquid crystalline polymer whilst applying a stress field. The level of anisotropy of the polymer chains in materials prepared using the latter approach will reflect both the intrinsic anisotropy and the strain applied. In contrast, monodomain liquid crystal elastomers prepared using a magnetic field, as in this work, will exhibit a level of chain anisotropy, which reflects the intrinsic coupling between the mesogenic units and the polymer chains.

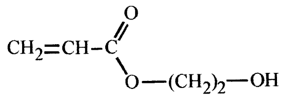
In order to understand quantitatively the nature of coupling in side-chain liquid crystalline elastomer systems, it is necessary to relate the level of preferred orientation of the side-chain mesogenic units to the orientation of the polymer backbone. The orientation of the mesogenic groups may be quite readily probed in a number of ways; at Reading, we have utilized X-ray scattering techniques since the mesogenic units, by virtue of their high electron density, provide the most visible (in terms of X-ray scattering) component of side-chain liquid crystalline polymers of the type under investigation [17]. Quantitative evaluation of coupling can therefore be reduced to the problem of measuring the orientation of the polymer backbone. Limited measurements have been made using small-angle neutron scattering [18,19]; however, the technique is costly in terms of experimental time as it requires isotopic substitution of the backbone hydrogens for deuterium and access to a neutron source. In this contribution, we discuss the use of monodomain elastomers as a probe for the backbone anisotropy; firstly, in order to evaluate the fit of the experimentally observed behaviour to theoretical models, and secondly as a potential tool for systematic studies of the properties of liquid crystalline elastomers. It is expected that in such samples, microscopic changes in polymer chain conformation will be reflected in the macroscopic behaviour of the sample. We shall adopt the approach of Warner [7] who has recently described how both shape changes at the nematic–isotropic transition and the stress-induced reorientation of monodomain samples can be used to determine the level of anisotropy in the polymer backbone.

2. Materials

The experiments described here utilized a side-chain liquid crystal copolymer based on [**I**] [20] containing 6 mol% of hydroxyethyl acrylate [**II**] to provide sites for subsequent cross-linking [12]. The polymer was produced by free-radical polymerisation initiated by AIBN at 55°C; the material produced was predominantly atactic with a weight average degree of polymerisation of ca. 200. The polymer showed a nematic phase with a nematic–isotropic transition (T_{NI}) at 123°C. Elastomers were produced by casting a small amount (~15 mg) of copolymer mixed with a small excess of cross-linking agent (di-isocyanatohexane) from dichloromethane onto a clean 'Kapton', sheet followed by holding the mixture at the required temperature until cross-linking was complete. Previously, measurements of the initial extensional modulus in the isotropic phase, together with swelling experiments have shown that this procedure yields material with a cross-link density in terms of monomer repeat units of ca. 1% [12].



I



$CH_2{=}CH{-}C({=}O){-}O{-}(CH_2)_2{-}OH$

II

Monodomain samples were prepared by cross-linking the films in the nematic phase at 118°C in a magnetic field. The majority of samples were prepared using a magnetic field of ca. 0.6 T, however, the mechanical deformations were performed on samples prepared with a field of 2.1 T; no quantitative difference in the behaviour of these latter films and those prepared at lower fields was observed [21]. Under such conditions, a macroscopic alignment was achieved relatively quickly; for example, in a uniform magnetic field of 2.1 T, a monodomain structure was obtained in ca. 900 s [16]. Previous experiments [22] have shown that conformational changes in the backbone resulting from coupling to the mesogen may lag behind

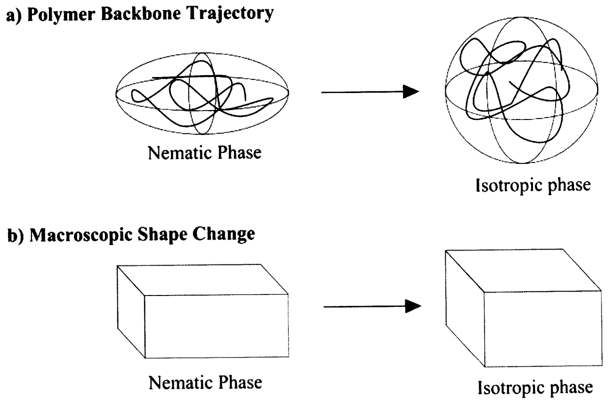


Fig. 2. Representation of the effect of a macroscopic shape change at the nematic–isotropic transition: in the isotropic phase, the loss of the anisotropic chain trajectory of the polymer backbone results in a change in sample dimensions parallel and perpendicular to the initial orientation.

the side-chain reorganisation, but not sufficiently to involve non-equilibrium conformations in the final sample, since cross-linking is a relatively slow process, typically taking ca. 24 h. The final cross-linked system exhibited a glass transition at ~35°C and a reversible nematic–isotropic transition at 123°C, i.e. similar to that recorded for the uncross-linked polymer. Polarised light microscopy confirmed the existence of a nematic phase and the monodomain structure.

The birefringence measurements were performed on an acrylate sample with a weight average degree of polymerisation of ca. 150 and a nematic–isotropic transition at 127°C. The materials were cross-linked with 1,4-methylenebis(phenylisocyanate). Three samples were prepared: a monodomain sample, using the procedure described in the previous paragraph, except that the cross-linking temperature was 100°C; a polydomain, also prepared at 100°C, but in the absence of an aligning field; finally, a sample was cross-linked in the isotropic phase at 140°C.

3. Experimental details

The dimensions of the monodomain sample were determined as a function of temperature using a travelling microscope fitted with a small temperature controlled oven. The sample dimensions were 5 mm × 8 mm, with a thickness of 0.15 mm. At each temperature, the dimensions were monitored for 6×10^5 s to ensure steady-state conditions, which were typically achieved in $\sim 2.5 \times 10^5$ s. At each temperature in the heating/cooling cycle, the dimensions of the samples were measured along a number of lines both parallel and perpendicular to the orientation axis.

All deformation experiments were performed at 80°C ($0.88T_{NI}$), using a miniature tensiometer equipped with an oven stable to ±1°C at this temperature. A strain rate of $0.02\ s^{-1}$ was used and when the sample was at the required extension it was held for 4×10^4 s prior to measurement (in fact, steady-state conditions were achieved in 3.6×10^3 s). Samples were held at the extremities by 'Kapton sellotape' and clamped between the jaws of the tensiometer, while the temperature was maintained at ≈10°C above T_g, and then heated to the operating temperature. Samples were deformed at a range of angles close to perpendicular (i.e. between 67 and 89°) to the direction of initial alignment of the mesogenic units, each experiment being performed on a freshly prepared sample of size 10 mm × 5 mm × 0.15 mm.

In situ X-ray scattering was performed using a charge coupled device-based area detector system which has been described in detail elsewhere [23]. The scattering at $s = 1.4\ \text{Å}^{-1}$ ($s = 4\pi \sin \theta/\lambda$, where 2θ is the scattering angle and λ the incident wavelength) arising from correlations between neighbouring mesogens was used as a probe of side-chain orientation. The scattered intensity at azimuthal angle $\phi = 0$–$360°$ was used to calculate the orientation parameter, $\langle P_2 \rangle = \langle 3 \cos^2\phi - 1 \rangle/2$, and a moment of inertia fit to a polar plot of scattered intensity vs. ϕ was used to estimate the angle, θ, between the director n and the extension axis. During such experiments, both the director orientation and orientation parameter were monitored between successive strains to ensure steady-state conditions. As an alternative probe of the director orientation, an optical method was used; here the intensity of laser light passing through a sample held between crossed polarisers was used [24]. Birefringence measurements in the isotropic phase were performed on monodomain samples viewed under polarised light using a Carl Zeiss Jenalab microscope incorporating a Senarmont compensator [25].

4. Results

4.1. Shape changes

For a side-chain liquid crystalline polymer, theory [6] has highlighted the possibility that the orientational order of the mesogenic units in the liquid crystal phase has an influence on the polymer backbone conformation; this can take up an anisotropic arrangement with alignment broadly parallel or perpendicular to the direction of mesogen alignment depending upon the sign of the coupling. In the isotropic phase global alignment of the mesogens is lost and consequently the polymer backbone will take up a broadly isotropic trajectory provided the cross-linking is sufficiently light to allow reversibility. The samples prepared here allow us to observe the resultant shape change of the polymer chain at a macroscopic level as illustrated in Fig. 2: firstly, because the monodomain sample prevents different domains nullifying each other; secondly, because the polymer network allows the microscopic conformational changes to be transformed to the macroscopic level.

The cross-linked samples prepared here exhibit a stable monodomain structure in the nematic phase, i.e. in the absence of any external aligning field, they retain the

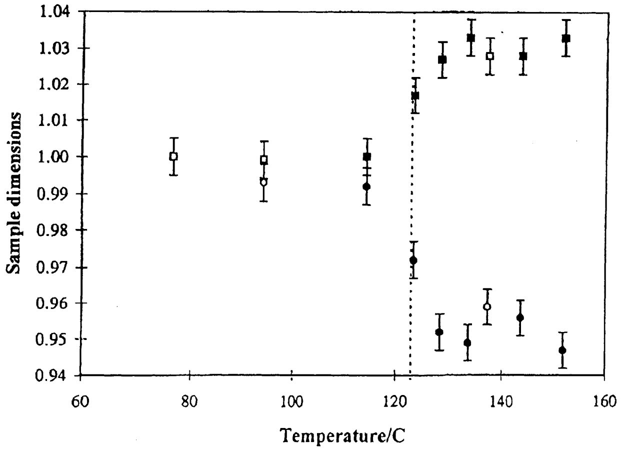


Fig. 3. A plot of the dimensions parallel (●) and perpendicular (■) to the director of a monodomain sample of a liquid crystal elastomer relative to the dimensions measured at 78°C, as a function of temperature. The effect was found to be reversible and broadly independent of whether the data was obtained on heating or on cooling. (The open symbols (○) and (□) refer to data obtained on cooling.) The dotted vertical line corresponds to the mid-point temperature of the transition from the nematic to the isotropic phase, which typically occured over a 2° range.

same director alignment and the same magnitude of order. X-ray patterns were obtained from a cross-linked sample held in the nematic phase in the absence of any further aligning field. The orientation parameter for the side-groups for the sample studied here was found to be $\langle P_2(\cos\alpha)\rangle = 0.5$. When the sample was heated into the isotropic phase, the high levels of order associated with the nematic phase were lost; for example, no ordering could be observed by X-ray scattering measurements; however, low levels of order could be observed by birefringence — see below. On cooling to the nematic phase, the previous director orientation was established immediately while the level of orientational order was found to gradually return to the initial values.

Fig. 3 shows a plot of the relative dimensions of the sample parallel and perpendicular to the orientation axis of the monodomain; the data were taken at various fixed temperatures in both the nematic and isotropic phases. For convenience, these are presented as values relative to those obtained at 78°C. From these data, it appears that within each phase the shape of the sample remains more or less constant. However, at the phase transition, there is a marked change in the shape of the sample. In the direction parallel to the orientation axis, the sample contracts by ~5% and in the direction perpendicular to the orientation axis the sample expands by ~3%. The effect was completely reversible. In contrast, a sample which had been cross-linked in the isotropic state showed no observable dimensional changes (presumably the change in length associated with the volume change at the nematic–isotropic transition is too small to detect by the method employed here).

The measurements shown in Fig. 3 provide a clear indication that the alignment of the mesogenic units is coupled to the polymer network. The shape change arises as a consequence of the alignment of the polymer backbone relative to the mesogenic groups. The alignment results in an elongation in the direction parallel to the orientation axis in the nematic phase. This indicates that the polymer backbone aligns parallel to the mesogenic units in this polymer, in line with a number of other studies of this system. These data are discussed in a more quantitative fashion below.

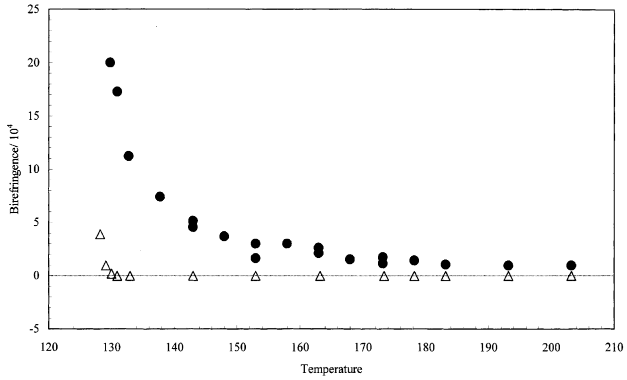


Fig. 4. Birefringence measured as a function of temperature for (●) a monodomain liquid crystalline elastomer heated into the isotropic phase; the alignment direction indicated by this birefringence is unchanged from that found in the nematic phase. (△) A sample cross-linked in the isotropic phase at 140°C; the rapid loss of all birefringence is particularly noticeable.

Analysis of the shape change data relies on the absence of net orientation in the isotropic state. In order to test this, it was decided to monitor any global orientation in the isotropic phase using birefringence as a probe [26]. Fig. 4 shows that a monodomain sample heated above T_{NI} gives rise to a small but finite, uniform birefringence in the same direction as that of the original director; the sign of the birefringence was positive. This birefringence was very small when the temperature was well above T_{NI}, in line with previous measurements on monodomain samples in the isotropic phase [14]. The level of birefringence at a temperature T was found to be approximately proportional to $1/(T - T_{\mathrm{NI}})$. The observation of this birefringence in the isotropic phase indicates ordering (although the level of order is too small to be quantified by X-ray scattering) and consequently the presence of an aligning field. This field arises by virtue of the network elasticity associated with the polymer backbone. Clearly, the influence of this aligning field extends well into the isotropic phase. In contrast, a sample cross-linked in the isotropic phase exhibited no observable birefringence above the nematic–isotropic transition. This presumably reflects the absence of macroscopic anisotropy in the polymer chain trajectory present at the time of cross-linking.[1]

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[1] A sample cross-linked in the nematic phase, but in the absence of any aligning field, also showed local birefringence but at lower levels (ca. 50% of that observed from the monodomain sample); naturally, no net global orientation was observed from the sample, but the experiment serves to illustrate that the coupling in these systems arises from conformational preferences (the hinge effect) [6] rather than the influence of the nematic field.

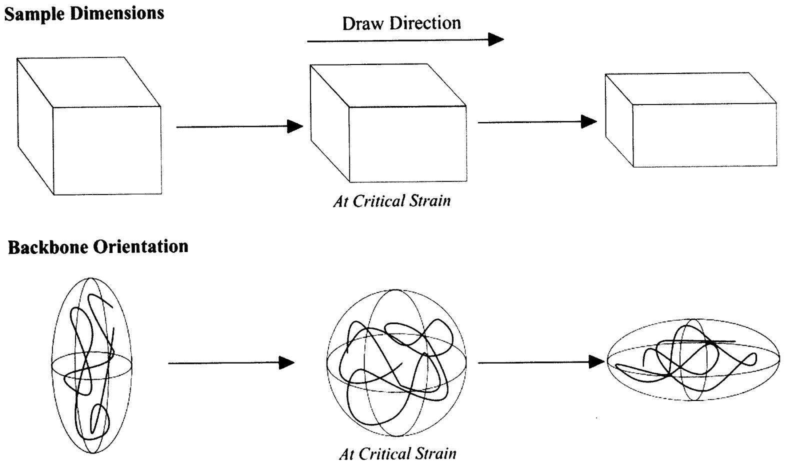

Fig. 5. Illustration showing the effect on a monodomain sample of a strain applied perpendicular to the alignment direction. In order to realign the backbone with the applied mechanical field, at some critical value of the strain, the backbone will pass through an isotropic state.

4.2. Mechanical deformation

A fundamental property of a side-chain liquid crystalline elastomer is that an applied stress producing anisotropy in the polymer backbone, results in a macroscopic alignment of the director by virtue of coupling. The stress–strain behaviour of monodomain samples can be understood since the director orientation and reorientation can be readily related to the relative orientation θ of the liquid crystal director and the applied field [21,27]. Warner and coworkers [28,29] have considered this problem in some detail and have developed two models to describe the behaviour. In one model, which has been particularly applied to samples of the type described here [28,29], they suggest that there exists a barrier to director rotation if the field is applied perpendicular to n_0, due to the anisotropic shape of the polymer chain, which is defined at the time of cross-linking. The theory defines a strain tensor that constrains both chain shape and shear relaxation. Where the deformation angle with respect to the director is less than $\pi/2$, the director is predicted to rotate in a continuous fashion with increasing strain; of particular interest, however, is the geometric arrangement where the director and the applied field lie perpendicular, as indicated in Fig. 5. In this arrangement, there is expected to be a jump in the value of θ at a critical strain λ_c, such that the director aligns with the applied field. This threshold field is analogous to the electric or magnetic-field induced Fréedericks transition, although it arises from an entirely different physical mechanism [27]. Quantitative extension to this theory reveals that for the $\pi/2$ arrangement (i.e. where θ, the angle between the director and the applied strain λ is 90°) the critical extension ratio (λ_c) can be related to the step lengths of the polymer backbone trajectory perpendicular ($l^0_\parallel$), and parallel ($l^0_\perp$) to the nematic director (Eq. (1)). This theory can be extended such that alternative geometries with $\theta < 90°$ can also be used to determine the value of λ_c. The formula linking the angle θ between the applied strain and the director, and the extension λ derived by Warner et al. is given by Eq. (2), where $\Delta = \theta - \alpha$ and α is the angle between the applied strain and the initial director orientation.

$$\lambda_c = \left(\frac{l^0_\perp}{l^0_\parallel}\right)^{1/3} \tag{1}$$

$$\tan 2\Delta = \frac{2(\lambda_c^3 - 1)\sqrt{\lambda}\sin 2\alpha}{(\lambda_c^3 + 1)(\lambda^2 - 1/\lambda) + (\lambda_c^3 - 1)(\lambda^2 + 1/\lambda)\cos 2\alpha} \tag{2}$$

The second model described by Warner [30,31], ties in closely with the observations of Finkelmann and his coworkers [32], in this case, director reorientation is associated with both an extensional and a shear deformation. Here an extension at 90° to the director orientation gives rise to a threshold extension λ_1. At extensions above this threshold value, there is a gradual rotation of the directors with the applied strain, until at an extension λ_2 a rotation of 90° is achieved, whereupon no further reorientation is possible. To distinguish between the two approaches, we have used the terminology of Ref. [30], here the anisotropy of the backbone λ_c is denoted as r. This is related to the director reorientation by Eq. (3). A particularly striking feature of this behaviour is the development of striped domains during the reorientation process [32].

$$\theta = \pm\arcsin\left[\frac{r}{r-1}\left(1 - \frac{\lambda_1^2}{\lambda^2}\right)\right]^{1/2} \tag{3}$$

Fig. 6 shows data obtained from experiments in which the influence of an applied stress on the director orientation was monitored for monodomain samples stretched at different angles to the director. At angles close to 90°, there is a rather marked jump in director orientation at a critical strain of about 1.15; as the angle is reduced, the director re-orientation

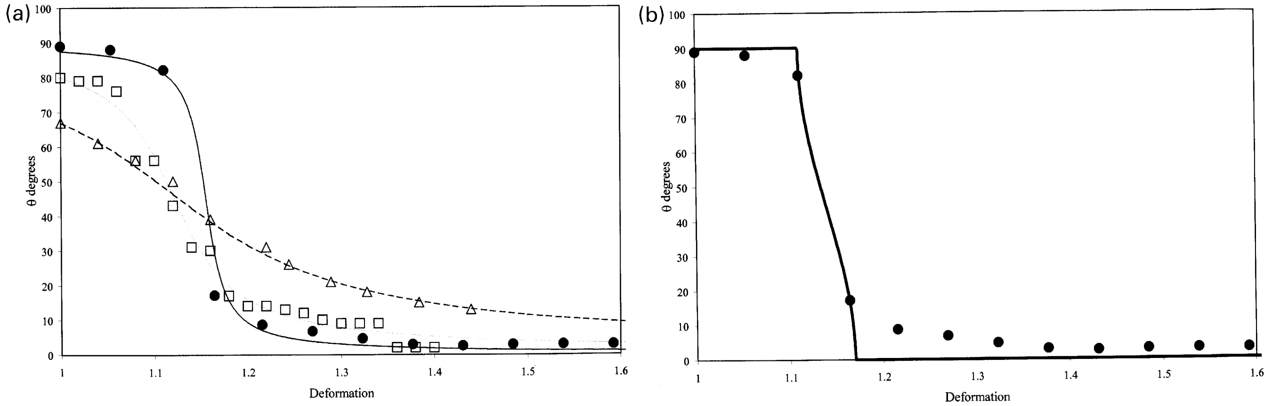

Fig. 6. (a) Orientation of mesogenic side-groups as a function of strain for a monodomain liquid crystalline elastomer deformed at varying angles to the initial director: (1) (●) at 89°; (2) (□) at 80°; (3) (△) at 67°. The curves shown represent a least-squares fit to the data using the theory of Warner et al. [28,29]. (b) The data shown in Fig. 6(a) fitted according to the alternative theory of Warner et al. (Eq. (3)) [30], which predicts the occurrence of striped domains.

becomes a more gradual process. Although it should be noted that we were unable to observe the predicted discontinuity at $\theta = 90°$, we attribute this to the extreme position sensitivity of the system, and more importantly to the inhomogeneous nature of the sample, consistent with the low levels of orientation attained. The data shown in Fig. 6 was fitted to the theoretical model represented by Eq. (2) using a least-squared method, and the curves are shown. This 'best-fit' data was obtained by calculating the differences between the experimental values for θ and those calculated from Eq. (2) at equivalent extensions using a range of values of θ and λ_c. The least-squares minimum was relatively insensitive to changes in λ_c and we estimate an error of ca. 2% for the value given. In addition, the calculated value of θ was particularly sensitive to the experimental values at high extensions where the relative error was the greatest (we estimate a maximum error of ca. 2° in the values for θ). The data points shown in Fig. 6 were taken using three different samples prepared under the same conditions, each at a different initial value of the angle between the director orientation and the applied stress field. The angles chosen were 89, 80 and 67°. The first two sets of data were obtained using X-ray scattering, the latter data set was obtained using an optical arrangement in which the director orientation was monitored using birefringence measurements. From our curve fitting calculations, the following values were obtained for λ_c: 1.16 at 89°; 1.13 at 80°; 1.19 at 67°. Although data was only obtained for three different values of θ, the fit of these data to Warner's theory is particularly encouraging, and the deviation of less than 3% around the mean value of 1.16 for λ_c is well within the error limits of these measurements, particularly given the variations which might occur during sample preparation.

The data obtained for the sample extended at 89° to the initial director has also been fitted to Eq. (3) as shown in Fig. 6(b). The best fit was obtained with a value for r and λ_1 of 1.11. The fit is particularly good at smaller extensions, and deviations at high extensions may be attributed to the slight deviation of the initial angle from perpendicular, and to fluctuations of the director about the mean value. On the basis of this evidence, we cannot distinguish between the two models, however, it is clear that if the sample is deforming in a manner consistent with the second theory, then such deformation should be accompanied by the formation of striped domains. We have searched unsuccessfully for evidence of such domains in these acrylate samples, both optically and using X-ray scattering. Both here and in previous investigations [27], only two peaks could be observed in the scattering pattern throughout the deformation process. In addition, changes in the optical texture of the sample were small and gradual. In contrast, when we have looked at samples based on a polysiloxane chain [33] similar to those described by Finkelmann [32], the formation of striped domains was readily apparent from both X-ray and optical studies. It should be noted that these polysiloxane samples generally exhibit a rather high level of anisotropy compared to the acrylate systems described here. The model of Ref. [30] predicts that for a system with low levels of anisotropy, there is only a narrow range of extensions over which striped domains are visible; this range could be experimentally unobtainably narrow. However, since there is no evidence that this mechanism is in operation in the discussion which follows, we have used the data obtained from fits to Eq. (2) rather than Eq. (3), although the values in the levels of backbone anisotropy predicted by either model are not markedly different.

5. Discussion

In the liquid crystal elastomer samples studied here, we attribute the macroscopic shape changes to a conformational change from the ordered backbone arrangement associated with the nematic phase to the isotropic conformation associated with the isotropic phase. In other words, the shape changes are a direct measure of the conformational change at the phase transition and hence a direct measure of the extent of coupling in the liquid crystal phase. Underlying such changes there will of course be a general expansion due to increasing molecular volume. If we consider this change taking place in a film with uniaxial symmetry, the recorded dimensional changes give a volume increase of ~0.01% at T_{NI}, a value typical for a liquid crystal–isotropic transition (however, this value is close to the precision limits of our experiment). In order to convert the dimensional changes of the sample to information regarding the anisotropy of the polymer chain conformation, we need to have knowledge of the link between microscopic and macroscopic strain. It is essentially the reverse problem of network elasticity in which it has often been assumed that the network points deform affinely with the macroscopic strain.

For a side-chain liquid crystal system, the potential describing the ordering of the polymer chains S_b with respect to the nematic director in the absence of macroscopic phase separation may be written for a mean field model in a similar way to that employed by Warner and others [34,35] by Eq. (4) (where S_a is the order parameter of the mesogenic units, f_a the fraction of mesogenic units, μ a coefficient describing the coupling between the mesogenic units and the polymer backbone, and Γ the coefficient detailing the interaction between the polymer chains). We have chosen a value of Γ to reproduce the nematic ordering of a hydrocarbon chain at the appropriate temperature relative to the T_{NI} for the complete system [36]. The fact that the ordering temperature for the backbone is substantially lower than that for the side-groups means that the contribution to the ordering of the chains due to the chain–chain interactions is negligible, except at relatively low temperatures. The coupling coefficients are expressed in terms of the mesogen–mesogen interaction parameter. Negative and positive values of μ lead to a preferentially perpendicular or parallel arrangement, respectively. The fact that the sample contracts at the clearing point, in a direction parallel to the liquid crystal director indicates directly that the chain configuration must be extended in that direction in the nematic phase. In other words, the coupling parameter μ must have a positive value in this specific case. The precise value for μ will determine the extent of the shape change at the phase transition, since in the isotropic phase all orientational order is lost. If we assume that in the isotropic state, the configuration of the chains between the junction points is random, then the shape change in the direction parallel to the liquid crystalline director is a measure of the chain extension in the nematic phase due to the coupling of its configuration to the liquid crystalline ordering. The effective extension, α, obtained from the dimensions parallel to the liquid crystal director is 1.05.

$$U_b = P_2[f_a \mu S_a + (1 - f_a)\Gamma S_b] \tag{4}$$

We can estimate the order parameter for the polymer chains by utilising standard network models (i.e. $S_b = [\alpha^2 - \alpha^{-1}]/5N$, where N is the number of statistical chain segments between cross-link points [37]) since the departure of the chain from isotropy is small. There must be some uncertainty as to the nature of a statistical segment of the polymer backbone in the liquid crystal phase, but taking it to correspond to several monomer repeat units, then an extension of ~1.05 corresponds to an order parameter for the polymer chain of 0.002. Using the order parameter measured by the X-ray scattering of the undeformed sample, which is essentially due to the side-chains, we can deduce a ratio for the two order parameters S_b/S_a. Calculations based on a simple mean-field model [38] within the range of realistic values for μ yield Eq. (5) where the precise value for β depends upon the values for Γ and f_a, but the value falls in the range 0.9–1.1. This relationship is only valid when $\Gamma < 1$ and the cross terms are small [38].

$$\frac{S_b}{S_a} = \beta\mu \tag{5}$$

In essence, this is the regime when the temperature is above the ordering transition for the polymer chain, and therefore the chain orders paranematically. Since these are most realistic assumptions for this system, we may use this approach to obtain the value of the coupling coefficient; from these shape changes, $\mu \sim 0.004$.

The critical extension λ_c measured from the reorientation of the monodomain samples by a stress field can be taken to be the change in dimension required to alter the polymer backbone from an anisotropic arrangement (with the long axis perpendicular to the applied stress) to an isotropic one. As a consequence, this deformation should correspond closely to the shape change observed at the nematic–isotropic transition; clearly, this is not the case. Repeating the calculation for the value of 1.16 obtained at angles close to 90°, we obtain a value for μ of ca. 0.008, close to the values of 0.006 and 0.007 estimated from mechanical measurements of polydomain samples [39] and neutron scattering data [18], respectively. Although minor corrections are needed to account for the different temperatures of the experiments, we believe these to be small because the orientation parameters are relatively invariant in the temperature range of these experiments; consequently, the agreement between these latter approaches is encouraging. The data obtained from the shape change at the nematic–isotropic transition appears to show a significantly smaller level of backbone anisotropy, and therefore a smaller coupling constant. This may indicate some departure from the theoretical expectations. One particular problem in experiments of this type is the time lag between side-chain ordering and the response of the backbone [12,38], however, we have taken particular care to avoid kinetic complications in these measurements by allowing substantial times for equilibration to occur and by performing experiments at temperatures well above the glass transition temperature.

A further consideration, which could influence the shape change data is the possibility of residual global orientation in the isotropic phase; for example, were the backbone to retain an overall level of anisotropy of 2% above the nematic–isotropic transition temperature, then a simple calculation gives a coupling constant of ca. 0.006 based on the data presented in Fig. 3. The birefringence measurements shown in Fig. 4 confirm that there is some ordering in the isotropic phase. The questions remain both as to whether this is sufficient to account for the differences in the values of the chain anisotropy obtained through the three routes, and to the precise origin of this birefringence.

It is not easy to quantify the level of global orientation of either the mesogenic units or the skeletal units, on the basis of the birefringence measurements alone. However, a brief consideration of some related systems provides some understanding of the ordering processes present in this system. We can relate the measured birefringence Δn to the underlying molecular order parameter S through Eq. (6), where Δn^0 is the birefringence for a perfectly ordered system. The stress-induced birefringence of methyl acrylate networks has been studied by Saiz [40] and was found to be small and negative; we estimate on the basis of that data, the birefringence for a perfectly ordered polymer is $\Delta n^0 = -3.5\times 10^{-3}$. In contrast, birefringence levels in a wide range of liquid crystalline units have been measured and values are usually large and positive. Taking a typical value for a benzoate ester, $\Delta n \sim 0.15$ at $(T_{\mathrm{NI}} - 10)$ [26], we estimate that for a system with perfecting ordering, $\Delta n^0 \sim 0.3$. This suggests that it is quite possible that the level of birefringence for temperatures above the clearing temperature is dominated by the mesogenic side-groups and not the polymer backbone

$$\Delta n = \Delta n^0 S \tag{6}$$

We have previously shown for this family of side-chain liquid crystal polymers, that the magnitude of the coupling between the mesogenic groups and the polymer backbones is largely related to the conformational preferences of the chemical bonds in the coupling chain, the so-called 'hinge' effect [41]. As such, we do not expect the interactions between the side-groups and the polymer chain to significantly change at the clearing point. In particular, we anticipate that the sign of the coupling will remain positive for this particular polymer. As a consequence, it is clear that the positive value of birefringence arises from a limited level of ordering of the mesogenic units, simple scaling suggests order parameters in the range of 10^{-2}–10^{-3} in the temperature range studied above the clearing point. Similar levels of birefringence were observed by Schätzle et al. [42,43] for a methacrylate-based side-chain liquid crystalline elastomer extended with a strain of 5% in the isotropic phase.

The observation of pre-transitional nematic-like fluctuations in the isotropic phase of low molar mass liquid crystal systems is well established both from experiment and from theory [44,45]. Of course to observe such fluctuations, it is necessary to apply an external field, such as a magnetic field. The fact that we observe a low level of birefringence compatible with such fluctuations for the monodomain sample above the clearing temperature indicates directly that there is an aligning field present. In this case, the aligning field arises by virtue of the presence of order in the polymer network. This order must be a remnant of the order present during cross-linking. This conclusion is supported by the fact that no birefringence is observed above the clearing temperature for the liquid crystal elastomer sample prepared in the isotropic phase. It is interesting to note that the polydomain liquid crystal elastomer prepared in the nematic phase also shows birefringence above the clearing point. For this sample, there is no global extinction, but locally, over microscopic regions, the material exhibits similar temperature dependence of the birefringence as observed for the monodomain sample.

We can attribute the apparent differences in the backbone anisotropy derived from the different experimental approaches to the fact that above the clearing temperature, the orientational order of the polymer network is non-zero. We are certain that this is not due to non-equilibrium effects, since we have taken particular care to ensure that the samples were studied over substantial periods of time. de Gennes [1] was the first to propose that chains cross-linked in nematic and smectic phases would be able to attain isotropic conformations when the nematic and smectic fields were removed. This was in contrast to the predicted behaviour of a polymer chain cross-linked under cholesteric conditions would be unable to attain an isotropic conformation. Such expectations are based on the behaviour of ideal polymer networks. We attribute the retention in the isotropic phase of a component of the anisotropy of the polymer network induced during cross-linking in the nematic phase, to the non-ideal nature of the network.

In a recent development of the theoretical understanding of liquid crystalline elastomers, Verwey and Warner [31] have considered the fluctuations in the composition of polymer chains in a liquid crystalline elastomer. Such fluctuations can arise as a consequence of random copolymerisation and result in variations in the anisotropy of the polymer chains. Their model predicts a small level of chain anisotropy in the isotropic state for materials cross-linked in the nematic phase, and no anisotropy for materials cross-linked in the isotropic phase. Thus, the behaviour observed here fits well with this model, although a contribution to the backbone anisotropy in the isotropic phase from topological effects cannot be ruled out.

The presence of the network anisotropy in the isotropic or more correctly paranematic state has important implications for the observation of soft elasticity [8,29,46]. The fact that previous experiments, for example, on electric field induced shape changes [47–49] have not been able to observe the phenomena of soft elasticity, supports the view that the non-ideal behaviour of nematic networks is the norm. Furthermore, the presence of fluctuations in network anisotropy can provide an approach for understanding the different mechanically induced reorientation effects observed in nematic monodomains of acrylate and siloxane based elastomers [27,30,32].

6. Conclusion

The measurements described above show different methods of determining the level of anisotropy of the polymer backbone in a side-chain liquid crystal elastomer. Data obtained by stretching a monodomain sample perpendicular to the director provide values for backbone anisotropy, which agree rather closely with data obtained previously from neutron scattering experiments. In contrast, direct measurement of the sample dimensions, and in particular, changes which occur on the loss of nematic ordering at the nematic–isotropic transition temperature, give a rather smaller value for the level of backbone anisotropy and hence the coupling constant. This reduction in the apparent chain anisotropy is attributed to the retention of a small component of the chain anisotropy in the isotropic phase; essentially above the ‘clearing’ temperature the elastomer is in a weak paranematic state. This arises from non-ideal behaviour of the polymer network due to fluctuations in the initial chain anisotropies.

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