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P. M S Roberts [a] , G. R Mitchell [a] , F. J Davis [a] & J. A Pople [a]

[a] Polymer Science Centre, JJ Thomson Physical Laboratory, University of Reading, Reading, Berkshire, RG6 6AF, England

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MECHANICAL SWITCHING AND SOFT ELASTICITY IN LIQUID CRYSTAL ELASTOMERS

PHILIP M S ROBERTS, GEOFFREY R MITCHELL, FRED J DAVIS, JOHN A POPLE.
Polymer Science Centre, JJ Thomson Physical Laboratory, University of Reading, Reading, Berkshire, RG6 6AF, England

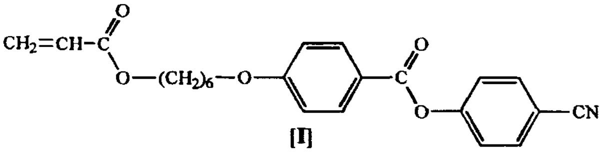
Abstract The application of a mechanical field is seen to cause a switching of the director orientation in a monodomain liquid crystal elastomer. This switching is most dramatic when the strain is applied normal, or nearly normal to the initial director as a sharp jump of 90° in orientation is seen. This molecular rearrangement is accompanied by a decrease in orientation parameter, $\langle P_2 \rangle$, during the rotation. Wide-angle x-ray scattering (WAXS) and optical microscopy studies have revealed a single director orientation throughout the switching process; broad optical-texture variations are observed after the director flip has occurred, although the sample remains optically clear throughout the process.

INTRODUCTION

The complex interactions between mesogenic side group and polymer backbone in a side-chain liquid crystal polymer force the backbone to adopt a locally anisotropic trajectory.[1] The introduction of chemical cross-links between chains effectively defines the state of lowest energy for the system and stabilises the molecular arrangement at the time of cross-linking.[2] When the cross-linking is performed on a system with a single director orientation, a so called monodomain, the equilibrium arrangement is a globally anisotropic network.[3] Monodomain liquid crystal elastomers have been prepared using both magnetic[4] and mechanical fields.[5] The presence of an anisotropic network allows the possibility of macroscopic shape changes around T_{NI} and, more interestingly, strain induced switching.[6,7] Bladon[8] and Warner[9] suggested the possibility of 'soft' deformation modes (for a geometry where a strain is applied at 90° to the initial director orientation); here deformation occurs at no cost to the free energy of the system, up to a characteristic threshold strain, whereupon there is a discontinuity in director orientation to allow alignment with the applied field. Preliminary experiments[6a] have confirmed this possibility. The interaction of curvature elasticity and network elasticity is central to this process and recently Kundler *et al*[7] have observed a slow rotation of the director, and the formation of complicated striped domains for a siloxane based elastomer subject to such a deformation. More recent theory, taking into account non-uniform deformations and local shear[10,11], has been able to explain these results. In this contribution we explore the response of an acrylate based elastomer to a mechanical field using in-situ WAXS and polarised optical microscopy.

MATERIALS

The elastomers were prepared from a side-chain liquid crystal copolymer based on [I] containing 6 mole % of hydroxyethyl acrylate to provide sites for subsequent cross-linking.[10] The cross-linking procedures and monodomain formation are described in more detail elsewhere.[12, 13]



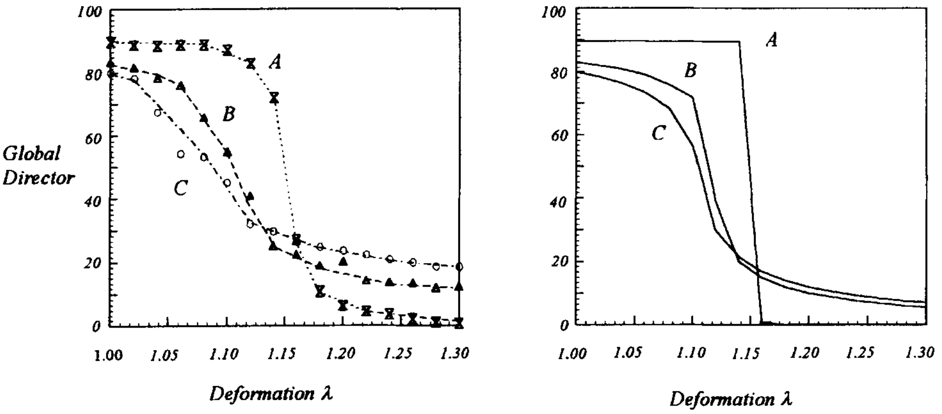
[I]

MECHANICAL SWITCHING

Mechanical fields effects are observed in liquid crystal elastomers, in contrast to their low molar mass counterparts, due to the presence of a permanent network. Perturbations of the backbone will influence the side-chains due to their coupling. For example, mechanical strains of ≈ 10% produce global orientation in the side-groups for a side-chain liquid crystal polydomain elastomer; typically producing a global orientation parameter of ≈ 0.6.[1] Detailed interpretation of such effects is made simpler through the use of elastomers with a single director orientation.

Bladon[8] considered the effects of application of a mechanical field, at some arbitrary angle, θ, to the initial director orientation, and showed that at $\theta=90^\circ$ there exists a critical extension given by $\lambda_c=(l^0_{//}/l^0_{\perp})^{1/3}$, ($l^0_{//}$ and $l^0_{\perp}$ refer to polymer step lengths parallel and perpendicular to the director orientation respectively), at which point the director is predicted to jump by 90° from the initial orientation to align with the applied field. This director jump has been observed experimentally in previous studies in an acrylate based elastomer.[6a] Recently Kundler *et al*[7] have observed different behaviour for siloxane based elastomers, which has been explained by extensions to the theory by Verwey *et al.*[10,11] Here a slow director reorientation is seen together with the development of optically opaque textures which correspond to microscopic defects of alternate orientation.

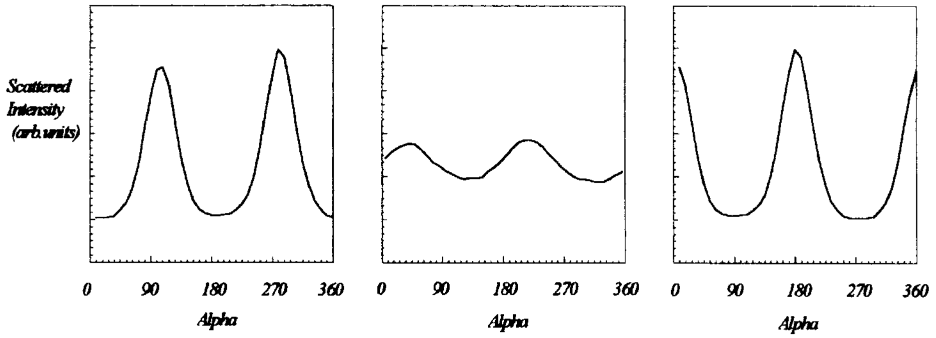
Using the combined techniques of in-situ time-resolved WAXS and optical microscopy we have performed mechanical strain experiments to test the uniformity of response of the acrylate system. Samples approximately 8 x 3 x 0.1 mm were deformed in a miniature tensiometer equipped with an oven at a strain rate of $0.1 s^{-1}$ at 80°C. The response time to an initial strain was typically 20 minutes although samples were left for 1 hour between steps to ensure equilibrium. On removal of the strain the original director orientation was recovered but over a much longer time scale, typically 200mins.



(a) (b)

Figure 1 (a) The response of the director angle vs. deformation for a monodomain elastomer extended at 89° (curve A), 83° (curve B) and 80° (curve C) to the initial director angle, (b) Shows a fit to the model of Bladon.

Figure 1 (a) shows data obtained using in-situ WAXS for a monodomain liquid crystal elastomer extended at 89°, 83° and 80° to the initial director orientation. **Figure 2** shows the azimuthal distribution of intensity at Q = 1.4 A^{-1}. It is clear that there is rotation of a single director. There is no evidence for the splitting or distortion of the peaks which would indicate the onset of a more complicated reorientation process as reported by Kundler[7] and Beatie.[14] **Figure 1 (b)** shows a fit to the theoretical model of Bladon. There is quantitative correlation between the two plots but there are considerable deviations, especially at deformations corresponding to the director jump. The curves indicate a critical strain $\lambda_c \approx 1.15$ which would correspond to the point, if the strain was performed at exactly 90°, at which the network would be truly isotropic and thus impart zero order to the side groups. The critical strain is related to the extent of anisotropy of the network and is found to be in good agreement with previous neutron scattering experiments[1] and other measurements.[15]



(a) (b) (c)

Figure 2 Representation of WAXS pattern obtained during deformation (at 89° to initial director) (a) $\lambda = 1.00$, (b) $\lambda = 1.15$, (c) $\lambda = 1.30$.

The director reorientation was accompanied by a characteristic decrease in orientation parameter, $<P_2>$, during the rotation, this subsequently increased on further strain as can be seen for the curves in **Figure 2**. **Figure 3** shows the variation in orientation parameter as a function of deformation for a sample strained at 89° to the initial orientation, here $<P_2>$ was a minimum at 16% extension. For samples deformed at 83° and 80° $<P_2>$ was a minimum at 12% and 8% extension respectively, although the minima were not so well defined.

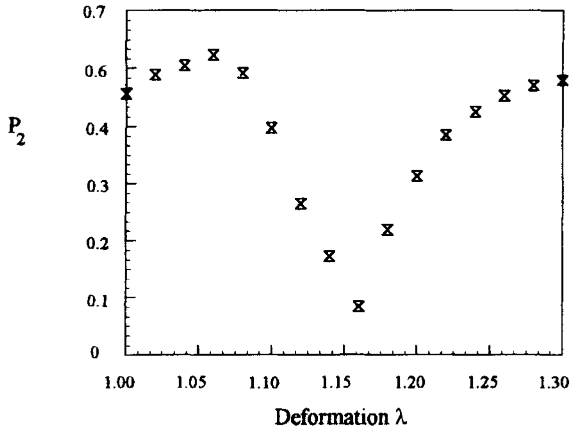


Figure 3 Variation in orientation parameter, $<P_2>$, for an elastomer deformed at 89° to the initial director axis.

We have explored the effects of the change in orientation parameter in more detail through the use of polarised optical microscopy, where the director orientation was mapped out over the full extent of the sample by the extinction axis, as the crossed polarisers were rotated about the sample. During the deformation the sample remained optically clear when viewed with unpolarised light as observed in the initial experiments[6a], and the pattern of reorientation with strain followed that shown in **Figure 1** over the central region, in that there was always a single director orientation. Over the sample as a whole there was some spread about this single director orientation reflecting the distribution of strains in the sample and the departure from a single uniaxial geometry (about 5°). After the director jump had occurred, for samples deformed at 90° to the initial director orientation, some structure developed on the scale of 300 μm but this did not correspond to abrupt director orientation changes, or to the generation of defects. The fact that the sample remained optically clear is in marked contrast with the development of optically opaque texture as seen by Kundler *et al.*[7] Moreover siloxane elastomers do not show a jump in the director orientation.

The initial model of Bladon was based on a constant order parameter, which is clearly not completely the case, but proves to be an appropriate model for the acrylate systems studied here.

SUMMARY

We have described experiments on monodomain elastomers in which a strain was applied at angles approaching 90° to the initial director orientation which led to a simple jump in the director orientation in agreement with the initial theory of Bladon.[8] WAXS revealed a decrease in orientation parameter, $<P_2>$, and optical microscopy revealed a single director orientation throughout the full extent of the sample during reorientation.

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