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Memory Effects in Monodomain Liquid Crystal Elastomers Produced in Magnetic Fields

P. M S Roberts [a] , G. R Mitchell [a] & F. J Davis [a]
[a] Polymer Science Centre, JJ Thompson Physical Laboratory, University of Reading, Reading, Berkshire, RG6 6AF, England

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MEMORY EFFECTS IN MONODOMAIN LIQUID CRYSTAL ELASTOMERS PRODUCED IN MAGNETIC FIELDS

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

Abstract Magnetic fields have been used to produce macroscopically oriented side-chain liquid crystal polymer films which were subsequently cross-linked to form monodomain liquid crystal elastomers. The orientation process is shown to be complete in minutes, in a modest magnetic field while the relatively slow cross-linking reaction is complete in around 60 hours. Films thus obtained show a memory of the state of order at cross-linking even after prolonged annealing in the isotropic phase. We find that the uniform memory is lost when the elastomer contains > 50% free chains by incorporating a controlled percentage of uncross-linkable homopolymer. We have thus lowered the effective modulus and looked in more detail at the coupling between mesogen and polymer backbone.

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INTRODUCTION

In side-chain liquid crystal polymer systems[1] any manifestations of the interaction between the polymer backbone and the mesogenic side-chain will be transmitted to the macroscopic level if chemical cross-links are introduced between polymer backbones to form liquid crystal elastomers. Such behaviour was predicted by de Gennes[2] and subsequently a number of phenomena have been observed experimentally including electrically-induced shape changes[3,4], strain-induced switching[5,6] and memory effects[7,8]. The effect of cross-linking is to provide a bias towards the backbone configuration present at the time of network formation. Any distortion of this configuration is opposed by the elasticity of the network; consequently, such materials display a memory of both backbone anisotropy and (by virtue of coupling) side-chain director orientation. In this contribution we describe a route to production of monodomain liquid crystal elastomers in which a magnetic field was used to produce a single director

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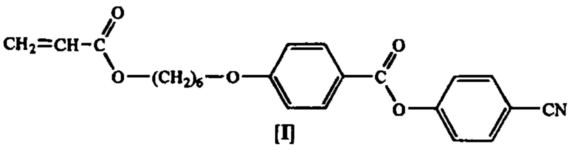
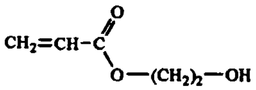
orientation prior to cross-linking. In particular the relationship between the level of cross-linking and the quality of memory was probed by changing the gel-sol composition of the system through the incorporation of an uncross-linkable but chemically similar polymer.

MATERIALS

In this study we have made exclusive use of a side-chain liquid crystal copolymer based on [I] containing 6 mole % of [II] to provide sites for subsequent cross-linking.[9]



[I]



[II]

Elastomers were produced by casting a small amount (~15mg) of copolymer mixed with a small excess cross-linking agent (di-isocyanatohexane) from dichloromethane onto a clean Kapton sheet followed by annealing the mixture at the required temperature until cross-linking was complete. DSC, optical microscopy and wide angle x-ray measurements indicated a nematic phase above the glass transition; on subsequent heating the samples became isotropic.[10]

MONODOMAIN FORMATION

Prior to cross-linking it was necessary to ensure a single director orientation for the mesogenic side-chains, and that the polymer backbone should adopt the required equilibrium conformation commensurate with this orientation. Clearly for monodomain formation, the orientation and the cross-linking must occur on very different times scales if the procedure is to be successful. To confirm this, the global orientation of the side groups was monitored using birefringence and wide angle x-ray measurements.

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Orientation can be induced *via* mechanical, electrical and magnetic fields;[11] for practical reasons of film preparation magnetic fields were used for these investigations. It was found that the orientation of the mesogens into a single domain was complete in around 15 minutes using a field of 2.1 Tesla. Previous experiments[12] have shown that the backbone rearrangement may lag behind the side chain reorganisation, but not sufficiently to cause a problem. The use of plasticisers (in particular a low molecular-weight liquid crystal 'E44') to reduce this time-lag has met with some success. Cross-linking was monitored from the growth of the gel content of the sample during the reaction, and from careful Infra-red measurements (using the intensity of the 'OH' vibration as a probe). Both methods showed the reaction to be complete in around 60 hours. Thus the relaxation of the polymer backbone due to orientation with the applied magnetic field was complete before substantial cross-linking had occurred (**Figure 1**).

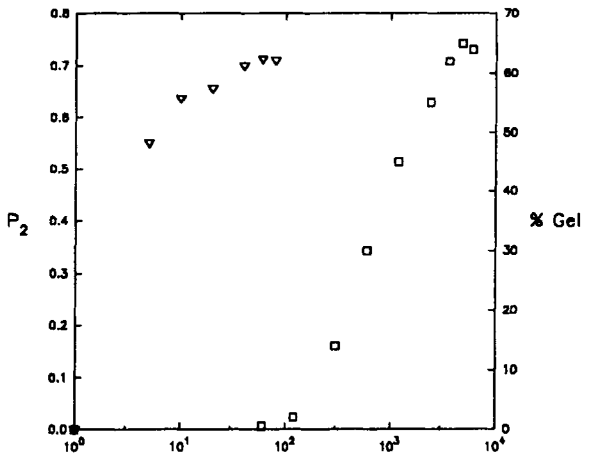

Figure 1 Increase in macroscopic order parameter (□) is complete in ~15 minutes while increase in gel fraction (Δ) is complete in ~ 60 hours.

The films obtained were optically uniform, transparent, and showed the expected highly directional birefringence. WAXS revealed diffuse arcs at $Q \sim 1.4\ \text{Å}^{-1}$ consistent with an aligned nematic phase.[4]

The major advantage of using a magnetic field to produce the monodomain lies in the ability to produce director orientation in any direction with respect to the surface of

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the film. In future studies it is intended to investigate the influence of mechanical fields on a range of different alignment geometries; in particular, parallel and perpendicular alignment relative to the films' surface will be compared (both arrangements show a good memory effect).

MEMORY EFFECT

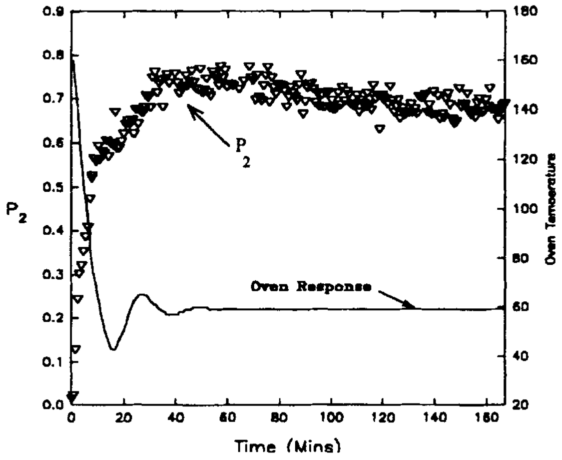

Figure 2 Plot showing timescale of recovery of order for an elastomer cooled to the nematic phase after being annealed in the isotropic phase for 5 hours.

The elasticity associated with simple rubbers arises as a result of an entropic drive towards the isotropic coil which was present at the time of cross-linking[13]. For liquid crystal elastomers the backbone adopts an anisotropic trajectory. On cooling such a sample from the isotropic phase in the absence of a magnetic field the anisotropic coil now forces the side-chains to align into a single domain. Any change in the level of order or director orientation would produce distortions in the network causing a departure from the state of lowest energy defined at the time of cross-linking. **Figure 2** shows a plot of the orientation parameter, $<P_2>$, for a sample which has been left at a temperature above T_{NI} for 5 hours and subsequently cooled to the nematic phase. Both the order and director orientation are recovered in minutes.

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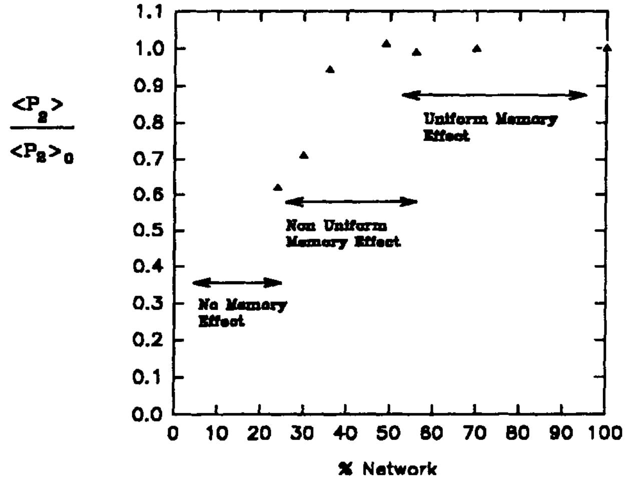

Figure 3 Ratio of recovered, $<P_2>$, to initial $<P_2>_0$ order, after prolonged annealing above T_{NI} showing uniform stable monodomain structures down to 50% network.

The introduction of a known amount of uncross-linkable homopolymer of monomer [I] should act as a swellant and reduce the effective modulus of the network. The absence of cross-links means that such chains will have no preferred orientation in relation to the network and in the monodomain elastomer will act in direct competition with the anisotropic network. At low concentrations they will be expected to conform to the trajectories of the bulk network and indeed it was found that up to 50% w/w could be added without disrupting the monodomain structure. As can be seen from **Figure 3**, these samples showed an orientation comparable to the aligned polymer and uniform extinction between crossed polarisers. Between 30% and 50% gel the network was no longer effective enough to recover the fully extended trajectory and consequently, the extent of order recovered was found to be diminished. Such samples did not appear uniform by microscopy although the initial director and shape of the elastomer were retained. Below 30% gel there was no memory of order, director or shape even when the swellant was removed suggesting inadequate network formation. This memory does not arise from polymer kinetics causing a very slow relaxation to an unoriented state, indeed, the structure is recovered after annealing above T_{NI} for many days. The uncross-linked copolymer never recovers orientation even after only a few seconds in the isotropic phase. Kinetic effects were seen in the lightly cross-linked mixtures where a uniform memory was observed for a sample containing only 30% gel when annealed above T_{NI} for only a few minutes, here entanglements will produce a temporary network and thus, large relaxation times. On further annealing the level of order was seen to decrease.

SUMMARY

We have described a reproducible route to production of monodomain liquid crystal elastomers and have explored the consequences of the strong coupling between side chain and network. The monodomains produced displayed a complete and permanent memory of both the backbone and side chain orientation present at cross-linking due to this very coupling. The network could support up to 50% soluble uncross-linked polymer before the uniform memory was lost due to the competing influences of sol and anisotropic gel configurations.

ACKNOWLEDGEMENTS

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