

# Imprinting chiral structures on liquid crystalline elastomers

Craig D. Hasson, Frederick J. Davis and Geoffrey R. Mitchell

Polymer Science Centre, University of Reading, Whiteknights, Reading, UK RG6 6AF.  
E-mail: g.r.mitchell@reading.ac.uk

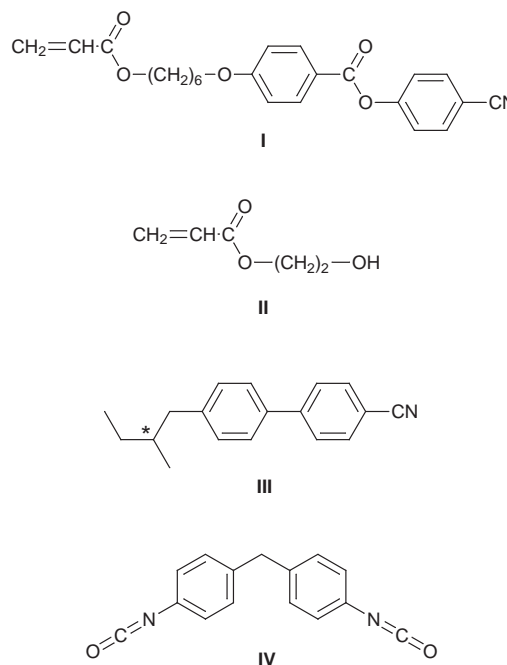
Received (in Cambridge, UK) 28th July 1998, Accepted 13th October 1998

**Cross-linking achiral liquid crystalline polymers in the presence of a removable low molecular weight chiral mesogen produces a liquid crystalline elastomer in which a chiral structure has been imprinted.**

In 1969 de Gennes published a paper speculating on the properties of a polymer chain lightly cross-linked in a liquid crystalline phase.<sup>1</sup> Using symmetry arguments, he showed that a chiral nematic would give rise to a permanent chirality of the polymer network. The essentials of de Gennes ideas<sup>2</sup> and other theoretical scientists<sup>3,4</sup> concerning nematic liquid crystalline elastomers have been confirmed experimentally,<sup>5,6</sup> however, we believe de Gennes's theory has remained essentially untested to date, probably because of the difficulty of incorporating a polymer backbone into a liquid crystalline phase. Some early work by Tsutsui *et al.*<sup>7,8</sup> attempted to resolve this issue through cross-linking an acrylate polymer in the presence of poly(benzyl-L-glutamate), however it is not clear that this system involved the types of mesogenic interaction originally envisaged by de Gennes. This issue is clearly of some importance in view of the volume of work involving cross-linking in a liquid crystalline solvent.<sup>9</sup> Here we show how low levels of cross-linking can be used to imprint a memory of a chiral mesophase into an elastomer with no imbalance in localised chiral centres.

Scheme 1 shows the principal features of our experiment. An achiral liquid crystalline polymer containing cross-linking sites was mixed with a chiral liquid crystal. The material was then cross-linked in the chiral nematic phase and finally the chiral liquid crystal was removed. Any chiral behaviour would then reflect a memory of the orientation imposed on the sample at the time of cross-linking in the same way that a magnetic<sup>10</sup> or mechanical field<sup>11</sup> imposes a permanent macroscopic order on the sample.

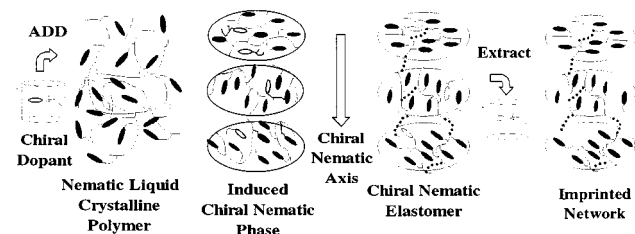
The system used was chosen to give a cholesteric phase with a helical pitch such that the material exhibited the well-known property of selective reflectivity in the visible portion of the electromagnetic spectra.<sup>12</sup> To this end the 4-cyanobenzoate containing acrylate **I**<sup>13</sup> was copolymerised with hydroxyethyl acrylate **II** (6 mol%, introduced to provide sites for cross-linking). This random atactic copolymer exhibited a nematic phase with a nematic-isotropic transition of 128 °C. Solutions were prepared in CH<sub>2</sub>Cl<sub>2</sub> (dried over alumina) of this polymer and the chiral cyanobiphenyl **III** (available from Merck as CB15) and films were cast from these solutions onto glass slides



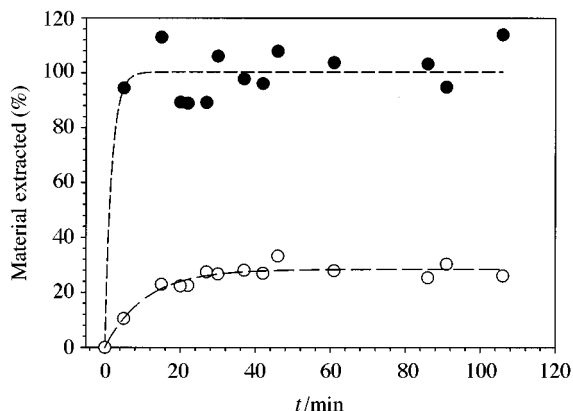
coated with a rubbed film of polyimide. The composition range over which a chiral nematic phase was formed was then determined. It was found that at compositions below *ca.* 60 mol% CB15 a chiral nematic phase could be observed. At lower compositions between *ca.* 20 and 35% CB15 films of the mixture showed selective reflection of visible light. For example, the 30% sample showed a selective reflection at 730 nm at 50 °C and it is this composition which will be used for the subsequent studies. Further films were cast containing the polymer, CB15 and a sufficient quantity of the diisocyanate **IV** to react with all the hydroxy units in the polymer. The solvent was removed at room temperature and the film allowed to dry overnight before heating slowly (2 °C min<sup>-1</sup>) to the required cross-linking temperature (in this example 50 °C). The sample was held at this temperature for 1 h, whereupon a polyimide sheet was placed on the surface, and 12.5 μm polyimide spacers were used to define the thickness. The material was then cross-linked for 16 days at 50 °C after which time it was found to consist of 72% gel by mass, in line with expectations based on the polydispersity of the sample.<sup>14</sup> The level of cross-linking was light, ~1mol% of the monomer units.

A portion of the elastomer produced from the above procedure was retained for further study, and the remainder of the sample was treated with refluxing acetone to remove both the chiral dopant and any soluble polymer. The extraction process was monitored by UV-visible spectroscopy and as Fig. 1 shows complete removal of both components was achieved after *ca.* 40 min.

The phase behaviour of the materials (*i.e.* mixture, cross-linked elastomer with dopant and cross-linked elastomer with dopant removed) was examined by optical microscopy and UV-visible spectroscopy to probe the pitch of any chiral ordering within the samples. The mixture and the elastomer samples

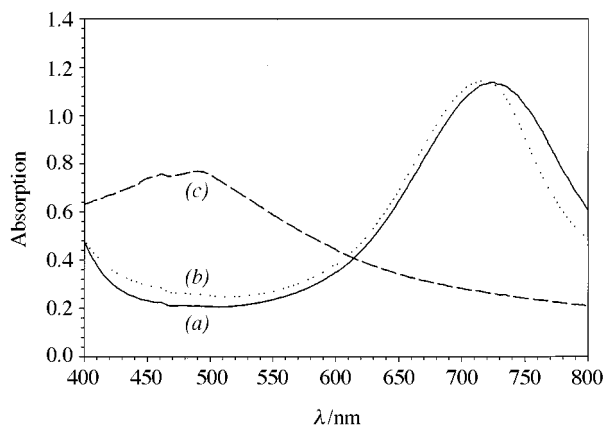


**Scheme 1** Description of procedure used to imprint a chiral structure onto a liquid crystalline elastomer: a chiral dopant is added to produce a chiral nematic phase, the polymer is cross-linked and finally the dopant is removed.



**Fig. 1** Plot of the mass of the extracted material (expressed as a mass fraction relative to the initial composition) as a function of the extraction time in refluxing acetone: (●) CB15 and (○) copolymer. The solid lines serve as guides.

cross-linked at 50 °C were visibly coloured, and their absorption spectra are shown in Fig. 2. Clearly, all three samples exhibited a cholesteric reflection, and by implication a chiral nematic phase. In the case of the initial uncross-linked mixture and the cross-linked material in which the dopant was retained, the maximum absorption ( $\lambda_{\text{max}}$ ) was at 730 nm at 50 °C, although the elastomer showed a much smaller variation of  $\lambda_{\text{max}}$  with temperature. Both these materials could be heated reversibly to the isotropic phase, but both passed through a biphasic region on heating in which nematic polymer coexisted with isotropic dopant. For the sample in which the dopant had been removed the maxima in the absorption spectrum moved to a much shorter wavelength, namely 500 nm at 50 °C (if this change were



**Fig. 2** Absorption spectra obtained from thin films of the liquid crystalline polymers and elastomers studied here: (a) mixture, (b) elastomer and (c) imprinted network. The peaks arise from selective reflection of visible light from the chiral material and are not observed for samples held at temperatures above the clearing point of the polymer.

simply due to the presence of the dopant in lower concentrations a shift to higher wavelengths would be expected). Initial measurements suggest that the change in  $\lambda_{\text{max}}$  is related in a proportional manner to the change in volume of the sample arising from removal of both dopant and the sol fraction. Interestingly,  $\lambda_{\text{max}}$  for this sample remained invariant with temperature until the material became isotropic at 128 °C. On cooling from the isotropic the chiral nematic phase reappeared and an identical absorption spectrum to that initially observed was obtained.

We have shown that cross-linking an achiral side-chain liquid crystalline polymer in an induced chiral nematic phase results in material which retains a memory of the chirality upon removal of chiral dopant, by virtue of the orientation imposed on the mesogenic side-groups by the chiral nematic phase, and the coupling between the mesogenic side-groups and the polymer backbone. This is a soft imprinting and arises from subtle molecular interactions in contrast to the properties of rigid highly cross-linked networks prepared through photopolymerisation of multifunctional monomers.<sup>9</sup> We believe firstly, these experiments confirm the theory outlined by de Gennes; secondly, this represents a novel route to imprinted materials, not least because of the enhanced behaviour arising from the relatively low levels of cross-linking (for example, they will readily uptake solvent and are not glassy); thirdly this represents a route to materials with new properties which merit further exploration.

This work is supported by the EPSRC. We thank Dr U. Singh of the University of the West Indies for discussions and Merck R&D UK for supplying the chiral dopant CB15.

## Notes and references

- 1 P. G. de Gennes, *Phys. Lett.*, 1969, **28A**, 11.
- 2 P. G. de Gennes, *Compt. Rend. Acad. Sci.*, 1975, **B281**, 101.
- 3 M. Warner, in *Side-Chain Liquid Crystal Polymers*, ed C. B. McArdle, Blackie, New York, 1989.
- 4 M. Warner and E. M. Terentjev, *Progr. Polym. Sci.*, 1996, **21**, 853.
- 5 G. R. Mitchell, P. M. S. Roberts, K. H. Ahn, F. J. Davis, C. D. Hasson, H. Hirschmann and J. A. Pople, *Macromol. Symp.*, 1997, **117**, 21.
- 6 J. Schatzle, W. Kaufold and H. Finkelmann, *Makromol. Chem.*, 1989, **190**, 3269; 1991, **192**, 1235.
- 7 T. Tsutsui, R. Tanaka and T. Tanaka, *J. Polym. Sci., Polym. Lett. Ed.*, 1979, **17**, 511.
- 8 T. Tsutsui and R. Tanaka, *Polymer*, 1981, **22**, 117.
- 9 See for example, S. M. Kelly, *J. Mater. Chem.*, 1995, **5**, 2047.
- 10 C. H. Legge, F. J. Davis and G. R. Mitchell, *J. Phys. II*, 1991, **1**, 1253.
- 11 J. Küpfer and H. Finkelmann, *Makromol. Chem., Rapid Commun.*, 1991, **12**, 717.
- 12 P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, Clarendon Press, Oxford, 1993, ch. 3.
- 13 F. J. Davis, A. Gilbert, J. Mann and G. R. Mitchell, *J. Polym. Sci.: Polym. Chem.*, 1990, **28**, 1455.
- 14 P. M. S. Roberts, G. R. Mitchell and F. J. Davis, *Mol. Cryst. Liq. Cryst., Sect. A*, 1997, **299**, 223.

Communication 8/05891A