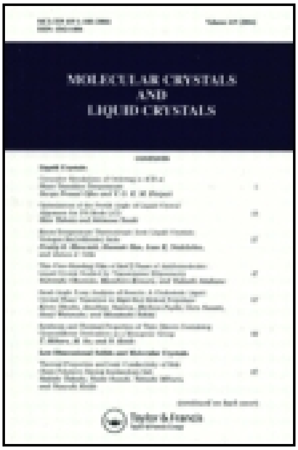

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Imprinting Chiral Structure on Liquid Crystalline Elastomers

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Imprinting Chiral Structure on Liquid Crystalline Elastomers

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Networks have been prepared which exhibit a chiral nematic phase without the presence of a net overall local chirality. These materials were formed by cross-linking a nematic achiral side chain polymer in a N* phase induced through the addition of chiral dopant. The dopant was then totally removed and the resultant elastomer continued to show an N* phase. The phase was monitored by selective reflection and circular dichroism and was recovered on cooling from the isotropic phase. The pitch of the N* helix was observed to have decreased to 70% of its initial value. In contrast to the behaviour of a mixture of the polymer and dopant, the imprinted network exhibited a marked reduction in the temperature dependence of the pitch of the N* phase.

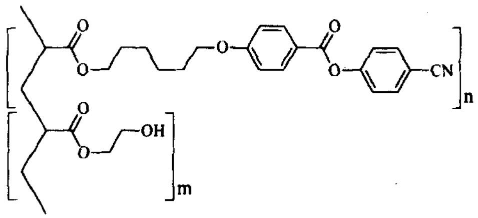
Keywords: chiral nematic elastomers; chiral memory; imprinted networks

INTRODUCTION

Polymer networks exhibit a memory function which relates to the configuration of the polymer chains at the point of cross-linking. Distortions away from this initial configuration result in energy penalties which are largely entropic in origin. We have shown how this memory function can be used to prepare stable nematic monodomain elastomers by cross-linking a side-chain liquid crystal polymer system held in a uniform magnetic field [1,2]. The stable monodomain arises due to a combination of the memory function and coupling between the order of the mesogenic units and the polymer chains. Both properties are required. We have shown recently how this concept may be extended to chiral nematic systems [3]. We have detailed the preparation of chiral nematic (N*) elastomers from achiral side-chain liquid crystal polymers by means of cross-linking whilst in an N* phase induced by a low molecular weight chiral dopant. On removal of the dopant the N* phase structure is retained by the elastomer. *In this paper we report on the optical properties of these novel materials.*

EXPERIMENTAL

The side-chain system used in this work is a random atactic copolymer, I, of a mesogenic monomer and 6mol% hydroxyethyl acrylate [4]. This copolymer (CBZ6) exhibits a nematic phase with the N-I phase transition at 128°C.



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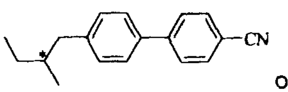

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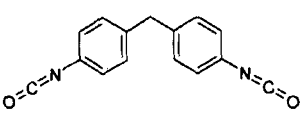

III

Mixtures of the copolymer CBZ6, and the chiral dopant CB15 Merck (II) were prepared using a co-solvent process. Each component (10mg) was dissolved in dry dichloromethane (10ml) and portions of these solutions were mixed to yield a solution with the desired molar ratio of the two components. The solution was concentrated by evaporation and then cast as a film on rubbed polyimide coated glass. These cast films were left for 1 hour to allow the solvent to evaporate before heating to 50C and applying a glass cover slide.

Elastomers were prepared from solutions containing I & II and the cross-linking agent, 4,4'-methylene-bis-phenylisocyanate (III) in dichloromethane (1mg ml^{-1}) in sufficient quantity to react with all of the hydroxy groups. The solution was concentrated by evaporation before casting as a film on to rubbed polyimide-coated glass. The cast film was allowed to dry overnight in a dessicator before heating at 2Cmin^{-1} to the cross-linking temperature of 60C. After one hour a polyimide sheet was placed on the surface of the sample. 12.5 μm polyimide spacers were used to define the sample thickness. The material was then cross-linked for 16 days. The chiral dopant, and soluble polymer fraction were removed from the elastomers by extraction with refluxing acetone. The composition of the solution was evaluated continuously using UV spectroscopy to obtain the mass of both the CB15 and the uncrosslinked polymer extracted. The samples (mixtures, elastomers and elastomers with the dopant removed) were examined using polarised light microscopy, UV/visible absorption and circular dichroism (CD) spectroscopy. The circular dichroism was measured using a single-channel spectrometer based on an Instruments S. A. photodiode array spectrograph, together with a white light source, broadband linear polariser, a rotatable pair of Fresnel rhombs and a single Fresnel rhomb as a source of left and right circularly polarised light over the range 400 to 800 nm[5].

RESULTS

Figure 1 shows a phase diagram for the mixtures of CB15 and CBZ6. The chiral nematic phase of the mixtures could be identified by the visual observation of the selective reflection of light and confirmed using CD spectroscopy as shown in Figure 2(a). The position of the maximum in the CD is proportional to the pitch, P_0 of the N* phase with $\lambda_{max} = \bar{n}P_0$, where $\bar{n}$ is the average refractive index . Measurements of CD on mixtures with differing compositions show that the pitch is inversely related to the fraction of chiral dopant present within the mixture. The elastomer was prepared within the N* single-phase region with a composition of 30mol% CB15 at 60C.

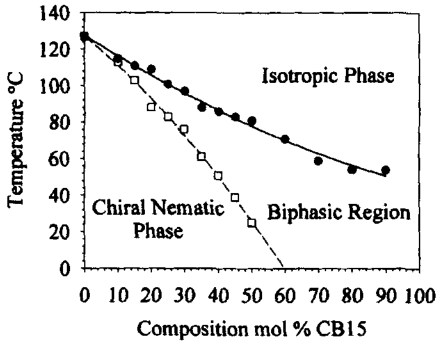

FIGURE 1 Phase diagram for mixtures of CBZ6 and CB15

After the cross-linking reaction was complete (16 days) the elastomer had a gel content of 72% by mass of the polymeric component. This is in line with expectations based on the polydispersity of the initial polymer [2]. The elastomer displayed an N* phase with an enantiotropic N*-I transition at 104C.

The N* phase was confirmed by the CD spectrum shown in Figure 2(b). Consideration of the positions of the maxima in Figure 2(a,b) shows that the pitch of the elastomer is similar to the uncrosslinked mixture from which it was prepared. The chiral dopant extraction procedure was applied to part of the elastomer sample. When spectroscopic analysis of the extract showed that all of the chiral dopant had been removed, the elastomer was removed from the refluxing acetone and residual solvent evaporated at room temperature. This elastomer sample, without any chiral dopant, exhibited an N* phase with an enantiotropic N*-I transition at 128C, a value similar to nematic elastomers of CBZ6 [6]. The sample showed selective reflection of light which was clearly visible to the naked eye. The chiral nature of the structure of this material was confirmed by the CD spectra shown in Figure 2(c). Clearly the pitch for the imprinted network is significantly shorter than that of the elastomer containing the chiral dopant (Figure 2(b)). At a qualitative level the shorter pitch can be attributed to a change in volume resulting from the removal of soluble material from the elastomer. If the chirality in the imprinted elastomer resulted from a

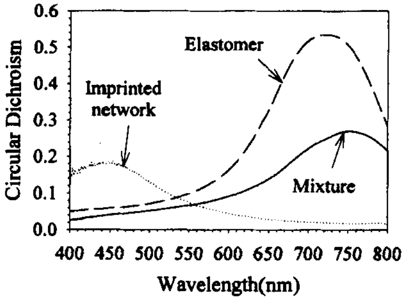

FIGURE 2 Circular dichroism ((Abs$_L$-Abs$_R$)/(Abs$_L$ + Abs$_R$)) as a function of wavelength at 60C for (a) mixture, (b) elastomer, (c) imprinted network

small amount of residual dopant we would expect a larger pitch than observed in the initial mixture as reducing the concentration of dopant increases the pitch.

It is emphasised that the memory of the N* phase is not kinetic in origin. The dopant extraction process results in considerable swelling of the sample which serves to eliminate any kinetic memory of the N* phase of the mixtures. The imprinted network exhibits an isotropic phase above the clearing temperature and recovers the N* phase on cooling from the isotropic phase. The presence of the helical director arrangement is visible to the naked eye through the selective reflection of light. The basis of the chiral memory effect is similar to that observed in nematic monodomain elastomers. The chiral dopant in the mixtures gives rise to a helical arrangement of the local director. Due to the coupling between the mesogenic units and the polymer backbone, the principal axis of the local radius of gyration tensor of the polymer chain also exhibits a helical arrangement. Cross-linking stabilises such an arrangement. Removal of the chiral dopant does not influence the spatial arrangements of the network except via the volume reduction. As a consequence of the helical arrangement of the network anisotropy, coupling results in a helical arrangement of the local nematic director. This gives rise to the chirality even though there is no net imbalance of the populations of any localised chiral centres.

Figure 3 shows the temperature dependence of the pitch, expressed as the wavelength at which the maximum circular dichroism is observed, for the mixture, the elastomer and the imprinted elastomer. The mixture shows the expected strong temperature dependence of the pitch as the N*-I transition is approached. The elastomer shows a greatly reduced temperature variation in λ_{max} and clearly some of this variation could be accounted for through the temperature variation of the average refractive index. The curves for the pitch variation in the mixture and the elastomer cross at the temperature at which the network was formed. The pitch of the imprinted network shows almost no variation with temperature. This invariance arises from the fact that the pitch of this material is defined by the network rather than the localised asymmetric interactions between dopant molecules and the mesogenic units.

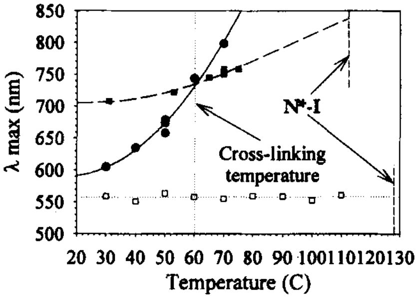

FIGURE 3 A plot of the wavelength of the maxima in CD of the mixture (●), elastomer (■) and imprinted network (□) as a function of temperature.

The results obtained in this work confirm the proposal of de Gennes [7,8], made some thirty years ago, that on the basis of a topological argument, any network which was formed within a chiral nematic phase would exhibit a memory of this phase. After de Gennes proposal, Tsutsui *et al* [9,10] presented limited evidence for such phenomena based on a complicated system of interpenetrating networks prepared within a lyotropic chiral matrix. In this work we have exploited the coupling between the mesogenic units and the polymer chains to transmit the induced chirality to the network. This provides a simple and direct route to realising these novel materials.

SUMMARY

Liquid crystalline elastomers have been prepared and imprinted with the structure of an induced N* phase. This chirality is not caused by the presence of defined molecular chiral centres, as with the dopant, but rather it is a result of a macroscopic chiral structure within the network. The induction and preservation of this structure is a result of coupling between the liquid crystalline order and the polymer backbone and provides a possible route to further novel materials.

Acknowledgements

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