Side-chain liquid crystalline elastomers: the relationship between the orientational ordering of the polymer backbone and the length of the coupling chain

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Abstract

The influence of cross-linking on the phase behaviour of a series of side-chain liquid crystalline elastomers has been studied. For samples cross-linked in the temperature range corresponding to the nematic phase, the phase transition was shifted compared to that observed when an identical sample was cross-linked in the isotropic phase. This shift represented a stabilisation of the nematic phase in the former case, in line with theoretical expectations. By utilising a novel, slow cross-linking method, which allows the polymer backbone to take up an equilibrium conformation prior to network formation, it proved possible to monitor the shifts in phase transition temperature as a function of the length of the methylene chain coupling the mesogenic units to the polymer backbone. The results obtained are related to the backbone anisotropy and indicate that the level of orientational order of the polymer in the nematic phase backbone increases with a reduction in the length of the coupling chain. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

For a side-chain liquid crystalline polymer orientation of the mesogenic side-units is accompanied by reorientation of the polymer backbone. Such orientation may be at a local microscopic level, as is the case for a polydomain sample or (in the presence of a suitable aligning field) global, as is the case for a monodomain sample. The level of order in the polymer backbone is determined by both the liquid crystal field and the constraints imposed by the attachment linkage. The nature and extent of this coupling of the long range orientational order of the mesogenic units to the conformation of the polymer backbone was explored both theoretically [1,2] and experimentally [3,4]. The ordering of the polymer chain can be observed by making direct measurements through small-angle neutron scattering (SANS) studies of mixtures of deuterium and hydrogen labelled polymer chains, [5–7], or indirectly through the observation of novel phenomena such as macroscopic shape changes of monodomain elastomers at the clearing temperature [8], or mechanically induced phase transitions [9].

The coupling of the order of the mesogenic side-groups to the polymer backbone trajectory arises both from their nematic-like interactions and from the restrictions resulting from the chemical nature of the coupling chain which joins the two components. Previous experiments have suggested that the nature of the coupling chain is the dominant component of such interactions [10–12], and hence the natural expectation is for the level of coupling to increase as this chain is shortened in length. To date, no systematic measurements of the influence of the chemical configuration of the coupling chain on the magnitude of coupling were made, not least because of the experimental difficulties inherent in such measurements.

Warner et al. have proposed that the phase behaviour of a cross-linked liquid crystal polymer system depends critically on the state of order at the point of cross-linking [13] and this has been confirmed experimentally for a nematic and a smectic side-chain liquid crystal polymer [14,15]. Warners' proposal is that for a system cross-linked in the nematic phase, the anisotropic network produced must become deformed at the nematic–isotropic transition, as all orientational order is lost in the isotropic phase. The additional energy required for this deformation naturally increases the temperature of the nematic–isotropic transition relative to an uncross-linked system. The opposite

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Table 1
Composition of the acrylate copolymers used in this study

Polymer[a]	Spacer chain length n	Feed ratio[b]		M_n[c]	M_w[c]	M_w/M_n[c]	DP_w[c]	Methacrylate unit in side-chain (%)[d]
		I	II					
CBZ2(I)	2	0.94	0.06	6.8×10^4	2.4×10^5	3.5	750	—
CBZ4(I)	4	0.94	0.06	9.8×10^4	3.1×10^5	3.2	890	—
CBZ6(I)	6	0.94	0.06	7.2×10^4	2.9×10^5	4.0	770	—
CBZ2(M)	2	0.90	0.10	7.3×10^4	2.2×10^5	3.0	700	5.8
CBZ4(M)	4	0.90	0.10	8.5×10^4	2.4×10^5	2.8	710	5.2
CBZ6(M)	6	0.90	0.10	9.8×10^4	3.5×10^5	3.6	960	5.2

[a] (I) refers to material cross-linked through the reaction of pendant isocyanate units (M) refers to material cross-linked through the thermal reaction of pendant methacrylate units.

[b] Copolymer composition was found to be equivalent to feed ratio of monomers according to ^{1}H NMR.

[c] Obtained from GPC data relative to polystyrene standards; values normalised to account for difference in molecular weight of monomer units.

[d] As mole fraction of repeat units evaluated from ^{1}H NMR.

effect is proposed for a system cross-linked in the isotropic phase. The difference, ΔT, in the clearing temperature for a nematic elastomer and an equivalent uncross-linked polymer is given by Eq. (1) [13].

$$\Delta T = 4Nk_BT\frac{D}{A}(S_x^2 - S_0^2) \qquad (1)$$

N is the number of cross-links, D and A are coefficients in a Landau-de Gennes type expansion of the free energy in terms of the order parameter, S_x is the order parameter of the network at the point of cross-linking and equates to the order of the backbone (S_b). S_0 is the order parameter at the clearing temperature. Clearly if the sample is cross-linked in the nematic phase range, there will be an increase in the clearing temperature, and if cross-linked in the isotropic phase range there will be a decrease in the mesophase stability. The extent of the variations will depend upon the state of order at the point of cross-linking and the value for D/A, which may be seen as a parameter describing the coupling. Thus, by comparing liquid crystal elastomers in which the cross-linking was performed in the nematic phase range and in the isotropic phase, it is possible to evaluate the strength of coupling. In this presentation we describe investigations using this approach. We shall show that particular care is

needed to establish equilibrium conformations of the polymer backbone, and describe a cross-linking procedure suitable for such experiments. The methodology is used to estimate the coupling in a particular liquid crystal elastomer system in which the chemical configuration is fixed, other than the nature of the coupling chain, which is varied from 2 to 4–6 alkyl units.

2. Experimental

Copolymers of monomer **I** (with $n = 2, 4, 6$) and hydroxyethyl acrylate **II** were prepared by polymerisation in de-oxygenated chlorobenzene solution (10% w/v) under reduced pressure for 18 h at 55°C using 1 mol% of AIBN as initiator as described previously [14]. The characteristics of these random copolymers are shown in Table 1. The cross-linking of these materials was achieved in two ways: firstly, by reacting the hydroxyl side-groups with di-isocyanatohexane as described previously; secondly, using a novel procedure which is described in detail elsewhere [16], but which involves the (slow) thermal reaction of pendant alkene groups as shown in Fig. 1. It would appear that this latter approach cross-linking involves the adventitious generation and reaction of free radicals, as
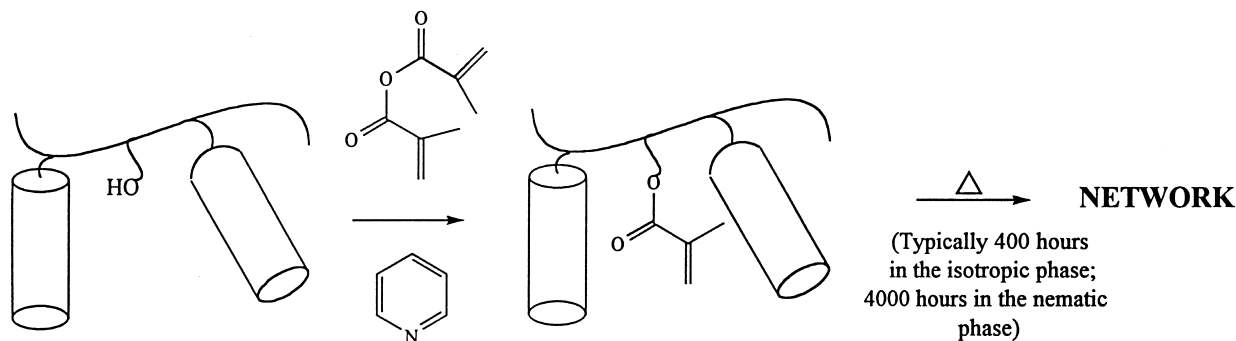

Fig. 1. Schematic representation of the methacrylate cross-linking process. The time scale of cross-linking, which is presumed to occur through adventitious radical formation is sufficient to allow the polymer backbone to achieve an equilibrium conformation.

Table 2
Efficiency of the methacrylate cross-linking reaction

Polymer[a]	Spacer length	Phase present at cross-linking temperature	% Cross-link density[b]	% Cross-link efficiency[c]
CBZ2(I)	2	Nematic	_[d]	_[d]
		Isotropic	0.94 ± 0.10	13
CBZ4(I)	4	Nematic	1.34 ± 0.10	19
		Isotropic	_[d]	_[d]
CBZ6(I)	6	Nematic	1.40 ± 0.25	20
		Isotropic	1.55 ± 0.21	22
CBZ2(M)	2	Nematic	0.48 ± 0.05	18
		Isotropic	0.66 ± 0.06	25
CBZ4(M)	4	Nematic	0.51 ± 0.05	22
		Isotropic	0.69 ± 0.06	30
CBZ6(M)	6	Nematic	0.69 ± 0.06	26
		Isotropic	0.86 ± 0.10	33

[a] (I)Refers to material cross-linked through the reaction of pendant isocyanate units (M) refers to material cross-linked through the thermal reaction of pendant methacrylate units.

[b] Network points as a function of the repeat unit.

[c] Measured cross-link density compared to that expected on complete reaction of the cross-link sites.

[d] Samples not of sufficient quality to allow measurement.

in separate experiments it was found that the rate of gel formation could be slowed by the addition of 5% of 2, 6-di-*t*-butyl 4-methylphenol (BHT). Methacrylic groups were introduced under anhydrous conditions by the reaction of hydroxyl groups from the hydroxyethyl acrylate comonomer with a twofold excess of methacrylic anhydride together with an excess of pyridine. ^{1}H NMR spectra showed that approximately 50% of the available hydroxyl groups were esterified. Films of the modified polymers were cast on to polyimide sheet from concentrated solutions (∼20% w/v) in dichloromethane. The films were dried at room temperature and then placed in an oven at the selected
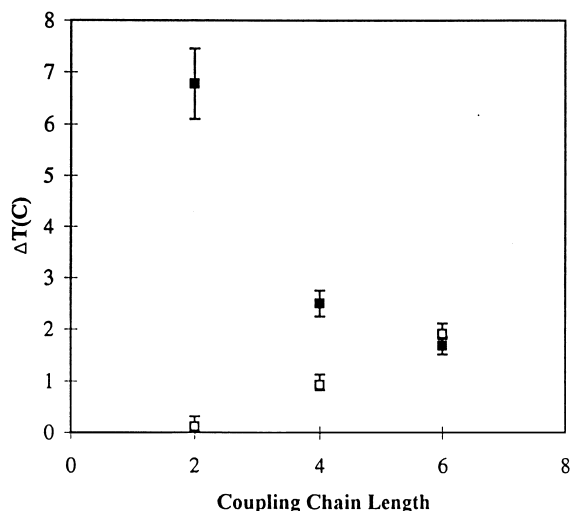

Fig. 2. Plot showing influence of coupling chain length on the difference in phase transition temperatures for acrylate polymers cross-linked in the nematic and in the isotropic phases. filled circles refer to samples cross-linked by the thermal reaction of pendant methacrylate groups described in the text. The open circles represent a sample cross-linked using the isocyanate method [14,17].

temperature. For samples cross-linked in the isotropic phase this was 132°C and for those cross-linked in the nematic phase the temperature was 78°C. The kinetics of the cross-linking reaction was monitored by the growth of the gel fraction. For samples cross-linked in the nematic phase a steady state value for the gel content was achieved after ∼4000 h, for samples cross-linked in the isotropic phase the equivalent time was ∼400 h.

The cross-link density of the elastomers prepared using both the routes described above, together with the cross-linking efficiency is shown in Table 2. For the samples cross-linked with di-isocyanatohexane the extent of cross-linking was evaluated using mechanical measurements of the modulus in the isotropic phase, [16]. For materials cross-linked via the reaction of methacrylate side-groups, where only relatively small samples were prepared, the cross-link density was obtained from the results of equilibrium swelling measurements in toluene using an interaction parameter obtained from the isocyanate cross-linked material in which both swelling and mechanical measurements were made.

The phase behaviour of the resultant elastomers was evaluated using a polarised light microscope equipped with a thermal stage and a photodiode coupled to a recording device which allowed the transmitted light intensity through the microscope to be plotted as a function of temperature. The nematic–isotropic phase transition could be readily evaluated by noting the temperature at which there was a sudden drop in intensity.

3. Results

All the uncross-linked polymers and the elastomers subsequently prepared show textures indicative of a nematic phase, and reversible phase transitions to the isotropic
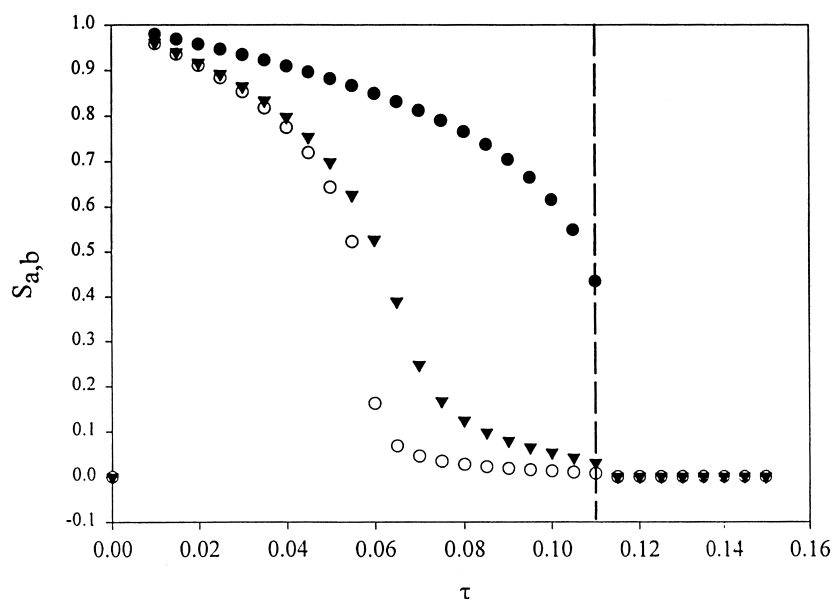
Fig. 3. Calculated values for the magnitude of the order parameters S_a and S_b as a function of the reduced temperature $\tau = kT/V_{aa}$ (●) side chain orientation S_a, backbone orientation S_b (○) $\mu = 0.01$, (▼) $\mu = 0.04$. The lower values for τ (<ca.0.8) are inaccessible owing to the glass transition.

phase. In order to ensure that the phase transition temperatures recorded for these networks were truly equilibrium in nature, great care was taken to ensure that each sample was fully equilibrated in the nematic phase prior to measurement. For samples which had been cross-linked in the isotropic phase an annealing time of several hundred hours was necessary to obtain consistent results. Fig. 2 shows the difference in temperature between the clearing point for the elastomer cross-linked in the nematic phase and that prepared in the isotropic phase for each of the three materials studied; also shown is the data recorded for elastomers, prepared by an alternative route using an isocyanate cross-linking reaction [14,17] in which cross-linking is essentially complete after ca. 40 h. For the system with spacer length 6, similar results are obtained by the two routes; in contrast, samples with the smaller coupling chains showed considerably reduced temperature differences when the isocyanate method was used. In these samples the polymer backbone has not attained an equilibrium conformation before substantial cross-linking has taken place and it is this which necessitates the use of an extremely slow cross-linking reaction.

In order to make a quantitative comparison between the phase transition shifts for the different material systems we must also take account of the level of cross-linking and the level of orientational order at the point of cross-linking. The data in Table 2 shows that there is some variation in the cross-linking density for the different systems. As the level of cross-linking is slightly lower for the networks with the shorter coupling chains, it is clear that the change of ΔT with reducing coupling chain length would be even more marked for samples with equivalent cross-link densities. Equally, for each pair of samples with the same coupling chain length, the cross-link density is slightly lower for the sample

prepared in the nematic phase compared with the sample cross-linked in the isotropic phase. This will also serve to reduce the values of ΔT observed.

In these materials the polymer backbone is ordered owing to the coupling of the nematic ordering to the polymer chains. We have explored the nature of the chain ordering with respect to the mesogenic units using a mean field model, similar to that employed by Warner and others [13,18]. The model considers the system as a two component mixture and is simplified by the presence of chemical bonding between the mesogenic unit and the polymer chain which serve to inhibit compositional fluctuations. The potential H describing the ordering S_b of the polymer chain with respect to the nematic director is given by Eq. (2), where S_a is the order parameter of the mesogenic chains, ϕ_{ab} are the fractions of the species in the system, μ is the coupling constant between the mesogenic unit and the polymer chain and λ is the coefficient describing polymer chain-polymer chain interactions. The coefficients are expressed as dimensionless parameters in relationship to the mesogenic–mesogenic interaction parameter $V_{(aa)}$. We can derive similar potentials to the one shown in Eq. (2) for the ordering of the mesogenic units and using a self-consistent approach, obtain values for the order parameters S_a and S_b as a function of the reduced temperature $\tau = kT/V_{(aa)}$. A typical result is shown in Fig. 3. As the temperature is reduced the mesogenic order parameter shows a discontinuous change at the nematic–isotropic transition and continues to increase as the temperature is reduced further. The order of the polymer chain shows a similar variation, although the level of order is much lower than that of the mesogenic side-groups for temperatures close to T_{NI} and is strongly dependent upon the value selected for μ. At much lower temperatures, the chain undergoes a second order
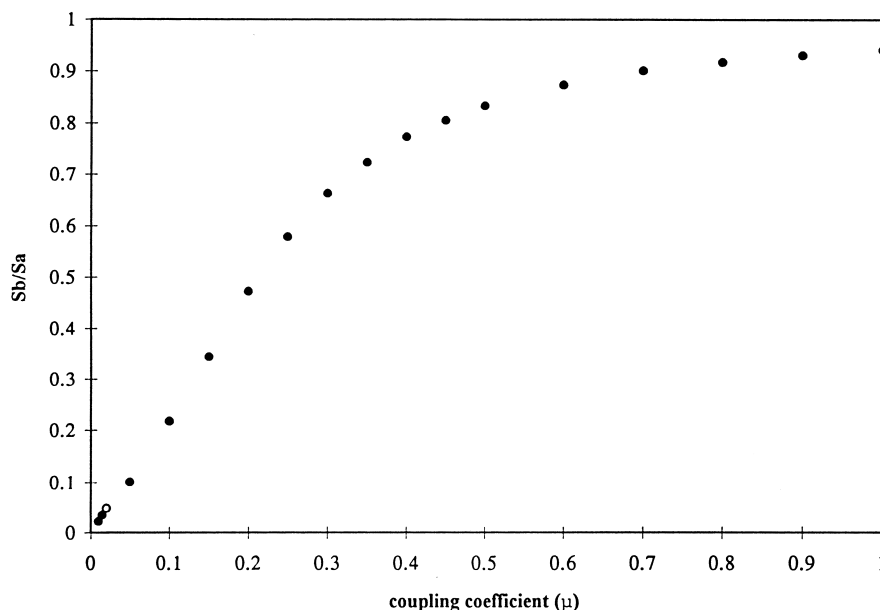
Fig. 4. The level of chain ordering (S_b) relative to the mesogenic order parameter (S_a), as a function of the coupling coefficient μ. For values of $\mu < 0.2$ the relationship is linear.

transition to a highly ordered state, at a temperature largely defined by λ. However, in this work we have only accessed temperatures in the range of $T_{NI} - 0.88T_{NI}$ (most of the temperature scale shown in Fig. 3 is not accessible in real materials owing to the glass transition).

$$H = -P_2(\cos\alpha)[\phi_a\mu_aS_a + \phi_b\lambda S_b] \qquad (2)$$

In this work we are interested in the relationship between the coupling coefficient and the orientational order of the polymer chains S_b. It is clear from Fig. 3 that for temperatures close to T_{NI}, S_b varies little with temperature. In Fig. 4 we show a plot of the level of chain ordering relative to the mesogenic order parameter as a function of the coupling coefficient μ. For values of $\mu < 0.2$ the relationship is linear. Using the levels of chain ordering for CBZ6 reported previously using neutron scattering and mechanical deformation it is clear that the value for μ is $\mu \ll 0.2$ in other-words for the material studied here it is reasonable to assume that the level of chain ordering shows a broadly linear correlation with the coupling coefficient μ.

Previous infra-red dichroism measurements [19,20] have shown that the order parameter of the mesogenic side-groups of equivalent polymers with coupling chain lengths $n = 2, 4, 6$, are broadly similar, if considered on a reduced temperature scale. As a consequence, any variation in the orientational order of the polymer backbone for systems with different coupling chains must be a result of a variation in the coupling coefficient. We observe this ordering through its effect on the phase transition shift, the magnitude of which is related both to the extent of ordering and to the value of the coupling coefficient. In otherwords, coupling both induces the chain order and provides a mechanism whereby this ordering effects the transition temperature.

The first effect arises as a consequence of the chemical attachment of the mesogenic units to the polymer backbone; the second effect, directly measured in this work, is a consequence of the network structure. As for samples with equivalent values of S_a, the backbone ordering is proportional to the coupling coefficient, we can substitute the side-group ordering into Eq. (1). ΔT is therefore proportional to the product of the coupling coefficient μ and $(\mu S_a)^2$; i.e. ΔT is proportional to μ^3 [and hence$(S_b)^3$]. Thus the ratio $\Delta T_6/\Delta T_2$ equates to $(S_6/S_2)^3$ with similar relationships for the other combinations

We have a direct measure of the order parameter, S_6, for the material with $n = 6$ from both SANS [6] and from macroscopic shape changes in monodomain elastomers [8]. Those measurements showed that for the $n = 6$ system, the radius of gyration parallel to the director was $\sim 10\%$ larger than the value recorded perpendicular to the director. This translates to an effective extension ratio of ~ 1.05 and an order parameter of the chain of $S_6 \sim 0.01$ [6]. Using the ratios given above and the values in Fig. 2, we can estimate that and $S_4/S_6 \sim 1.1$ and $S_2/S_6 \sim 1.5$; if we correct for the slightly different cross-link densities given in Table 2 (using the linear relationship between ΔT and the cross-link density in Eq. (1)) we obtain more precisely $S_4/S_6 \sim 1.2$ and $S_2/S_6 \sim 1.8$. It must be emphasised that this analysis is semi-qualitative in nature, as the methodology is rather indirect relying on a number of theoretical assumptions. However, the principle disadvantage of this technique is the extremely long time required for cross-linking. This is unavoidable if the polymer chain is to attain an equilibrium conformation. With this regard, the method compares favourably with techniques such as neutron scattering, where non equilibrium conditions must also be considered and avoided if

necessary. The increased coupling coefficient with shorter chains can be directly related to the reduced conformational freedom as the number of methylene units in the coupling chain is decreased. This underlines the important role of the coupling chain in determining both the magnitude of the coupling, as shown here, and the sense of the coupling, as reported in earlier work [10–12].

4. Summary

We have utilised the theory of Warner et al. in order to obtain a quantitative estimate of the magnitude of the coupling between the mesogenic unit and the polymer backbone in a liquid crystalline polymer system. In line with natural expectations, systems with shorter coupling chains showed a greater level of coupling between the two components. However, in order to observe this enhanced coupling, particular care had to be taken to ensure that non-equilibrium conditions did not mask the effect. We attribute the increased coupling coefficient to the reduced conformational freedom in the coupling chain as n is reduced.

Acknowledgements

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