Oligomers as molecular probes of orientational coupling interactions in polymer melts and networks

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Simultaneous measurement of infrared dichroism and birefringence was used to study orientational coupling effects between a series of monodisperse polybutadiene oligomers and the surrounding matrix, which consisted of either polybutadiene polymer melt or polybutadiene network. The oligomers had molecular weights ranging from well below the critical molecular weight for entanglement M_e, to several times M_e. For the oligomer/network system, the magnitude of the coupling coefficient was found to remain constant at about unity over the range of network crosslink densities, oligomer molecular weights and degrees of swelling examined, thereby confirming the D n.m.r. experiments performed on the same samples. For the oligomer/polymer system, orientational coupling effects were examined as a function of oligomer molecular weight and temperature. It was found that unentangled oligomers experienced almost complete coupling, while fully entangled melts were subject to a much lower coupling. In addition, it was found that the magnitude of the coupling is independent of temperature, indicating that these orientation correlations are entropic in nature, arising from the packing entropy of chain segments. An orientational dependent lattice model, proposed originally by DiMarzio, was found suitable for predicting experimental results.

(Keywords: oligomers; melts; networks)

INTRODUCTION

A large body of experimental evidence has indicated the existence of local correlations in the orientations of neighbouring molecules in various polymeric systems[1–18]. The first experimental indications came from the observation of a concentration-dependent stress-optical coefficient of polymer networks swollen with different solvents[1]. It was observed that solvents with spherically shaped molecules caused a strong decrease in the stress-optical coefficient. From these results, it was concluded that chain–chain interactions constitute additional contributions to the anisotropy of the polarizability of chemical bonds along polymeric chains, and that the presence of solvent molecules reduces these interactions, resulting in decreased anisotropy of orientation and leading to a smaller measured stress-optical coefficient. More recently, it was found that small molecules embedded in an oriented polymeric medium will adopt a preferential orientation in the direction of the orientation of the surrounding matrix[2–4]. This effect is not limited to free probe molecules, but also influences the orientation of chain segments in an unswollen polymer melt or network by creating a certain degree of cooperativity in segmental orientation[6,10].

The use of small-angle neutron scattering (SANS)[19] together with deuterium nuclear magnetic resonance (D n.m.r.)[8] pointed out that the orientational anisotropy of short polymer chains dissolved in a strained elastomer is effective at very short length scales, i.e. at the bond level. Significant probe orientation was observed by using D n.m.r., which is a technique that measures average bond orientation since n.m.r. interactions are local in nature and provide information at the level of the polymer chain's primary structural elements. On the other hand, no probe distortion was detected by SANS, which is a technique that probes relatively large length scales on the order of the radius of gyration of a polymer chain and is insensitive to anisotropies on the bond-length scale.

A large number of experiments have been made with small molecules as probes to examine orientation correlations in deformed elastomers. These experiments have investigated the effects of probe size and shape, concentration, network extension ratio and temperature on the magnitude of the coupling between probe molecules and the stressed network chains[3,4,20,21]. In addition, experiments using oligomers as probes in polymer networks that have the same chemical structure as the oligomers have examined the effects of oligomer molecular weight and concentration on the coupling strength[7,9,12,17,18]. More recent studies have concentrated on investigating orientation correlations between different components of a polymer melt[13,14,22] and between segments of fully entangled polymer chains[11,15]. A summary of all these results is given in the next section.

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The aim of the work described here has been twofold. The primary goal has been to examine the effects of both temperature and probe entanglements on the orientational coupling between probe oligomers and the surrounding matrix, where the oligomers are dissolved in a polymer melt of fully entangled chains that have the same chemical structure as the oligomers. Therefore, step-strain experiments are made with a series of oligomers with molecular weights ranging from well below the entanglement molecular weight, M_e, to several times M_e. A secondary part of this work has been to verify the D n.m.r. results for the orientation of deuterated oligomers in stretched networks[7].

For the main goal of this study, overall sample orientation as well as oligomer orientation are measured simultaneously as a function of time following a step strain (dynamic orientation). To examine temperature effects, the step-strain experiments are repeated at different temperatures. The transient measurements are made with a simultaneous i.r. dichroism and birefringence rheo-optical technique, where the orientation of the deuterium labelled oligomers is calculated from the measured dichroism, and the overall sample orientation is calculated from the measured birefringence. Next, in order to verify the D n.m.r. results, the same optical technique is used to measure the steady-state orientations of both the probe oligomers and the stretched network at various oligomer sizes, concentrations and network extensions. The procedure to calculate oligomer and sample orientations together with polymer synthesis, sample preparation and experimental method are given. The experimental results are presented and discussed, as are the implications of these results together with a possible lattice model representation for orientation correlations in this system. Finally, a summary of this work is given in the concluding section.

PREVIOUS EXPERIMENTAL RESULTS

Experiments studying orientational coupling interactions aim at establishing a relationship between the orientation of the probe molecules and that of the overall sample, and examine the effects of varying the probe molecular structure and its environment such as temperature and probe concentration. Basic understanding of orientation correlations in polymeric systems is necessary in order to understand and predict orientation-dependent properties of polymers, especially elastomers. All experimental results that examine orientation correlations in polymeric systems have shown that in the presence of such correlations a bulk state of orientation produces an orientational order in the bonds of the probe molecules following the relationship:

$$\langle u_i u_j \rangle_{\text{probe}} = \varepsilon \langle u_i u_j \rangle_{\text{bulk}} \qquad (1)$$

where the vector $\boldsymbol{u}$ describes the orientation of the chemical bonds and the indices i and j denote the vector component. The terms $\langle u_i u_j \rangle_{\text{probe}}$ and $\langle u_i u_j \rangle_{\text{bulk}}$ describe the state of orientation of the probe molecules and the bulk matrix in which the probes are dissolved, respectively, and ε is the orientational coupling constant. It is a measure of the strength of the orientation correlation, where $\varepsilon = 0$ indicates no coupling and $\varepsilon = 1$ indicates complete coupling. It is necessary to emphasize that ε is a measure of orientational coupling interactions between fully relaxed probes that do not support any stress and stress-oriented matrix chains. Some experimental results have indicated that ε can be a function of $\langle u_i u_j \rangle_{\text{bulk}}$ for very large matrix deformations[20,23]. The relationship between the local orientation vector $\boldsymbol{u}$ and the more coarse-grained Rouse vector $\boldsymbol{r}$ is shown in *Figure 1*. The probe in equation (1) can be a small molecule, oligomer or chain segment. Note that the determination of orientation correlations using oligomers or chain segments requires that the probe and the matrix orientations obey the same time dependence.

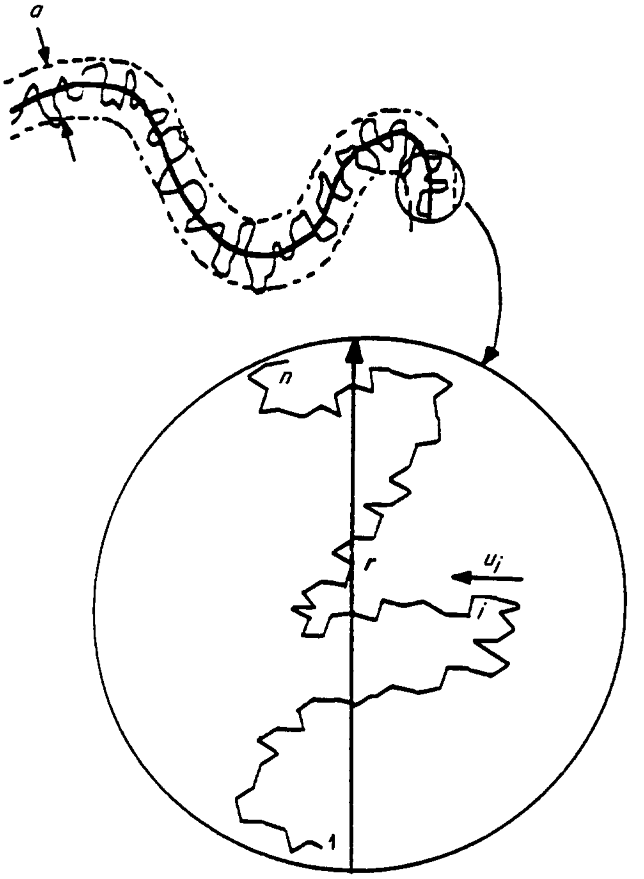

Figure 1 Illustration of the distinction between the statistical-segment level and the chemical-bond level (the diameter of the reptation tube is *a*)

In order to establish the motivation for the work described here, a detailed literature survey of the experimental results concerning orientation correlations in polymeric systems will be given next. This detailed summary will serve as a review of both published and unpublished results that are related to the work presented in this paper.

Small molecules

Deloche and Samulski[2] used deutero-benzene (C_6D_6) and deutero-chloroform ($CDCl_3$) as swelling agents in elongated polyisoprene networks to examine orientational coupling interactions with D n.m.r. spectroscopy. In these experiments, the order parameter of the network was determined separately by extending D n.m.r. measurements to labelled unswollen and swollen networks. The results show that both the anisotropic solvent probe and the polymer segments experience short-range orientation correlations in extended networks and that the order parameter of the probe molecules is linearly proportional to that of the network chains. When probe concentration effects are considered, it was found that the degree of its orientation decreases as the network is increasingly swollen, and that the ratio of the order parameter of the probe molecules to that of the network is proportional to the network volume fraction raised to the (4/3) power. When temperature effects are considered, the results indicate that the probe degree of orientation decreases with increasing temperature. Later, similar studies were made with C_6D_6 as D n.m.r. probe in elongated poly(dimethyl siloxane) (PDMS) networks, and it was found that the orientational coupling coefficient, ε, is 0.56 for this system[6], indicating moderate coupling strength.

The orientation of over 100 symmetrical aromatic molecules in extended polyethylene films was studied by Thulstrup and Michl[3] using u.v.–visible dichroism. It was found that the degree of orientation of the aromatic probe molecules in stretched polyethylene films is dominated primarily by molecular shape, where generally the larger the aspect ratio of the probe molecule, the greater its orientation in the anisotropic matrix. In addition to the probe size, small changes in the chemical structure seemed to influence the degree of orientation correlations, leading to the conclusions that orientational coupling interactions are due to the finite volume of the probe molecules and that geometrical packing requirements can explain in part the anisotropic interaction. The sensitivity of orientational coupling interactions to small substitutions in the chemical structure of the probe indicates that other factors, such as induced dipole interactions, can be important in determining the nature of such interactions. To study temperature effects, probe orientations at two different temperatures are measured. It was found that in general probe orientation decreases with increasing temperature. However, orientation dependence on temperature is sensitive to the probe chemical structure, where the orientation of probes with larger aspect ratio is less sensitive to temperature.

A similar study using a series of ketones as molecular probes in stretched polyethylene films was made by Schmidt and Schneider[4]. The probes consisted of symmetric ketones with two identical n-alkyl hydrocarbon arms having 2 to 17 carbons, and ketone orientations were measured by using i.r. dichroism. The degree of orientation of the ketones was found to increase with increasing probe length, where ketones with long and straight chains had the largest orientation. Increasing the experimental temperature produced a decrease in the orientation of not only the probe ketones, but also the matrix chains. The sensitivity of ketone orientation to temperature decreased with increasing molecular weight, but all the ketones lost orientation faster than the matrix chains with increasing temperature.

Using fluorescence polarization methods, Erman *et al.*[20] studied the orientation of rigid rod-like diphenyl polyalkene probes of variable length in uniaxially deformed polyisoprene networks[20]. A distinct coupling of the probe orientation to that of the stretched network was observed. The magnitude of the coupling coefficient ranged from 0.1 to 0.8 and the coupling strength decreased with increasing probe length. The same type of study was performed by Queslel *et al.*[21] using fluorophores with flexible n-alkyl groups as probes in deformed polyisoprene networks. The results indicate that increasing probe length increases its orientation. In addition, the measured values for ε for this system were 0.4 to 0.8. The main difference in the orientational behaviour with increasing probe length between the two systems is due to the flexibility of the probes, where stiffness could allow the rod probes only selective correlations with specific network configurational sequences.

Oligomers

Several researchers have examined the effects of orientation correlations on oligomers of the same chemical structure as the network polymer chains. Using deuterium-labelled polybutadiene oligomers that are 10 monomers long in unlabelled polybutadiene networks, Jacobi *et al.*[5,7,17,18] made D n.m.r. measurements to study the orientational coupling interactions in the system. By using undeuterated polybutadiene networks swollen to different extents with deuterated oligomers, it was shown that the oligomer orientation extrapolated to infinite dilution is approximately twice as large as the orientation of network segments in an unswollen network[7]. This finding is very surprising because the orientation of the network chains provides the driving force for the oligomers to orient. Therefore, one would not expect the oligomers to be more oriented than the network chains themselves. Further investigation of these results indicated inconsistency in data analysis, where the *cis* and *trans* splittings (*cis* and *trans* splittings refer to the signal due to the CD_2 groups located near *cis* and *trans* repeating units, respectively) were extrapolated to zero oligomer concentration and compared to the splitting due to the deuterated network[5] to obtain the coupling magnitude, but it was assumed that there is no distinction between *cis* and *trans* splittings in the network. Subsequent experiments proved that the observed splitting in the spectra of the deuterated network is due to the narrower *cis*-CD_2 units[18]. Therefore, only the 'inner' splitting of the oligomers had to be compared to the network splitting to obtain a measure for the coupling. After adjusting the data to account for this new factor, it was found that $\varepsilon = 1$ for all the elastomer crosslinking densities and oligomer volume fractions used[18]. In addition, it was found that the coupling is independent of oligomer length for oligomers with molecular weights between 500 and 4000.

Sotta *et al.*[9,12] used D n.m.r. to study the orientation of PDMS oligomers of variable length in extended PDMS networks. Additionally, the effects of oligomer concentration and the presence of a solvent diluent were investigated. It was found that the ratio of the oligomer order parameter to that of the network is independent of oligomer molecular weight for the four oligomers used. These oligomers have molecular weights between 300 and 10 000, all below the entanglement molecular weight for PDMS. For all the oligomers studied, it was found that the degree of probe orientation increases linearly with that of the network, and for all cases the orientational order of the oligomers is equal to that of the network chains, giving $\varepsilon = 1$[9]. Also, it was found that within experimental error ε is independent of oligomer concentration for the range studied (5–20%). Moreover, in the presence of small solvent molecules, it was found that orientation coupling interactions between chain segments and the solvent molecules are reduced greatly[12]. Therefore, it was concluded that orientational order induced in strained networks is related to the nature of the local chain confinement, where the introduction of oligomers does not perturb this order. However, these orientation correlations are sensitive to the presence of small solvent molecules. These conclusions are in agreement with the results discussed so far for both oligomers and solvent molecules in strained networks.

Tassin *et al.*[16] used unentangled polystyrene oligomers in long fully entangled polystyrene polymer melts to examine orientation correlations in polymer melts. Two oligomers with different lengths and two polymers with different molecular weights were used. The relaxations of all the samples were monitored as a function of time by using i.r. dichroism measurements. For all the samples studied, the oligomer orientation linearly followed that of the polymer with a coupling constant $\varepsilon = 0.26$. Such a low coupling constant is not surprising because polystyrene has a bulky side group (benzene ring), so it does not pack very well. Therefore, polystyrene cannot produce efficient coupling interactions because these interactions arise from steric effects.

Chain segments

The presence of orientational coupling interactions in bidisperse melts was detected by using simultaneous i.r. dichroism and birefringence. By simultaneously measuring the transient orientation of the melt and of its two components following a step strain, it was found that the relaxation of the short chains is slowed down[13,14]. In these experiments, three sets of bidisperse poly(ethylene propylene) blends were examined. The molecular weight ratio of long to short chains varied between 2.3 and 7, and both species in all the blends had molecular weights that were several times M_e (fully entangled melts). Each set consisted of five blends containing 10, 20, 30, 50 and 75% by volume longer chains. It was found that all three sets exhibit clear effects of orientational coupling interactions, where the shorter species' relaxation is significantly retarded when longer chains are added to the melt. In addition, the shorter chain relaxation was observed to become slower as the matrix content of longer chains is increased. Following a step strain, it was observed that the longer chains' relaxation is slightly increased with increasing shorter chains in the sample. This was interpreted in terms of orientation correlations in the melt, which couple the orientations of both species to that of the average sample, thereby increasing the shorter species' orientation and decreasing the longer species' orientation. For all three sets, the coupling coefficient was found to equal 0.45, indicating that ε is independent of molecular weight for fully entangled melts. To study the temperature dependence of the coupling coefficient in this system, step-strain experiments at four different temperatures (0, 20, 40 and 60°C) were made on a blend containing 50% longer chains in a 53 K/125 K blend. The results showed no temperature dependence of the coupling coefficient[24], leading to the conclusion that these coupling correlations must be entropic in nature.

I.r. dichroism measurements on monodisperse isotopically labelled block polystyrenes indicated that the chain ends experienced orientational correlation effects with coupling coefficient between 0.6 and 0.7[11]. Moreover, isotopically labelled star polystyrenes were examined by using i.r. dichroism[25], and it was found that the arm ends retain some residual orientation, which is attributed to the interactions with the surrounding media of partially oriented chains.

Simultaneous i.r. dichroism and birefringence step-strain experiments were recently made on three almost monodisperse isotopically labelled block copolymers[15]: a diblock polybutadiene with a short end-segment labelled, a triblock polybutadiene with a short centre-segment labelled, and a triblock poly(ethylene propylene) with two equal end segments labelled. Experimental results indicate the presence of orientational coupling interactions in all three block copolymers, where the orientations of chain ends (which relax first according to the physical picture of reptation) and chain centres (which relax last according to reptation) are coupled to the average chain orientation. The coupling coefficient for the two polybutadiene block copolymers is 0.4, and for the poly(ethylene propylene) block copolymer, it is 0.45, in agreement with the value obtained for the same polymer in bidisperse melts.

Recently, Amram *et al.*[26] investigated the orientation of strained polyisoprene networks at different temperatures with two different techniques. The results obtained using fluorescence polarization indicated that chain-segment orientation decreases with increasing temperature, while results from dichroism measurements showed no temperature dependence of chain-segment orientation. This apparent conflict has a simple explanation: the presence of the fluorescent label in the former experiment and its absence in the latter, where it was argued that changes in temperature may affect the conformational properties of bonds around the label leading to artificial temperature dependence of segmental orientation[26].

Summary

In summary, a large variety of orientation phenomena in polymeric systems are due to local orientation correlations. Therefore, it is necessary to gain a fundamental understanding of these interactions in order to understand the orientation-dependent properties of polymer blends and elastomers and to develop appropriate constitutive equations that describe the flow behaviour of polymeric systems. Although the exact nature of such interactions are not well understood yet, the experimental data collected so far in the literature allow some conclusions to be drawn.

First, for moderate strains, there is a linear relationship between the order parameter of the probe and that of the oriented matrix, where the second moment of the orientational distribution function of the probe is proportional to that of the surrounding matrix and the proportionality constant, ε, provides a measure of the strength of the orientational coupling interaction.

Secondly, in the ketone experiments, where the probes are a series of low-molecular-weight molecules, the coupling increases with increasing molecular weight. However, in the PDMS oligomer experiments, the coupling is independent of molecular weight. Also, a linear PDMS tetramer in a strained PDMS network gives $\varepsilon = 1$, while a cyclic PDMS tetramer in the same system and under the same conditions gives a significantly lower value for ε[27]. These results lead to the conclusions that the effect of molecular weight saturates for chains of more than a few tens of backbone bonds in length, and that linear probes are better oriented with the surrounding chains than cyclic probes of the same size.

Thirdly, orientational coupling interactions act on the bond-length scale, which is must smaller than the length scale treated by reptation, and chains oriented only by coupling correlations do not contribute to the state of stress of the sample containing them. This conclusion has important implications for the theoretical treatment of orientation correlations.

Finally, conflicting results are obtained when temperature effects are considered. Most experimental results show that ε is a function of temperature, a fact supporting the idea that these coupling correlations are 'nematic-like', enthalpically driven[2–4]. On the other hand, a few recent results indicate otherwise[24,26].

When the strength of orientational coupling is considered, the results in the literature are in conflict. However, a general trend can be detected if the results for the polystyrene oligomers ($\varepsilon = 0.26$)[16] are excluded. (The unusually bulky geometry of polystyrene decreases the efficiency of coupling interactions.) As the size of the probe molecule is increased, the coupling strength is increased, in agreement with the idea that orientation correlations act on the bond level in an additive fashion. This effect saturates for sufficiently long oligomers, about 10 monomers. Complete coupling ($\varepsilon = 1$) is obtained for linear oligomers dissolved in networks that have the same chemical structure as the oligomers. On the other hand, the value of the orientational coupling coefficient is much lower for fully entangled monodisperse or bidisperse melts ($\varepsilon = 0.4$ to 0.7), and increasing the molecular weight of the blend constituents does not change ε, indicating saturation in orientational coupling effects in fully entangled melts. At this saturation limit, it is expected that different polymers should have different values for ε, where the range in literature varies between 0.4 and 0.7. Such a difference is not surprising since in the absence of attractive interactions ε should be quite sensitive to the detailed geometric shape of a monomer and hence not be expected to have a universal value.

An important observation regarding the temperature dependence of ε can be deduced from the conclusions of Jacobi *et al.*[18] and Sotta *et al.*[9] for oligomers in strained networks. In both studies, D n.m.r. was used to measure the values of ε, and it was found that $\varepsilon = 1$ for all oligomer sizes considered and concentrations used. Although these experiments were all made at room temperature, an important observation regarding the temperature dependence of ε can be deduced from the results reported. If ε were a function of temperature as reported by others[2–4], then it is expected to decrease with increasing temperature. Equivalently, it is expected that ε should increase if the D n.m.r. experiments were to be conducted at below room temperature giving $\varepsilon > 1$, which is not a physically possible condition since it implies that the probe oligomers are more oriented than the surrounding network chains. Therefore, the measured value of $\varepsilon = 1$ in these experiments indirectly dictates that ε should be independent of temperature.

MATERIALS AND METHODS

Polymer synthesis and characterization

The polymers used in this study are anionically polymerized polybutadienes that vary in size from very short oligomers to fully entangled polymers. For the oligomer/polymer part of this study, six deuterated oligomers with molecular weights ranging from 500 to 22 000 are dissolved in fully entangled, undeuterated polybutadiene polymer with molecular weight 268 000. The properties of the pure oligomers and of the polymer are given in *Table 1*. The statistical copolymer at the bottom of the table is used to perform control experiments, as will be discussed later.

Table 1 Properties of the pure polymers

Sample code	MW	M_w/M_n	%D[a]
PB0.5	500	1.15	70.7
PB1	1000	1.13	69.0
PB2	2000	1.14	73.2
PB4	4000	1.12	70.0
PB8.5	8500	1.13	74.3
PB22	22 000	1.13	71.5
PB268	268 000	1.30	0
Statistical copolymer	117 000	1.04	8.0

[a] This is the fraction of hydrogens at the CH_2 groups replaced by deuterium

Table 2 Properties of the oligomer-polymer samples

Sample code	Concentration of oligomers	%D[a]
PB0.5 in PB268	0.191	13.5
PB1 in PB268	0.203	14.0
PB2 in PB268	0.194	14.2
PB4 in PB268	0.203	14.3
PB8.5 in PB268	0.202	15.0
PB22 in PB268	0.207	14.8

[a] This is the fraction of hydrogens at the CH_2 groups replaced by deuterium

Polymerization was conducted anionically in cyclohexane at room temperature with *sec*-butyl lithium as the initiator. The first six oligomers in *Table 1* were prepared from butadiene deuterated at the CH_2 groups in the 1,4 position with a degree of deuteration of approximately 70%. Synthesis procedure and characterization results for PB0.5, PB1, PB2 and PB4 are reported in detail in another publication[28]. PB8.5 and PB22 were prepared and characterized in the same manner. The polymer (PB268) was prepared from normal butadiene by following the same synthesis technique and the statistical copolymer was prepared by using both normal and deuterated butadienes, with deuterated monomer content of about 11%. The overall molecular weights for the first five oligomers in *Table 1* were measured by vapour pressure osmometry, while the molecular weights for the remaining three polymers were determined by using membrane osmometry. Polydispersity of all the samples was measured by gel permeation chromatography. Deuterium content in the pure oligomers was measured by n.m.r., while the copolymer content of deuterium was obtained from *FT*i.r. measurements using PB2 as the reference.

The oligomer/polymer samples used in this work were prepared by dissolving approximately 20% oligomers in the long polymer. Oligomer concentration in the sample along with the deuterium content of the samples are given in *Table 2*.

Polybutadiene networks swollen with polybutadiene oligomers were also studied in this work mainly to verify the D n.m.r. results discussed earlier[18]. The networks were prepared anionically by crosslinking precursor chains in solution with a *bis*(1,2,4-triazoline-3,5-dione) crosslinking agent. This method yields networks with a well-defined number of chemical linkages[29]. Three networks with different degrees of crosslinking were used in

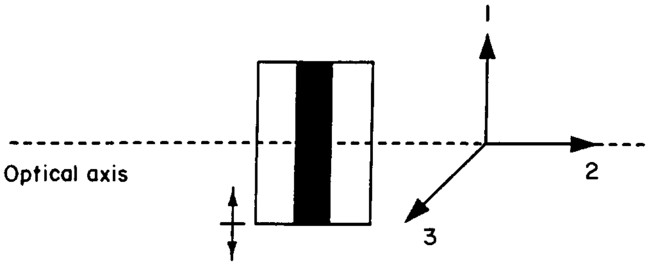

Figure 2 Flow-cell geometry showing the optical axis parallel to the 2-axis and normal to the plates of the flow cell, shown as open rectangles. The sample is sheared by translating one of the plates in the 1-direction as shown

our experiments: 0.8%, 1.0% and 1.5%. Four different oligomers (the first four in *Table 1*) having molecular weights ranging from 500 to 4000 were used as swelling agents in these networks. A practical upper limit to the oligomer molecular weight that can be studied is set by the slow diffusion of longer chains into the network. In swelling the networks, ample time was provided to establish a homogeneous distribution of oligomers in the networks. Samples of three different degrees of swelling (oligomer volume fraction) were used: 0.1, 0.3 and 0.5. The swollen network samples used in these experiments were approximately 20 mm × 3 mm × 0.5 mm in size.

Theoretical basis for experiments

The coupling coefficients for the samples can be obtained from measuring simultaneously both the dichroism and the birefringence of each sample. These two properties are measures of sample optical anisotropy. They arise from the deviatoric part of the full refractive index tensor of the material, n_{ij}, which is the sum of real and imaginary parts:

$$n_{ij} = n'_{ij} + in''_{ij} \qquad (2)$$

The real part describes how the material retards light and the imaginary part describes how it attenuates light. Anisotropy in the refractive index of a polymer material is fundamentally related to anisotropy in the orientation distribution of polymer segments. In our experimental set-up, the sample is sheared along the 1 direction, while light propagates along the 2 direction, as shown in *Figure 2*. Therefore, the measured birefringence equals the difference in the eigenvalues of the real part of the observed refractive index tensor projection:

$$\Delta n' = n'_{11} - n'_{33} \qquad (3)$$

where $\Delta n'$ is the measured birefringence. On the other hand, at infrared wavelengths, the measured dichroism has a strong wavelength dependence determined by the absorption spectrum of the samples. Labelling the oligomers used in our samples with deuterium shifts one of their absorption peaks to a wavelength at which they would otherwise be transparent. Consequently, at the C–D bond absorption wavelength, only the deuterated oligomers will give rise to the observed dichroism. So the dichroism provides a measure of the anisotropy of orientation of the oligomers in the samples, which equals the difference in the eigenvalues of the imaginary part of the observed refractive index tensor projection:

$$\Delta n'' = n''_{11} - n''_{33} \qquad (4)$$

where $\Delta n''$ is the measured dichroism.

Optical train

The optical apparatus used in these experiments has sufficient sensitivity for linear viscoelastic measurements, has a response time of 50 μs and allows the simultaneous measurement of the transient dichroism and birefringence of a sample. A detailed description and a diagram of the optical train used is given elsewhere[13]. The light source is an infrared (i.r.) diode laser operating at the frequency of the C–D bond stretching vibrational absorption, 2190 cm^{-1}. The i.r. beam passes through a polarizer (oriented at 0°) and a photoelastic modulator (oriented at 45°) before impinging on the sample, which is held between two parallel windows in the flow cell. The flow cell used in these experiments has a parallel-plate geometry and 50–60 ms response time for step strains. A detailed description of its design can be found elsewhere[30]. The transmitted beam leaving the flow cell is first intercepted by a beam splitter (oriented at less than 5° with respect to the optical axis, so the polarization of neither beam is significantly changed), then it is observed by two separate detectors: the dichroism detector, which receives the transmitted beam, and the birefrigence detector, which receives the reflected beam through a second polarizer oriented at $-45°$. Data acquisition and control of the step-strain experiments are accomplished by a microcomputer.

Signal processing and data acquisition

The optical train is readily analysed by using the Mueller formalism[31]. The analysis gives a relationship between the experimental variables and the amplitude of harmonics of the photoelastic modulator carrier frequency ω in the intensity observed by each detector. The light intensity at each detector is demodulated to determine the dichroism or the birefringence. The signal measured by each detector has the form:

$$I = I_{\mathrm{DC}} + I_{\omega}\sin(\omega t) + I_{2\omega}\cos(2\omega t) + \cdots \qquad (5)$$

where ω is the photoelastic modulator frequency, which is 42 kHz in these experiments. In an earlier work[13] it was found that the dichroism is proportional to $I_{2\omega}$ obtained at the dichroism detector and the birefringence is proportional to I_{ω} obtained at the birefringence detector.

The output from the dichroism detector is sent through a high-speed pre-amp to a lock-in amplifier set to a reference frequency of 2ω. Therefore, the output from this lock-in amplifier is $I_{2\omega}$ and it is proportional to the dichroism, which can be obtained from $I_{2\omega}$ and I_{DC} measured at the dichroism detector as follows:

$$\frac{I_{2\omega}}{I_{\mathrm{DC}}} = 2J_2 \tanh v \qquad (6)$$

where J_2 is the value of the Bessel function and v is proportional to the dichroism through the relationship:

$$v = \frac{2\pi d}{\alpha}\Delta n'' \qquad (7)$$

where α is the wavelength of light (1/2180 cm) and d is the path of light in the sample which equals the thickness of the sample.

Similarly, the output from the birefringence detector is amplified and sent to a lock-in amplifier set to a reference frequency of ω. Therefore, the output from this lock-in amplifier is I_{ω} and it is proportional to the birefringence, which can be obtained from I_ω and I_{DC} measured at the birefringence detector as follows:

$$\frac{I_\omega}{I_{DC}} = 2J_1 \frac{\sin \mu}{\cosh \nu} \qquad (8)$$

where J_1 is the value of the Bessel function and μ is proportional to the birefringence through the relationship:

$$\mu = \frac{2\pi d}{\alpha} \Delta n' \qquad (9)$$

The output from the two lock-in amplifiers and the signal from the displacement tranducer on the flow cell are simultaneously recorded by using an analogue–digital converter. The I_{DC} at each detector is measured by using a multimeter. Care must be taken to subtract background i.r. radiation. The Bessel functions are calculated from calibration experiments where the sample is replaced by a quarter-wave plate with $\mu = \pi/2$, where it was found that $J_1 = 0.48 \pm 0.01$ and $J_2 = 0.13 \pm 0.01$. The sample thickness is directly measured to determine d. Therefore, from equations (6)–(9), the dichroism and the birefringence of the sample can be calculated. The coupling coefficient ε is determined from:

$$\varepsilon = \frac{K}{\Phi} \frac{\Delta n''}{\Delta n'} \qquad (10)$$

where Φ is the volume fraction of the C–D bonds in the sample and is given in *Table 2* and K is a calibration factor that arises due to the fact that the dichroism and the birefringence have different molecular origins. K is determined from control experiments made with the statistical copolymer. Following a step strain, all the segments along the statistical copolymer chains should have the same average orientation. Therefore, the randomly distributed labelled chain segments (giving rise to the dichroism) will have the same average orientation as the average segment in the sample (giving rise to the birefringence). From the control experiments, K can be calculated as

$$K = \Phi \frac{\Delta n'}{\Delta n''} \qquad (11)$$

where Φ is the volume fraction of the C–D bonds in the statistical copolymer, which equals 0.08 from *Table 1*. From the experimental results using the statistical copolymer, K was found to equal 0.25 ± 0.01.

For the experiments involving the polybutadiene elastomers, an alternative way of recovering ε is used. Owing to the chemical linkages in the elastomer host, oligomer orientation is not time variant, but it is dependent on the degree of deformation. This can be exploited to reduce experimental error by recovering ε from the dependencies of dichroism and birefringence on deformation rather than from their value at a single extension ratio. The classical theory of rubber elasticity dictates that orientation in uniaxially extended elastomers is proportional to $\lambda^2 - 1/\lambda$, where λ is the extension ratio (the ratio of extended length to unextended length). As a result, plots of dichroism and birefringence *versus* $\lambda^2 - 1/\lambda$ should be linear. It follows, therefore, that the ratio of the slope of the dichroism plot to that of the birefringence plot for a given sample can be used to determine ε by substituting that ratio for $\Delta n''/\Delta n'$ in equation (10).

Experimental procedure

The optical experiments for the oligomer/polymer samples were made in the same manner described in previous work[13,14]. Step-strain relaxation experiments were made on all samples at room temperature. In addition, two samples (PB2 in PB268 and PB8.5 in PB268) were used to study temperature effects on the coupling constant, where step-strain experiments using these two samples were repeated at four different temperatures: 0, 20, 40 and 60°C. Heating and cooling of the flow cell was achieved by using a circulating bath, and the sample temperature was calculated from a calibration curve that relates bath temperature to sample temperature[15]. The reproducibility of the results was confirmed for each sample and at each temperature. For the elastomers, extension ratios of 1 to 1.33 were used. For the melts, sample thicknesses of 0.56–1.65 mm were used and strains of 30–45% were applied. At the end of each experiment the thickness of the melt sample is measured directly by using a micrometer and the signal from the displacement transducer together with the sample thickness are used to determine the exact magnitude of the strain. It was confirmed that the experiments were made in the linear viscoelastic regime by comparing results obtained with different strain magnitudes. For both melts and elastomers, the collected data for the dichroism have lower signal to noise ratio than the birefringence since the dichroism signal is about two orders of magnitude than the birefringence signal.

To perform optical experiments on the elastomers, the flow cell was slightly modified to accommodate uniaxial extension. The parallel i.r. windows (and their holders) were replaced by a pair of mounts which clamp an elastomer sample at opposite ends. One mount is attached to the stationary plate of the flow-cell translation stage, while the other is secured to the mobile plate. Samples were elongated by manually turning the flow-cell drive shaft. Extension ratios were determined from the separation of the upper and lower mounts. Measurements at 6 to 12 extension ratios were typically obtained for each experiment. Experiments on each sample were repeated several times after unloading the sample and rotating its orientation. Slopes of dichroism and birefringence *versus* $\lambda^2 - 1/\lambda$ were obtained from least-squares fits of the data and values of ε were computed according to equation (10) with the ratio of the slopes substituted for $\Delta n''/\Delta n'$.

The raw data for the step-strain experiments on the melts are tabulated at logarithmically spaced time points (25 points per decade). The transient data for both the dichroism and the birefringence are shifted to the same reference baseline, zero. Such shifting is necessary because the signal from the laser can experience a gradual change in intensity that causes baseline shifts in the lock-in signals. Since different fractions of the beam reach each detector, the lock-ins that measure the dichroism and the birefringence can have different baseline shifts. Transient data at times up to 200 ms and greater than 10 s are discarded since at $t < 200$ ms, the data is not completely reliable due to the possible stress contribution at short times to measured oligomer orientations for some of the samples, and at $t > 10$ s, the measured signals become too small and noise can dominate. Then $\Delta n'$ and $\Delta n''$ are calculated at each data point and the results are averaged and used in equation (10) to obtain ε. This procedure is repeated for each data file obtained by using the same

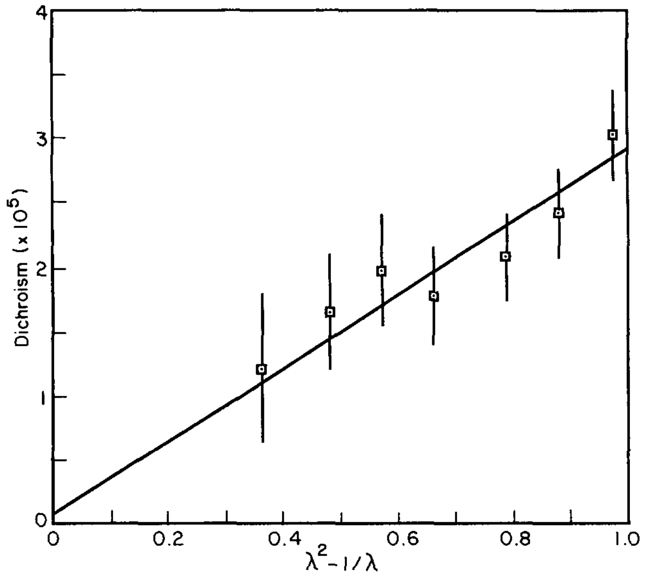

Figure 3 Dichroism of strained network

sample, where a data file is the average of 15–25 experiments and the final reported results for ε are the average of two to five data files. Therefore, each reported value for ε is the average of 1200–4000 data points.

RESULTS AND DISCUSSION

Oligomers in strained networks

Twelve samples of different network crosslink densities, oligomer molecular weights and degree of swelling are studied. These samples were previously studied by D n.m.r.[7,18], where it was found that ε is approximately unity over the ranges of network crosslink densities (0.8–1.5%), oligomer molecular weights (500–4000) and degrees of swelling (0.1–0.5) studied. The coupling coefficient for each of the samples is determined by the simultaneous i.r. dichroism and birefringence technique described above. *Figures 3* and *4* illustrate typical plots of the dependence of dichroism and birefringence on the extension ratio for one sample (network crosslink density = 0.8%, oligomer $M_n = 500$, degree of swelling = 0.3). The data plotted are the averages of five experiments and uncertainty bars depict the standard deviations of the measurements. Least-squares analysis of the data reveals that within experimental uncertainty the data are linear. The extrapolated fits are expected to pass through the origin since for no strain there should be no orientation. The offset from the origin is relatively minute and may be attributed to uncertainties in dichroism and birefringence measurements and/or small errors in λ values due to the uncertainty in determining the zero elongation position. From the ratio of the slopes of these plots, a coupling coefficient of 1.05 ± 0.10 was computed. Within experimental error, this value for ε is in agreement with the D n.m.r. study.

All other samples yielded similar values for the coupling coefficient ($\varepsilon = 1$), which is in agreement with the D n.m.r. results, indicating that ε should be constant over the range of the parameters studied. The physically unreasonable positive deviations from unity are attributed to small surface defects on the samples, which are believed to anisotropically scatter light and artificially enhance the measured dichroism, resulting in a slightly inflated value of ε. This explanation is supported by the observation that samples with greater surface roughness (as observed under an optical microscope) tended to yield larger deviations from unity.

Oligomers in polymer melts

In order to explain the experimental results, two important molecular characteristics in polymer melt rheology will be reviewed. First, the entanglement molecular weight of a polymer, M_e, is the average weight between entanglements in fully entangled melts. Polymer chains with molecular weights greater than M_e are considered entangled. For polybutadiene, $M_e = 2000$. Therefore, from *Table 1* it is evident that PB0.5, PB1 and PB2 are not entangled. The second significant molecular weight in melt rheology is M^*, the critical molecular weight at which the plateau modulus appears in the polymer relaxation modulus. For polybutadiene, $M^* \approx 20\,000$–$24\,000$ ($M^* = 10$–$12M_e$). Therefore, from *Table 1*, it is found that PB22 is at M^*, with PB4 and PB8.5 between M_e and M^*.

All the oligomers with molecular weights less than M^* can be considered Rouse chains with stress relaxation times much less than the experimental timescale. For the first five oligomers in *Table 1*, the Rouse relaxation times are less than 10^{-9} s, while the experimental timescale is greater than 10^{-3} s. For PB22 the reptation relaxation time is less than 10^{-2} s, so all the oligomer probes used in these experiments can be considered fully relaxed at the beginning of data collection at $t = 200$ ms. Consequently, the experimentally observed dichroism is due only to oligomer orientation by coupling interactions with the long polymer segments. As a result, both the oligomer relaxation and the overall sample stress relaxation will have the same time dependence. This is observed in all samples studied, where the normalized transient birefringence and dichroism are identical, as can be seen in *Figure 5*, which gives the normalized oligomer orientation and the overall sample orientation as a function of time. This sample was chosen because of its high signal–noise ratio, and the results in *Figure 5* are the average of 25 experiments.

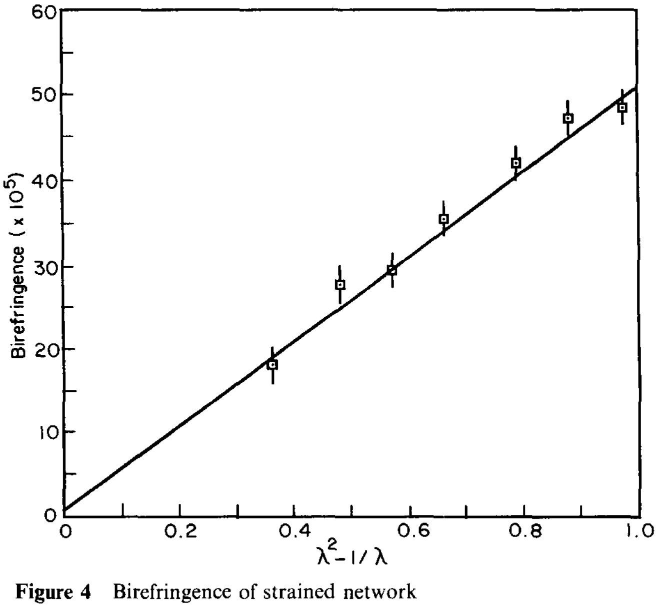

Figure 4 Birefringence of strained network

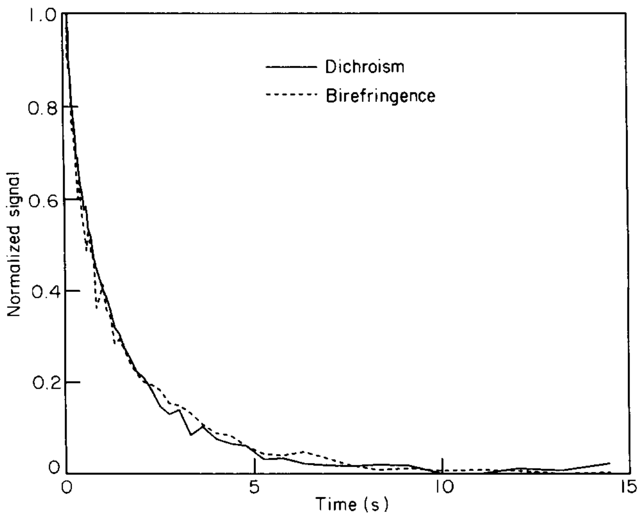

Figure 5 Normalized dichroism and birefringence following a step-strain for PB4 in PB268

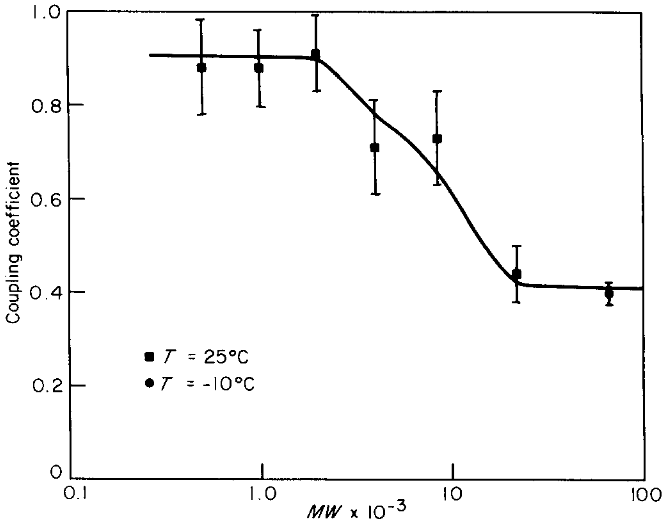

Figure 6 Coupling coefficient for polybutadiene oligomers in polybutadiene polymer as a function of oligomer molecular weight

When the experimental results are reduced as described earlier, the orientational coupling coefficient is obtained. The calculated values for ε from room-temperature experiments are shown in *Figure 6*, where the solid curve is drawn to guide the eye. The data point at $MW = 66\,000$ on the figure is from our previous results on isotopically labelled block copolymers where the experiments were performed at $T = -10^{\circ}C$[15]. From *Figure 6*, it can be concluded that short oligomers with $MW \leqslant M_e$ experience almost complete orientational coupling to that of the surrounding matrix chains. The coupling strength does not change with increasing oligomer length provided the oligomer molecular weight does not exceed M_e. This is in agreement with previous results on oligomers in deformed elastomers[9,17,18]. On the other side of the molecular weight axis results giving a much smaller coupling coefficient ($\varepsilon = 0.4$) for fully entangled polybutadienes ($MW \geqslant M^*$) prevail. Also, in this region of the oligomer size, ε does not change with molecular weight. This is again in agreement with previous findings[11,14,15]. For oligomers with molecular weights between M_e and M^*, the coupling coefficient is in between the two limits discussed above, $0.9 > \varepsilon > 0.4$. The exact nature of ε-dependence on oligomer molecular weight in this region cannot be determined from the available results. The transient nature of these observations is qualitatively shown in *Figure 7*, where the second moment of the orientation distribution is given as a function of time for different blend components.

Experiments made at a fairly wide range of temperatures with two samples containing polybutadiene oligomers with molecular weights 2000 and 8500 in polybutadiene polymer indicate that for this system ε is independent of temperature, as can be seen in *Figure 8*. Representative error bars in this figure are placed only on one data point for each sample. The same magnitude of error applies to the remaining data points, but the bars were omitted for the sake of clarity. The observed lack of temperature dependence of ε is in agreement with previous results for fully entangled poly(ethylene propylene) melts[14]. Therefore, it has been demonstrated that here that orientational coupling interactions in polymer melts are independent of temperature for a wide range of probe molecular weights ranging from unentangled short oligomers to fully entangled polymers. Consequently, it can be concluded that orientation

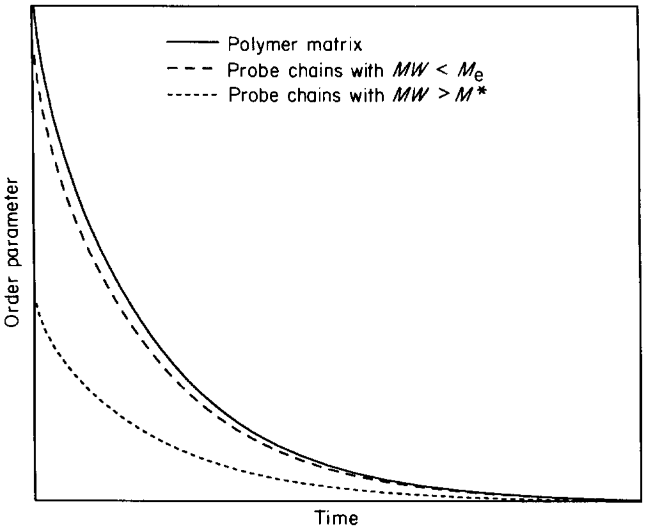

Figure 7 Qualitative representation of the time-dependent order parameter

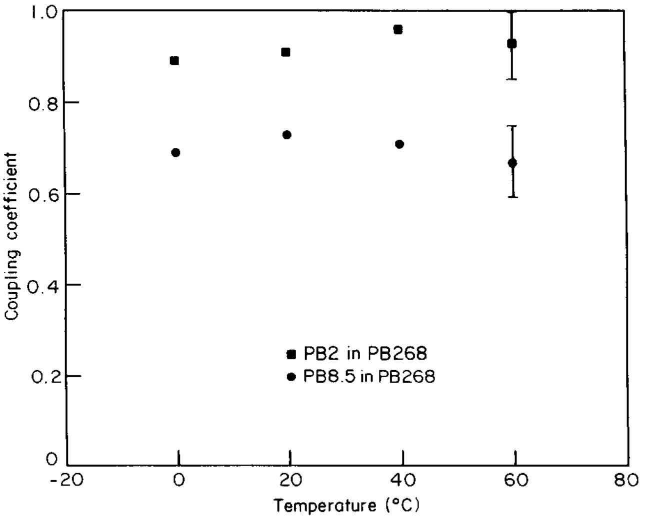

Figure 8 Coupling coefficient as a function of temperature

correlations in polymeric systems have entropic, rather than enthalpic, origin.

In the experiments described in this paper the probe has the same chemical structure as the matrix. A temperature dependence of the coupling coefficient was observed in several other experiments[2–4], where the probe and the matrix had different chemical structures. This difference in the temperature dependence of ε between our results and the results reported in references 2–4 is expected, since the measured quantity, ε, is the relative average orientation of the probe chains with respect to the overall sample average orientation. With increasing temperature, all chain segments in the sample become more mobile with respect to each other since more conformations will be available with increasing thermal energy. This will affect the average orientation of each species in the sample by the same magnitude (owing to their similar chemical structure). Therefore, the relative coupling between short and long chains remains constant, giving a constant ε. In the experiments in references 2–4, the coupling between two different species was measured giving a decreasing ε with temperature. It is expected that different species will acquire different enhancement in their mobility with increasing thermal energy giving a changing ε with temperature. In addition, in references 2–4 the probes were small molecules, so they have extra degrees of freedom when compared to the surrounding matrix. Therefore, the probes are expected to lose their orientation faster than the matrix chains even if the interaction force remains the same. Moreover, D n.m.r. results for PB oligomers in PB networks[18] and for PDMS oligomers in PDMS networks[9] indirectly indicate that ε should be independent of temperature, as argued earlier.

Theoretical models for orientation correlations in polymer melts

The classical theory of rubber elasticity describes the entropy change of a flexible chain network (crosslinked or temporary) as the sum of the contributions of single chains:

$$\Delta S = \sum_{i=1}^{N} \Delta s_i \tag{12}$$

where Δs_i is the entropy of an isolated chain. Equation (12) implies that the entropy of a chain is not altered by the dense packing in the bulk material. When a free probe molecule is placed in a deformed network, this molecule will be relaxed, and within the framework of the classical theory it will not contribute to the stress or to the entropy change. Consequently, probe molecules in a deformed matrix should not be oriented. However, experimental evidence indicates otherwise. Therefore, the classical theory for rubber elasticity is not adequate for describing orientational coupling effects in deformed polymeric systems.

Several attempts have been made over the years to correct the 'gas-like' theory for rubber elasticity by accounting for orientation correlations between chain segments[2,12,23,32–36]. These correctional models adopt two main approaches in modelling orientational coupling effects: enthalpic and entropic. Several researchers have attributed coupling effects in deformed networks to energetic effects and used a temperature-dependent potential to describe the contribution of orientation correlations to the free energy of the system[2,12,23,34]. In addition, recently the effects of orientation correlations on Rouse chains were modelled by using a Maier–Saupe potential, giving a coupling coefficient that is inversely proportional to temperature[37] (see equation (7) in reference 37). The entropic approach to model the problem was first attempted by DiMarzio in 1962[32]. He accounted for the intermolecular interferences due to excluded-volume effects by using a three-dimensional lattice model. All other entropic-based theories are mainly attempts to improve or modify the DiMarzio lattice model[33–36].

In the light of our experimental evidence showing that coupling strength is temperature-independent, it is concluded that orientation correlations must be a consequence of the dense packing or excluded-volume effects (only weak Van der Waals interactions might contribute additionally). However, it is important to emphasize that orientation correlations take effect only when external work is applied to the system, leading to some type of stress-induced orientation of the matrix. This point will be used when discussing the predictions of the lattice model of DiMarzio towards the end of this section.

After reviewing available information in the literature correlating probe size with the strength of coupling interactions, it was concluded that ε increases with probe molecular weight until the probe is several monomers in length, then the effect of molecular weight saturates. However, the results in this chapter indicate that when the oligomers are long enough to participate in entanglements, the magnitude of ε starts to decrease until a second saturation limit with respect to probe molecular weight is reached for fully entangled melts[14,15]. This can be attributed to the effects of entanglements since the loops and bends that entangled probe chains have to follow can interrupt the perfect coupling observed for unentangled probes with the surrounding matrix chains.

For fully entangled polymer chains a simple picture will be used to explain the saturation in the value of ε for fully entangled melts. A fully entangled polymer chain is assumed to participate in two types of entanglements: weak and strong. The weak entangelements are those at the ends of the chain (the terminal 5 or 6 entanglements) and the strong ones are those located towards the centre. During stress relaxation, the weak entanglements only play a minor role in the temporary network formed by entanglements that gives rise to the plateau modulus for polymer melts. Therefore, chains with few entanglements (less than 10–12) do not exhibit a well-defined plateau modulus. The molecular weight at which strong entanglements begin to form is M^*. A similar argument can be outlined for orientation correlation effects in melts. Weak entanglements affect ε differently from strong entanglements. Therefore, when the probe molecular weight exceeds M^*, only strong entanglements are formed with increasing chain length, and no change in ε with molecular weight takes place.

In the following analysis it will be shown that the lattice model of DiMarzio is adequate to predict the magnitudes of coupling observed experimentally. According to this model, the total configurational entropy of the system is divided into two contributions:

$$S = S_c + S_p \tag{13}$$

where S_c is the configurational entropy of chains from the classical rubber elasticity theory, which depends only on the end–end length of the chain. While S_p is the

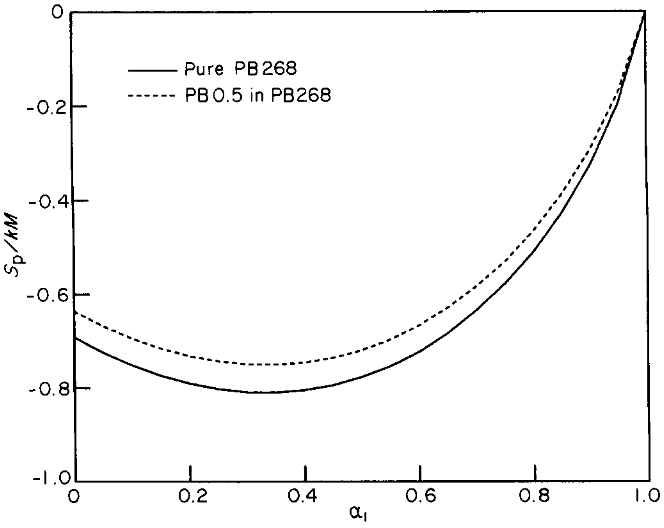

Figure 9 Packing entropy as a function of orientation

packing entropy, which arises from the excluded-volume effects in chain packing. In this analysis S_p depends on the orientation distribution of monomer segments in the chains. Therefore, S_p arises from a contribution at the bond-length scale, which is the length-scale influenced by orientation correlations. Since mutual interference due to excluded-volume effects reduces the total configurational entropy, $S_p \leqslant 0$.

In order to calculate S_p, DiMarzio used the Flory lattice theory to account for excluded volume in deformed networks. To describe the packing entropy in a monodisperse polymer melt, the equation obtained by DiMarzio for S_p in swollen networks is modified to give:

$$\frac{S_p}{kM} = -\frac{1}{r}\ln\frac{1}{r} + \sum_{i=1}^{3}\left(1 - \alpha_i\frac{r-1}{r}\right)\ln\left(1 - \alpha_i\frac{r-1}{r}\right) \qquad (14)$$

where k is the Boltzmann constant, M is the total number of lattice sites, r is the degree of polymerization and α_i is the fraction of total bonds in direction i with $\alpha_1 + \alpha_2 + \alpha_3 = 1$. The packing entropy as a function of α_1 for PB268 is given in *Figure 9*. It has a minimum at $\alpha_1 = 1/3$ when the system is isotropic. Increasing α_1 corresponds to shear or extension in direction 1. When $\alpha_1 = 1$ all the chains are oriented as rigid rods in direction 1. If S_p were the only term in the configurational entropy, then *Figure 9* indicates that flexible chains in a polymer melt should spontaneously orient to maximize the entropy. However, amorphous polymers do not exhibit spontaneous order because the gain in S_p is smaller than the loss in S_c due to ordering.

When the system is deformed due to applied mechanical strain (reducing S_c), monomer segments of the chains will orient in the deformation direction to maximize S_p, reaching a new balance point between S_c and S_p. This situation was examined by Tanaka and Allen[33]. They used the lattice model of DiMarzio to calculate the enhancement in chain-segment orientation due to packing effects for small deformations. Using the restricted lattice-walk approximation, they found that the relative increase in orientation due to packing in an elongated dry network is 50%. Since crosslinking is not explicit in this theory, it can be applied to fully entangled polymer melts that behave as a temporary network under deformation, yielding $\varepsilon = 0.5$. This value is consistent with our experimental results for fully entangled polybutadiene with $\varepsilon = 0.4$. Note that in their treatment, Tanaka and Allen ignored the relative stiffness of the chains. Such a factor can affect the magnitude of the orientational coupling coefficient. This effect was recently demonstrated by Erman *et al.*[36] where they modified the DiMarzio lattice model to account for chain stiffness. They found that coupling is decreased for flexible chains and increased for chains with rigid segments. Therefore, ε is expected to vary about 0.5 depending on chain flexibility. This is in agreement with our experimental results where relatively flexible polybutadiene chains gave a coupling coefficient that is 20% less than the predictions of Tanaka and Allen without accounting for chain flexibility.

Adding short unentangled oligomers to a matrix of fully entangled polymer chains does not change the concept of packing entropy, so S_p for the system becomes the weighted sum of the contributions of both polymer and oligomer chains. Since the oligomers have a much smaller degree of polymerization than the polymer, the packing entropy for pure oligomers is larger than that for a pure long polymer, as can be deduced from equation (14). Therefore, adding oligomers will raise the packing entropy curve for the system without changing its shape as shown in *Figure 9*. Maximum packing entropy is achieved when all the bonds in the system (belonging to polymer chains or oligomers) are oriented in direction 1. If α_1 is the fraction of polymer bonds in direction 1 (the shear direction) and γ_1 is the fraction of oligomer bonds in direction 1, then maximum packing entropy is achieved when both α_1 and γ_1 are maximized. Since α_1 is determined by the imposed deformation and γ_1 cannot physically exceed α_1, S_p is maximum when $\gamma_1 = \alpha_1$, giving $\varepsilon = 1$. This is again consistent with the experimental results where $\varepsilon = 0.9$ to 1.0 for oligomers in a polymer melt or in a network. In a real system the oligomers are not expected to orient exactly with the surrounding matrix because the oligomers are free chains unbound by entanglements, so they are expected to have additional rotational mobility at the ends. Therefore, a real system is expected to give a value for ε that is similar to the theoretically predicted value, $\varepsilon = 1$, but slightly smaller due to the rotational effects at the oligomer chain ends discussed above.

Finally, owing to the lack of experimental data, the exact nature of the change in ε with oligomer size between M_e and M^* is not known.

CONCLUSIONS

The simultaneous measurement of infrared dichroism and birefringence of uniaxially extended polybutadiene networks swollen with deuterated polybutadiene oligomers was used to determine the coupling coefficients of the swollen networks. For the systems studied here, values of ε were found to remain constant at approximately unity over the range of network crosslink densities, oligomer molecular weights and degrees of swelling examined, thereby confirming the D n.m.r. experiments made on the same samples.

Use of oligomers with systematically varying molecular weights dissolved in a polymer that has the same chemical structure as the oligomers permitted the study of orientational coupling interactions in polymer melts as a function of probe molecular weight. At room temperature, three distinct regimes were found: unentangled oligomers experienced almost complete orientational coupling to the matrix chains ($\varepsilon \approx 0.9$); fully entangled melts were subject to a much lower coupling ($\varepsilon = 0.4$); and oligomers with molecular weights between M_e and M^* experienced an intermediate orientational coupling ($0.9 > \varepsilon > 0.4$).

Experiments made at different temperatures on two samples, one containing unentangled oligomers and the other oligomers with few entanglements, indicate that ε is independent of temperature, leading to the conclusion that the observed orientation correlations in the system have an entropic origin. Furthermore, the lattice model of DiMarzio, which is based on the concept of packing entropy, was found to be adequate in predicting experimental results.

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