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Temperature Effects on the Magnitude of Orientational Coupling Interactions in Polymer Melts

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1. Introduction

A large body of experimental evidence has indicated the existence of local correlations in the orientations of neighboring molecules in various polymeric systems.[1–17] For example, it was found that small molecules embedded in an oriented polymer network will adopt preferential orientation in the direction of the orientation of the surrounding matrix.[2–4] This effect is not limited to free probe molecules but influences the orientation of chain segments in polymer melts[12–14] and unswollen networks by creating a certain degree of cooperativity in segmental orientation.[6,10]

Since orientation correlations are widely present in oriented polymeric systems, a complete understanding of the nature of such interactions is necessary. It has been believed that these correlations are enthalpically driven since experimental results have shown that orientation correlations exhibit a distinct temperature dependence.[2–4] However, in these experiments, orientational coupling effects were measured between two chemically different species (the probes and the polymer matrix have different chemical structures). Since the measured quantity is the strength of the coupling, which is the relative average orientation of the probe chains with respect to the overall sample average orientation, the measured temperature dependence may be due to different degrees of mobility enhancement for the chemically different species with temperature. Therefore, these systems are not good models to examine the nature of orientation correlations.

In a recent publication we have shown that orientation correlations between short, unentangled polybutadiene oligomers dissolved in a fully entangled polybutadiene melt and the chain segments of the melt are independent of temperature.[18] Since coupling between chemically identical species is measured in this case, temperature effects due to different mobility enhancements for the probes and the matrix chains are ruled out. Therefore, it was concluded that these correlations between short probes and the surrounding matrix are entropic in nature, arising from excluded-volume effects.

The objective of this work is to generalize our conclusions regarding the entropic nature of orientation correlations. Therefore, the temperature dependence of orientation correlations in a fully entangled poly(ethylenepropylene) melt is examined. These correlations were shown to exist in this system in another publication.[13]

2. Materials and Method

The sample used in these experiments is a bidisperse blend of short and long poly(ethylenepropylene). The short polymer has a molecular weight of 53 000 and characteristic relaxation time of 0.35 s, while the long polymer has a molecular weight of 125 000 and characteristic relaxation time of 7.0 s. The sample contains 50% long polymer, 40% short polymer, and 10% deuterated version of the short polymer. The short polymer and its deuterated version have identical degrees of polymerization, identical rheological properties, and a negligible tendency toward phase separation.[12] A detailed description of polymer synthesis and characterization can be found elsewhere.[12]

The optical apparatus used in these experiments has sufficient sensitivity for linear viscoelastic measurements, parallel-plate flow cell, 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, together with a description of data acquisition and signal demodulation, is given elsewhere.[12] Step-strain experiments were performed at 0, 20, 40, and 60 °C. Sample thicknesses of 0.46–0.63 mm were used, and strains of 30–40% were applied. The reproducibility of the results was confirmed at each temperature, and in each case it was confirmed that the experiments were conducted in the linear viscoelastic regime by comparing results obtained with different strain magnitudes. The raw data were tabulated at logarithmically spaced time points (25 points/decade) and normalized by using the signal at 100 ms (to allow for the mechanical response time of the flow cell). Each reported data curve is the average of 25–60 experiments.

3. Results and Discussion

For a bidisperse polymer melt, it was shown by Doi et al. *that the strength of orientational coupling interactions* can be measured by using the overall sample and short-chain relaxations at times much greater than the reptation time of the short chains.[19] At such long times the following relationship holds[19]

$$(S/S_0) = \epsilon(G/G_0) \qquad \text{for } t \gg \tau_s \qquad (1)$$

where S/S_0 is the normalized short-chain relaxation, G/G_0 is the normalized bulk relaxation, and ϵ is the orientational coupling parameter and its magnitude is a measure of the strength of this coupling, where an ϵ value of one indicates complete coupling and a value of zero indicates no coupling. From eq 1 a plot of S/S_0 as a function of G/G_0 should be a straight line passing through the origin with a slope equal to ϵ.

The terminal relaxations of this blend at the experimental temperatures for times greater than 20 s are shown in Figure 1. From this figure, the effects of orientation correlations in polymer melts can be clearly seen, where the normalized relaxation of the short chains is proportional to that of the bulk at times >20 s, although the short polymer has a characteristic relaxation time of 0.35 s. From the results, it is clear that local orientation correlations in this system are independent of temperature. Data collected at four different temperatures ranging between 0 and 60 °C almost collapse on the same line and have the same slope. The measured values for ϵ at different temperatures are given in Figure 2. Within experimental error, the measured ϵ is independent of temperature and has an average value of 0.45, which is identical with that measured at room temperature for bidiperse blends of the same polymer for a variety of blend compositions (10–75% by volume longer chains) and component molecular weights (53K/125K, 125K/370K, 53K/370K).[13]

The above results, combined with our findings regarding oligomers in polymer melts,[18] lead to the conclusion that orientation correlations in polymeric systems arise due to excluded-volume effects that change the configurational entropy of the system.

The lattice model of DiMarzio[20] can be used to predict orientational coupling effects in polymer melts. This model accounts for excluded-volume effects, usually ignored by the classical theory of rubber elasticity, by adding a negative term (the packing entropy) to the configurational entropy of the system. Under external

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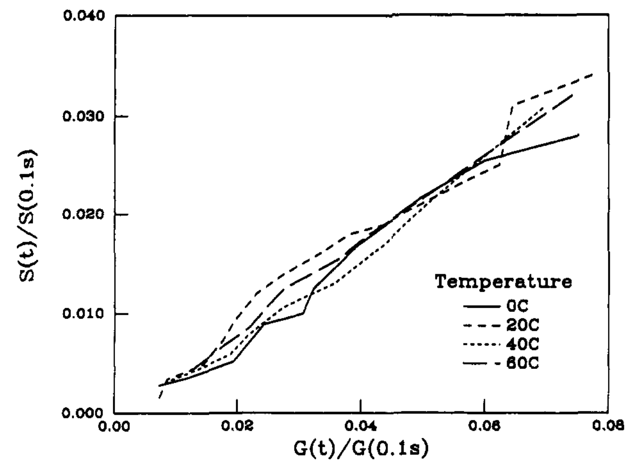

Figure 1. Normalized short-chain dichroism as a function of normalized sample birefringence in the terminal relaxation region at different temperatures.

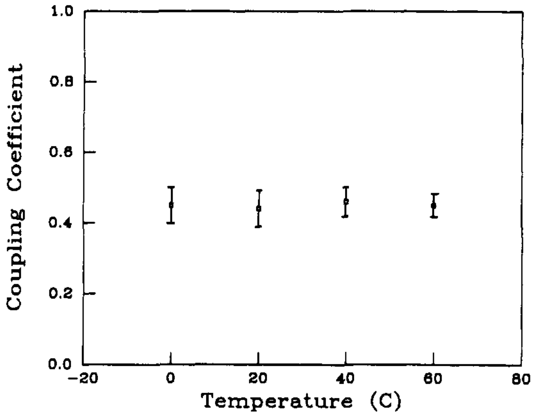

Figure 2. Orientational coupling coefficient as a function of temperature for the blend.

stress, the system will maximize its entropy by exhibiting orientational coupling effects. Tanaka and Allen[21] have used this model to calculate the enhancement in chain-segment orientation in dry rubbers 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 cross-linking is not explicit in this theory, it can be applied without any modifications to fully entangled polymer melts that behave as a temporary network under deformation. The system examined in this work is a fully entangled bidisperse melt, and the conclusions of Tanaka and Allen can be applied, yielding $\epsilon = 0.5$. From Figure 2 it is clear that within experimental error, this value is in agreement with our experimental results for fully entangled poly(ethylenepropylene).

Finally, we have shown that orientation correlations in fully entangled polymer melts are independent of temperature. Therefore, these correlations must be entropically driven. In addition, the lattice model of DiMarzio was found to be successful in predicting the observed orientation coupling effects.

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Registry No. Poly(ethylenepropylene) (copolymer), 9010-79-1.