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Relaxation of Binary Blends of Long and Short Chains: Evidence for Orientational Coupling

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Introduction

Various experimental studies have revealed the existence of local orientational correlations between molecules in a large variety of systems. For example, short-range order has been detected by depolarized Rayleigh scattering and Raman spectroscopy in *n*-alkane liquids.[1-4] Deuterium magnetic resonance studies have also shown that solvent molecules, even those of nearly spherical shape, as well as oligomers are oriented in deformed networks.[5,6] Free polymer chains dispersed in a deformed network also exhibit a segmental orientation[7] even though their overall dimensions remain isotropic.[8] An abnormally high orientation of a fluorescent molecule, covalently incorporated in a polyisoprene network[9,10] or at the end of a dangling chain,[11] has been detected by fluorescence polarization measurements. The orientational behavior of both rigid[12] and flexible[13] free probe molecules has also been related to the probe geometry.

The possibility that the same kind of interaction might exist in polymer melts has been recently put forward.[14-16] Infrared dichroism measurements on isotopically labeled block copolymers of linear and star polystyrenes have shown a higher orientation of the ends of the arms of the stars relative to that of linear chains.[14] Recent results, obtained by using an infrared dichroism based rheooptical technique,[16] also indicate that in a bimodal blend the relaxation of the short chains after a step–shear was slowed down when the concentration of the long chains was increased. These observations cannot be accounted for by the tube theories,[17-19] even if constraint release effects[20-23] are taken into account. To explain these results, a nematic-like interaction between chain segments in the melt has been proposed. The influence of this interaction on the relaxation dynamics has been theoretically treated independently by Merrill et al.[24] and Doi et al.[25]

The aim of this note is to present further evidence of this orientational coupling between chains in deformed melts and to test the recent theoretical modeling of this phenomenon. To this end, infrared dichroism measurements have been performed on blends of deuterated short PS chains ($M < M_e$) and nondeuterated long PS chains ($M \gg M_e$), where M_e is the molecular weight between entanglements. Such a technique has recently proved to be powerful for the study of the dynamics of relaxing systems.[14,26,27]

Table I
Characteristics of the Different Polymers

material	$10^{-5}M_w$	M_w/M_n
PS160	1.63	1.1
PS1000	11.90	1.4
PSD10	0.10_7	1.07
PSD27	0.27	1.06

Experimental Section

Blends containing 15 wt % deuteriated short PS chains in long-chain PS matrices were studied. This composition was chosen to ensure a reasonable accuracy in the dichroism measurements especially for the deuteriated species without having concentrations of the short chains which were too high. The characteristics and designation of the short chains and matrices are given in Table I. The mixtures were prepared by dissolving a weighted amount of the individual components in distilled benzene at a total polymer concentration of 6%. The polymer films were prepared according to a well defined procedure.[14,26,28] The glass transition temperature T_g of the resulting films was 108 ± 1 °C. No drop of T_g with respect to the long-chain homopolymer has been detected due to the presence of deuteriated short chains.

Films were uniaxially stretched up to a draw ratio $\lambda = 4$, at a constant strain rate of 0.1 s^{-1} and at a temperature of 115 ± 0.4 °C. The films were held at fixed strain and allowed to relax for a given aging time.[28] They were then quickly quenched to room temperature. Short and long times have been reached by varying the stretching temperature and applying time–temperature superposition.[14,28]

The orientation of the PS chains and of the deuteriated species was obtained by using a Nicolet 7199 Fourier transform spectrometer, according to a method detailed in the literature.[14,26] The orientation is quantified in terms of the second moment of the orientation distribution function, $\langle P_2(\cos\theta)\rangle = (1/2)\langle 3\cos^2\theta - 1\rangle$, where θ is the angle between the chain axis and the stretching direction. We estimate that our experimental uncertainty is ± 0.005 P_2 units.

The possibility of a phase separation of the samples in this binary isotopic mixture[29] seems unlikely because of the relatively high value of the χ parameter for the single-phase stability ($\chi_s = 3.3 \times 10^{-2}$) due to the combinatorial entropy of the low molecular weight deuteriated species. We also do not believe the segregation is due to stretching[30] since the critical draw ratio would be on the order of 30.

Results

Hereafter, the orientation of the long and short chains is reported as a function of the aging time t at 115 °C and expressed in seconds.

The relaxation of both components of the blend PS1000–PSD10 (with a volume fraction of short chains $\phi_s = 0.15$) is presented in Figure 1. The long chains undergo a rapid relaxation at short times $-1 < \log t < 1.5$ and a much slower one at longer times. Their orientation seems to go through a plateau in the time scale $2 < \log t < 4$. The orientation of the short chains is always significantly lower, but their relaxation shows a behavior rather similar to

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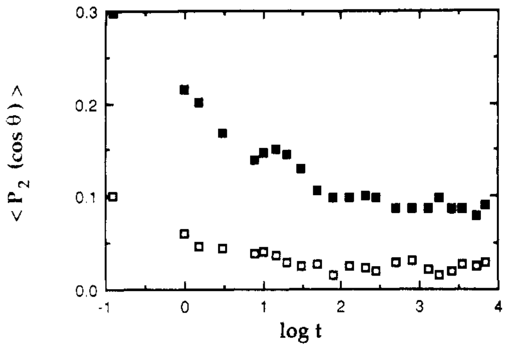

Figure 1. Relaxation of the orientation of PS1000 chains (■) and PSD10 chains (□) in the blend PS1000–PSD10.

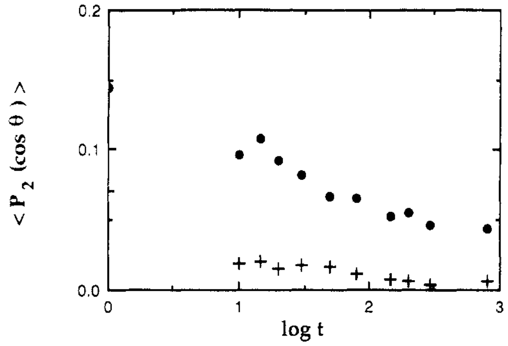

Figure 2. Relaxation of the orientation of PS160 chains (●) and PSD10 chains (+) in the blend PS160–PSD10.

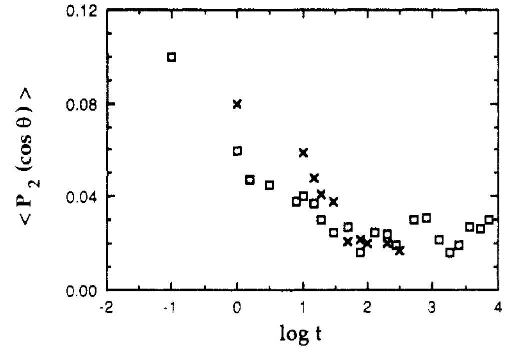

Figure 3. Relaxation of the orientation of the PSD10 chains (□) in the blend PS1000–PSD10 compared with that of the PSD27 chains (×) in the blend PS1000–PSD27.

that of the long chains, in the sense that a nearly constant orientation is observed over a broad range of time.

The same deuteriated chains have been blended at the same volume fraction with PS160, i.e., a matrix consisting of chains shorter than PS1000. The relaxation of the PSD10 and PS160 chains is shown in figure 2. At long times, a lower orientation with respect to the previous blend is observed for both types of chains. Such a result is expected for the long chains.[31] However, the PSD10 chains appear to have a lower orientation in the lower molecule weight matrix, exhibiting thereby a matrix effect.

To determine the dependence of the relaxation of the short chains on their length, experiments were conducted on a third blend consisting of PSD27 chains in the PS1000 matrix. The results, given in Figure 3, are compared with the behavior of the PSD10 chains in the same matrix. At short times, a higher orientation of the PSD27 chains is observed, whereas at longer times the same level of orientation is reached for the two lengths of chains. The orientation of the PS1000 chains, on the other hand, is the same in these two binary blends.

These experimental results show that the relaxation of short chains is sensitive to their length at short times and also to the length of the surrounding matrix chains.

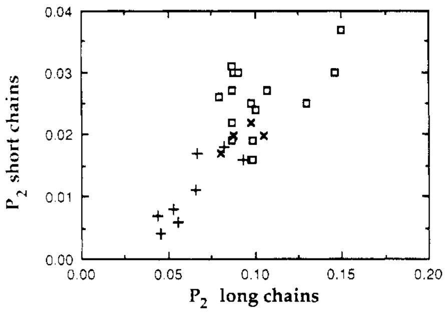

Figure 4. Orientation of the short chains as a function of the orientation of the long chains in the different blends and for sufficiently long times: (□) PS1000–PSD10; (×) PS1000–PSD27; (+) PS160–PSD10.

Discussion

Our data indicate a special kind of matrix effect on the relaxation of the short chains which cannot be accounted for by constraint release processes. In order to explain this observation, some considerations dealing with the respective relaxation times of the chains are required.

Previous studies[26,31] have shown that the relaxation of orientation experienced under our experimental conditions could be interpreted in the context of the Doi–Edwards model.[18,19] This treatment applies only to long entangled chains, the behavior of the short chains being better described by a Rouse type relaxation.[32]

The relaxation time τ_A associated with the relaxation of a chain of a molecular weight M_e (=18 000 for PS) with fixed ends has been estimated to be approximately 28 s at 115 °C.[28,31] Since this relaxation time scales as M^2 and is decreased by a factor of 2 due to the constraints imposed on the ends of the chain, one can estimate that the Rouse relaxation times of our short unentangled chains are $\tau(\text{PSD10}) = 17$ s and $\tau(\text{PSD27}) = 124$ s at a temperature of 115 °C. We therefore expect the short chains to have relaxed their orientation on the time scale of τ, i.e., for $\log t > 1.2$ and $\log t > 2.1$ for PSD10 and PSD27, respectively. Such behavior is not observed experimentally and could not explain the matrix effect.

The main difference between the two matrices relies more on the different anisotropy induced by stretching than on the length of the matrix chains themselves, which are very long compared to the short ones. At times longer than their own relaxation time, the short chains remain oriented due to an orientational coupling with the oriented segments of the surrounding chains.

These experiments can be used for a rough test of a recent theory on orientational coupling in polymer melts. As quoted by Doi et al.,[25] the total measured orientation can be considered as the sum of two contributions: one from the chain itself; the other from an orientational coupling with the oriented surroundings characterized by an efficiency ϵ. In our case, at sufficiently long times, the short chains are relaxed by themselves so that their intrinsic orientation is equal to 0. Under this condition, it can easily be derived from ref 25 that

$$\frac{\bar{Q}_s(t)}{\bar{Q}_L(t)} = \frac{\epsilon(1-\phi_s)}{1-\epsilon\phi_s} \tag{1}$$

in which the subscripts S and L refer to the short and long chains, respectively, $\bar{Q}(t)$ is the total measured orientation at time t, and ϕ is the volume fraction.

In Figure 4, we have reported the orientation of the short chains versus that of the long ones for the different blends in the time scale where eq 1 should hold. The orientation of the short chains is clearly correlated with that of the long species for the different matrix molecular weights. The experimental data seem to indicate a linear relationship between the orientation of the long and short species from which the parameter ϵ can be calculated. We find $\epsilon = 0.26 \pm 0.03$.

This value is rather close to that obtained by Kornfield et al.[16] on hydrogenated polyisoprene melts (0.3–0.4). It is, however, much less than what is found in elastomeric networks where ϵ is close to one[7] or even higher.[6] The difference between the behavior in melts and networks seems to be an open question at the present time.

Conclusion

The experiments reported here show that the relaxation of polymer melts cannot be solely accounted for by reptation and constraint release concepts. The orientation of the chain segments is influenced, in addition to the contribution of their own dynamics, by an orientational coupling with the surroundings. Binary blends of long and short chains are ideal candidates to reveal this interaction. The experimental data are in agreement with the theoretical treatment of this orientational coupling proposed by Doi et al.

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Molecular Orbital Studies on Model Compounds of Simple Silane and Germane Polymers

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Introduction

Poly(organosilanes) [–SiRR′–], where R and R′ represent in general various alkyl and aryl groups, are the focus of intense scientific and technological interest. In particular, their fascinating physical and chemical properties lend themselves toward numerous applications, including as UV photoresists in microlithography, as radical photoinitiators, as impregnating agents for strengthening ceramics, as precursors for silicon carbide fibers, and even as dopable electrical conductors and semiconductors.[1-5] More recently, Miller et al.[6] have synthesized a series of poly(organogermanes) [–GeRR′–] which exhibit many physical and electronic properties similar to the analogous polysilanes.

Among their more unusual properties, polysilanes and, more recently, polygermanes exhibit a marked bathochromic shift in λ_{max} of their electronic spectra associated with an increase in the bulk of the R and R′ substituents.[1-9] In addition, the electronic spectra of di-*n*-hexylsilane and higher alkyl homologues are highly and reversibly thermochromic: below approximately 40 °C they adsorb red-shifted near λ_{max} = 370–380 nm whereas above 40 °C bands near λ_{max} = 320–325 nm dominate.[7,8]

These phenomena have been attributed by some to a combination of side-chain crystallization and the occurrence of trans–gauche conformational transitions along the silicon backbone.[1-4,10] Specifically, melting of the side chains occurring at temperatures above 41 °C allows for conformational transitions away from the trans state, which in general is the one preferred, from the standpoint of side-chain packing efficiency and conformational energy considerations, to the conformationally higher energy gauche states. As temperatures increase, the gauche states become more populated relative to the alternative trans state; hence the chain experiences a gradual and characteristic blue shift in λ_{max} associated with these rod-to-coil transformations.

Several theoretical studies,[8-18] using both molecular mechanics (MM)[8-15] and, more recently, molecular orbital

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