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Fourier Transform Infrared Dichroism Study of Orientation Relaxation Using Isotopically Labeled Polystyrene Stars

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ABSTRACT: Infrared dichroism has been used to measure the orientation relaxation of six-arm polystyrene stars. Block copolymers of perdeuteriated and protonated styrene were used so as to separate the relaxation of the branch point, arm center, and chain end of the star. The results are compared with analogous measurements on linear chains, and the effects of branching are discussed.

Introduction

The manner in which branched polymer chains relax after an imposed strain is one of the remaining questions in molecular viscoelasticity. It is of particular interest to understand this relaxation in the simplest case, which is star polymers. A relaxation mechanism that is different from the reptative motion of a linear chain is suggested by dynamic linear viscoelastic studies on various star polymers.[1–3] It is the aim of this investigation to study the effects of branching on orientation relaxation, especially at short and intermediate relaxation times. While rheological measurements are useful, there is a limit to the detail which they can provide. Much more information can be obtained by studying the relaxation of specified portions of the macromolecules. These require that the portions be labeled and the difference in behavior between labeled and unlabeled units be followed spectroscopically.

The technique used to study molecular viscoelasticity in this investigation is Fourier transform infrared (FTIR) dichroism. Infrared dichroism measurements reveal the chain segment orientation, as averaged over all the chain segments bearing the chemical group of interest. This orientation is induced by an applied strain, and its decay with time is completely analogous to stress relaxation. By use of selectively deuteriated materials, it is possible to distinguish the motions of different segments of a polymer molecule. This method has proven useful in the study of linear chains[4–8] where chain ends are observed to relax faster than chain centers. In this study, the molecular relaxation of star polystyrenes with six arms, deuteriated at either the ends or the central branch point, is measured and compared with the previously studied relaxation of linear chains.[8,9] The results are discussed in light of existing theories of molecular relaxation, and the effects of branching on orientation relaxation are discussed.

Experimental Section

Star block copolymers of perdeuteriated styrene and hydrogenous styrene were prepared by anionic polymerization following the procedure described in ref 10. The parent blocks and the resulting copolymers were characterized by gel size exclusion chromatography (SEC) at 30 °C using THF as the mobile phase. The molecular weights are summarized in Table I, and the resulting stars are shown schematically in Figure 1. The SEC columns (μ-Styragel) were calibrated via the use of 16 polystyrene standards (Goodyear, Polymer Labs, and Toyo Soda). The molecular weights of the previously studied linear chains are also given in the table.

Solutions of each star copolymer were prepared at 8% in distilled benzene and were stirred continuously for 3 days to ensure homogeneous dissolution. Polymer films were obtained by casting these solutions on clean plate glass, followed by drying at room temperature. The resulting 100-μm films were cut to the desired geometry and annealed under vacuum for 70 h at 150 °C to remove residual solvent and internal stress. The samples were annealed on a reticulated plaque to obtain an irregular surface and thereby avoid internal reflectance artifacts in the spectroscopic measurements. The glass transition temperature (T_g) of the resulting films was 108 ± 1 °C. T_g measurements were made with a Du Pont Instruments 1090 thermal analyzer at a scanning rate of 20 °C/min.

The uniaxial stretching measurements were performed with a hydraulic tensile testing apparatus developed in our laboratory.[11] Experiments were performed at 114.9 ± 0.4 °C. For the three longest aging times, experiments were performed at 138.0 ± 0.4 °C, and the measured orientation was shifted to the reference temperature of 115 °C by a standard WLF factor using the coefficients $C_1 = -9.76$ and $C_2 = 64.8$ (for a reference temperature of 115 °C). Similar applications of time–temperature superposition are well established.[12] After equilibration to the oven temperature, the samples were stretched in uniaxial extension at a constant strian rate of 0.1 s^{-1} to an overall draw ratio of $\lambda = 4$. (Possible variation in the macroscopic draw ratio was checked via experiments using films inscribed with ink markers. Only films with consistent draw ratios were used for the spectroscopic measurements.) The films were held at fixed strain and constant temperature for the desired aging time and then quickly quenched to room temperature. This method freezes the residual orientation of the polymer and allows its subsequent evaluation via spectroscopic measurements at ambient temperature.

Infrared spectra were obtained with a Nicolet 7199 Fourier transform spectrometer at a resolution of 2 cm^{-1} with a total of 128 scans. The polarization of the infrared beam was obtained by use of a SPECAC gold wire grid polarizer; samples rather than polarizer were rotated 90° in order to obtain the two polarization measurements. Dichroic ratios were calculated as $R = A_\parallel/A_\perp$ where $A_\parallel$ and $A_\perp$ are the respective measured absorbances for the electric vector parallel and perpendicular to the stretching direction.

Theory

(1) Determination of the Orientation. The orientation function $P_2(\cos\theta)$ is related to the dichroic ratio (R) by

$$P_2(\cos\theta) = \frac{R_o + 2}{R_o - 1}\,\frac{R - 1}{R + 2}$$

where $R_o = 2\cot^2\alpha$, α is the angle between the dipole

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Table I

material and designation		deuterated block			hydrogenous block	
		position	$10^{-4}M_w$	M_w/M_n	$10^{-5}M_w$	M_w/M_n
poly(styrene-h_8–styrene-d_8)$_6$	STAR-a[a]	chain end	3.70	1.05	1.88	1.05
poly(styrene-h_8–styrene-d_8)$_6$	STAR-b[a]	branch pt	3.06	1.04	2.15	1.05
poly(styrene-h_8–styrene-d_8)	L1-a[b]	chain end	2.70	1.03	1.57	1.05
poly(styrene-h_8–styrene-d_8–styrene)-h_8)	L1-b[b]	center	3.00	1.03	0.79	1.03
poly(styrene-d_8–styrene-h_8–styrene-d_8)	L2[b]	chain end	3.88	1.03	4.24	1.08
poly(styrene-h_8)	L6[c]				11.9	1.4

[a] This study. [b] Reference 8. [c] Reference 9.

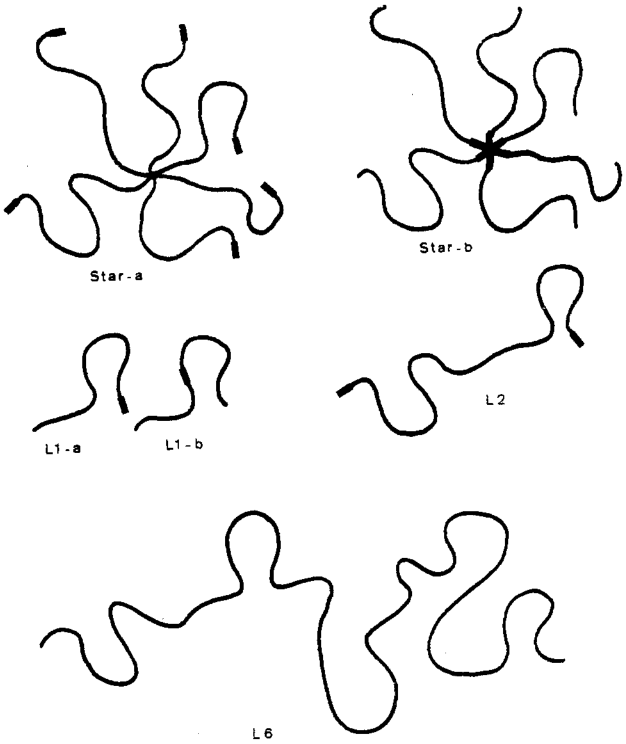

Figure 1. Schematic representation of materials: (—) poly(styrene-h_8), (■) poly(styrene-d_8).

moment of the considered vibration and the chain axis, and θ is the angle between the chain axis and the stretching direction.

In the case of a block copolymer, clearly separated absorbances must be chosen in order to follow the variation in R for each block. The absorbance at 906 cm^{-1} was chosen to monitor the PSH block. This absorbance corresponds to the out-of-plane ν_{17b} mode of the benzene ring for which $\alpha = 35°$.[13]

The absorbances at 2195 and 2273 cm^{-1} were used to monitor the PSD block. They correspond to assymetric stretching vibrations of CD$_2$ groups and stretching vibrations of aromatic CD groups, respectively.[14] The angle is not known for these absorbances, but it has been shown[4] that the orientation function is algebraically related to R as follows:

$$P_2(\cos\theta) = -3.8\left(\frac{R-1}{R+2}\right)_{2195}$$

$$P_2(\cos\theta) = -2.7\left(\frac{R-1}{R+2}\right)_{2273}$$

Once the orientations of the PSH and PSD blocks were known, the average orientation of the entire star copolymer was calculated as the weighted average of the blocks. As a caveat, the possibility of nonideal mixing in the melt due to isotope effects has been considered[15] and is assumed to be negligible for these copolymers.

Similar methodology was followed in the previous studies on linear polystyrenes.[8,9] Where necessary, the previous data have been shifted by a standard WLF factor to this experimental temperature.

(2) Predictions of the Orientation. Before we discuss the theoretical developments for relaxation in star polymers, it is appropriate to briefly recapitulate the theories for linear chains from which the newer work derives. The initial reptation concept of de Gennes[16] is now widely recognized as a useful means of envisioning polymer relaxation. This early description of curvilinear diffusion of a chain along a tube defined by its topological constraints has been elaborated by Doi and Edwards.[17,18] The model of Doi and Edwards describes polymer relaxation in terms of three characteristic times: τ_A, the time for Rouse motion of chain subsections between entanglements; τ_B, the time for retraction of the deformed chain inside its deformed tube to recover its equilibrium curvilinear length (this motion is only important for large deformations); and τ_C, the time for reptation of the chain through its deformed tube.

Though originally devised to describe the motion of a free chain in a net of fixed obstacles, this model can be made self-consistent to account for the motion of the surrounding chains. Previous work from this laboratory[7-9] has established the applicability of the Doi–Edwards model to linear chains.

In the case of star polymers, the reptative mode of relaxation is expected to be quenched by branching.[19] The general picture of entangled chains has been used by Doi and Kuzuu[20] and Pearson and Helfand[21] to treat the case of relaxation in star molecules. These authors were mainly interested in the long time motions where the reptation mechanism is suppressed. The relaxation involves the retraction of the arms along their tube axes by large-scale fluctuation processes. Both theories agree with the longest relaxation time showing an exponential dependence with the number of entanglements per arm, the prefactors being somewhat different. Before reaching this long time limit, we can expect that a star polymer will exhibit relaxation motions rather analogous to linear polymers: i.e., a short time Rouse-like relaxation independent of the molecular weight, followed by the retraction of the deformed arms inside the deformed tubes to regain their equilibrium length, and possible coupling with the chain length fluctuation process. We will focus our attention in the present paper on the short and intermediate time behaviors. Advantage will be taken of the block structure of our copolymers to discuss the relaxation of segments located close to the branch point or further away or near the chain ends and to make comparisons with similar segments on linear chains.

Results

Hereafter the measured orientation relaxation is reported in terms of the Rouse relaxation time, τ_A. This relaxation time is a convenient normalizing factor since

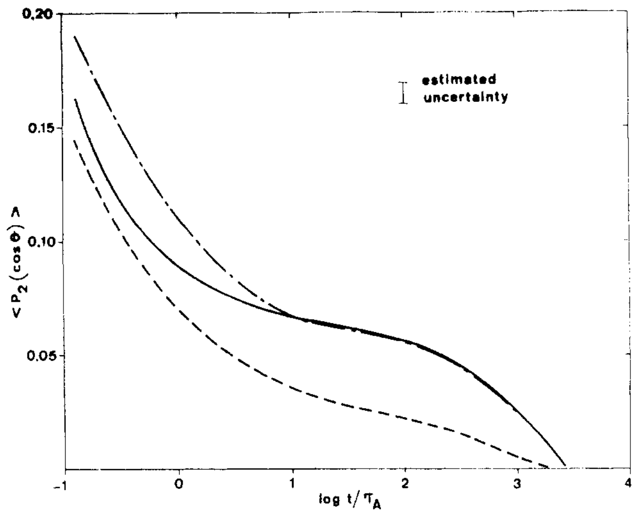

Figure 2. Orientation function versus time for STAR: (-·-) branch point, (—) central block of an arm, (---) chain end.

it is independent of molecular weight. In the case of polystyrene, τ_A = 28 s at this experimental temperature of 115 °C.[6] Nearly 5 decades of time are spanned by the measurements. The resulting data allow the examination of orientation relaxation at short and intermediate times ranging from below τ_A to above τ_B.

Since comparisons are made between several polymers in the following sections, a brief aside for nomenclature is perhaps in order. As described in Table I and in Figure 1, we compare a six-armed star polymer with linear chains whose lengths are comparable to one, two, and six arm lengths. These material will be referred to as STAR, L1, L2, and L6, respectively. With the exception of L6, each of these materials is a copolymer of styrene and perdeuteriated styrene. The perdeuteriated block represents 15% of the copolymer and is located at either the chain end, the chain center, or the branch point as differentiated in the nomenclature by -a and -b. By comparing the appropriate copolymers and by selecting the proper infrared absorbances, as outlined in the preceding section, it is possible to measure the orientation of the chain end (terminal 15%), the central block of the chain or arm (central 85%), the center of the chain (central 15% of linear chain), the branch point (central 15% of star), and the overall average.

(I) Orientation Relaxation in Star Molecules. The utility of isotopic labeling is evident in Figure 2 where the relaxations of different segments within a star polymer are compared. The branch point (15% around the branch point) appears initially more oriented than the central block of the arm (85% around the branch point). The central block, in turn, is more oriented than the chain end. As the materials relax at fixed strain, the chain end orientation decays rapidly. At long times, the relaxation of the central block orientation is similar to the relaxation of the branch point. The end block is always less oriented and shows a more rapid relaxation. This behavior suggests that orientation relaxation in the arms of the star first occurs at the chain end and then progresses along the central block toward the branch point.

(II) Comparison between Linear and Star Molecules. The relaxation of the average orientation of the six-armed star is compared with that of linear polymers in Figure 3. The short time behavior does not appear very different from that of linear chains. This result is not surprising since our previous studies on linear chains have shown that the relaxation at short times can be attributed to local relaxation modes, thus independent of the molecular architecture of the chain. In contrast, the relaxation of the star molecule is different at long times from that of a linear chain with a length equal to the length of either one arm (L1), two arms (L2), or even the same overall molecular weight (L6). The orientation of the branched chain at an intermediate time scale lies between that of the L2 and L6 linear polymers. This behavior indicates that the relaxation of the star molecule is more rapid than that of a linear chain of equal mass, emphasizing the role of the molecular structure of the chain. The relaxation of an arm is less facile than that of an unbranched chain of equal length, suggesting that long time modes are suppressed by branching. This leads to the appearance of a rather long plateau in the relaxation of the star which was not as pronounced in the linear chains.

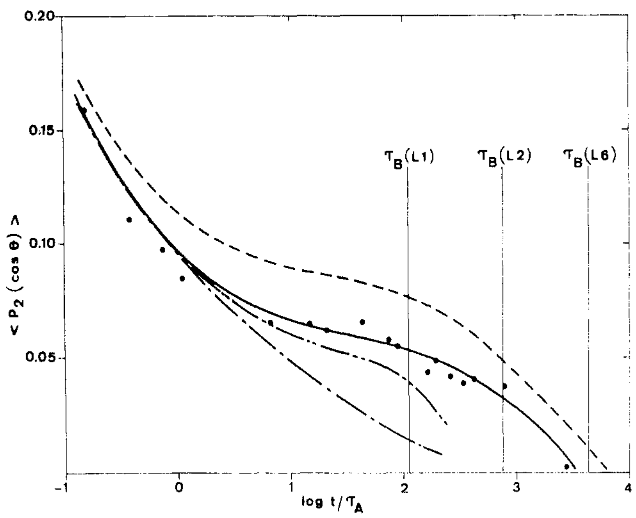

Figure 3. Overall average orientation function versus time for various polystyrenes: (---) L6, (—) STAR, (-··-) L2, (-·-) L1.

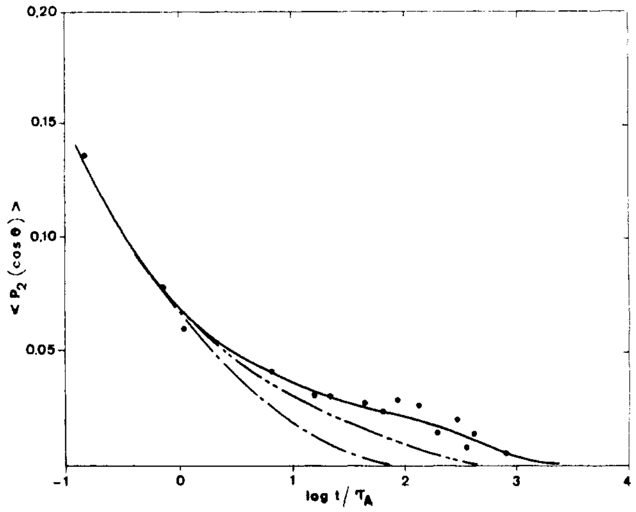

Figure 4. Chain end orientation function versus time for various polystyrenes: (—) STAR, (-··-) L2, (-·-) L1.

In order to check whether chain ends or the central part are responsible for this behavior, the orientation of both blocks has been compared in linear and star molecules. The relaxations of orientation of chain ends of the star, L1, and L2 polystyrenes are presented in Figure 4. The highest orientation is obtained for the end part of the arm of the star. It has been shown that the relaxation of an end part of a chain is sensitive to its length and to the overall length of the chain. This accounts for the differences in the orientation of the L1 and L2 chain ends. The end segment of the arm of the star is slightly shorter than that of the L2 copolymer, and the total length of the L2

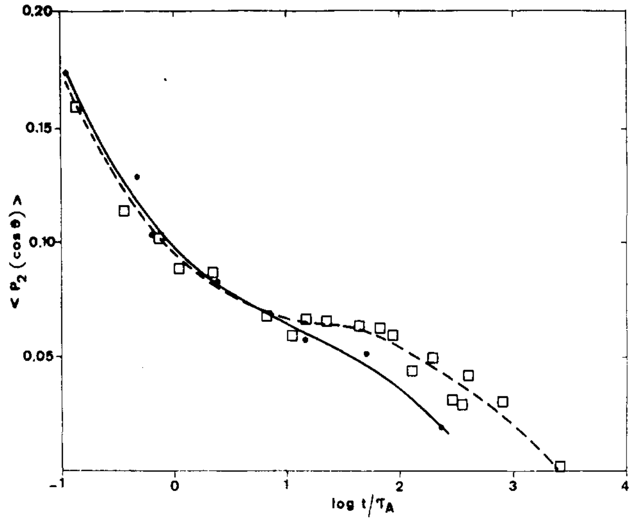

Figure 5. Orientation function versus time for central block of STAR (- - -) and central block of L2 (—).

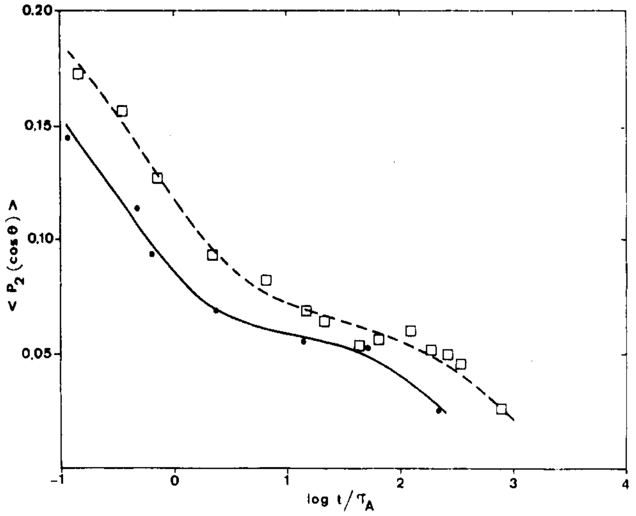

Figure 6. Orientation function versus time for branch point of STAR-b (- - -) and central block of L1-b (—).

copolymer is slightly higher than twice the length of the arm. For these reasons, a lower orientation of the end block of the arm as compared to that of the linear chain is expected. This experimental result suggests that the relaxation of the end part of an arm in the star polymer might be intrinsically slower than that of the linear chain because of the suppression of a relaxation mode (like the reptation mechanism). Another conjecture is that the chain end remains more oriented thanks to the existence of an orientational coupling with the surroundings which are more oriented for stars than for linear chains (see Figure 3).

The behaviors of the central part of the L2 copolymer (protonated block of molecular weight 4.24×10^5) and of the star (protonated block of star) are compared in Figure 5. As in the previous cases, the short time relaxation is identical in both materials. An important difference can be noted at long times ($\log t/\tau_A \geq 1$), where the central part of the star remains more oriented. Here again, a plateau is evident for the star but not for the linear polymer. To be very accurate in this comparison, it must be noted that the two blocks do not have exactly the same length and are not located on "chains" having the same molecular weight. The block of the star under consideration is slightly smaller than that of the linear chain and may therefore present a higher orientation. But the length of the chain is higher than twice the length of one arm which should lead to a lower orientation for the star polymer. These two effects act in opposite directions and may balance each other. We therefore claim that the observed behavior is not an effect of the different lengths of the polymers under consideration (since they are quite comparable) but reflects the effect of "pinning" the center of the chain and thereby suppressing the reptation motion.

Another comparison dealing with shorter central sequences is of value. In Figure 6, we have plotted the relaxation of the orientation of the deuteriated central block of the L1-b copolymer and that of the deuteriated central block of star-b. The orientations of the different blocks show a distinctly different behavior at short times, the center of the star polymer being significantly more oriented than the center of the linear chain. Differences in the overall molecular weight cannot account for this observation since short time relaxation is molecular weight independent. On the other hand, the differences in the molecular weights of the chains do affect the long time relaxation, and we can state that the center of the star will relax at longer times than the linear chain. The shift between the two curves can be related to the lengths of the chains as a first approximation. Since reptation does not reach the central part of the chain in this time scale, the relevant relaxation time is τ_B and scales as M^2. Hence, a shift of $\log (M_{\text{star}}/M_{\text{lin}}/2)^2 = 0.8$ decade of time can be expected. Our results roughly indicate between 0.5 and 0.6 decade. Therefore, we can argue that the relaxation of the central part of the star copolymer in this time scale is not significantly slower than that of the linear polymer, equivalent to the center of L2. Moreover, our results tend to suggest that the relaxation of the center of the star might be even more rapid.

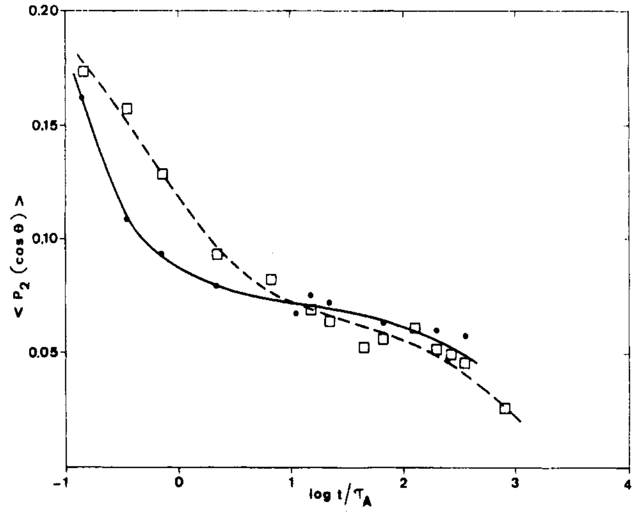

Figure 7. Orientation function versus time for the branch point of star (- - -) and external block of star (—).

In order to examine this assumption, we have plotted the relaxation of the central part of the star (deuteriated block of star with $M = 3.0 \times 10^4$) and that of the middle part of the arm (i.e., arm minus central point minus end block) in Figure 7. We thus compare a 30K central part with a 171K "external" part. The higher orientation of the 30K block, which was already noted at short times on the previous figure, is still apparent here. At longer times, the orientation of the central part is similar, probably even slightly lower than that of the external block. Although this effect is rather tiny, it is very surprising. Indeed, if we consider that the relaxation originates from the end of the chain, we expect a lower orientation for the external block. Such a result is not obtained experimentally, suggesting that the relaxation of the center is more rapid than expected.

Discussion

In this discussion, we would like to emphasize some important points that have been raised in the preceding section.

The first point concerns the difference between the relaxation of average orientation in the star, in the L2 copolymer, and in the L6 polymer. This point is not trivial, since we know that the zero shear viscosity is dominated by the total molecular weight of the polymer and enhanced in the stars with regard to the linear polymer of the same molecular weight (in this range of molecular weights).[2,22] Our results indicate that, in the time scale of our experiments, the relaxation of orientation is not dominated by the reptation of the branches. On the other hand, the relaxation of orientation appears slower than for the linear polymer with M_w equal to the length of one arm. This is not surprising but gives an estimate of the effect of pinning one end of the chain. It is also interesting to note that the relaxation of orientation is slower than for the L2 copolymer. This is more surprising, since it is very tempting to model the relaxation of one arm in the intermediate time scale as that of a linear chain with a molecular weight twice that of the arm. This slowing down of the relaxation of the star (even in this time scale) must be attributed to different dynamics for the relaxation of one arm by comparison to that of a linear chain.

The second point concerns the high orientation of the ends of the arm. From the study on linear polymers,[8] we know that the lower orientation of chain ends can be attributed to the retraction and chain length fluctuation motions. Reptation is not important here, since the orientation is completely relaxed (at least theoretically) by the fluctuation mechanism (the ends being considered are rather short).[23] Therefore, we expect equivalent behavior for the ends of the star. Nevertheless, we know[8,24] that part of the orientation of chain end segments is due to an orientational coupling with the oriented surroundings. We believe that the higher orientation of ends of arms is the result of this type of interaction with the surrounding media, which is more oriented in the case of stars.

The third point deals with the high orientation of the central part of the star especially at short times. A higher orientation of chain segments can arise from a smaller distance between entanglements. From melt viscoelastic measurements, we know that the plateau modulus of the star is the same as for linear polystyrenes,[2] implying that the molecular weight between entanglements is unchanged. Moreover, at the present molecular weight, we can estimate that the average distance between branch points of stars is on the order of the radius of gyration of one arm. Therefore, it seems unreasonable to believe in a special interaction due to close branch points. In our opinion, this behavior originates from the so-called core of the star which is described by a dense region of stretched segments.[25] We can put forward an analogy between the orientation of the segments inside the core and the orientation of segments in spherulites. In the latter case, segments rotate in the direction of the stress, rather than extend, like in amorphous chains.[26] A direct consequence is that a high orientation can be obtained. (Values of P_2 currently range around 0.8–0.9 for deformations of 300%.) Although the core region only extends over $f^{1/2}$ statistical segments,[25] i.e., a molecular weight of roughly 2500 or 1/10th of our central block (f being the functionality of the star), this might be sufficient to produce an orientation of the central block higher than expected.

The last point that we would like to mention concerns the relaxation of the central part of the arm. It appears somewhat more rapid than anticipated. This is surprising and indicates that the relaxation is not simply a process which begins at the end of each arm and moves inward. At the present time, we do not possess an adequate explanation for this behavior.

Conclusions

These measurements on six-armed polystyrene stars reveal the usefulness of FTIR dichroism in understanding molecular viscoelasticity. Orientation relaxation has been measured over nearly 5 decades of time. Block copolymers of styrene and perdeuteriated styrene have been used to separate the relaxation of the chain end, arm center, and branch point of the star. When compared with analogous measurements on linear chains, several striking differences are observed. The overall average orientation relaxation of an arm of the star polymer is slower than that of a comparable chain in the absence of branching. Residual orientation of the chain ends is observed and attributed to the surrounding media of partially oriented chains. Branching is seen to hinder significantly molecular relaxation.

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Registry No. Polystyrene, 9003-53-6.

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