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Deuterium NMR Study of Phenyl Group Motion in Glassy Polystyrene and a Blend of Polystyrene with Polyphenylene Oxide

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ABSTRACT: Deuterium solid echo line shapes were measured as a function of temperature and echo delay time on glassy polystyrene and a blend of polystyrene with poly(2,6-dimethyl-1,4-phenylene oxide). The spectra were strongly temperature dependent from room temperature to the glass transition, indicating motion on the time scale of tens to hundreds of microseconds. The line shape signature of π flips is present in these spectra. The time scale and temperature range overlap the β process seen in dynamic mechanical spectroscopy on both pure polystyrene and in the blend. A quantitative interpretation of the phenyl dynamics was based on a simultaneous description of phenyl group rotation which allows for small angle jumps and π flips. A fairly broad distribution of correlation times was introduced through the use of the stretched exponential correlation function. The quantitative interpretation reinforces the time/temperature overlap of the phenyl group motion with the β process though the apparent activation energies from different approaches are difficult to compare due to the limited temperature range and the overlap with the α process.

Introduction

The dynamics of glassy polystyrene have been investigated with a wide variety of experimental and theoretical approaches. Dielectric[1-3] and dynamic mechanical response[4-8] data on this polymer are quite complete and provide the starting point for any NMR study. Proton,[9-13] carbon-13,[14] and deuterium[15,16] NMR have all already been applied to this polymer though the interpretations vary somewhat.

The mechanical, dielectric, and NMR experiments have generally concluded that the β process is involved with phenyl group motion though some of the reports associate lower temperature relaxations with phenyl group motion as well. The β process is close to the glass transition in temperature and overlaps it at the higher frequencies typically employed in NMR experiments. Even typical mechanical measurements at 1–10 Hz show the β process as a low-temperature shoulder on the glass transition process.[5] The glass transition temperature is near 400 K and the β process is within 50 deg of this temperature in most of the experimental data.[5] The proximity to the glass transition in temperature and frequency interferes with all the experimental approaches, limiting the information that can be extracted.

Calculations on isolated chain fragments[17-19] and on bulk amorphous polystyrene[20] indicate phenyl group motion is quite restricted in contrast to the interpretations developed from the experimental data. Solution dielectric[21] and NMR studies[22] indicate the presence of phenyl group rotation on a time scale comparable to segmental motion. These solution measurements are best compared with the isolated chain fragment calculations. For bulk polystyrene, deuterium line shape data on phenyl-labeled material points to the presence of π flips,[15,16] with the most recent study[16] indicating the participation of all phenyl groups in this motion. Earlier solid-state NMR studies[14,15] involving more limited data sets resulted in interpretations involving the flipping of only a small fraction of the phenyl groups.

The present study uses phenyl deuterium labeled polystyrene but in contrast with the earlier studies phenyl-d_4-labeled polystyrene is employed here with the para position left protonated. This is important since any rotational motion of the phenyl group in polystyrene about the symmetry axis will not affect the para phenyl line shape. Thus in the studies employing phenyl-d_5-labeled polystyrene, the unaffected para line shape is superimposed on the line shape of the other phenyl deuteron positions which contain the dynamic information of interest. Some assumption about this unaffected line shape must be made in order to interpret changes in the composite line shape patterns. This is further complicated in the typical echo study since intensity reduction produced by motion on the time scale of the echo delay occurs.[23] Frequently, 80% of the signal from the deuterons affected by motion can be lost over the duration of common echo delay times, which could make the para deuteron line shape a significant contributor to the pattern, obscuring the information on ring rotation dynamics.

In addition to the improvements obtained by using polystyrene-d_4, the effects of blending on phenyl dynamics will be studied. Mechanical data are again available on the blend[24,25] of PS with poly(phenylene oxide) (PXE), and a β relaxation process is evident in these blends. In fact, the β relaxation becomes a more distinct feature of the mechanical response as a function of temperature as PXE is added to the PS. The glass transition temperature of the blend also rises significantly[26] as PXE is added since PXE has a considerably higher glass transition temperature relative to PS. This resolution of the β relaxation due to the raising of the α relaxation by the addition of a high-T_g blend component is not unexpected. Glass transition dynamics of pure PS and blends of PS and PXE have been studied by two-

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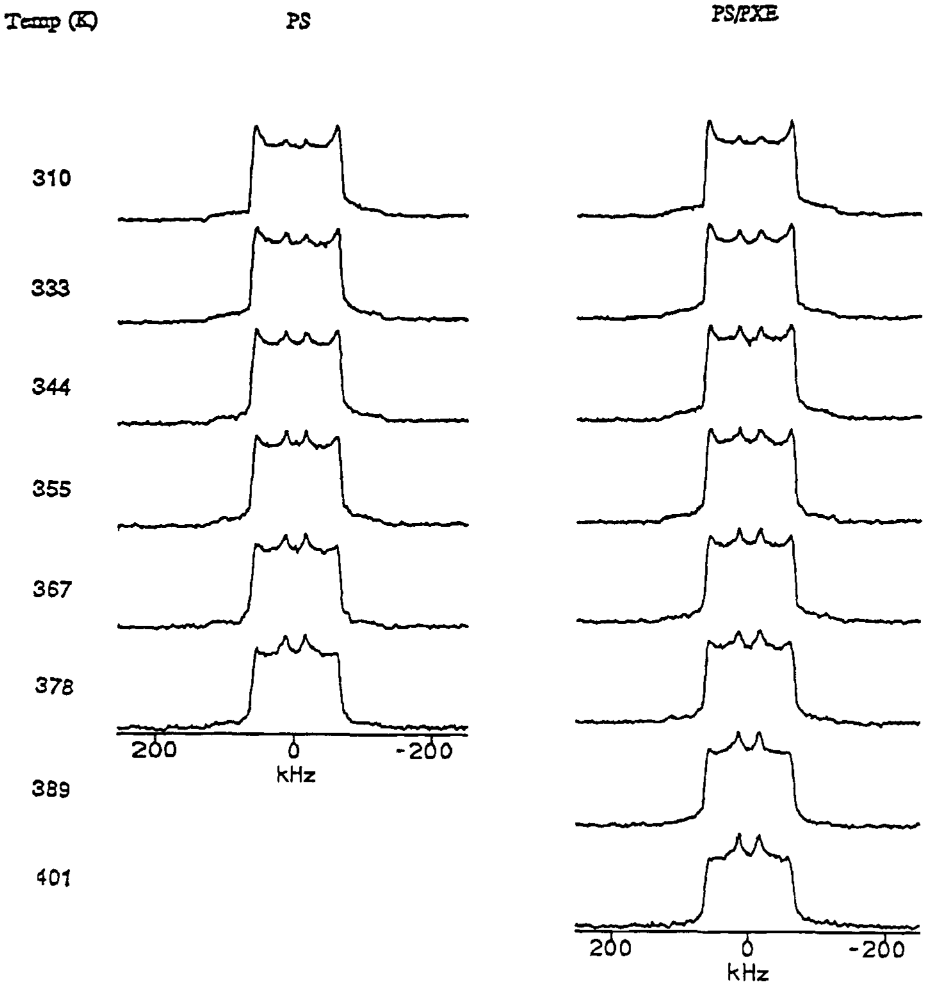

Figure 1. Experimental one-dimensional deuterium spectra as a function of temperature for PS and the 25/75 blend of PXE/PS at an echo delay time of 20 μs.

dimensional deuterium NMR.[27,28] It is hoped that the NMR study on the phenyl-labeled PS reported here will indicate the role of the phenyl group motion not only in pure PS but also in the blend, with the added prospect of determining the effects of blending on this motion. When PMMA is added to polycarbonate,[29,30] the main sub-glass transition relaxation process involving phenyl group motion of the polycarbonate is suppressed. The possibility of such a phenomenon occurring in this blend will be directly addressed in this study.

Experimental Section

Phenyl-deuterated polystyrene (PS-d_5) was purchased from Cambridge Isotope Laboratories, and poly(phenylene oxide) (M_n = 17 000 and M_w = 34 000) was obtained from General Electric. The PS-d_5 was converted to PS-d_4 (M_n = 29 494 and M_w = 70 210) by replacing the para deuteron first by bromination and then by hydrogenation.[31] A 25–75 wt % blend of PXE and PS, respectively, was prepared as reported in an earlier NMR study of this system.[32] DSC analysis of the blend showed a single glass transition at 128 °C, in agreement with those reported on fully protonated polymers.[25]

One dimensional deuterium fully relaxed solid echo experiments were performed on a Bruker MSL 300 at a deuterium frequency of 46.073 MHz. A Bruker HP-300BB (broad band) probe with a 5 mm coil was used, and sample temperature was regulated by a Bruker VT-1000 temperature controller. The temperature was calibrated with a thermocouple placed in a sample tube within the 5 mm coil. The $\pi/2$ pulse width was 2.5 μs and echo delay times of 20, 50, 100, and 150 μs were employed. A recycle delay time of 20 s was used, which is at least 5 times the observed spin–lattice relaxation time.

Results

Experimental one-dimensional deuterium spectra obtained at an echo delay time of 20 μs on PS-d_4 at temperatures from 310 to 378 K are shown in Figure 1 along with comparable spectra on the 25–75 blend at temperatures from 310 to 401 K. Figure 2 contains spectra at a series of echo delay times for both pure PS and the blend at temperatures of 333 and 378 K.

Interpretation

At all temperatures shown in Figure 1 two inner peaks are present which are indicative of the presence of a rapid π flip motion of the phenyl groups about their symmetry axis, rapid being defined as fast compared to the frequency breadth of the ^{2}H quadrupole powder pattern ($\approx 10^5$ Hz). The inner peaks grow in amplitude at the expense of the relatively rigid Pake pattern as temperature is raised. This is in reasonable agreement with the qualitative features seen in the spectra reported earlier[15,16] on PS-d_5 but the relative amount of inner peak intensity corresponding to rapid π flippers is greater as would be expected since this motion does not affect deuterons in the para position.

Qualitatively, the variable-temperature spectra on the 25–75 blend (PXE/PS) are very similar except spectra

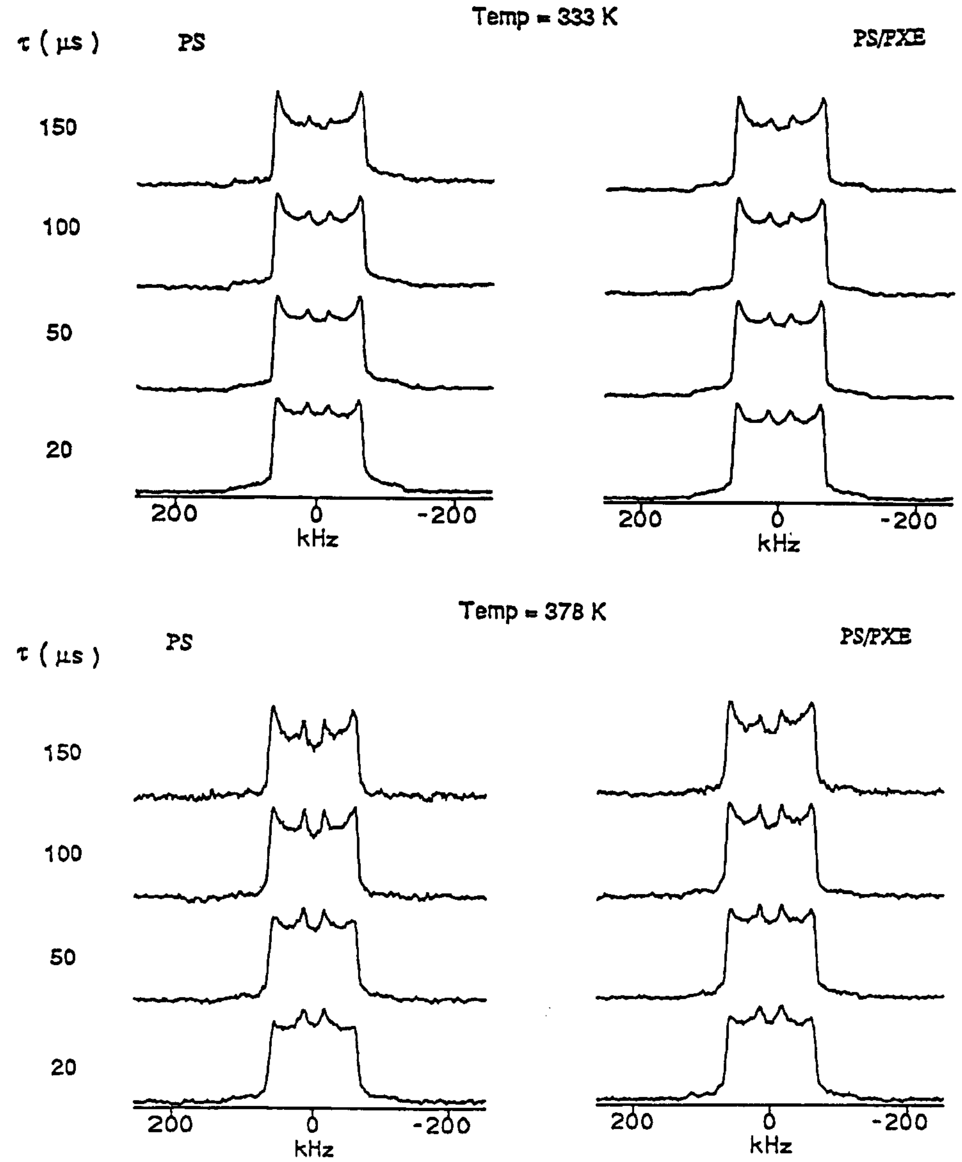

Figure 2. Experimental ^{2}H spectra as a function of echo delay time (τ) at 333 and 378 K for PS and the blend PXE/PS.

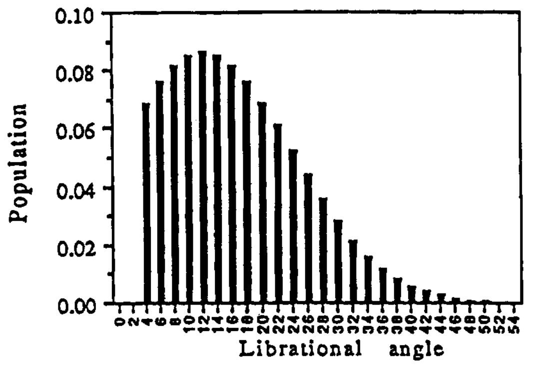

Figure 3. Distribution of librational amplitudes used to characterize the motion of the nonflipping population of PS phenyl rings.

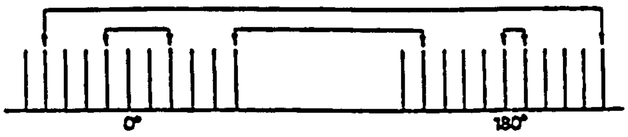

Figure 4. Schematic of the simultaneous model for oscillation and flips between two conformational minima separated by 180°. The example shown is for 22 sites with 4 typical jumps; all jumps are equally probable.

can be taken at higher temperatures because of the higher glass transition of the blend. At the higher temperatures the line shape component from rapid flippers becomes the predominant feature.

The variable echo time spectra on PS-d_4 and the blend are also quite similar and show the expected trend of a decreasing contribution of the rapid flippers to the line shape as the echo delay time is lengthened. Both the temperature dependence of the line shape and echo delay time dependence indicate motion on the microsecond time scale at these temperatures. This temperature regime and time scale correspond to the β process seen in dielectric and mechanical response in pure PS.[5]

To quantitatively described the dynamics in this system, simulation of the spectra can be undertaken based on the values of the static quadrupolar coupling tensor and descriptions of motion already developed for application to other synthetic polymer systems. For the π flip motion there are quite a few dynamic models to choose from though many of the models are closely related. The first common feature of the models is to allow for only a fraction of the phenyl groups to flip[14,15] or to assume that a fraction flip more rapidly.[16] In the

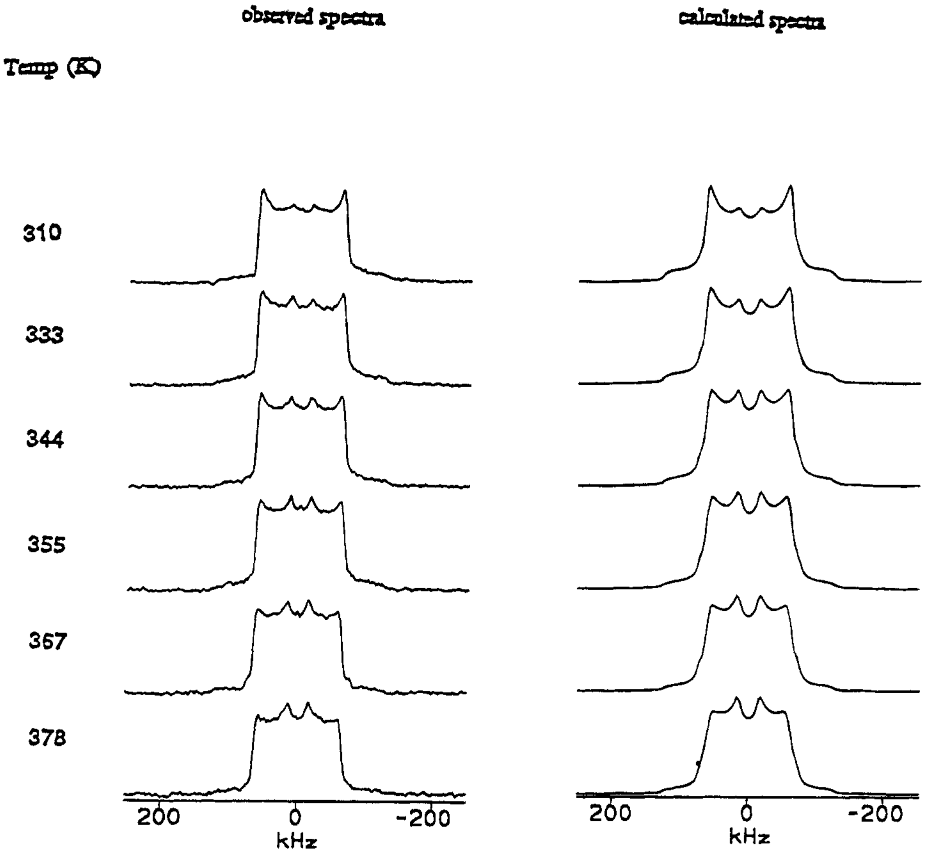

Figure 5. Experimental and calculated ^{2}H spectra for PS as a function of temperature at an echo delay time of 20 μs.

model employed here, one parameter is the fraction of phenyl groups that flip.

The fraction of phenyl groups that do not flip are often assumed not to be completely static and are assumed to undergo rapid librational motion about the symmetry axis of a limited angular amplitude. This approach is implemented here and in fact a Gaussian distribution of librational amplitudes is employed following the simulation methodology by English et al.[23,33-35] The distribution of librational amplitudes is often allowed to increase with temperature but a single distribution shown in Figure 3 is employed here since the fraction of nonflipping groups is small and the simulations do not depend strongly on the exact nature of the distribution of librational amplitudes.

The fraction of phenyl groups that do flip are often found to have more complex dynamic characteristics than a single jump angle and a single rate.[33-35] English et al. use a Gaussian distribution of jump angles centered around the conformational minimum.[33-35] Distributions of correlation times are frequently employed and may cover several decades of time.[16-18,32] Theoretical simulations of phenyl group motion in amorphous polystyrene indicate the presence of small oscillations, short jumps, and rather a few large-amplitude jumps close to π flips.[20] The signature of the π flip process is clearly present in the spectra. The challenge of developing an interpretation is to allow for all the various motions occurring in combination with the flips and yet have a manageable number of parameters. Given this situation and the data base in hand, there is no unique model choice in this regard, and we have chosen a simultaneous model[36] which allows for small-angle jumps and large-angle jumps centered in angular amplitude around 180° with the time scale described by a stretched exponential. This model allows for both a distribution of time scales through the stretched exponential form which may be written as a sum of exponentials[37] and a distribution of jump angles including but not limited to the flip process.

The parameters controlling the time scales are the fractional exponent α and the characteristic time τ_p of the stretched exponential form of the correlation function $\phi(t)$.

$$\phi(t) = \exp[-(t/\tau_p)^{\alpha}] \tag{1}$$

The exponent effectively effectively controls the breadth of the distribution of time scales in terms of exponential correlation times.

Angular disorder is introduced in the simultaneous model by allowing for jumps of equal probability between a set of regularly spaced sites centered around 0 and 180°. The basic twofold character of the motion is introduced by having the sites centered at 0 and 180°, and angular disorder is introduced by allowing jumps between all available sites. Figure 4 shows how this introduces both small- and large-amplitude jumps. The parameters are the spacing or step size of the sites and the breadth of the wells around 0 and 180° which contain the sites.

The various quantities entered into the simulation can be summarized as follows. The principal values of the quadrupolar coupling tensor determined from low-temperature spectra (e^2qQ/h = 170 kHz) and a value of T_2 (320μs) also determined at low temperatures are entered as fixed quantities. The fraction of phenyl groups that flip is considered to be constant at all temperatures. The fractional exponent α, time scale τ_p, site step size, and breadth of the angular well around 0 and 180° are adjusted at each temperature. Figure 5

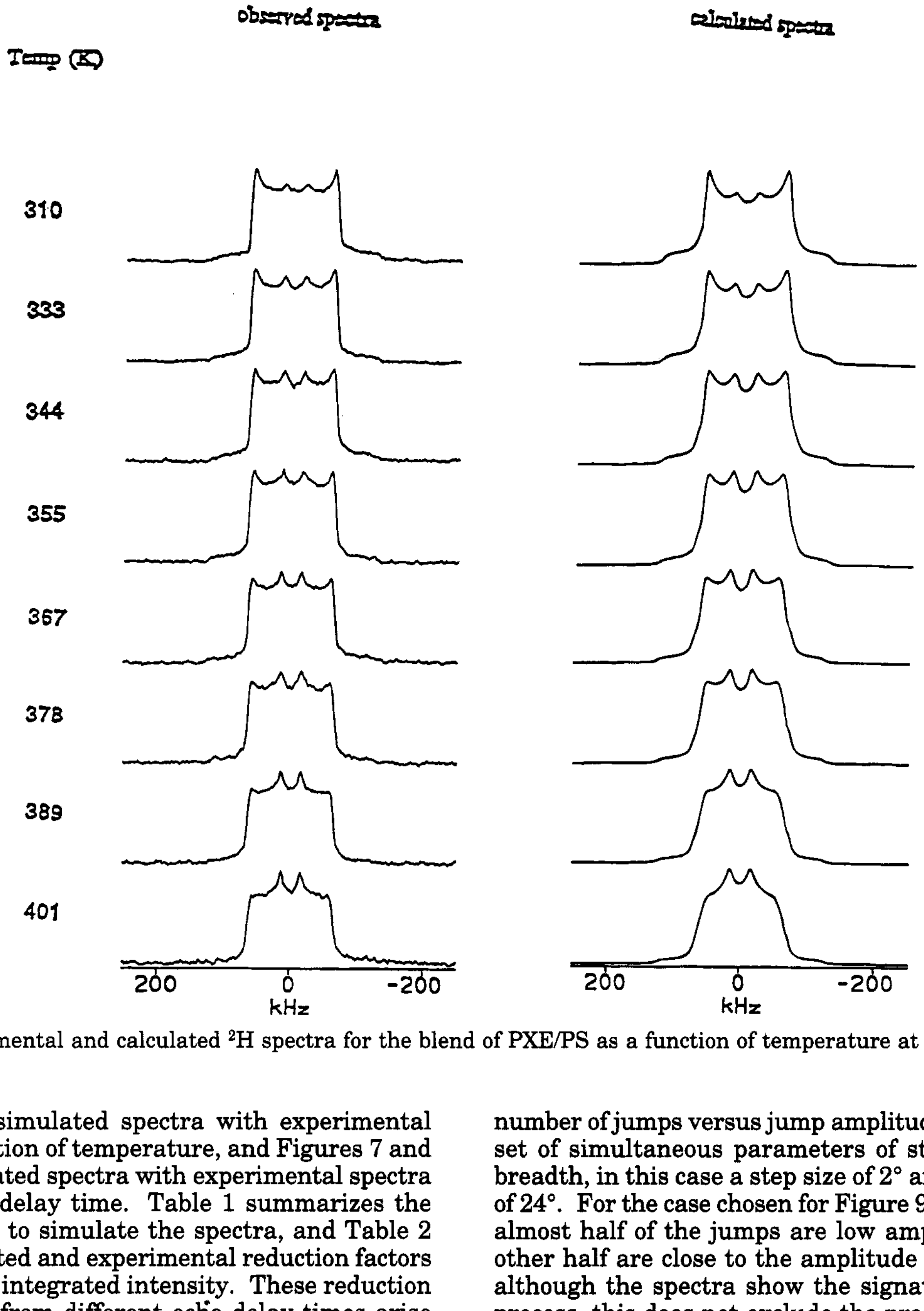

Figure 6. Experimental and calculated ^2H spectra for the blend of PXE/PS as a function of temperature at an echo delay time of 20 μs.

and 6 compare simulated spectra with experimental spectra as a function of temperature, and Figures 7 and 8 compare simulated spectra with experimental spectra as a function of delay time. Table 1 summarizes the parameters used to simulate the spectra, and Table 2 compares simulated and experimental reduction factors determined from integrated intensity. These reduction factors obtained from different echo delay times arise from both T_2 effects and the loss of intensity due to motion occurring on the same time scale as the echo delay time.

Discussion

The line shape features as a function of temperature and echo delay time can be reasonably reproduced by the simulation procedure. For pure polystyrene, the percentage population of phenyl groups undergoing jumps including π flips is 82%. This result is much higher than the early estimates[14,15] of the fraction of flipping phenyl groups but is not as high as the fraction found by Kulik and Prins,[16] who report that 100% of the groups are flipping though their model is based on a description which allows for both fast and slow flippers.

While the percentage of phenyls allowed to jump is 82%, the simultaneous model actually allows for comparable amounts of small-amplitude jumps and large-amplitude jumps or flips. Figure 9 shows the relative number of jumps versus jump amplitude for a particular set of simultaneous parameters of step size and well breadth, in this case a step size of 2° and a well breadth of 24°. For the case chosen for Figure 9, which is typical, almost half of the jumps are low amplitude while the other half are close to the amplitude of a π flip. Thus although the spectra show the signature of the π flip process, this does not exclude the presence of an equal amount of small-angle jumps. The effect of small jumps on the line shape is not as distinctive and is therefore not as readily noticed. This does not completely remove the discrepancy between the NMR line shape interpretations and the theoretical simulations of ring dynamics in amorphous polystyrene[20] but it certainly comes closer to the theoretical results which stresses the presence of small-angle jumps.

An apparent activation energy can be calculated from the temperature dependence of the characteristic time τ_p of the stretched exponential correlation function. An Arrhenius plot is shown in Figure 10 which leads to an activation energy of 69 kJ/mol. This is below the mechanical and dielectric results[5] of 125–146 kJ/mol for the β process as well as the value of 233 kJ/mol of Kulik and Prins[16] for the slow flippers. However, the correlation times obtained from the NMR data reported here can be compared with the mechanical data of Illers and Jenckel.[4] This is accomplished by using the time scale and distributional width for the phenyl motion to

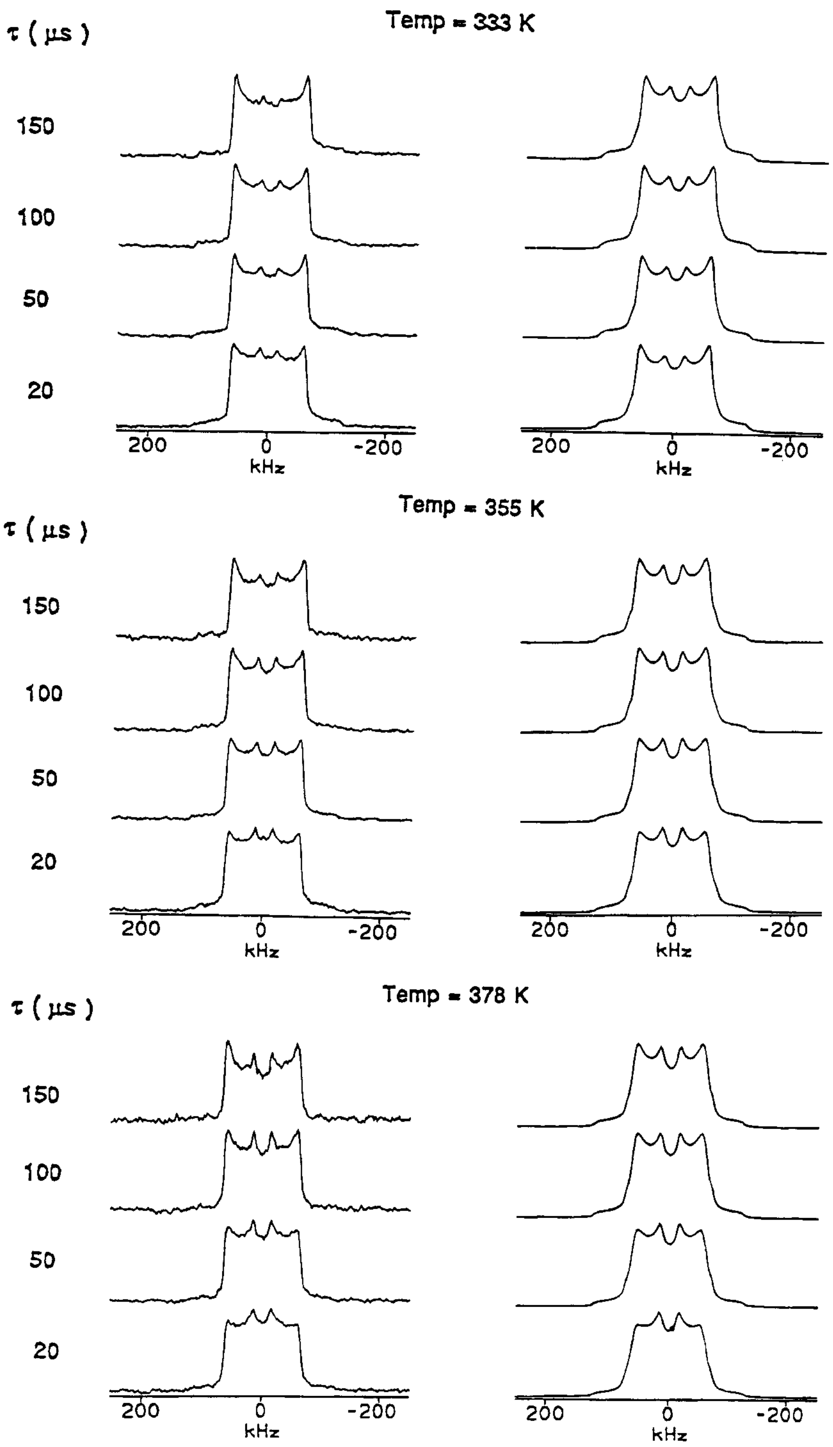

Figure 7. Experimental and calculated ^{2}H spectra for PS as a function of echo delay time (τ) at 333, 335, and 378 K.

calculate a temperature and frequency of maximum loss using the equation[38]

$$G(\omega)^{\text{loss}} = \frac{\langle \sigma(0)^2 \rangle}{kT} \int_0^\infty \sin(\omega t)[-\phi'(t)]\,\mathrm{d}t \qquad (2)$$

where $\phi'(t)$ is the derivative of the correlation function and $\langle \sigma(0)^2 \rangle$ represents the magnitude of the coupling to the molecular event. The position of maximum loss at the selected temperatures calculated in this manner from the NMR data are shown in Figure 11 alongside the data of Illers and Jenckel. The time/temperature correspondence between the NMR and mechanical data is clear. The wide variation in apparent activation energies stems from the limited temperature range over which the β process can be studied and the overlap of the β process with the glass transition whether the experimental method employed is NMR, dielectric, or mechanical. Thus we conclude that disordered angular jumps of the phenyl groups including the presence of π flips is the repeat unit level motion which NMR line shape studies can identify occurring at the same time scale of the β process.

Some of the earlier interpretations[39] of the β process suggest a coupling of the phenyl group motion with backbone libration or oscillation. Kulik and Prins note little change in the backbone line shapes of chain-deuterated polystyrene in the same temperature range so there is little evidence from deuterium line shape

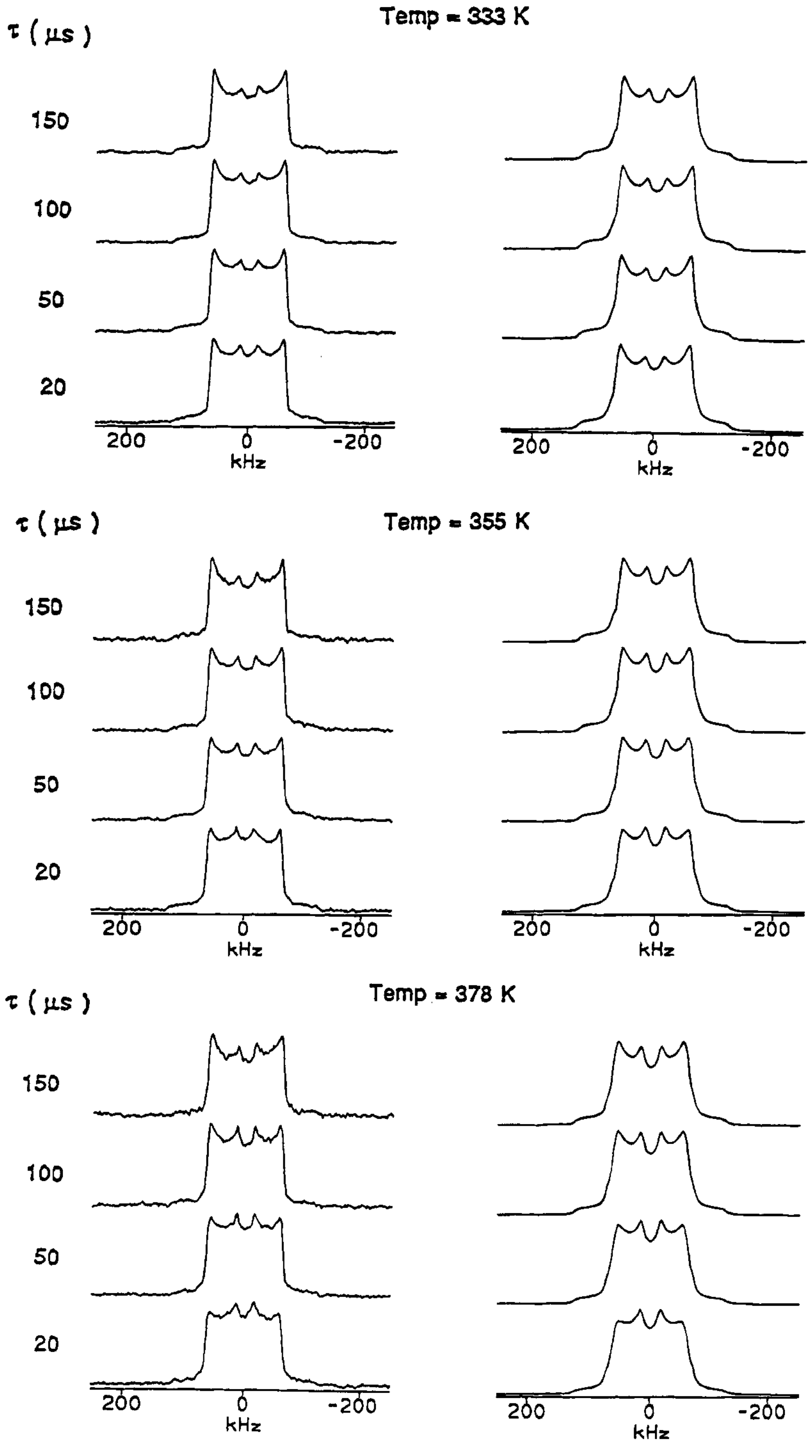

Figure 8. Experimental and calculated ^{2}H spectra for PXE/PS as a function of echo delay time (τ) at 333, 355, and 378 K.

data to support this interpretation. The line shape data reported here offer no insight into this possibility.

The breadth of the time scale of phenyl motion is contained in the fractional exponent α, which varies from 0.20 to 0.55 as temperature is raised. This corresponds to quite a broad distribution of exponential correlation times extending over several decades of frequency. This heterogeneity of time scale in combination with the distribution of jump angles indicates significant complexity in the phenyl group motion. It is quite possible that an alternative simulation of the line shapes could be produced with a different mix of angular and time scale heterogeneity but both must figure prominently in our view of this sub-glass transition motion.

Table 1[a]

temp (K)	τ_p (s)	α	angular breadth (±deg)	step size (deg)
310	5.00×10^{-3}	0.20	12	2
333	1.00×10^{-3}	0.30	14	2
344	3.00×10^{-4}	0.35	14	2
355	2.00×10^{-4}	0.40	16	2
367	9.00×10^{-5}	0.45	16	2
378	4.00×10^{-5}	0.50	18	3
389	3.00×10^{-5}	0.52	18	3
401	2.00×10^{-5}	0.55	20	4

[a] Population of flippers is 82% for PS and 80% for PS/PXE and population of nonflippers is 18% for PS and 20% for PS/PXE at all temperatures.

Table 2

	PS		PS/PXE	
τ (μs)	exp	sim	exp	sim
	Temperature = 333 K			
20	1.000	1.000	1.000	1.000
50	0.635	0.636	0.761	0.643
100	0.355	0.388	0.439	0.397
150	0.286	0.258	0.308	0.265
	Temperature = 355 K			
20	1.000	1.000	1.000	1.000
50	0.739	0.664	0.755	0.671
100	0.456	0.421	0.481	0.429
150	0.275	0.285	0.290	0.292
	Temperature = 378 K			
20	1.000	1.000	1.000	1.000
50	0.699	0.677	0.713	0.683
100	0.377	0.423	0.434	0.428
150	0.205	0.281	0.317	0.287

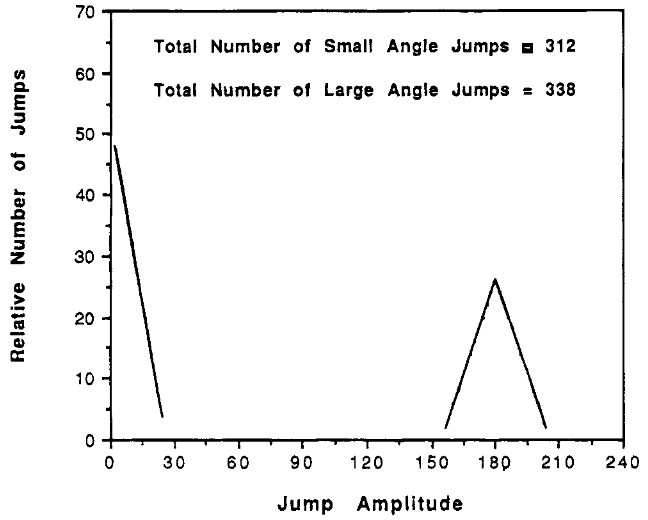

Figure 9. Relative number of jumps versus amplitude for the simultaneous model for a step size of 2° and a well breadth of 24°.

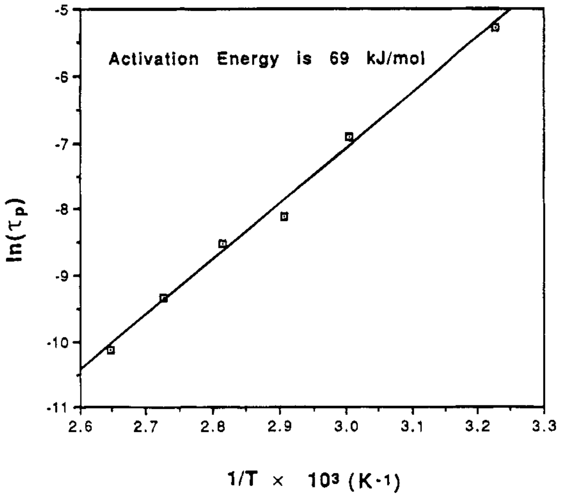

Figure 10. Arrhenius plot of the temperature dependence of the characteristic correlation time (τ_p) for the ring jump motion.

This basic motion of the PS phenyl groups is little altered as PXE is blended with the PS. Table 1 shows the simulation parameters for both pure PS and the 25–75 blend, which are identical except the fraction of phenyl groups jumping in the blend is slightly less than in pure PS. Since the phenyl motion is almost unchanged in the blend while the glass transition of the blend moves upward almost 30°, the β relaxation process is better resolved from the glass transition, which is apparent in the mechanical data.[24,25] The level of suppression of phenyl motion is far below that observed in blends of polycarbonate and PMMA.[29,30] The significant change in the temperature of the glass transition relative to no shift in the time scale or temperature of the β process could be associated with the longer range of motion characteristic of the glass transition and the localized nature of the β process. The very low level of the suppression of the β process in the PXE–PS blends relative to the sub-T_g process in polycarbonate/PMMA blends is a different question. The β process in PS is a side-chain motion while the sub-glass transition motion in polycarbonate is a main-chain motion. This distinction needs to be substantiated in a number of blend studies before it should be accepted as a general rule.

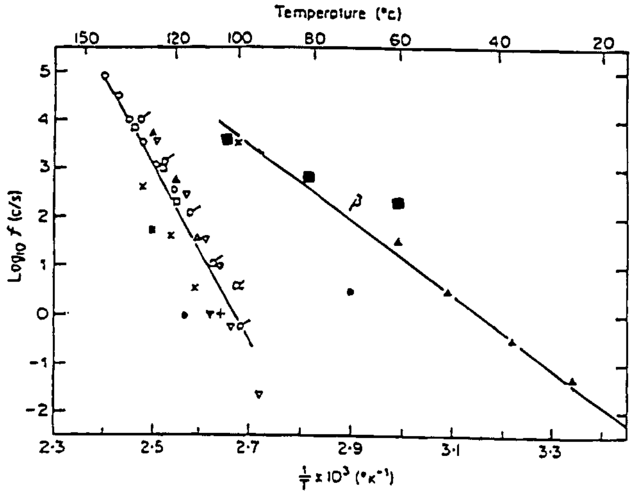

Figure 11. Frequency/temperature locations of the α and β relaxations in polystyrene. The squares represent the prediction from the NMR analysis and the other data are from Illers and Jenckel.[4] The two relaxations, α and β, are clearly delineated in the mechanical data at lower frequencies, the β peak being observed as a shoulder on the low-temperature side of the α peak.

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References and Notes

(1) Curtis, A. J. *SPE Trans.* **1962**, *2*, 82.
(2) Adamec, V. *J. Polym. Sci., Part B* **1968**, *6*, 687.
(3) McCammon, R. D.; Saba, R. G.; Work, R. N. *J. Polym. Sci., Part A-2* **1969**, *7*, 1721.
(4) Illers, K. H.; Jenckel, E. *Rheol. Acta* **1958**, *1*, 322.
(5) Yano, O.; Wada, Y. *J. Polym. Sci., Polym. Phys. Ed.* **1971**, *9*, 669.
(6) Sinnott, K. M. *SPE Trans.* **1962**, *2*, 1962.
(7) Crissman, J. M.; McCammon, R. D. *J. Acoust. Soc. Am.* **1962**, *34*, 1703.
(8) Crissman, J. M.; Woodward, A. E.; Sauer, J. A. *J. Polym. Sci., Part A* **1965**, *3*, 2693.
(9) Odajima, A.; Sohma, J.; Koike, M. *J. Phys. Soc. Jpn.* **1957**, *12*, 272.
(10) Slichter, C. P. *Makromol. Chem.* **1959**, *34*, 67.
(11) Hunt, B. I.; Powles, J. G.; Woodward, A. E. *Polymer* **1964**, *5*, 323.
(12) Connor, T. M. *J. Polym. Sci., Part A-2* **1970**, *8*, 191.
(13) Linder, P.; Roessler, E.; Sillescu, H. *Makromol. Chem.* **1981**, *182*, 3653.
(14) Schaefer, J.; Sefcik, M. D.; Stejskal, E. D.; McKay, R. A.; Dixon, W. T.; Cais, R. E. *Macromolecules* **1984**, *17*, 1107.

(15) Spiess, H. W. *Colloid Polym. Sci.* **1983**, *261*, 13.
(16) Kulik, A. S.; Prins, K. O. *Polymer* **1993**, *34*, 4635.
(17) Abe, J.; Tonelli, A. E.; Flory, P. J. *Macromolecules* **1970**, *3*, 294.
(18) Reich, S.; Eisenberg, A. *J. Polym. Sci., Part A-2* **1972**, *10*, 1397.
(19) Tonelli, A. E. *Macromolecules* **1973**, *6*, 682.
(20) Rapold, R.; Suter, U. W.; Theodorou, D. N. *Macromol. Theory Simul.* **1994**, *3*, 19.
(21) Stockmayer, W. H.; Matsuo, K. *Macromolecules* **1972**, *5*, 766.
(22) Jones, A. A. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 863.
(23) Schadt, R. J.; Cain, E. J.; English, A. D. *J. Phys. Chem.* **1993**, *97*, 8387.
(24) Yee, A. F. *Polym. Prep. (Am. Chem. Soc., Div. Polym. Chem.)* **1976**, *17* (1) 145.
(25) Yee, A. F. *Polym. Eng. Sci.* **1977**, *17*, 213.
(26) Stoetling, J.; Sarasz, F. E.; MacKnight, W. J. *Polym. Eng. Sci.* **1970**, *10*, 133.
(27) Kaufmann, S.; Wefing, S.; Schaefer, D.; Spiess, H. W. *Macromolecules* **1990**, *23*, 3431.
(28) Chin, Y. H.; Inglefield, P. T.; Jones, A. A. *Macromolecules* **1993**, *26*, 5372.
(29) Landry, C. J. T.; Henrichs, P. M. *Macromolecules* **1989**, *22*, 2157.
(30) de los Santos Jones, H.; Liu, Y.; Inglefield, P. T.; Jones, A. A.; Kim, C. K.; Paul, D. R. *Polymer* **1994**, *35*, 57.
(31) Kambour, R. P.; Bendler, J. T. *Macromolecules* **1986**, *19*, 2679.
(32) Chin, Y. H.; Zhang, C.; Wang, P.; Jones, A. A.; Inglefield, P. T. *Macromolecules* **1991**, *25*, 3031.
(33) Hirchinger, J.; Miura, H.; Gardner, K. H.; English, A. D. *Macromolecules* **1990**, *23*, 2153.
(34) Miura, H.; Hirschinger, J.; English, A. D. *Macromolecules* **1990**, *23*, 2169.
(35) Schadt, R. J.; Cain, E. J.; Gardner, K. H.; Gabara, V.; Allen, S. R.; English, A. D. *Macromolecules* **1993**, *26*, 6503.
(36) Roy, A. K.; Jones, A. A.; Inglefield, P. T. *J. Magn. Reson.* **1985**, *64*, 441.
(37) Weiss, H. G.; Dishon, M.; Long, A. M.; Bendler, J. T.; Jones, A. A.; Inglefield, P. T.; Bandis, A. *Polymer* **1994**, *35*, 1880.
(38) Yee, A. F.; Smith, S. A. *Macromolecules* **1981**, *14*, 54.
(39) Pschorn, U.; Roessler, E.; Sillescu, H.; Kaufmann, S.; Schaefer, D.; Spiess, H. W. *Macromolecules* **1991**, *24*, 398.

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