all the cases studied here, the best model is case IIC1 which has distributed slow beads with the slowest beads in the interior of the chain and elastically coupled via the medium with a spring constant approximately 10^{-2} that for the in-chain entropy springs.

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NMR Relaxation Time Studies of Polystyrene

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ABSTRACT: Proton spin–lattice (T_1) and spin–spin (T_2) relaxation times are reported for polystyrene (PS) samples of low (10 K) and high (2×10^6) molecular weights and varying surface areas in oxygen, ambient, and in vacuo. The measurements were made in order to elucidate the molecular dynamics responsible for the various NMR and dielectric relaxation processes in PS and so clarify several sources of discrepancy in earlier literature data and interpretation. Correlation frequencies are determined from NMR data as well as data from other sources in the literature. A molecular weight dependent α relaxation was observed which is in good agreement with previously reported data. Variations in the positions and intensities of low-temperature T_1 data are traced to spin diffusion to end groups and either direct relaxation by O_2 or spin diffusion to O_2 or a combination of these. The intrinsic γ relaxation is observed in the T_1 data but in the T_2 data only in the presence of O_2. By analogy with poly(n-vinylcarbazole) the γ process is attributed to low-amplitude torsional libration of the phenyl group. At low temperatures O_2 contributes to the dipolar field causing a reduction in T_2. Above the temperature corresponding to about 10^4 Hz for the γ relaxation, the lifetime of the O_2 phenyl ring complex is short and rapid relative reorientation of O_2 with respect to the proton spin system causes an increase in T_2. As a result there is a change in the T_1 mechanism from spin diffusion to direct paramagnetic relaxation by the diffusing O_2 molecules.

A large volume of molecular relaxation data obtained from dielectric, mechanical, and nuclear magnetic resonance (NMR) techniques has been accumulated on the molecular motions of polystyrene (PS). These techniques have revealed the existence of multiple relaxations. With the exception of the glass transition (α relaxation) there appears to be considerable disagreement on the interpretation of the relaxation time data.

Dynamic mechanical[1] and dielectric[1] relaxation of PS samples including thermally degraded samples have shown five relaxations below the glass transition at a frequency of 10 kHz. The β relaxation found at 360 K is attributed to local oscillation of backbone chains while the γ peak at 180 K due to phenyl rotation is observed only in the mechanical measurements. The γ' peak at 100 K is observed only in the dielectric relaxation of bulk polymerized samples and is assigned to the motion of weak polar bonds involving oxygen atoms in the chain. A peak at 55 K in dynamic mechanical measurements is believed to result from lattice defects caused by the placement of a syndiotactic diad between isotactic sequences or vice versa. The relaxation mechanism for the newly reported ϵ peak at 25 K is not known.

The NMR data on PS exhibit considerable variation in the number of transitions, the temperature at which they occur, and the assignment of the molecular processes responsible for them. The available data are voluminous and no attempt will be made here to review them; however, the conclusions of some of the more widely referenced studies will be discussed. Hunt, Powles, and Woodward[2] measured the spin–lattice relaxation times (T_1) of PS as a function of temperature. Three relaxations corresponding to T_1 minima at $\simeq$500, 260, and 130 K were observed. The high-temperature minimum was identified with the α process. By comparing polystyrene with poly(phenyl-L-alanine) it was suggested that the low-temperature minima might be due either to oscillation of the phenyl ring or to reorientational motion of impurities such as residual monomer which could lead to relaxation of the polymer by spin diffusion, or to a combination of these two processes. Examination of PS sample purified by reprecipitation from toluene with methanol and dried in vacuum showed T_1 behavior above 300 K similar to that of the previous sample. However, a deep minimum which was observed at 160 K disappeared on heating to 520 K and the repeated T_1 plot was now similar to that of the previous sample. The authors concluded that the low-temperature minimum at 160 K was due to the presence of low molecular weight solvent. Connor[3] examined a series of atactic PS samples of very narrow molecular weight distributions, over a wide molecular weight range. Three relaxation regions were found in T_1 and $T_{1\rho}$. The α relaxation was molecular weight dependent and minima in T_1 and $T_{1\rho}$ shifted to higher temperatures with increasing molecular weight. The intensity of the low-temperature minima was molecular weight dependent while its position on the temperature scale was not. From the activation energies calculated for this process it was argued that this relaxation resulted from spin diffusion to the mobile end groups. The γ relaxation was manifested as a tail on the low-temperature side of the α relaxation in the T_1 plot and as a slight depression in $T_{1\rho}$ at 223 K. An activation energy of 7.6 kcal/mol was calculated for the process and the origin of the motion was not specifically assigned. Subsequent low-temperature T_1 results of Crist[4] clarify the contribution of end groups to the overall T_1 behavior.

Wardell, McBrierty, and Douglass[5] reported T_1 and T_2 data for homopolymers of PS and polybutadiene and a copolymer of the two. A small change in T_2 at 170 K and a strong T_2 transition at 400 K were observed in polystyrene. Annealing was found to reduce T_2 and shift the low-temperature transition to around room temperature. In the block copolymer the low-temperature T_2 transition occurred over a broader temperature range than in the homopolymer beginning at 170 K and leveling off at room temperature. In addition to the α relaxation above 420 K the T_1's of an unannealed sample showed a deep minimum at approximately 180 K. The low-temperature minimum was assigned to impurity relaxation. Annealing removes the 180 K minimum and the T_1 plot showed two low-temperature minima at ~150 and 258 K in agreement with data of Hunt et al.[2] The T_1's of the annealed samples below 350 K are larger than those of either the unannealed sample or those of Hunt et al.[2] The authors did not comment on the origin of the T_2 transition and the two T_1 transitions at low temperatures; however, they did conclude on the basis of Tonelli's calculations[6] that the sub-T_g transitions (in T_1, T_2, and $T_{1\rho}$), or equivalently, assignment of the γ transition from other measurements to phenyl group motion, are unlikely.

Recent NMR relaxation studies on poly(n-vinylcarbazole) (PVK)[7] have revealed three intrinsic relaxation processes in this polymer. Low molecular weight samples exhibit T_1 minima at 250 K while high molecular samples with a broad molecular weight distribution show a minimum at approximately 120 K. These minima are assigned to the motion of chain ends and low molecular weight fractions, respectively. High molecular weight samples of narrow molecular weight distribution do not show either of these minima. The α relaxation associated with T_g exhibits a high-temperature T_1 minimum accompanied by a change in T_2 at lower temperatures. Molecular complexation of the carbazole ring with O_2 leads to an additional contribution to the dipolar field below 220 K indicating a lifetime for the complex greater than $\simeq 10^{-4}$ s. A change in T_2 reflecting the onset of motion of oxygen with respect to the proton spin system is coincident with the oxygen-induced dielectric relaxation.[11] A minimum in T_1 in the 400 K range is observed for the γ relaxation and is associated with local carbazole group motion. Since the γ relaxation is dielectrically inactive in the absence of oxygen, torsional oscillation about the nitrogen-backbone carbon bond (C_{2v} symmetry axis) is proposed as the molecular motion responsible. The weak T_1 minimum indicates a fairly low amplitude motion. The onset of the torsional oscillation appears to significantly reduce the lifetime of the oxygen carbazole complex. At low temperatures (<220 K), T_1 is dominated by spin diffusion to paramagnetic oxygen. High surface area samples indicate more efficient relaxation near the surface. At high temperatures (>220 K) oxygen translational motion becomes more rapid than spin diffusion, a uniform spin temperature is achieved in the polymer, and direct relaxation by the paramagnetic oxygen is consistent with the results in this region. The structural similarities between PVK and PS are manifested in the transition plots for the two polymers.

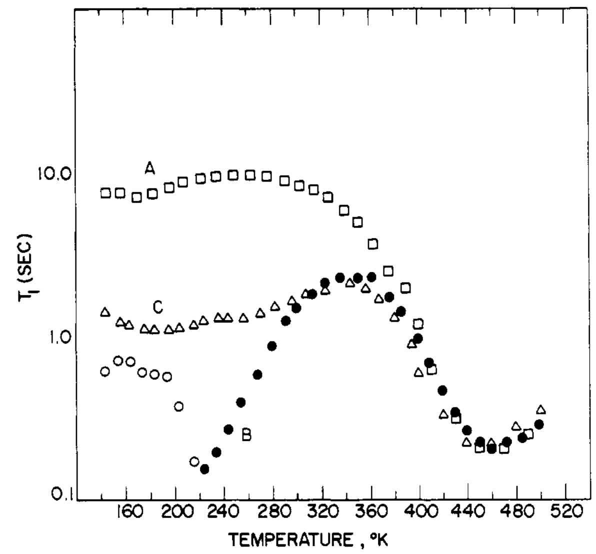

Figure 1. A plot of T_1 vs. temperature for (A) an evacuated sample of PS (mol wt = 1×10^4), (B) PS in ambient, and (C) sample B cooled after heating to 500 K. (A) and (B) are high surface area powders, (C) is a low surface area glass. Open circles represent temperatures at which the magnetization recovery is nonexponential.

It seems clear from the published relaxation data that there is some uncertainty concerning the existence and origins of the sub-T_g relaxations in polystyrene. The magnitude of the NMR relaxation times and the number of low-temperature transitions appear to be sensitive functions of the physical characteristics of the polystyrene samples. We have conducted a study of the NMR relaxation time data in PS samples selected for their molecular weight and molecular weight distribution, as well as the method of preparation. The results and interpretation are discussed in the light of recent findings for PVK and many of the inconsistencies in the previously published data for PS are clarified.

Experimental Section

The polystyrene samples used in these measurements were obtained from Pressure Chemical Co., of Pittsburgh, Pa. The samples were $M_w = 1 \times 10^4$ (MWD = 1.06) and $M_w = 2 \times 10^6$ (MWD < 1.20). Evacuated samples were obtained by pumping the samples to $\simeq 10^{-5}$ mm at 80 °C for 12 h. Samples which were measured in oxygen or ambient were first degassed in NMR tubes attached to nylon valves and then re-equilibrated in the respective atmospheres.

The NMR data were obtained on a Bruker SPX-90 NMR spectrometer at 90 MHz. The 90° pulse width was 3.5 μs with a recovery time of 6 μs. The magnetic field was generated by a 12 in. shimmed electromagnet operated in the current regulated mode. The temperature was controlled by a gas flow thermostated system and controlled to an accuracy of ±1°.

Spin-lattice relaxation times (T_1) were measured by the 180–τ–90° pulse technique.[12] Spin-spin relaxation (T_2) times were obtained from the free induction decay (FID) following the 90° pulse. T_2 was taken as $t_{1/2}/\ln 2$ where $t_{1/2}$ is the time required for the FID to fall to one-half its original value.

Results

Plots of log T_1 vs. temperature for three samples of the low molecular weight material are shown in Figure 1. Sample A is a thoroughly evacuated sample. Sample B was thoroughly

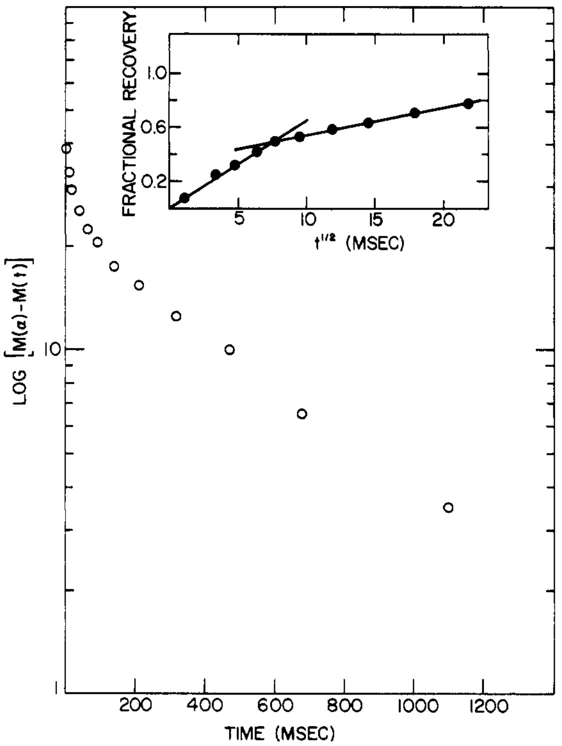

Figure 2. Magnetization recovery vs. time following a 90° pulse for PS (mol wt = 1 × 10^4) in air.

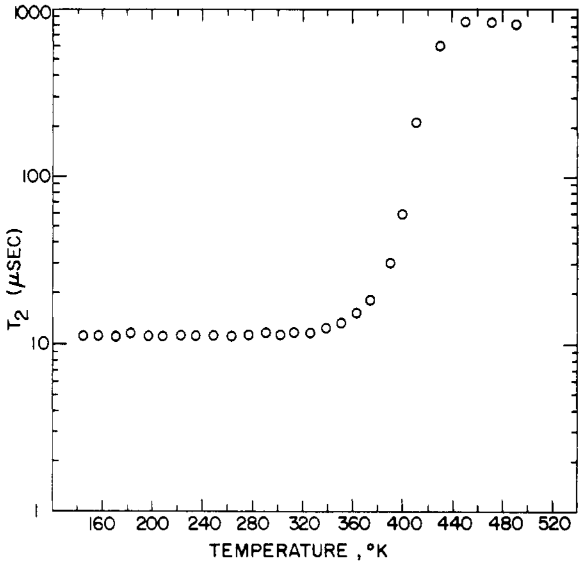

Figure 3. A plot of T_2 vs. temperature for an evacuated sample of PS (mol wt = 1 × 10^4).

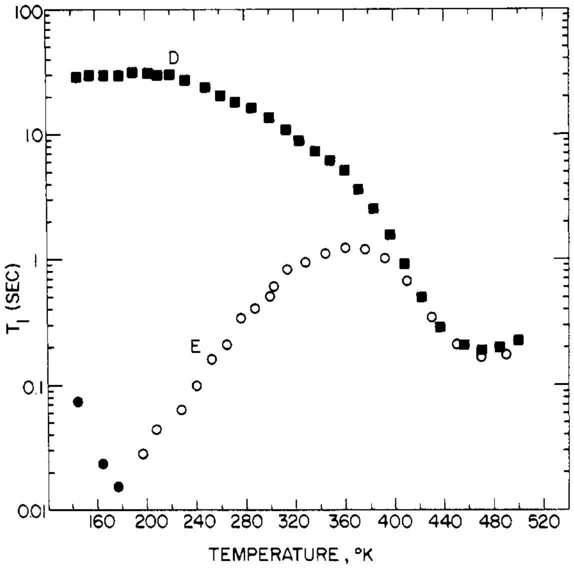

Figure 4. A plot of T_1 vs. temperature for PS (mol wt = 2 × 10^6) (D) evacuated and (E) equilibrated with O_2. (D) and (E) are high surface area powders. Closed circles represent temperatures at which the magnetization recovery is nonexponential.

evacuated, re-equilibrated under ambient, and sealed, while C is B which has been cooled rapidly after relaxation time measurements up to 500 K. Samples A and B were finely powdered material while sample C was a transparent glass. All three samples exhibit almost identical behavior above 380 K with T_1 decreasing to a minimum at 460 K. Below 380 K the evacuated sample has the longest T_1 and a considerable variation can be seen for the three samples. Sample A shows a weak minimum at approximately 160 K. Sample B exhibits enhanced relaxation at low temperatures and a well-defined minimum almost two orders of magnitude smaller than that of the evacuated sample. Similar results have been observed in poly(methyl methacrylate).[13] At temperatures below 220 K the magnetization recovery (Figure 2) is nonexponential at short times. The inset in Figure 2 is a plot of the fractional magnetization recovery vs. (time)$^{1/2}$ for short times. The plot consists of two distinct straight-line segments. This type of behavior is expected if the recovery is dominated by spin diffusion to paramagnetic impurities with certain constraints which have been discussed.[7-10] Sample C exhibits somewhat complicated behavior at low temperature. The T_1's are intermediate between those of samples A and B and there is a broad minimum which appears to consist of overlapping relaxations with minima at 180 and 260 K. T_2 of sample A (Figure 3) is constant at 11 μs up to 340 K and T_2 increases sharply by about two orders of magnitude above that temperature.

Plots of log T_1 vs. temperature for the high molecular weight material are shown in Figure 4. Sample D is thoroughly evacuated and exhibits T_1's which are much longer than any of the other samples. In the low-temperature region T_1 is constant at 30 s. Between 240 and 360 K there is a change in the slope of T_1 and at higher temperatures T_1 decreases sharply to a minimum at 470 K. Sample E is an evacuated high molecular weight sample re-equilibrated in oxygen. T_1's are very sensitive to the presence of oxygen and the sample exhibits vastly enhanced relaxation. A minimum in T_1 is observed at 180 K, three orders of magnitude less than the evacuated sample. At temperatures below 180 K the magnetization recovery (Figure 5) is also nonexponential and as the insert demonstrates a plot of fractional magnetization recovery vs. (time)$^{1/2}$ consists of two distinct regions for short times. Above 400 K T_1's for both the evacuated and oxygenated samples are almost identical. The change in slope of T_1 observed in the evacuated sample between 240 and 360 K is not found in sample E. However, the T_2 plots (Figure 6) of samples D and E show a low-temperature transition at about 200 K only in the presence of O_2. Both samples show the large increase in T_2 at 360 K similar to that of the low molecular weight materials.

Discussion

The T_1 behaviors of evacuated samples A and D are similar above 380 K in the region of the α relaxation but sample A exhibits its minimum about 10 K lower than sample D. The origin of the α relaxation is well known and results from the extensive motion of the polymer chain as it goes through the glass transition. The rapid rise in T_2 beginning at ~340 K for

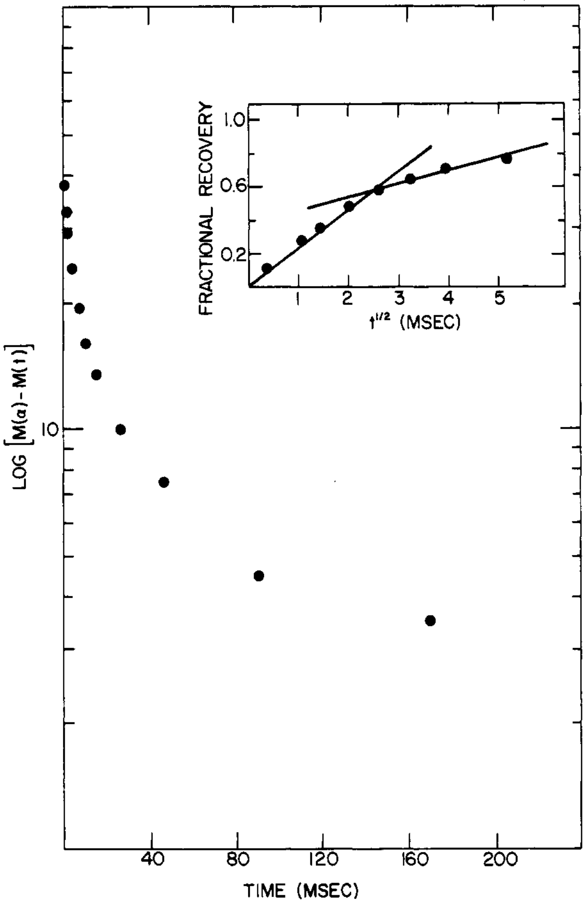

Figure 5. Magnetization recovery vs. time for PS (mol wt = 2 × 10^6) in O_2.

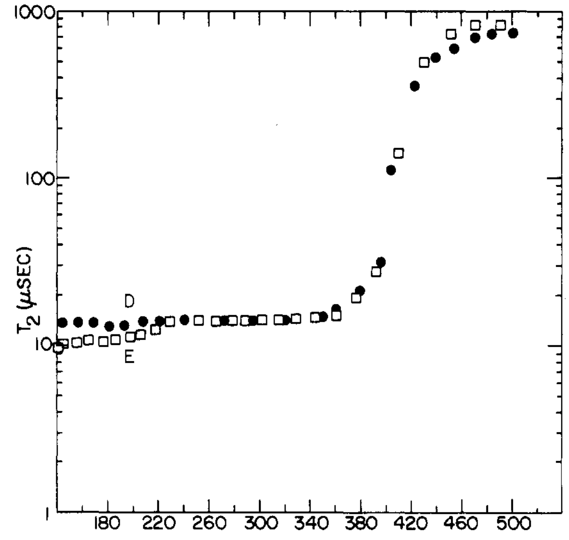

Figure 6. A plot of T_2 vs. temperature for PS (mol wt = 2 × 10^6 (D) evacuated and (E) equilibrated with O_2.

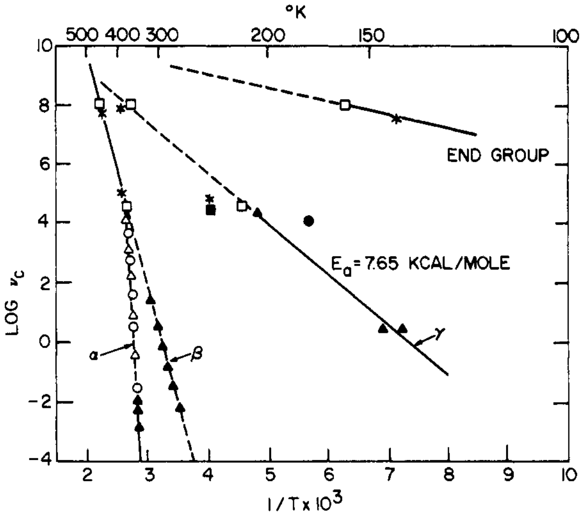

Figure 7. Transition map for PS where ☐ corresponds to the present NMR data; * NMR T_1 and $T_{1\rho}$ data, ref 3; ■ NMR T_2 data, ref 4; △, ● dielectric data references in ref 3; ▲ mechanical references in ref 3; ○ mechanical, ref 1.

A and 360 K for D is further evidence for large-scale motion. The T_2 transition is observed in the transition map (Figure 7) at $\simeq 10^4$ Hz where the α and β processes intersect. Consequently, the α and β transitions cannot be resolved in the T_2 data and at the temperatures of the T_1 minimum both processes may be described by a composite $\alpha\beta$ process.[3] At low temperatures there are large differences in the T_1 behavior of these samples. The contrast between the low molecular weight T_1 minimum and the relatively temperature independent T_1's of the high molecular weight sample has been observed previously.[3] Connor found that the position of this minimum was independent of molecular weight but its intensity was not. This is consistent with spin diffusion to the chain ends and is responsible for the efficient T_1 relaxation in this region.[3]

The γ relaxation is observed as a change in the slope of T_1 of sample D between 240 and 360 K. The minimum is broad and no corresponding transition is observed in the T_2 data for the evacuated samples indicating a very low amplitude motion and inefficient relaxation. Interference from the end groups prevents the observation of this transition in the low molecular weight sample A. In PVK,[7] poly(*N*-ethyl-2-vinylcarbazole) (P2VK), and poly(*N*-ethyl-3-vinylcarbazole) (P3VK)[14] similar γ relaxations are observed in T_1's within the same temperature range. The corresponding transition in T_2[7] and dielectric data[11] for PVK are only observed in the presence of oxygen, while dielectric relaxations of P2VK, P3VK,[15] and poly(3-chloro-*N*-vinylcarbazole) (ClPVK)[11] are observed in evacuated samples. It was therefore concluded that the γ relaxation is due to torsional motion of the carbazole ring in all of these carbazole polymers. However, in the case of PVK the motion is about the C_{2v} symmetry axis of the ring and as such is not dielectrically active. The formation of an oxygen complex, however, results in an off-axis dipole and an oxygen induced dipolar field both of which are modulated by motion of the ring system giving rise to a dielectrically active transition and a change in T_2. This is also observed for polystyrene in an oxygen atmosphere (Figure 6). T_2 increases by about 4 μs beginning at approximately 190 K. The frequency points corresponding to the T_1 and T_2 transitions for this relaxation are plotted on the transition map (Figure 7) giving an activation energy of approximately 7.7 kcal/mol compared to 8 kcal/mol for the similar relaxation in PVK.[7] We have therefore concluded that similar to PVK, P2VK, P3VK, and ClPVK, polystyrene does exhibit a γ relaxation due to low amplitude motion of the phenyl ring.

The T_1 values of polystyrene in air and oxygen are much smaller than those of the degassed sample. The essential features of the degassed samples are retained at high temperatures but a new minimum and nonexponential magnetization recovery appear at low temperatures. The limiting cases of diffusion limited and rapid diffusion to paramagnetic oxygen have been dealt with previously.[16] For the case of diffusion-limited relaxation the initial magnetization recovery is described by a (time)$^{1/2}$ dependence at short times giving way to an exponential dependence at longer times. This type of behavior is observed for polystyrene in both air and oxygen (Figures 2 and 5) at temperatures below the T_1 minimum at 220 and 180 K, respectively (Figures 1 and 4). The fractional recovery plot is composed of two regions. Similar behavior has been observed for PVK and has been shown to result from surface and bulk oxygen effects.[7] The polymers apparently preferentially adsorb O_2 at the surface so that surface O_2 concentration is larger than bulk O_2 concentration. A corresponding shift in the T_1 minimum for high surface area samples to lower temperatures reflects the change from a diffusion-limited mechanism to a rapid-diffusion process.[7] On the high-temperature side of these minima the magnetization recovery is exponential. The region of the T_1 minimum coincides with the beginning of the transition in T_2 in the presence of oxygen (Figure 6). It is known the PS forms a molecular complex with oxygen.[17] The dynamical behavior of this complex can account for the O_2-induced effects in T_1 and T_2 similarly to PVK.[7] The oxygen-induced dipolar field is averaged at the onset of motion of the phenyl ring (γ relaxation) due to rapid reorientation of the O_2 molecule relative to the polymer. As the temperature is increased above the T_1 minimum the thermally activated hops of the O_2 molecule between the phenyl rings are governed by the diffusion constant of O_2 which is orders of magnitude larger than the spin-diffusion constant[7] resulting in a uniform spin temperature so that the magnetization recovery becomes exponential.[7] The activation energy for this process appears to be related to the internal motions of the polymer which is not of sufficient amplitude to produce a T_2 transition in its own right.

The data for a sample C (Figure 1) show that the features of the T_1 plot are extremely sensitive to the physical characteristics of the sample. Sample C is a low surface area glass and its T_1 plot exhibits features due to both end-group effects and the interaction with O_2. Because of the low surface area of C the concentration of surface O_2 is less than that in the bulk. The T_1 minimum due to bulk O_2 occurs at higher temperatures than that of surface O_2.[7] Consequently, the low-temperature T_1 features are sensitive functions of not only the number of end groups present but also the surface area of the sample.

Conclusions

T_1 and T_2 relaxation time measurements have been made on several PS samples with various molecular weights in the presence and absence of O_2. These measurements have clarified the origin of several discrepancies and disagreements in interpretation in the earlier literature. The interpretation of the α relaxation and its molecular weight dependence is in good agreement with the results of Connor.[3] The γ relaxation which exhibits its T_1 minimum at approximately 360 K does not show a corresponding transition in T_2 in evacuated samples. In the presence of air or molecular O_2, complexation of O_2 with the phenyl ring leads to an additional contribution to the dipolar field. This contribution is averaged when motion of the oxygen molecule with respect to the proton spin system approaches $\sim 10^4$ Hz and gives rise to a transition in T_2. The weak T_1 minimum due to the γ relaxation indicates a low amplitude motion and the similarities with carbazole-containing polymers have led to the conclusion that this relaxation is due to torsional libration of the phenyl ring accompanied by a decrease in the lifetime of the styrene–O_2 complex.

The low-temperature relaxation time behavior is complicated. Evacuated samples show T_1's which are a function of molecular weight as a result of being dominated by spin diffusion to the end groups in the case of the low molecular weight materials. Samples in ambient and O_2 atmospheres are dominated by spin diffusion to the paramagnetic O_2 sites below the minimum in T_1. In both of these cases the T_1 minimum due to the γ relaxation is obscured. The surface area of the sample is critical in determining the position and intensities of the T_1 minimum in the presence of O_2. Consequently the low-temperature behavior can be extremely complicated giving the appearance of multiple relaxations or a broad relaxation at low temperatures depending on the molecular weight and physical characteristics of the sample. These findings account for the apparent discrepancies observed in the reported literature relaxation data of polystyrenes and they emphasize the care that must be taken to exclude oxygen, especially in aromatic containing polymers which tend to complex with O_2, in order to observe the intrinsic molecular relaxations of the polymer.

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