Mixing effects on the mid-kilohertz mobility of polystyrene in glassy polystyrene–diluent blends

Laurence A. Belfiore
Department of Agricultural and Chemical Engineering, Colorado State University, Fort Collins, Colorado 80523, USA

and Stuart L. Cooper
Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin 53706, USA

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Low molecular weight additive effects on the mid-kilohertz mobility of atactic polystyrene (PS) at 25°C via n.m.r. spin–lattice relaxation experiments in the rotating frame ($T_{1\rho}$) are analogous to the results of a previous study of diluents in glassy bisphenol-A polycarbonate. The diluent with a relatively low glass transition temperature (T_g), dioctylphthalate, increases the spectral density of thermal motions of the chain backbone and the pendant group in PS on the order of 38.5 kHz. Of the ^{13}C nuclei in the glassy polymer, the relaxation behaviour of which can be differentiated by high-resolution, solid-state n.m.r., the $T_{1\rho}$'s of the aromatic carbons in the side group are affected most by dioctylphthalate. In contrast, the styrene oligomer, which has a higher T_g than that of dioctylphthalate, does not significantly alter the ambient temperature mobility of polystyrene at 38.5 kHz. The PS–styrene oligomer and PS–dioctylphthalate blends are examples of athermal and non-athermal mixtures, respectively. However, the effect of the enthalpy of mixing on the $T_{1\rho}$'s of the polymer is probably obscured by differences in blend mobility due to different blend T_g's.

(Keywords: Solid state nuclear magnetic resonance; spin lattice relaxation; polystyrene; plasticizer; blends)

INTRODUCTION

The results of previous n.m.r. spin–lattice relaxation experiments in the rotating frame ($T_{1\rho}$) indicate that the low-molecular-weight additives, dibutylphthalate and dibutylsuccinate, affect mid-kilohertz motions in glassy bisphenol-A polycarbonate in a co-operative manner at ambient temperature[1,2]. In this paper, $T_{1\rho}$ data at 38.5 kHz and 25°C are presented for atactic polystyrene-diluent blends to provide further evidence of diluent-induced changes in the mid-kilohertz mobility of a glassy polymer.

Most polymer–diluent blends of practical interest are characterized by a non-zero enthalpy of mixing. This is expected if co-operative interactions occur between the two components at the molecular level. Hence, there are both enthalpic and entropic contributions to the interaction free energy of mixing. This is rationalized using the results of the Flory–Huggins lattice theory of polymer–solvent mixtures[3]. The enthalpy and entropy changes upon mixing due to intermolecular interactions between polymer and diluent are:

$$\Delta H_{\text{int}} = -kT^2 N_A \phi_B \left(\frac{\partial \chi}{\partial T}\right) \tag{1}$$

$$\Delta S_{\text{int}} = -kN_A \phi_B \frac{\partial}{\partial T}(T\chi) \tag{2}$$

where N_A is the number of diluent molecules, ϕ_B is the volume fraction of polymer, T is the temperature, k is Boltzmann's constant, and χ is the polymer–diluent interaction parameter. The form of the temperature dependence of χ becomes apparent upon consideration of the mixing process. For example, if the enthalpic effects are the same for all contact sites between polymer and diluent, then the entropy of mixing is obtained, to a good approximation, by focusing solely on the conformational freedom of placing segments of the macromolecule in the lattice. In this case, χ is given by (constant) T^{-1}, ΔS_{int} vanishes, and the interaction free energy of mixing is independent of the temperature.

The blend of polystyrene and the low-molecular-weight styrene oligomer described herein is one example of an athermal solid solution. This implies that the free energy of mixing, which accounts for both conformational and interaction effects, is completely entropic in origin. From equations (1) and (2), one rationalizes that χ for this blend is a non-zero constant. The equation of state contribution to the polymer–diluent interaction parameter is responsible for the non-zero value of χ for athermal polymer

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solutions[4,5]. The data of Flory and co-workers[4,6] indicate that χ is typically in the range 0.3–0.5 for nearly athermal solutions in the limit of infinite dilution of polymer.

In the following discussion, carbon-13 $T_{1\rho}$'s obtained from high-resolution, solid-state n.m.r. spectra are compared together with calorimetric results for both athermal and non-athermal polystyrene–diluent blends. In this respect, the effect of ΔH_{int} on the mid-kilohertz mobility of the polymer is examined.

MATERIALS AND THERMAL CHARACTERIZATION

Atactic polystyrene (PS) was obtained from Pressure Chemical Co. with a number-average molecular weight ($\bar{M}_n$) of 1.8×10^6 and a polydispersity index ($\bar{M}_w/\bar{M}_n$) less than 1.3. The diluents used in this study are dioctylphthalate (DOP), obtained from Eastman Chemical Products (actually di-2-ethylhexylphthalate), and a styrene oligomer (SO) with a $\bar{M}_n$ of 800 (Pressure Chemical Co.). The materials were characterized by differential scanning calorimetry and the resulting thermograms are shown in *Figure 1*. In each case, the sample was quenched below the glass transition temperature (T_g) from the molten state and then scanned at a heating rate of 20°C min^{-1}. The T_g of the high-molecular-weight polystyrene is 111°C and that of the styrene oligomer is between 15° and 20°C. Dioctylphthalate has a T_g of -83°C, which is in excellent agreement with the data of Garfield and Petrie[7].

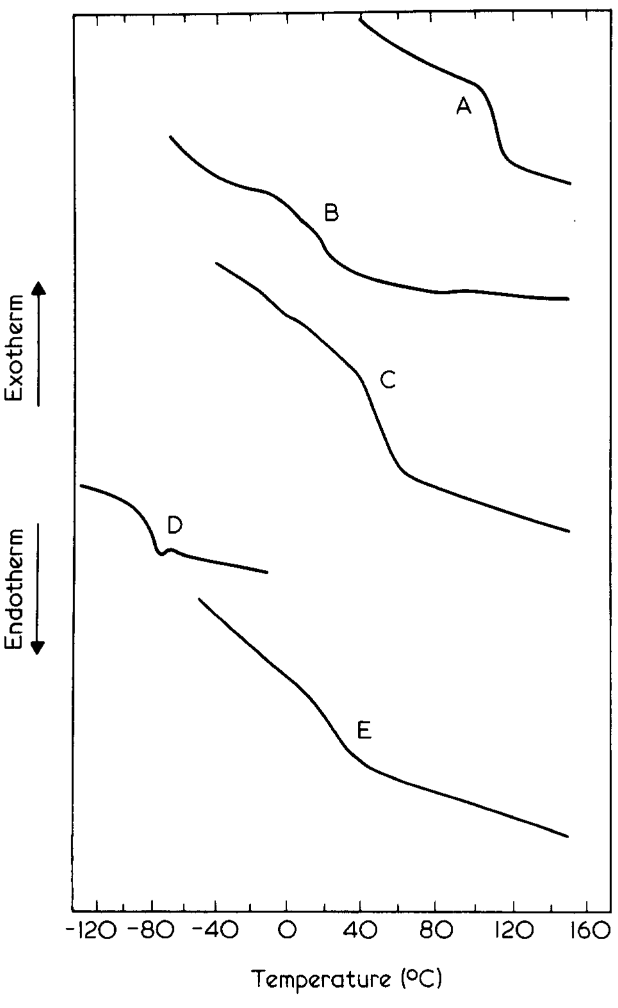

Figure 1 D.s.c. thermograms of A, polystyrene; B, styrene oligomer; C, 50% polystyrene–50% styrene oligomer; D, dioctylphthalate; E, 70% polystyrene–30% dioctylphthalate, in the vicinity of T_g

Polystyrene–diluent blends devoid of any traces of crystallinity were prepared from methylene chloride solutions upon evaporation of the solvent, and subsequent high-temperature moulding. The details of this procedure are described in a previous publication on polycarbonate–diluent blends[1]. The d.s.c. thermograms of the blends in *Figure 1* reveal a single T_g intermediate between the pure component T_g's. This suggests that polystyrene is compatible with either diluent and that ΔH_{int} in the blend of PS and dioctylphthalate does not substantially hinder the mixing process. However, the breadth of the glass transition region is much larger in the PS–DOP blend (27°C) relative to that in the undiluted polymer (9°C). This indicates that the mixing process is not completely homogeneous in the plasticized polymer. A similar conclusion holds for the athermal mixture of PS and the styrene oligomer.

HIGH-RESOLUTION ^{13}C N.M.R. SPECTRA OF POLYSTYRENE AND PS–DILUENT BLENDS

Proton-enhanced dipolar-decoupled ^{13}C n.m.r. spectra at 50.3 MHz for polystyrene and the PS–diluent blends obtained using magic-angle sample spinning (MASS) at 4 kHz are shown in *Figure 2*. Cross polarization and ^{13}C–^{1}H dipolar decoupling were carried out at 55 kHz. The ^{13}C free induction decays were acquired using spin–temperature alternation in the rotating frame[8] and quadrature detection.

Carbon-13 peak assignments for PS have been given previously[9]. Furthermore, Earl and VanderHart[10] have reported absolute ^{13}C chemical shifts for this polymer in the solid state. The resonance furthest downfield between 145 ppm and 146.5 ppm in *Figure 2a* (designated by 1) is due to the aromatic carbon (non-protonated) directly bonded to the chain backbone. Interestingly, the n.m.r. signal for this ring carbon is split into a complex pattern involving 20 peaks in solution[11]. This is a consequence of the configurational sequence distributions in atactic polystyrene. The other aromatic carbons (protonated) are grouped in a single intense resonance at 127 ppm (designated by 2 in *Figure 2a*). In hexachlorobutadiene at 105°C, the protonated aromatic carbons of atactic polystyrene are resolved into two distinct resonances[12] at 125.8 ppm (*para*) and 128.1 ppm (*ortho*, *meta*). The *ortho*- and *meta*-ring carbons are resolved by approximately 0.6 ppm only for highly stereoregular sequences that occur in the isotactic polymer[12]. However, one does not expect to resolve these peaks in the solid state. The resonance furthest upfield at 42 ppm (designated by 3) is assigned to the methine carbon in the backbone. The methylene carbon signal which appears slightly downfield from the methine carbon resonance is not well resolved in any of the solid-state spectra in *Figure 2*. This is partly due to the fact that the methylene carbon resonance coincides with a spinning sideband of the protonated aromatic carbons. In addition, methylene carbons in atactic PS exist in a multitude of solid-state conformations and configurations. This results in a complex resonance pattern. In solution, there are 12 closely spaced methylene resonances between 42 ppm and 47 ppm due to a variety of configurational sequences in PS[13]. The remaining low intensity signals in the spectrum in *Figure 2a* are spinning sidebands of the non-protonated aromatic carbons and Delrin (MASS rotor).

The spectra of the polystyrene–diluent blends are very similar to the spectrum of the undiluted polymer. This is not surprising because PS is the major component in the binary mixtures. In the PS–SO blend (*Figure 2b*), the resonances of the polymer and the oligomer coincide. In contrast, most of the aliphatic resonances of DOP appear upfield from the methine resonance of PS in the blend spectrum of polystyrene and dioctylphthalate in *Figure 2c*. In each case, the low-molecular-weight component does not substantially affect the isotropic chemical shifts of PS in the blend. It should be mentioned that digital subtraction techniques were not utilized to remove the spectral contributions of the diluents.

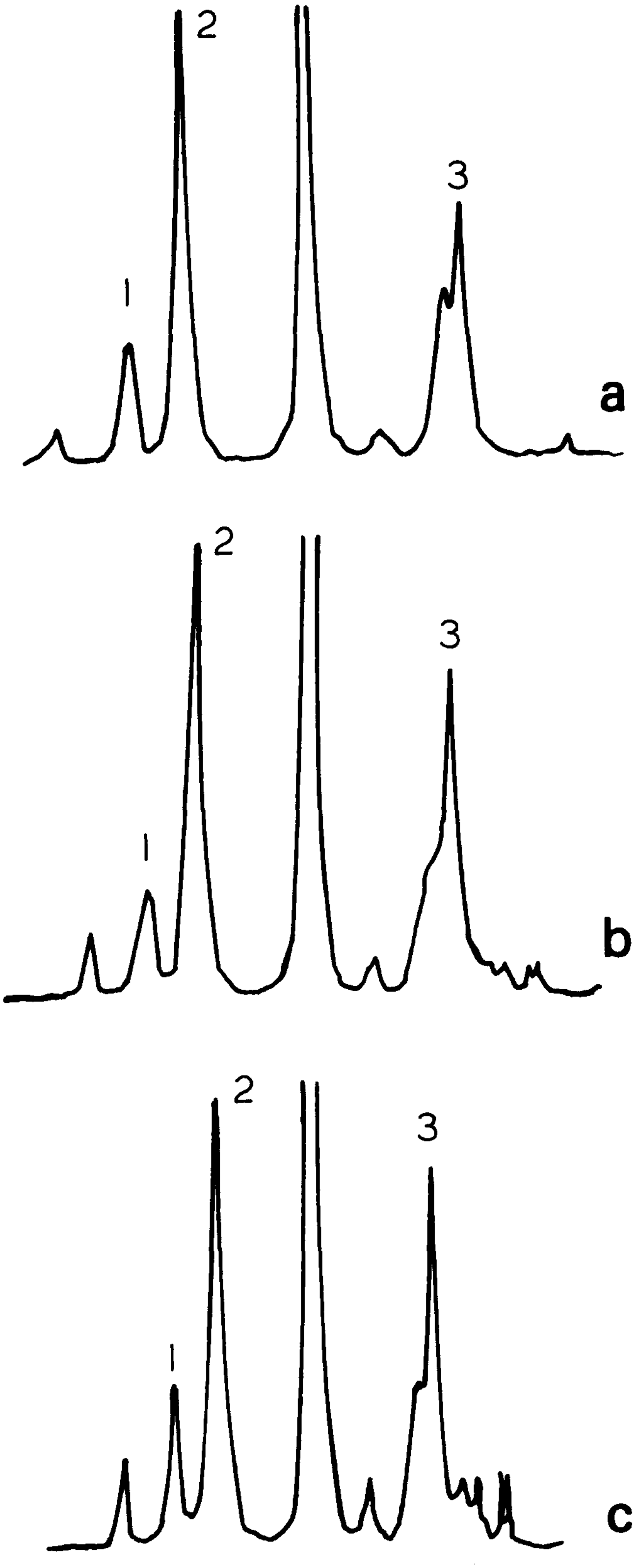

Figure 2 Proton-enhanced dipolar-decoupled MASS ^{13}C n.m.r. spectra of polystyrene and PS-diluent blends in the solid state. The strong resonance in the central region of each spectrum is due to the Delrin rotor used for MASS. Only the numbered peaks are analysed with the $T_{1\rho}$ experiment. (a) Polystyrene; (b) polystyrene + styrene oligomer; (c) polystyrene + dioctylphthalate

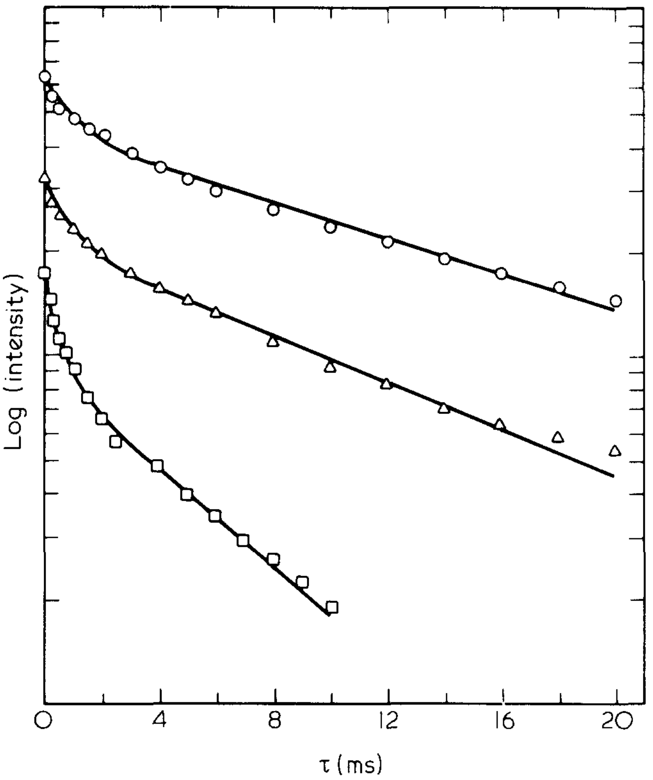

Figure 3 $T_{1\rho}$ curves at 38.5 kHz for the protonated aromatic carbons in polystyrene. The solid line is the nonlinear fit of the data points to equation (3) using the time constants given in *Table I*. The materials are: ○, polystyrene; △, 50% polystyrene–50% styrene oligomer; □, 70% polystyrene–30% dioctylphthalate

SPIN–LATTICE RELAXATION IN THE ROTATING FRAME

With individual resonance lines resolved for some of the chemically unique carbons in glassy polystyrene, the results of spin–lattice relaxation experiments in the rotating frame are interpreted unambiguously in terms of micro-Brownian motions of the chain backbone and the pendant (phenyl) group. It has been shown previously that carbon-13 $T_{1\rho}$'s in polymeric glasses are mainly sensitive to thermal motions in the low-to-mid kilohertz frequency range at ambient temperature[9,14,15]. The $T_{1\rho}$ experiments were carried out using the methodology of Schaefer *et al.*[16] at a ^{13}C r.f. field strength of 38.5 kHz.

The spin–lattice relaxation curves are shown in *Figures 3* and *4* for the protonated aromatic and methine carbons, respectively, in polystyrene. The materials being compared are (a) the undiluted polymer (PS), (b) 50% PS–50% styrene oligomer, and (c) 70% PS–30% dioctylphthalate. In *Figures 3* and *4*, the logarithm of the n.m.r. peak intensity is plotted as a function of the time τ that the ^{13}C magnetization was spin-locked in the rotating frame

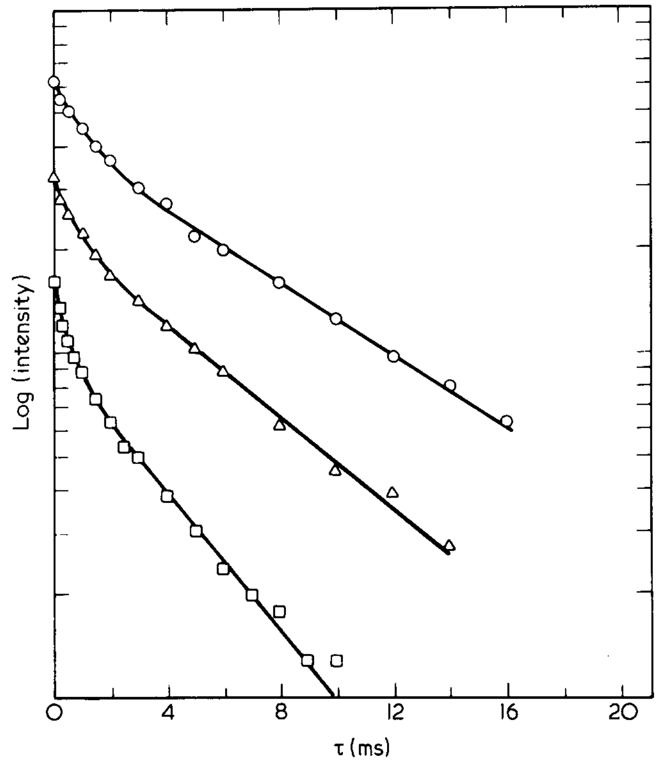

Figure 4 $T_{1\rho}$ curves at 38.5 kHz for the methine (backbone) carbon in polystyrene. The solid line is the nonlinear fit of the data points to equation (3) using the time constants given in *Table 1*. The materials are: ○, polystyrene; △, 50% polystyrene–50% styrene oligomer; □, 70% polystyrene–30% dioctylphthalate

Table 1 Carbon-13 $T_{1\rho}$ at 38.5 kHz (fast and slow components) for polystyrene and PS–diluent blends.

$$\left.\begin{matrix} T_{1\rho}\ \text{(short)} \\ T_{1\rho}\ \text{(long)} \end{matrix}\right\}\ \text{(ms)}$$

	Polystyrene resonances		
System	Non-protonated aromatic	Protonated aromatic	Methine
Polystyrene (T_g = 111°C)	0.9±0.5 45±5	1.1±0.3 17±2	1.1±0.4 8.3±0.9
50% Polystyrene 50% Styrene oligomer (T_g = 51°C)	0.4±0.2 34±3	0.9±0.4 13±2	0.8±0.2 6.5±0.6
70% Polystyrene 30% Dioctylphthalate (T_g = 32°C)	0.4±0.2 16±2	0.5±0.1 6.3±0.9	0.4±0.1 4.2±0.5

after breaking thermal contact with the abundant proton spin system. The absolute intensity $I(\tau)$ shown on the vertical scale is arbitrary. In each case, the semi-logarithmic decay of the peak intensities is considerably non-linear which implies that one relaxation time constant is not sufficient to characterize the relaxation behaviour. This is also observed in the $T_{1\rho}$ curves for polycarbonate and polycarbonate–diluent blends[1]. In this respect, the $T_{1\rho}$ data were analysed using a three-parameter, two-time-constant model in the following form:

$$I(\tau)=\exp\left\{-\frac{\tau}{T_{1\rho}(\text{short})}\right\}+\phi\exp\left\{\frac{-\tau}{T_{1\rho}(\text{long})}\right\} \quad (3)$$

where ϕ is the ratio of statistical weights for the slow and fast decay processes, respectively. The two relaxation times which characterize the fast [$T_{1\rho}$(short)] and slow [$T_{1\rho}$(long)] components of each non-linear intensity decay are given in *Table 1*. The uncertainty reported for the relaxation time constants is a consequence of fitting the three-parameter non-linear model using a maximum of 17 data points between $\tau = 10$ μs and 20 ms. The results of the model calculations, depicted as continuous lines in *Figures 3* and *4*, agree very well with the discrete data points for each n.m.r. peak intensity decay.

The $T_{1\rho}$ data for the undiluted polymer agree favourably with the results of Schaefer *et al.*[9,17]. At 32 kHz, the initial slope of the $T_{1\rho}$ curve (over the first 100 μs) for the composite methine and methylene carbon resonance is 0.8 ms (ref. 9) compared with $T_{1\rho}$(short) at 38.5 kHz here of 1.1 ± 0.4 ms. From a linear least-squares fit of the PS $T_{1\rho}$ decay between $\tau = 50$ μs and 1 ms at 37 kHz, Schaefer[17] reports time constants of 8.0 and 11.2 ms for the aliphatic and protonated aromatic carbons, respectively. The corresponding $T_{1\rho}$(long) data in *Table 1* for these two carbons are 8.3 ± 0.9 and 17 ± 2 ms. In comparing the results with the literature values, it is noteworthy that the range of τ (10 μs–20 ms) encompassed here by the nonlinear regression calculation of $T_{1\rho}$(long) greatly exceeds the upper limit of 1 ms used previously.

The low-T_g diluent, dioctylphthalate, substantially decreases $T_{1\rho}$(short) and $T_{1\rho}$(long) of the main- and side-chain carbons in PS. This results from a diluent-induced increase in the Fourier components of micro-Brownian motions at 38.5 kHz for the chain backbone and the pendant group. The interactions between polystyrene and dioctylphthalate which produce a significant change in the PS $T_{1\rho}$'s do not appear to be localized in a particular region of the macromolecule. However, of the ^{13}C nuclei in the glassy polymer the relaxation behaviour of which can be differentiated by high-resolution solid-state n.m.r., the $T_{1\rho}$'s of the aromatic carbons in the side group are affected most by the presence of dioctylphthalate. In contrast, the styrene oligomer produces only a small decrease in $T_{1\rho}$ in the 50/50 athermal mixture of PS and SO relative to the corresponding time constants in the undiluted polymer. For each carbon resonance in PS, the difference between $T_{1\rho}$ in the undiluted polymer and the athermal mixture is marginally detectable in view of the experimental uncertainty.

In the PS–DOP blend, it is difficult to determine the effect of the non-zero enthalpy of mixing on polystyrene $T_{1\rho}$'s using the limited data in *Table 1*. Although the relaxation time constants in the athermal mixture (PS–SO) are considerably longer than those in the non-athermal mixture (PS–DOP), it might be suspected that the difference between the ambient-temperature mid-kilohertz mobility in the two blends is primarily due to different blend T_g's. From *Figure 1*, the T_g of the 50/50 athermal mixture of polystyrene and the styrene oligomer is 51°C compared with the T_g of 32°C for PS plasticized by dioctylphthalate. It was suggested previously[1] that $T_{1\rho}$'s in different polymer–diluent blends should be compared at the same blend T_g or at an equivalent temperature interval below T_g. This is important if the Fourier components of motion associated with the primary (T_g) transition contribute significantly to the $T_{1\rho}$ spectral density functions in the frequency regime of interest.

CONCLUSIONS

Low-molecular-weight additive effects on the mid-kilohertz mobility of atactic polystyrene at 25°C via n.m.r. $T_{1\rho}$ are analogous to the results of a previous study of diluents in glassy bisphenol-A polycarbonate. The low-T_g diluent, dioctylphthalate, increases the spectral density of thermal motions of the chain backbone and the pendant group in PS on the order of 38.5 kHz. Of the ^{13}C nuclei in the glassy polymer the relaxation behaviour of which can be differentiated by high-resolution solid-state n.m.r., the $T_{1\rho}$'s of the aromatic carbons in the side group are affected most by dioctylphthalate. In contrast, the styrene oligomer, which has a higher T_g than that of dioctylphthalate, does not significantly alter the ambient temperature mobility of polystyrene at 38.5 kHz.

The PS–styrene oligomer and PS–dioctylphthalate blends are examples of athermal and non-athermal mixtures, respectively. However, the effect of the enthalpy of mixing on the $T_{1\rho}$'s of the polymer is probably obscured by differences in blend mobility due to different blend T_g's.

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