clude that the structure is due to optical effects (interference bands, reflection losses, etc.) but not chemical shifts of the carbonyl group. However, the observed mismatch at 1715–1720 cm^{-1} can be taken as suggestive evidence of the presence of an additional carbonyl absorption in the blend. Making a correction for the predicted minimum at the ~1720-cm^{-1} peak, the shifted carbonyl groups in the blend would be ~10–15 cm^{-1} lower in frequency than the normal carbonyl. From the difference spectrum intensity the lower frequency carbonyl can constitute no more than ~3% of the total carbonyl groups.

Conclusion

The experimental evidence presented in this paper points to the conclusion that the excess volume, enthalpy, and entropy of mixing for the PMMA–PSAN pair are extremely small in magnitude. In the terminology of the equation of state theory, the three reduced parameters, volume, pressure, and temperature, must be nearly identical both for the two-component polymers and for their mixtures.

The interaction between two macromolecules is manifested by a downward shift (~10–15 cm^{-1}) in the stretching frequency of the carbonyl group of PMMA. That the interaction is indeed weak is indicated by the low intensity of the displaced peak, contributed by no more than 3% of the PMMA segments in the blends.

We believe that we have found a rare case in which the physical properties of a polymer mixture approach the requisites of a "regular" solution.

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Compatibility in Blends of Poly(methyl methacrylate) and Poly(styrene-*co*-acrylonitrile). 2. An NMR Study

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Received May 26, 1978

ABSTRACT: Blends of poly(methyl methacrylate) and poly(styrene-*co*-acrylonitrile) have been examined by pulsed NMR and on the basis of T_1 and $T_{1\rho}$ data it is concluded that there is inhomogeneity on a characteristic length between limits of 20 and 150 Å determined by the experiment.

In part 1 of our study on the properties of mixtures of poly(methyl methacrylate) and poly(styrene-*co*-acrylonitrile) extensive mixing of the two components was indicated by dielectric and calorimetric measurements.[1] However, dimensional level of homogeneity remains unanswered. We explore this aspect further using the technique of pulsed nuclear magnetic resonance which is inherently sensitive to short-range interactions.

Experimental Section

Details of sample preparation have been given in part 1. Five PMMA/PSAN materials were studied for which the fraction by weight of PMMA ranged from 0 to 1.0 in 0.25 increments. Melt-blended films were cut into small pieces and sealed under vacuum in NMR tubes.

Data were recorded on a conventional Bruker B-KR301 spectrometer operating at a resonant frequency of 40 MHz. The solid echo sequence,[2] 90°–τ–90° (90° phase shift) provided an approximation to the complete free induction decay from which T_2 was measured as $t_{1/2}/\ln 2$ where $t_{1/2}$ denotes the time taken for the signal to decay to half the initial intensity. The 180°–τ–90° pulse sequence provided T_1[3] while $T_{1\rho}$ was obtained from the 90°–90° phase shift spin-locking sequence.[4] Rotating frame measurements were made at an radiofrequency field, H_1, of 10 G. In the region of the low-temperature $T_{1\rho}$ minimum, results were also taken from H_1 = 7.3 and 2 G. These low H_1 field data were recorded on a second spectrometer, described previously.[5] The Bruker temperature control facility provided sample temperatures to an accuracy of ±1 °C.

Results and Discussion

Spin–lattice, T_1, spin–spin, T_2, and rotating frame $T_{1\rho}$ data were recorded from −150 to +160 °C and are presented as a composite plot in Figure 1. It is apparent from the outset that T_2 data are uninformative in monitoring changes associated with blending and will not be discussed further. T_1 and $T_{1\rho}$ data at the minima associated with the onset of α-methyl motion[6] (at 0 °C and ca. −100 °C,

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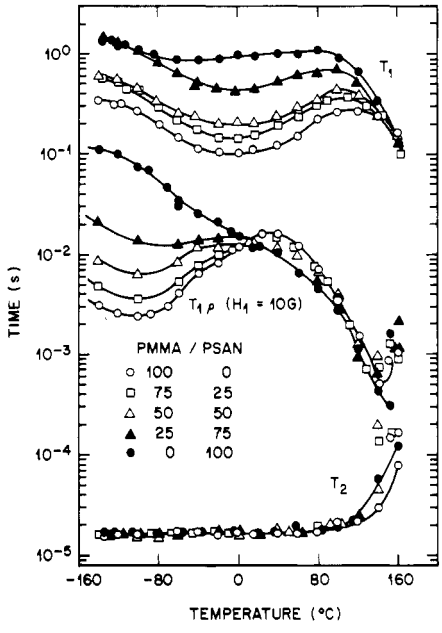

Figure 1. T_1, T_2, and $T_{1\rho}$ data for PSAN/PMMA blends as a function of temperature.

respectively) are, however, revealing. The observation of exponential decay in both sets of data (with the exception of marginally nonexponential $T_{1\rho}$ decay for the 75/25 PSAN/PMMA sample to be discussed later) is indicative of strong interaction, via the mechanism of spin diffusion, between the two-component polymers.[7,8] The α-methyl motion in the PMMA is relaxing the remaining protons in the PMMA and the protons in the PSAN. The effect may be quantified on the basis of the following simple model which, for completeness, includes the possibility that phenyl group motions in the PSAN may also be providing a relaxation site.[9] Let k_1^0 and k_2^0 respectively denote the intrinsic relaxation rate of a methyl proton and a phenyl proton. The weight fraction of PMMA is ω_1. If M_m, M_ϕ, and M_T are the magnetizations associated with α-methyl protons, phenyl protons, and the total magnetization, respectively, then

$$k_1^0 M_m + k_2^0 M_\phi = dM_T/dt \quad (1)$$

On the assumption of a common spin temperature this equation may be stated in terms of the corresponding numbers of protons present. Thus

$$k_1^0 \frac{N_m}{N_T} + k_2^0 \frac{N_\phi}{N_T} = k \quad (2)$$

where k is the observed spin–lattice (T_1^{-1}) or rotating frame ($T_{1\rho}^{-1}$) relaxation rate. In terms of the mass fraction of PMMA, eq 2 may be written

$$(7.1 + \omega_1)k = \omega_1[3k_1^0 - 3.5k_2^0] + 3.5k_2^0 \quad (3)$$

Thus, if spin diffusion allows all of the material to relax totally through the two relaxation sinks, but is not a rate-controlling step, the plot of $(7.1 + \omega_1)k$ vs. ω_1 should be linear. Figure 2 shows data at the T_1 minimum for both 30 and 40 MHz. The linearity of the 40-MHz data is ambiguous because of scatter; the 30-MHz data clearly support the model. An estimate of the maximum diffusive path length L may be derived from the approximate formula

$$L = (6D/k)^{1/2} \quad (4)$$

Typically, for $k = 2$ s^{-1} and a diffusion coefficient $D = 10^{-12}$ cm^2 s^{-1},[10] $L \approx 170$ Å. Therefore if aggregates of the

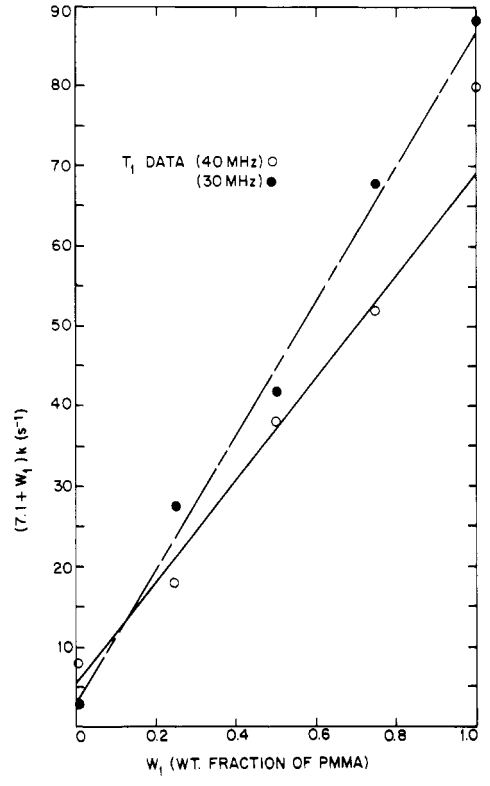

Figure 2. Plot of $(7.1 + \omega_1)k$ vs. ω_1, the weight fraction of PMMA. $k = T_1^{-1}$ at 0 °C.

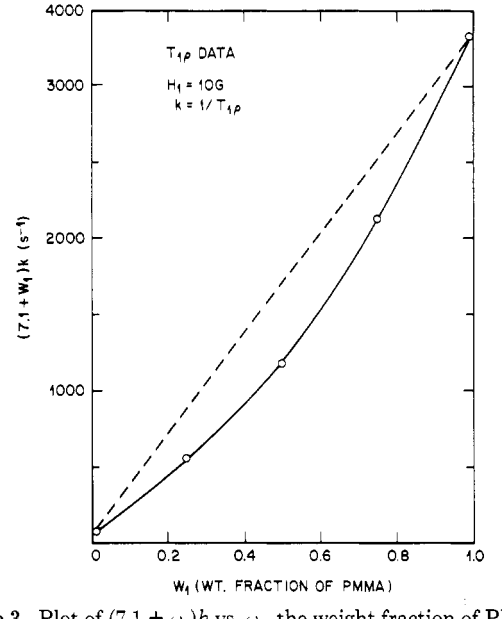

Figure 3. Plot of $(7.1 + \omega_1)k$ vs. ω_1, the weight fraction of PMMA. $k = T_{1\rho}^{-1}$ at −100 °C.

Table I
$T_{1\rho}$ and T_1 Magnitudes at −100 and 0 °C, Respectively

mass fraction of PMMA	$T_{1\rho}$, ms				T_1, ms, at ν_0 =	
	H_1 = 10 G	H_1 = 7.3 G	H_1 = 2 G short	H_1 = 2 G long	40 MHz	30 MHz
1.0	2.4	2.1	1.6		100	90
0.75	3.7	3.4	0.5	3.0	150	114
0.5	6.4	6.1	1.4	6.9	200	180
0.25	(12.5)	(12.9)	1.3	9.6	407	265
0	76.0	67	50		930	3500

component polymers are present their linear dimensions are certainly less than 170 Å on the basis of the T_1 data.

Following the same procedure for the $T_{1\rho}$ data at the

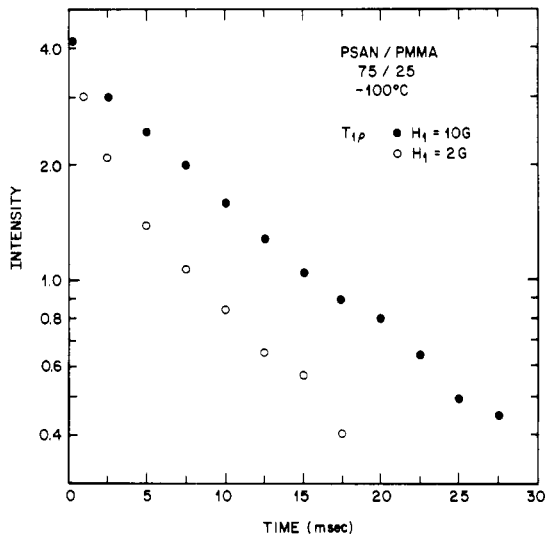

Figure 4. $T_{1\rho}$ decay for 75/25 PSAN/PMMA for H_1 = 10 and 2 G, respectively.

low-temperature minimum, Figure 3 shows that $(7.1 + \omega_1)k$ does not vary linearly with ω_1; the relaxation rate for the blends falls short of the magnitudes expected from a tightly coupled spin system. In this case, however, a diffusive path length of only about 17 Å would be required to eliminate spin diffusion as a rate-controlling step. These data therefore indicate that there is segregation on a scale between 20 and 150 Å.

The question now arises as to why simple exponential $T_{1\rho}$ decay is observed at $H_1 \approx 10$ g in most samples. One would expect nonexponential behavior for a segregated system with the overriding caveat that it is not possible to resolve two $T_{1\rho}$ components which are within a factor of 2, using only the 1.5 decades of decay observable with our system. In this context the marginally nonexponential decay observed in the 75/25 PSAN/PMMA blend alluded to in the earlier part of this section assumes critical significance. If nonexponential decay is to be observed at all, the 75/25 blend is the obvious candidate since there is greatest chance of having some of the PSAN material remote from the dilute PMMA. Furthermore, the curvature in the decay should increase at lower H_1 fields since $T_{1\rho}$ will decrease without altering the diffusive path length. Data recorded at H_1 = 7.3G and 2.0 G at -100 °C are listed in Table I. The nonexponential character of the $T_{1\rho}$ decays unambiguously increases as required to be consistent with component polymer segregation. Figure 4 compares the $T_{1\rho}$ decay for H_1 = 2 and 10 G in the 75/25 PSAN/PMMA material.

In summary, the NMR data presented in this paper indicate that there is inhomogeneity on a scale between 20 and 150 Å, determined by the experiment, in the PSAN/PMMA blends studied.

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Interaction Parameter in Polymer Mixtures

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ABSTRACT: An improved method has been devised to calculate, from melting point measurements, the interaction parameter between a crystalline and an amorphous polymer. The procedure takes into account the effect of morphological changes in melting point depression.

The determination of thermodynamic interaction between two polymers is crucial to the understanding of compatibility in mixtures. Of the several methods which have been applied recently to amorphous polymers, namely, small-angle neutron scattering,[1] gas–liquid (polymer) chromatography,[2–4] and vapor sorption,[5] none is readily adaptable to a mixture containing a crystalline polymer as one of its components. Nishi and Wang,[6] in their analysis of the lowering of the melting temperature of a crystalline polymer in the presence of an amorphous one, derived a simple equation which related the melting point depression directly to the interaction parameter. Their equation described satisfactorily the data obtained for mixtures of poly(vinylidene fluoride) and poly(methyl methacrylate)[6] or poly(ethyl methacrylate).[7]

From a study of isothermally crystallized samples, Nishi and Wang concluded that morphological changes such as imperfections in crystals and reduction in lamellar thickness were not major factors in the lowering of the melting point in a PVF_2–PMMA mixture. Nevertheless, it is worthwhile to examine the possibility that such morphological contributions may be important in other blends. A case in point is the mixture of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and isotactic polystyrene (PS) for which a reduction in the thickness of i-PS crystals has been indicated by small-angle X-ray studies.[8] In the present investigation, we have extended the treatment of Nishi and Wang to take morphological effects into account. A procedure has been devised so that both the interaction parameter and the morphological contribution can be calculated from melting point measurements.

The interaction parameter between PPO and PS has been determined by melting point measurements in two previous investigations. Shultz and McCullough[9] used ternary mixtures of PPO–PS–toluene and Berghmans and Overbergh[10] used isotactic PS and PPO. In both studies, the interaction parameter was found to be approximately

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0024-9297/78/2211-1267$01.00/0