Compatibility in Blends of Poly(methyl methacrylate) and Poly(styrene-*co*-acrylonitrile). 1. Physical Properties

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ABSTRACT: The compatibility of blends of poly(methyl methacrylate) and poly(styrene-*co*-acrylonitrile) was studied by measurements of density, specific heat, dielectric relaxation, and enthalpy relaxation. The results of these measurements point to the conclusions that there is extensive mixing of the segments of two macromolecules and that the excess volume, enthalpy, and entropy of mixing are very small in magnitude. The interaction between the two polymers is manifested by a downward shift ($\sim 10 - 15$ cm^{-1}) in the infrared stretching frequency of the carbonyl group but only about 3% of the PMMA segments contribute to the displaced peak.

Among polymers known to be compatible with each other, the pair poly(methyl methacrylate) and poly(styrene-*co*-acrylonitrile) is one of the few for which thermodynamic interaction has been measured.[1] With the aid of small-angle neutron scattering the molecularly dispersed character of the blend has been confirmed by measurement of the second virial coefficient of the binary solution. The miscibility of the two polymers, however, is dependent on temperature, and phase separation of initially compatible blends occurred at elevated temperatures.[2] This phenomenon is associated with the "lower critical solution temperature" and is now accepted, on both theoretical and experimental grounds, as a common occurrence in polymer mixtures.[3,4]

Except for the two interesting studies mentioned above, and an unpublished report on refractive indices,[5] little information is available about the physical properties of PMMA–PSAN blends. We have therefore undertaken measurements of density, specific heat, and dielectric relaxation of this system. We have also applied infrared spectroscopy in an attempt to identify the nature of the molecular interaction between the two polymers.

An additional reason for our interest in this system is the following: high molecular weight PMMA has almost the same glass transition temperature (T_g) as PSAN, and the pair therefore offers a unique opportunity to study the enthalpy relaxation of mixtures since annealing can be conducted at virtually the same temperature interval from the T_g's of the two constituent polymers in the mixture. To our knowledge, enthalpy relaxation in polymer mixtures has not been investigated previously in great detail.

Experimental Section

1. Materials. Poly(styrene-*co*-acrylonitrile), with an acrylonitrile content of 28.09% by weight from elemental analysis, was obtained from Union Carbide Corp. (UCC RMD 4520). It was purified by precipitating twice from a 2-butanone solution into a large excess of methanol. The intrinsic viscosity of PSAN in 2-butanone was 0.622 at 25 °C and the T_g of the polymer was 106.5 °C as measured by differential scanning calorimetry.

Two poly(methyl methacrylate) samples were used in our study. The first, PMMA-1, was supplied by Cellomer Associates Inc. and used without further purification. The number and weight average molecular weights were 3.32×10^5 and 6.06×10^5, respectively. The T_g of PMMA-1 was 103.5 °C. The second sample, PMMA-2, was obtained from the Rohm and Haas Co. (Plexiglas 100) and was purified by precipitating twice from a 2-butanone solution into a large excess of methanol. The intrinsic viscosity of PMMA-2 in benzene was 0.355 dL/g at 25 °C from which the viscosity average molecular weight was computed to be 1.45×10^5. The T_g of the polymer was 88.0 °C. (The presence of copolymerized units in this material is indicated by high-resolution NMR spectra.)

Model compounds used for infrared spectroscopic studies were methyl isobutyrate, methyl trimethylacetate, isobutyronitrile, and *n*-butyronitrile (all from Aldrich Chemical Co.) and were used without further purification.

2. Film Preparation. a. Melt-Blended Films. Pellets of PSAN and PMMA-2 were blended in a Brabender plastograph at 150 °C for 7 min at a rotor speed of 40 rpm. The mixtures appeared opaque at early stages of mixing but became transparent after about 3 min. For the purpose of attaining the same thermal history, the two component polymers were also passed through the Brabender plastograph under identical conditions. Films were pressed between aluminum sheets at 170 °C for 5 min and then quenched to room temperature by placing the sheets between the platens of a water cooled press. Film thickness of about 1.5×10^{-2} cm was used for density and calorimetric measurements while thicker films, about 0.13 cm, were used for dielectric relaxation studies.

b. Solution-Cast Films. Films of PMMA-1, PSAN, and their mixtures were cast from 4% solution in 2-butanone on glass plate at room temperature. The solvent was evaporated slowly under a stream of air and the resulting film was dried under vacuum at 85 °C for a week and then at 140 °C for 24 h. Film thickness was about 1.5×10^{-2} cm for density and calorimetric measurements but thinner samples, 7 to 15×10^{-4} cm, were used for infrared spectroscopy.

3. Density. The densities of polymer films were measured by the use of a gradient column composed of water and calcium nitrate.[6] All measurements were made at 22 °C. The resolution of the gradient column was 3×10^{-4} g cm^{-3} and the reproducibility of density measurements was within 1×10^{-3} g cm^{-3} for samples prepared at different times. The average of three measurements for each sample was taken as the experimental value.

In connection with enthalpy relaxation studies, densities were also measured after annealing at 85 °C. Annealing was carried out in an aluminum chamber under argon atmosphere. The temperature of the chamber was controlled within ±0.1 °C with a proportional temperature controller and the temperature of the sample was monitored by a copper–constantum thermocouple.

4. Calorimetry. A Du Pont differential scanning calorimeter, Model 990, was used for glass transition temperature and specific heat measurements. The temperature reading was calibrated with indium metal (mp 156.3 °C) and a sapphire disk was used for the calibration of specific heat.

The glass transition temperature was taken as the onset of the abrupt increase in the specific heat of the specimen. In order to obtain reproducible T_g and ΔC_p values, the same sample weight of 14 mg was used throughout our experiments. The samples were placed in aluminum pans at 140 °C with the dual purpose of obtaining good contact between sample and pan and of eliminating the effect of previous thermal history. The assemblies were then cooled on a copper block maintained at room temperature.

In enthalpy relaxation experiments, samples were heated in the calorimeter to 145 °C under nitrogen and then quenched at a cooling rate of about 300 °C/min to the glass state. Annealing of the quenched specimens was conducted at 85 °C under nitrogen in the calorimeter.

A heating rate of 5 °C/min was used in all the calorimetric experiments. A sensitivity setting of 0.1 mcal/s was used in ΔC_p determinations. A small stream of nitrogen gas, about 10 cm^3/min,

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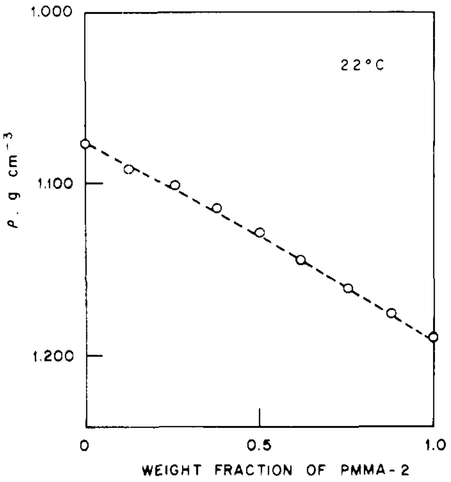

Figure 1. Densities of PSAN-PMMA-2 mixtures.

flushed the calorimeter during measurement. The reproducibility of T_g values was about ±0.6 °C, and that of ΔC_p about $\pm 7 \times 10^{-3}$ cal g^{-1} °C^{-1}.

5. Dielectric Relaxation. The Fourier transform dielectric spectrometer used has been described in previous papers.[7] Under computer control, a voltage pulse was applied to a sample and the integrated current response was recorded. This procedure was repeated with a capacitor which was equivalent to the vacuum capacitance of the sample. The complex permittivity of the sample was then calculated from the two current responses by the use of a computer program. The temperature of the environmental chamber which housed the sample was also controlled and programmed by the computer. Under the conditions of our experiments, useful data could be obtained in the frequency range of 1 to 10^4 Hz.

6. Infrared Spectroscopy. Experiments were carried out with a Model 620 Perkin-Elmer grating spectrometer and a Model 15B Digilab Fourier Transform spectrometer. Measurements on the latter were taken at 2-cm^{-1} resolution. The free-standing polymer films were mounted on holders and transmission spectra taken at normal incidence with the Fourier Transform spectrometer. The model compounds, liquids at room temperature, were placed in an adjustable NaCl cell and the spectra taken with the grating spectrometer. In order to examine the interaction between polymers and model compounds, swollen films were placed between KBr disks. Although absorbance was recorded over the entire frequency range of the instrument, attention was focused at the stretching band of the carbonyl group of the PMMA. The optical constants of the PSAN and PMMA films were determined using transmission and reflection methods and details will be reported elsewhere.[8]

Results and Discussion

1. Density. The densities of PSAN, PMMA-2, and their mixtures are shown in Figure 1. The observed values (open circles) are in excellent agreement with calculated ones based on the rule of volume additivity (dotted line). Almost identical results are obtained for PSAN and PMMA-1. Annealing at 85 °C does not seem to induce a significant increase in density (Figure 2).

It can be concluded from the density measurements that the excess volume of mixing is small and does not exceed the magnitude of experimental uncertainty, namely, $\pm 5 \times 10^{-4}$ cm^3 g^{-1}. Large, negative-excess volumes have been reported for other compatible mixtures,[9] although positive deviation from volume additivity has also been claimed.[10]

2. Glass Transition Temperature. Figure 3 shows T_g for mixtures of PSAN and PMMA-2 as a function of blend composition expressed in weight fraction. The experimental data fall nicely on a straight line. However, the T_g data can be correlated equally well with volume fractions of the components because the densities of the two polymers differ by only 10% and the value of volume fraction is within 0.02 units of the value of weight fraction. Thus, both Gordon-Taylor equation[11] using weight fraction W or Bueche-Kelley equation[12] using volume fraction ϕ are applicable to our results. The latter equation, derived from the assumption of additivity of free volume, is preferred because it gives excellent correlation even when the densities of two polymers are widely different as in the case of poly(vinylidene fluoride) and poly(methyl methacrylate).[13] In the Bueche-Kelley equation

$$T_g = (\phi_1 T_{g_1} + k\phi_2 T_{g_2})/(\phi_1 + k\phi_2) \qquad (1)$$

k is ratio of thermal expansion coefficient $\Delta\alpha_2/\Delta\alpha_1$, with $\Delta\alpha = \alpha(\text{liquid}) - \alpha(\text{glass})$. Apparently the value of k is unity in eq 1 for the PMMA-PSAN pair. This is borne out by the $\Delta\alpha$ values of the two polymers. The α_l and α_g values for PMMA have been reported to be $5.60-5.80 \times 10^{-4}$ °C^{-1} and $2.25-2.72 \times 10^{-4}$ °C^{-1}, respectively; therefore, $\Delta\alpha$ should be about 3.2×10^{-4} °C^{-1}. For PSAN, we have not been able to find the value of $\Delta\alpha$ in the literature. But if we assume that the thermal expansion coefficient of PSAN is the weight fraction average of the expansion coefficients of polystyrene[14] and polyacrylonitrile,[14] then $\Delta\alpha$ is estimated to be $3.1-3.2 \times 10^{-4}$ °C, identical to that of PMMA.

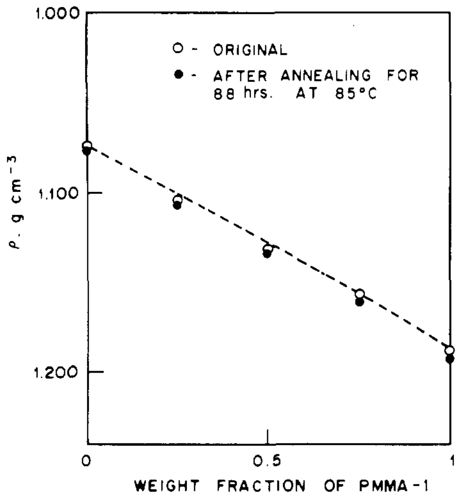

Figure 2. Densities of PSAN-PMMA-1 mixtures before and after annealing.

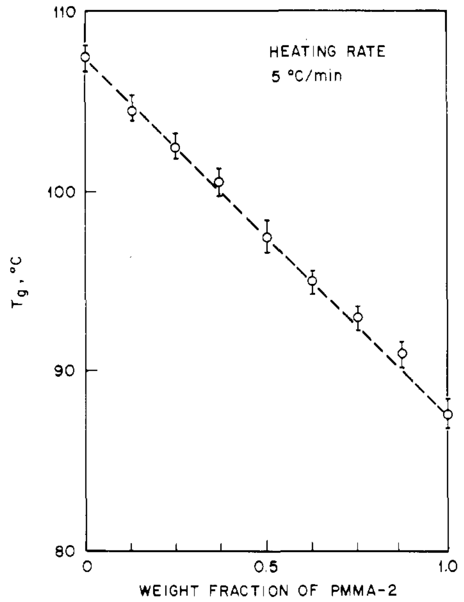

Figure 3. Glass transition temperatures of PSAN-PMMA-2 mixtures.

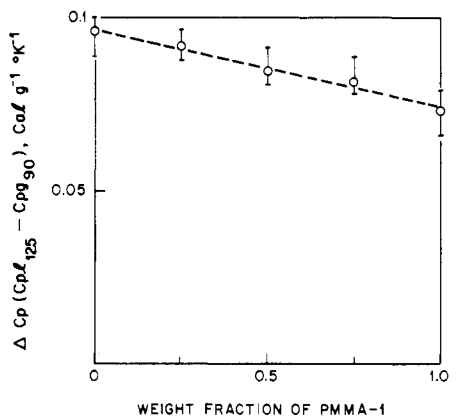

Figure 4. ΔC_p values accompanying glass transitions.

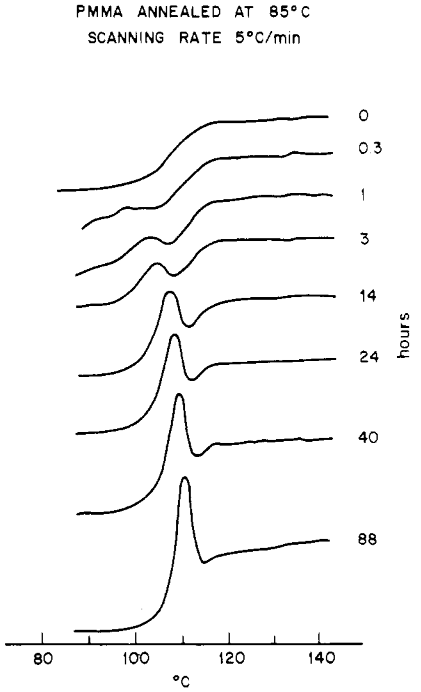

Figure 5. Effect of annealing on the specific heat of PMMA-1.

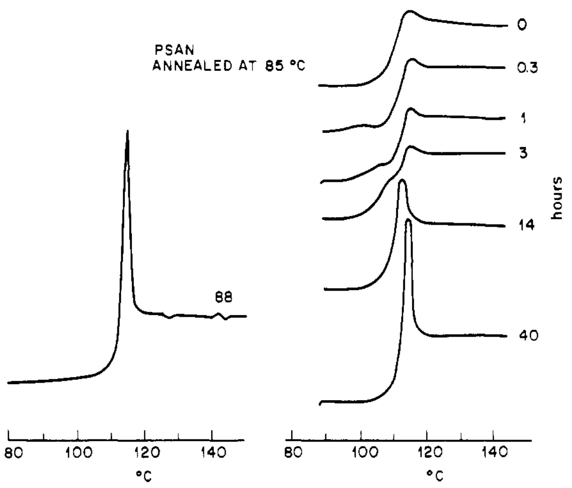

Figure 6. Effect of annealing on the specific heat of PSAN.

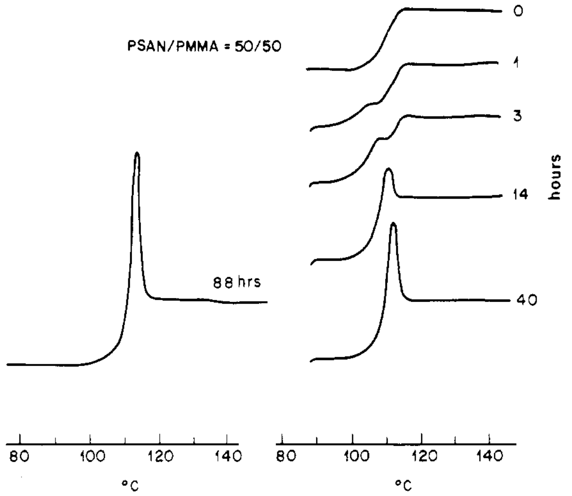

Figure 7. Effect of annealing on the specific heat of a 50/50 PSAN-PMMA-1 mixture.

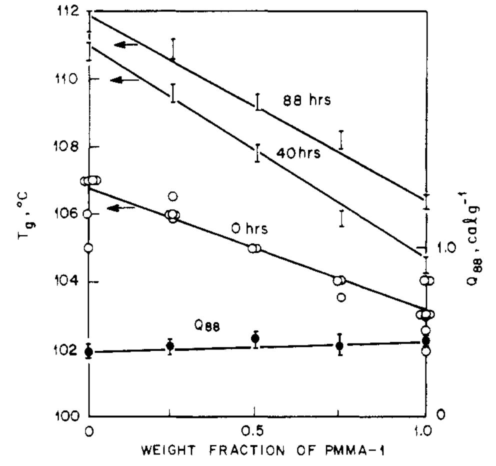

Figure 8. Glass transition temperatures and enthalpy relaxations of annealed PSAN, PMMA-1, and their mixtures.

The implication of eq 1 with regard to the additivity of free volumes suggests extensive mixing of the different segments. Furthermore, the configurational entropies must, to a first approximation, also obey the rule of additivity. The excess entropy of mixing is therefore expected to be very small. This conclusion is consistent with the results of neutron scattering studies[1] which yield a value for the partial molar excess entropy, ΔS_1^e, of only about -5.7×10^{-2} cal/K/mol of PMMA (MW $\approx 2 \times 10^5$) at a PSAN concentration of 1×10^{-2} g cm^{-3}.

3. ΔC_p Accompanying Glass Transition. The change in specific heat during the transition is taken as the difference in C_p values at 125 °C (liquid) and at 90 °C (glass). Excellent base lines are obtained in individual thermal scans and the error bars in Figure 4 indicate the variation in results from ten measurements including different specimens. As can be seen, an approximately linear relation between ΔC_p and blend composition is obtained for the PSAN-PMMA-1 pair.

4. Enthalpy Relaxation. Typical thermal scans of annealed samples are shown in Figures 5–7. When the samples were annealed for a short period of time at 85 °C, a shoulder appeared in the thermograms of both polymers below their normal T_g's. The origin of this shoulder is poorly understood and will not be elaborated here. At longer annealing times, the shoulder disappeared and pronounced endothermic peaks similar to those found for polystyrene and polycarbonate[15] were recorded. As annealing time increases, the onset of the C_p jump moves to higher temperatures. But the increase in T_g with annealing is small, less than 5 °C after annealing for 88 h in all the samples examined. The magnitude of the increase in T_g is to be compared with a corresponding value of about 18 °C for polystyrene annealed at 90 °C after 15 h. The shift

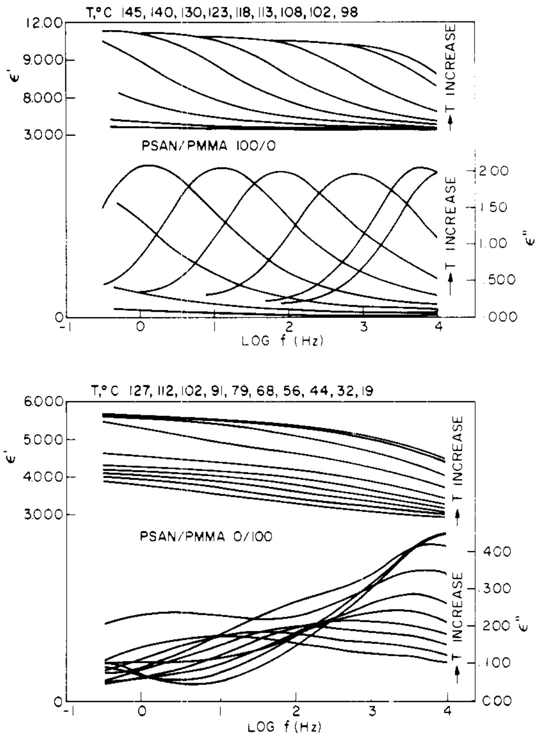

Figure 9. Dielectric relaxation curves of PSAN and PMMA-2.

in T_g is approximately proportional to blend composition, as shown in Figure 8.

The quantity Q_t, which represents the additional thermal energy absorbed during the glass-to-liquid transition by an annealed sample compared to a quenched one, is computed graphically from the respective thermograms. The values of Q_t at t = 88 h are fortuitously similar for PMMA and PSAN and the variation of Q_{88} with composition has the same magnitude as experimental uncertainty (Figure 8). These results are highly suggestive of only a weak interaction between the two polymers which exerts no measurable influence on enthalpy relaxation.

It might be argued that if the interaction between two polymers remains unchanged during the glass-to-liquid transition, then Q_t will not be altered by this interaction regardless of its magnitude. While the argument has merit, we feel nevertheless that in the present system the interaction is so weak in relation to the magnitude of Q_t that its effects are not discernible. In support of this view we would point out that a thermally induced phase separation occurs in some mixtures at only 150 °C where the interaction vanishes. As a point of reference, the partial molar excess enthalpy derived from neutron scattering studies[1] is only about −22.5 cal/mol of PMMA (MW $\approx 2 \times 10^5$) at a PSAN concentration of 1×10^{-2} g cm^{-3}.

5. Dielectric Measurements. The dielectric relaxation data for PMMA are shown in Figure 9. Both α and β relaxations are clearly identified and the results are in good agreement with literature values.[16] The ϵ' and ϵ'' values for PSAN in the α-relaxation region are also represented in Figure 9. There is no indication of β relaxation for this copolymer in the temperature range of our experiment. The normalized dielectric data for blends containing 75, 50, and 25% PSAN, respectively, are summarized in Figures 10 and 11. A single, well-defined α peak is observed for each mixture.

The changes in permittivity, $\Delta\epsilon$, for both β and α mechanisms are summarized in Table I. The magnitudes of $\Delta\epsilon$ for the α relaxations in mixtures obey the simple rule of additivity, as evidenced by the excellent agreement between experimental and calculated values. The characteristic WLF-type dependence of f_{max} vs. $1/T$ for α relaxation is noted for the component polymers as well as mixtures (Figure 12). This body of experimental data reinforces the conclusion that large-scale, main-chain motion of the two polymers occurs simultaneously and cooperatively in the α process, a situation rendered possible only when extensive mixing of the two polymers is achieved.

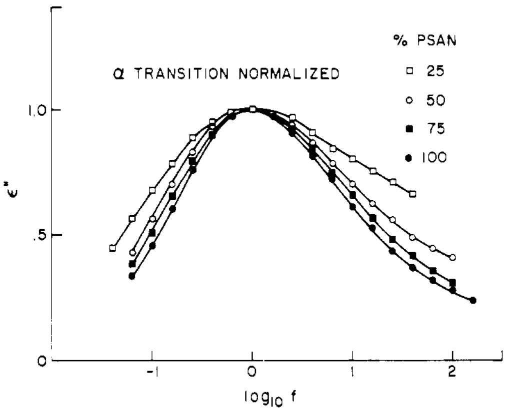

Figure 10. Normalized dielectric loss curves of blends—α transition.

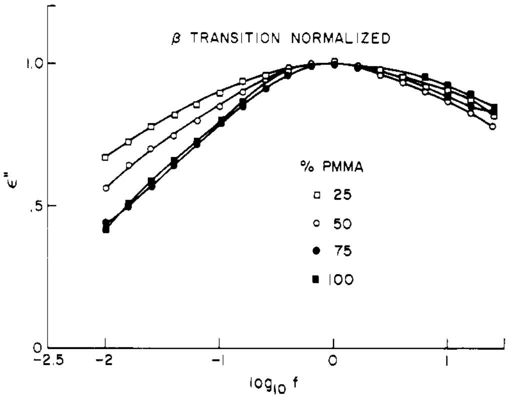

Figure 11. Normalized dielectric loss curves of blends—β transition.

Table I
Magnitude of $\Delta\epsilon$ for α and β Transitions as a Function of Composition

PSAN/PMMA	β	α_{exptl}	α_{calcd}
100/0	0.0	7.8	7.8
75/25	0.3	6.2	6.1
50/50	0.6	4.5	4.5
25/75	0.9	2.9	2.8
0/100	1.2	1.1	1.1

In the β process, the change in permittivity is directly proportional to the amount of PMMA in the mixture because PSAN does not undergo a β relaxation in the same temperature range. Therefore, we are concerned only with the motion of PMMA. The apparent activation energy of this process decreases from 20 to 14.5 K cal mol^{-1} as the PMMA content decreases from 100 to 25% in the mixture (Figure 13). Similar decreases in the activation energy of β relaxation have been reported for poly(methyl acrylate) containing diluents.[17] The β process in PMMA has been ascribed by many investigators to the rotation of the ester group in the side chain[18,19] although recent work on cross-linked PMMA[20] supports an alternative mechanism based on the local motion of main chain segments. Inasmuch as the presence of the PSAN molecule is not expected to change the rotational energy

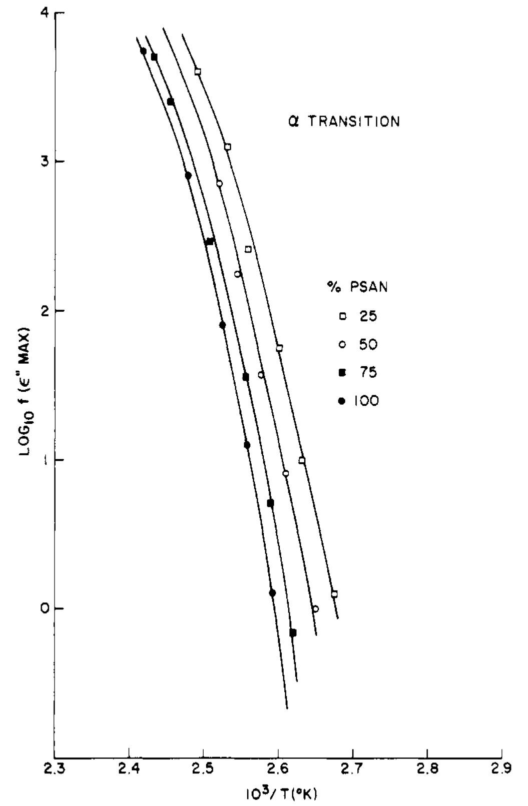

Figure 12. Dependence of the frequency of loss maximum (α) on temperature.

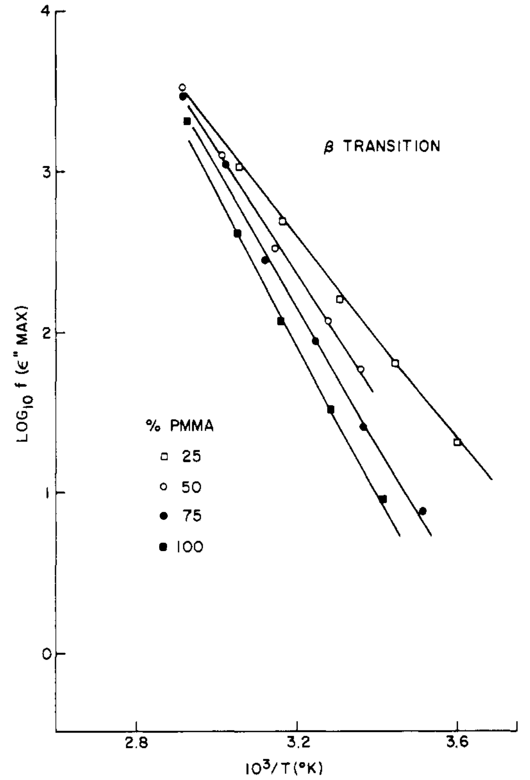

Figure 13. Dependence of the frequency of loss maximum (β) on temperature.

barrier of the ester group of PMMA, our results appear to favor the postulate of a local mode motion of the main chain.

6. Infrared Spectroscopy. The negative value of the partial molar excess enthalpy obtained from neutron scattering prompted us to search for the nature of specific interaction between PMMA and PSAN. We recognize that in the equation of state theory by Flory,[21] the enthalpy of mixing contains contributions arising from differences in reduced volumes and reduced temperatures in addition to the parameter X_{12} which describes the pair contact energy. Therefore, a small negative $\Delta\bar{H}_1$ does not necessarily imply the existence of specific interaction. Nevertheless, we are encouraged by evidences from Fourier Transform infrared spectroscopy that shifts in the stretching frequency of the carbonyl group occur in mixtures of PMMA with poly(vinylidene floride)[22] and of poly(vinyl chloride) with dioctyl phthalate.[23]

Table II
Carbonyl Stretching Frequencies of Model Compounds and Polymers[a]

	carbonyl stretching frequency, cm^{-1}	shift, cm^{-1}
methyl trimethylacetate (MTA)	1738 ± 1	
methyl isobutyrate (MIB)	1741 ± 1	
MTA + IBN (1:1 mol ratio)	1735 ± 1	−3
MIB + IBN (1:1 mol ratio)	1737 ± 1	−4
MIB + *n*BN (1:1 mol ratio)	1738 ± 1	−3
MIB + PSAN (1:3.5 wt ratio)	1731 ± 1	−10
PMMA	1729 ± 1	
PMMA + IBN (1:1 wt ratio)	1729 ± 1	0
PMMA + PSAN (1:1 wt ratio)	1729 ± 1	0
PMMA + PSAN (1:3 wt ratio)	1729 ± 1	0

[a] IBN = isobutyronitrile. *n*BN = *n*-butyronitrile.

The results of the model compound experiments showed small shifts in the carbonyl frequency, ~3 to 4 cm^{-1} (Table II). A concentrated solution of PSAN in methyl isobutyrate reveals a larger shift, about 10 cm^{-1}. However, a mixture containing equal weight percentages of PMMA and isobutyronitrile shows no shift at all for reasons which are not clear to us but are perhaps related to the poor solvent power of IBN for PMMA.

No obvious shifts were seen in visual comparisons of the PSAN–PMMA polymer film spectra. However, differences could be quantitatively characterized by computer calculation of difference spectra from the digitally recorded absorbance data. The procedure involved choosing a selected band, either C≡N or C═O, in the blend spectrum and then computationally adjusting the pure polymer spectrum containing that band until the peak maximum had exactly the same value as the band maximum of the blend. Subtraction then gave a zero difference at the peak maximum and differences in other portions of the band could be seen. The 2240 (C≡N stretch) and 1732 cm^{-1} (C–O stretch) bands of the blends were examined. The difference spectra all showed complicated structures with maxima and minima above and below the zero difference line. The difference peaks were stronger in the case of the carbonyl band and the values amounted to as much as ~3% of the intensity of the peak maximum of the polymer film carbonyl absorption. These structures were examined in more detail for the carbonyl absorption of the 75% PSAN sample by comparison of the experimental results with theoretical calculations of the difference spectra from the Fresnel optical relations[8,24] using previously measured optical constants of PMMA[8] and using a constant value of 1.45 for the refractive index of PSAN in the 1650–1800 cm^{-1} region (obtained from fringe band measurements). The calculations qualitatively matched the observed maxima and minima except for a minimum predicted at ~1720 cm^{-1} in contrast to an observed maximum at ~1715 cm^{-1}. Where the difference spectra match one can conclude 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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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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