Molecular Weight Effect on the Miscibility of Poly(ethylene oxide) and Isotactic Poly(methyl methacrylate) in Their Blends

C. Marco and J. G. Fatou

Instituto de Ciencia y Tecnologia de Polimeros, Juan de la Cierva 3, 28006 Madrid, Spain

M. A. Gomez,[†] Hajime Tanaka,[‡] and A. E. Tonelli[*]

AT&T Bell Laboratories, Murray Hill, New Jersey 07974. *Received June 6, 1989; Revised Manuscript Received November 8, 1989*

ABSTRACT: Blends of poly(ethylene oxide) and isotactic poly(methyl methacrylate) have been studied for a wide range of compositions and molecular weights of one of the components by differential scanning calorimetry and high-resolution, solid-state ^{13}C NMR spectroscopy. Proton spin-lattice relaxation times in the rotating frame, $T_{1\rho}$(H), as well as calorimetric data, indicate compatibility of the components of these blends in the amorphous phase, which were previously reported as immiscible, depending on the molecular weights of the components. Compatibility of the blend components in the melt state has been studied from the NMR dynamic parameters and also been found to be molecular weight dependent.

Introduction

Recently, a number of papers have been devoted to the study of the influence of the tacticity of poly(methyl methacrylate) (PMMA) on its blends with several other polymers, such as poly(vinyl chloride),[1-3] poly(vinylidene fluoride),[4,5] and poly(ethylene oxide) (PEO).[6-8] The differences in conformation and chain flexibility for the various PMMA stereoisomers seem to have an important effect on the phase behavior of their blends.

In the particular case of poly(ethylene oxide)/atactic poly(methyl methacrylate) blends, several studies have related their degree of intermixing to the observed depression of the melting point,[9-12] changes in the glass transition temperature,[11,12] and measurements of spherulitic growth[10,13,14] and overall crystallization rates.[10,12,15] For these studies, techniques such as solution ^{13}C NMR,[16] X-ray diffraction,[17] IR spectroscopy,[6,11] and inverse gas chromatography[18] have been used. From their results, it could be concluded that the components of these blends were compatible in the melt and in the amorphous phase.

The influence of the configurations of poly(methyl methacrylate) in its blends with poly(ethylene oxide) has been considered more recently.[7,8] Previous analysis by vibrational spectroscopy suggested that isotactic PMMA would be more miscible than syndiotactic PMMA.[6] However, studies of these blends by small-angle X-ray scattering and differential scanning calorimetry have shown that PEO is compatible with syndiotactic PMMA in the amorphous and melt state but not with isotactic PMMA. This conclusion has been obtained by using whole polymers with relatively broad molecular weight distributions and only a limited molecular weight range for the syndiotactic and isotactic samples. This limitation precludes any generalization and suggests the need to analyze the influence of the molecular weight of the amorphous component on the miscibility in a wide range of blend compositions.

The purpose of this work was to study the dependence of miscibility of the amorphous components of blended poly(ethylene oxide) and isotactic poly(methyl methacrylate) (IPMMA), on molecular weight and blend composition. Differential scanning calorimetry has been combined with solid-state ^{13}C NMR in order to establish the degree of homogeneity of the blends in the amorphous phase. Moreover, in order to better understand the influence of molecular weight on the miscibility of both components, molecular weight fractions of IPMMA have been used in a molecular weight range from 2×10^5 to 1.4×10^6.

One of the most common methods used to establish polymer miscibility is differential scanning calorimetry (DSC) where the detection of a single glass transition temperature, T_g, is considered evidence for compatibility. However, when a polymer can crystallize during a DSC scan, the results are not always unambiguous, and it is necessary to combine them with those provided by a different technique.

Solid-state ^{13}C NMR is a very useful technique that can provide information about polymer chain conformation and mobility. When applied to polymeric blends, it can also provide important information through a mechanism known as spin diffusion. The spin perturbation produced at a site can be dissipated through a sample due to strong dipolar interactions among nuclei. This can only occur if the nuclei are relatively close. Relaxation of spin polarization can give an indication of spatial proximity of polymeric chains and, in the case of blends, of the degree of intermixing of their components.

In the case of protons, spin diffusion is very efficient due to strong dipolar interactions. The spin-lattice relaxation time of protons in the rotating frame, $T_{1\rho}$(H), in solids represents an average value of the relaxation behavior over all the protons. In a blended material this value will be affected by the proximity of chains and will differ from that of the pure homopolymers in the case of homogeneously mixed blends. However, it is generally difficult to measure this parameter through ^{1}H NMR due to broad resonances and the overlapping of signals from different types of protons.

Schaefer et al. showed[19,20] that it was possible to measure indirectly the $T_{1\rho}$(H) attached to different carbons by high-resolution ^{13}C NMR in the solid state. In the usual cross-polarization experiment, the decay of the magnetization is given by the $T_{1\rho}$(H). This method has been

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[†] Permanent address: Instituto de Ciencia y Tecnologia de Polimeros, Juan de la Cierva 3, 28006 Madrid, Spain.

[‡] Permanent address: Department of Applied Physics and Applied Mechanics, Institute of Industrial Science, University of Tokyo, Roppongi 7-22-1, Minato-Ku, Tokyo 106, Japan.

0024-9297/90/2223-2183$02.50/0

successfully used to study several polymeric blends, some of which have both a crystalline and amorphous component[21-23] and is also applied here to the PEO/IPMMA blends.

Experimental Section

Materials. Poly(ethylene oxide) samples used in this study were fractions supplied by Hoechst Iberica and Union Carbide. They were purified by precipitation in ethyl ether from benzene solutions at room temperature and dried under vacuum for 2 days. Average molecular weights were obtained from viscometry with the following equation

$$[\eta] = 3.97 \times 10^{-4} M^{0.69}$$

appropriate for benzene solutions at 25 °C.[24]

Isotactic poly(methyl methacrylate) was synthesized by the method described by Goode[25] using phenylmagnesium bromide as initiator and toluene as solvent at 10 °C. The polymer was fractionated by precipitation at room temperature in the solvent–nonsolvent system benzene–methanol. The fractions were purified by precipitation with ether from methylene chloride solutions. Average molecular weights were determined by viscometry using the following equation[26]

$$[\eta] = 5.2 \times 10^{-5} M^{0.76}$$

appropriate at 30 °C for benzene as solvent. The tacticity of each fraction was determined from solution ^{1}H NMR spectra obtained on a Varian XL 300-MHz spectrometer. The analysis of the β proton region[27] and the corresponding integrals gave in all cases a 98% isotactic triad concentration.

Binary blends were prepared from 1% (w/v) chloroform solutions. IPMMA weight concentration ranged from 20 to 50% of the total polymer composition in order to allow for the crystallization of poly(ethylene oxide). The mixtures of polymers were maintained in solution for a period of 2 days with frequent stirring to assure homogeneity. The solvent was removed by a rotary evaporator at room temperature, and the resulting films were subjected to further drying under vacuum for a week.

Techniques. DSC measurements were carried out by using a Mettler TA 3000-DSC 30/TC 10 differential scanning calorimeter. Samples were melted at 120 °C for 10 min and then quenched in liquid nitrogen to reduce, as much as possible, crystallization of the system. DSC scans were run from −100 to 100 °C at 10 °C/min. In another set of experiments, blends were melted under the same conditions and then crystallized at 30 and 57 °C for 24 h. DSC scans were run at 10 and 1 °C/min, respectively, for these latter blends.

^{13}C NMR measurements in the solid state were carried out on a Varian XL-200 spectrometer operating at a static field of 4.7 T. A 45-kHz radio-frequency field strength was used for the dipolar decoupling (DD) of proton spins, with a decoupling period of 200 ms. Magic angle sample spinning was achieved with a Doty Scientific probe which utilizes a double air bearing design. All the samples were spun at speeds of ca. 3 kHz in aluminum oxide rotors with Kel-F (poly(chlorotrifluoroethylene)) end caps. Depending on the sample, 500–2000 scans were needed to obtain a good signal to noise ratio.

The proton spin–lattice relaxation times in the rotating frame, $T_{1\rho}$(H) measured at room temperature, were obtained from plots of the decay of the relative magnitude of the carbon magnetization versus proton–carbon contact time in the usual cross polarization sequence.

Variable-temperature experiments were performed by using the same Doty Scientific probe. The spin–lattice relaxation times, T_1(C), of the PEO signal at 90 °C in the pure polymer and in the blends were measured by the usual inversion–recovery sequence, and 200 scans were performed at this temperature for each point of the inversion–recovery sequence. Each T_1 was derived from seven experiments.

Results and Discussion

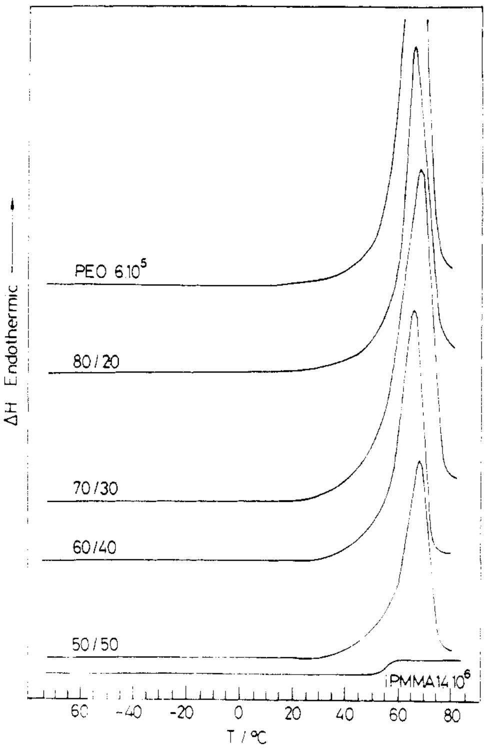

Figure 1. DSC traces of PEO(6 × 10^5)/IPMMA(1.4 × 10^6) blends crystallized at 30 °C.

The first point to be mentioned is related to the possible crystallization of IPMMA. It has been claimed[28,29] that this polymer does not crystallize from the melt but only when induced to do so by solvents. This fact has been corroborated, for the fractions and blends used in this work, by wide-angle X-ray diffraction where an amorphous halo has been exclusively observed for IPMMA, when the samples are quenched into liquid nitrogen or slowly cooled down from the melt. This means that the PEO/IPMMA blends to be considered correspond to the crystalline/amorphous types.

The amorphous IPMMA show a typical DSC curve with a glass transition temperature, T_g, about 55 °C, which is independent of molecular weight in the range considered.

After the PEO sample is quenched from the melt into liquid nitrogen, no glass transition temperature is detected. However, it has been considered to have a T_g = −60 °C,[30] for a totally amorphous sample, and this value will be used in the following discussions. A melting temperature about 66 °C is obtained. This is an apparent value that depends on the thermal history of the sample.

Poly(ethylene oxide) with 6 × 10^5 molecular weight has been blended with isotactic poly(methyl methacrylate) fractions with molecular weights of 2 × 10^5, 7 × 10^5, and 1.4 × 10^6. Blends ranging in composition from 20 to 50 wt% of IPMMA component were obtained to assure crystallization of PEO. Figure 1 shows typical thermograms obtained for mixtures of PEO(6 × 10^5)/IPMMA(1.4 × 10^6) isothermally crystallized at 30 °C. No glass transition is observed in any case for the temperature range studied. This suggests that the polymers are incompatible, and, consequently, two T_g's, one corresponding to each polymer, should be detected. However, this is an example in which the criteria of miscibility, based on the glass transition temperature, are not adequate. The glass transition temperature for IPMMA is 55 °C, a value too close to the melting temperature of poly(ethylene oxide) to be observed in the DSC curves, and the T_g of PEO cannot be detected as a consequence of the high crystallinity of this polymer. Furthermore the blends quenched in liquid nitrogen exhibit the same behavior as those iso-

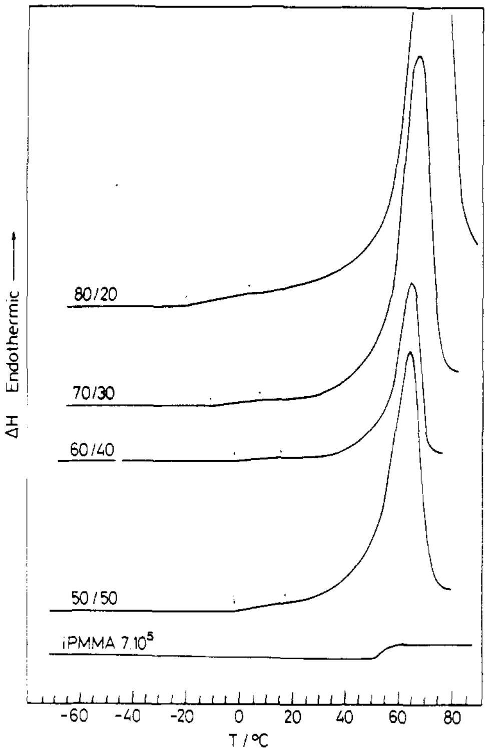

Figure 2. DSC traces of PEO(6 × 10^5)/IPMMA(7 × 10^5) blends crystallized at 30 °C.

thermally crystallized. Thus, one cannot unambiguously conclude from these data that the PEO(6 × 10^5)/IPMMA(1.4 × 10^6) blends have incompatible components. It seems likely, however, that they are incompatible because an intermediate T_g has not been observed as was the case for other blends (see below).

However, when the molecular weight of IPMMA is reduced, as is the case for the blend PEO(6 × 10^5)/IPMMA(7 × 10^5), the DSC curve shows in the temperature range from −20 to 10 °C a small change in the heat capacity, which at the higher temperature overlaps with the melting endotherm of PEO. This change in the base line in the thermogram, indicated by arrows in Figure 2, may be identified with the glass transition of the blend.

Similar evidence for component compatibility was also obtained for blends of PEO(6 × 10^5)/IPMMA(2 × 10^5).

There is no evidence of an exotherm due to crystallization prior to the melting of the system, so the poly(ethylene oxide) must crystallize during the cooling process. Thus, it was not possible to prepare pure, amorphous blends, and each of them has a crystalline fraction corresponding to poly(ethylene oxide) and an amorphous fraction of PEO and IPMMA, enriched in IPMMA with respect to the initial concentration of the blend.

From the enthalpy associated with the melting endotherm, the crystallinity of poly(ethylene oxide) in the blends can be obtained by taking 190 J/g as the enthalpy of fusion of 100% crystalline poly(ethylene oxide).[31] From the values of PEO crystallinity, it was possible to correct and determine the real composition of the amorphous component of the blends, as is reported in Table I.

The crystallinity of the poly(ethylene oxide) in the blends are listed in Table I. PEO crystallinity is also composition and molecular weight dependent for samples with identical thermal treatment. In PEO(6 × 10^5)/IPMMA(2 × 10^5) and PEO(6 × 10^5)/IPMMA(7 × 10^5) blends crystallinity decreases with increasing PMMA content, whereas in the case of PEO(6 × 10^5)/IPMMA(1.4 × 10^6) it seems not to be affected by IPMMA composition. These results may indicate that, in the first case, PEO is not allowed to crystallize completely when it is homogeneously blended with IPMMA. In the second case, poly(ethylene oxide) seems to crystallize completely without any effect of the addition of IPMMA, probably due to phase separation in the amorphous phase. On the other hand, the depression of the melting temperature for these blends seems to depend on the molecular weight of the amorphous components as predicted by the Flory–Huggins–Scott theory for the melting point depression. The apparent T_m for the blends, after crystallization at T_c = 30 and 57 °C, are shown in Figure 3. The blend PEO(6 × 10^5)/IPMMA(1.4 × 10^6) does not show a decrease of T_m with increasing concentration of IPMMA. However, when the molecular weight of the amorphous component is reduced, a significant decrease in the apparent T_m is observed when the concentration of IPMMA increases. These conclusions are only indicative of the compatibility of blend components. Analysis of the compatibility in crystalline/amorphous systems through evaluation of the depression of the melting temperature requires determination of equilibrium melting temperatures, and this type of analysis will be reported elsewhere.

The T_g values associated with the base-line changes in the DSC curves are in agreement with those obtained by using the Fox equation[32] and are listed in Table I.

$$1/T_g = \frac{w'_{\mathrm{PEO}}}{T_{g_{\mathrm{PEO}}}} + \frac{w'_{\mathrm{IPMMA}}}{T_{g_{\mathrm{IPMMA}}}}$$

Here w'_{PEO} and w'_{IPMMA} are the weight fractions of amorphous poly(ethylene oxide) and isotactic poly(methyl methacrylate), respectively. The T_g of pure poly(ethylene oxide) was taken as −60 °C, as previously reported, and the T_g of isotactic PMMA was measured as 55 °C by DSC.

From the previous discussion, it is clear that the study of the compatibility of PEO and IPMMA in their blends by thermal analysis presents some limitations. More definitive conclusions can be obtained by using solid-state ^{13}C NMR techniques, which provide information about the degree of component intermixing through mobility. The ^{13}C cross polarization, magic angle spinning spectrum of one of these blends and of both homopolymers is shown in Figure 4. As explained in the Introduction, in all cases the variation of the carbon magnetization was analyzed as a function of contact time between ^{1}H and ^{13}C in cross polarization experiments. From these plots it is possible to determine $T_{1\rho}$ of the protons attached to different carbons because of the spin-diffusion phenomenon. For these experiments samples of different blends and homopolymers were melted and isothermally crystallized at 35 °C, and all $T_{1\rho}$ measurements were conducted at room temperature.

In pure IPMMA the (measured) proton $T_{1\rho}$ values were 5.2 ms for 2 × 10^5 molecular weight and 5.9 ms for 1.4 × 10^6 molecular weight. In both cases the carbon magnetization was a single exponential decay and the values obtained from the various carbon lines differed by no more than 10%.

For pure PEO, there is a crystalline and noncrystalline component with a broad resonance superimposed on a narrow resonance, but with very different $T_{1\rho}$, the noncrystalline component having a much longer relaxation time, as previously reported.[33,34] Because we are primarily interested in the amorphous phase of the blends, only the slowly relaxing component was considered. The $T_{1\rho}$(H) measured was 20 ms for the amorphous component of PEO with 6 × 10^5 molecular weight and 15 ms

Table I
Thermal Data for PEO/IPMMA Blends

sample	w_{PEO}	ΔH_{blend}, J·g^{-1}	ΔH_{PEO}, J·g^{-1}	$(1-\lambda)_{PEO}$	w'_{PEO}	T_m,[a] °C	T_m,[b] °C	T_g,[c] °C
PEO(6 × 10^5)/IPMMA(1.4 × 10^6)	1	...	153.4	0.80	...	66.5	67.8	...
	0.8	118.1	147.6	0.78	0.47	69.0	67.7	-11
	0.7	113.1	161.6	0.85	0.26	70.1	67.9	15
	0.6	90.6	151.0	0.80	0.23	66.8	67.8	19
	0.5	78.5	157.0	0.83	0.15	69.6	67.6	30
PEO(6 × 10^5)/IPMMA(7 × 10^5)	0.8	108.2	135.3	0.71	0.54	66.5	67.1	-18
	0.7	90.9	129.9	0.68	0.42	66.0	66.8	-6
	0.6	74.5	124.1	0.65	0.34	65.3	66.6	4
	0.5	56.6	113.2	0.60	0.29	64.5	66.1	11
PEO(6 × 10^5)/(IPMMA(2 × 10^5)	0.8	113.8	142.3	0.75	0.50	66.1	67.1	-15
	0.7	93.5	133.5	0.70	0.41	65.7	66.6	-4
	0.6	71.9	119.9	0.63	0.36	65.0	66.3	2
	0.5	57.7	115.5	0.61	0.28	64.5	65.9	12

[a] T_c = 30 °C. [b] T_c = 57 °C. [c] Calculated from the Fox equation.

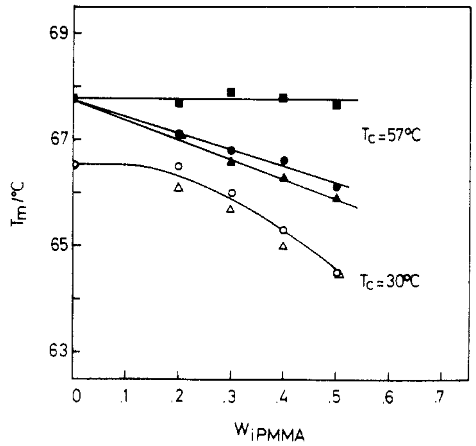

Figure 3. Variation of apparent melting temperatures with the composition for PEO(6 × 10^5)/IPMMA(1.4 × 10^6) (■), PEO(6 × 10^5)/IPMMA(7 × 10^5) (○, ●), and PEO(6 × 10^5)/IPMMA(2 × 10^5) (△, ▲) blends at indicated crystallization temperatures.

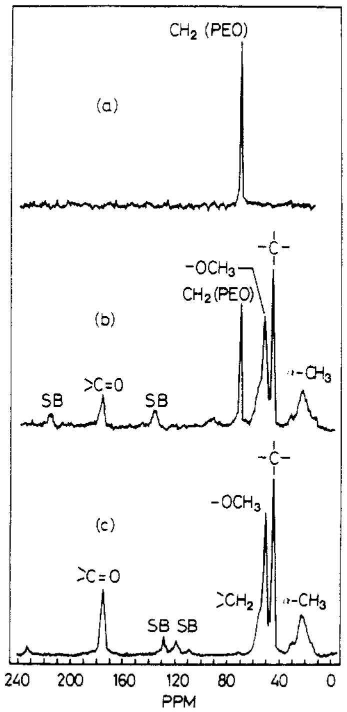

Figure 4. ^{13}C CP/DD MAS NMR spectra of (a) PEO (M = 6 × 10^5), (b) 80/20 PEO/IPMMA blend, and (c) IPMMA (M = 1.4 × 10^6), at room temperature.

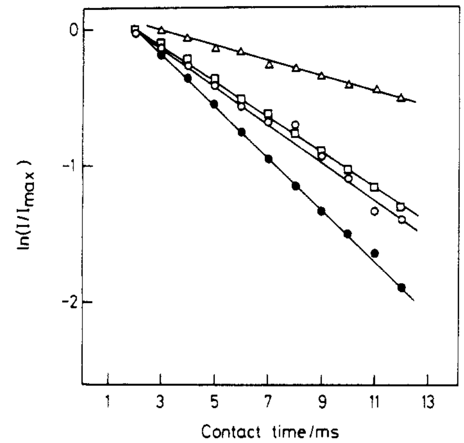

Figure 5. Plots of IPMMA (2 × 10^5) carbon magnetization versus cross polarization contact time for pure IPMMA (●) and PEO(6 × 10^5)/IPMMA(2 × 10^5) blends isothermally crystallized at 30 °C, with weight ratios of 80/20 (○) and 60/40 (□), compared with pure PEO (6 × 10^5) (△) carbon magnetization decay.

for 2 × 10^5 molecular weight samples. A similar trend with molecular weight has been observed by Dechter[33] and may result from a dependence of interlamellar spacing on molecular weights.

For blends with PEO(6 × 10^5)/IPMMA(2 × 10^5) molecular weights and 60/40, 80/20 compositions, the carbon magnetization was a single exponentially decreasing function of the contact time, over the range of contact times considered, as shown in Figure 5. Moreover, the values obtained for the blends from the IPMMA signal are 7.4 and 7.2 ms compared with 5.2 ms for pure IPMMA. The relaxation of IPMMA in the blends compared with that of pure IPMMA suggests that mixing of IPMMA chains with poly(ethylene oxide) in the amorphous phase must be intimate enough to produce an intermediate $T_{1\rho}$ for all blends. So it seems, as was also indicated from the DSC data, that for these molecular weights, some poly(ethylene oxide) molecules in the amorphous phase must be in contact with IPMMA molecules at relatively short distances.

Similar behavior was observed for blends of PEO(6 × 10^5)/IPMMA(7 × 10^5). Figure 6 shows the carbon magnetization decay of IPMMA for these blends with 60/40 and 80/20 compositions. The $T_{1\rho}$(H) of pure IPMMA(7 × 10^5) will be intermediate to pure IPMMA(2 × 10^5) and pure IPMMA(1.4 × 10^6), both shown in the figure. The values obtained for the 60/40 and 80/20 blends are 8.3 and 8.0 ms, respectively, as compared to 5.2–5.9 ms for pure IPMMA, which indicate, as commented on before, some miscibility of components in the amorphous phase of these blends.

As shown in Figure 7, the behavior observed for blends with PEO(6 × 10^5)/IPMMA(1.4 × 10^6) molecular weight is very different. For 60/40 and 80/20 compositions the

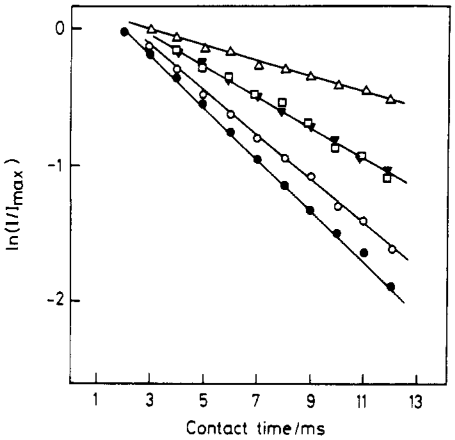

Figure 6. Plots of IPMMA carbon magnetization versus cross polarization contact time for pure IPMMA (1.4×10^6) (●), IPMMA (2×10^5) (○), and PEO(6×10^5)/IPMMA(7×10^5) blends crystallized at 30 °C with weight ratios of 80/20 (▼) and 60/40 (□), compared with pure PEO carbon magnetization decay (△).

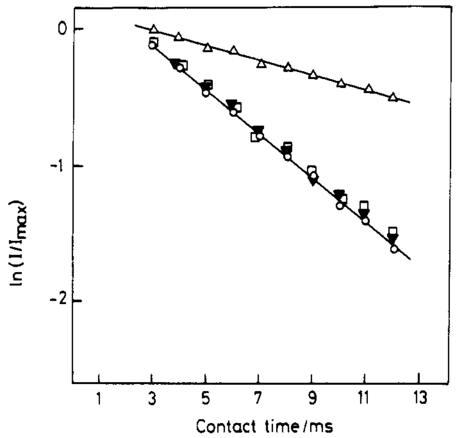

Figure 7. Plots of IPMMA carbon magnetization versus cross polarization contact time for pure IPMMA (1.4×10^6) (○) and PEO(6×10^5)/IPMMA(1.4×10^6) blends isothermally crystallized at 30 °C and with weight ratios of 80/20 (□) and 60/40 (▼), compared with pure PEO carbon magnetization decay (△).

relaxation of the IPMMA in the blends is very close to that of the pure homopolymer and the values measured are almost the same 6.0 and 5.9 ms as that of pure IPMMA(1.4×10^6). This indicates that the magnetization arises from domains where IPMMA is pure or surrounded by only a few chains of PEO. As was also pointed out by the DSC data, the results suggest the absence of significant interchain mixing in the amorphous phase at these compositions. Only in the 80/20 composition at very long contact times does the observed $T_{1\rho}$(H) seem to slightly deviate from the pure homopolymer. This behavior may indicate that even in phase-separated systems, there are boundaries or interphases in which some polymer mixing may occur.

An estimate of the distance scale on which the NMR study can probe component miscibility in blends may be obtained from the $T_{1\rho}$ measurements.[35,36] By assuming a spin-diffusion relaxation mechanism, an estimate of the maximum diffusive path length L may be derived from the approximate formula[35-37]

$$L = (6DT_{1\rho})^{1/2}$$

where D is the spin-diffusion coefficient. Typically D has a value of 10^{-12} cm^2 s^{-1}. Thus for $T_{1\rho} \approx 10^{-2}$ s, L is ~20 Å. In our NMR study if the heterogeneities are <20 Å the blend components are considered compatible from the $T_{1\rho}$ results.

Table II
Relaxation, T_1(C) (s), for PEO Pure and in Its Blends with IPMMA at 90 °C (Melt State)

samples		T_1(C), s[a]
PEO(6×10^5)		1.25
PEO(6×10^5)/IPMMA(2×10^5)	80/20	1.04
PEO(6×10^5)/IPMMA(2×10^5)	60/40	0.93
PEO(6×10^5)/IPMMA(1.4×10^6)	80/20	1.24
PEO(6×10^5)/IPMMA(1.4×10^6)	60/40	1.26

[a] T_1 data: ±5%.

The $T_{1\rho}$(H) of the blends were also determined from observation of the PEO ^{13}C signal. However, because the PEO resonance is a composite of crystalline and amorphous peaks, the ^{13}C NMR estimation of the degree of amorphous component miscibility in PEO/IPMMA blends has relied principally on the $T_{1\rho}$(H) relaxation of the amorphous IPMMA resonances. Nevertheless, the trend observed for the $T_{1\rho}$(H) values obtained from PEO was the same as that observed from the IPMMA ^{13}C peaks.

For PEO(6×10^5)/IPMMA(1.4×10^6) blends, the relaxation of PEO in the blends is the same as that of the pure homopolymer (20 ms) for both blend compositions. These blends would appear to be phase separated, and PEO(6×10^5) and IPMMA(1.4×10^6) are incompatible. $T_{1\rho}$(H) = 10 and 11 ms for the PEO(6×10^5)/IPMMA(7×10^5) and PEO(6×10^5)/IPMMA(2×10^5) blends, respectively, when observing the PEO resonance, while from the IPMMA resonances $T_{1\rho}$(H) = 7–8 ms for the same blends (see Figures 5 and 6). Though slightly different $T_{1\rho}$(H)'s are detected by observing PEO and IPMMA resonances, considerable, though not complete, averaging of $T_{1\rho}$(H) by spin diffusion occurs for both polymers in these blends. The $T_{1\rho}$(H) obtained from the PEO signal (10–11 ms) of these blends is considerably different from the 20-ms value observed for the pure homopolymer. Thus, for these molecular weights there appears to be a considerable mixing of the blend components.

In all blends, no significant changes in the chemical shifts of the PMMA (especially the carbonyl and the α-methyl) have been observed. As pointed out by an IR study[6] for compatible PEO/atactic PMMA blends, the intermolecular interactions between molecules of PEO and APMMA are very weak approaching those of the van der Waals type.

Until now, we have examined the degree of mixing of the blend components in the amorphous phase when the polyethylene oxide was already crystallized. But we were also interested in investigating the situation in the melt state. Consequently, we studied the blends by NMR at 90 °C where PEO is molten. The spin–lattice relaxation time, T_1, of the PEO signal for the homopolymer and in the blends was measured in order to check whether there was any change in the dynamic parameters of PEO upon blending. These values are reported in Table II. The results indicate that for PEO(6×10^5)/IPMMA(1.4×10^6) the percentage of IPMMA in the blends does not seem to affect the mobility of PEO in the melt, so even in the melt state these blends seem to be phase separated. T_1(C) data, when combined with the results of melting point depression measurements, corroborate the incompatibility of the two polymers in the molten state. When the system crystallizes, there are no IPMMA chains relatively close to those of PEO, as indicated by solid-state ^{13}C NMR recorded at room temperature.

For PEO(6×10^5)/IPMMA(2×10^5) blends, although differences in T_1(C) are not large, PEO mobility seems to be affected by the presence of IPMMA, as reflected in the decreasing $T_1(C)$ as the composition of IPMMA increases. When taken together with the DSC and melting point depression data, the solid-state NMR results permit us to conclude that in the melt there must be some entanglement between different chains, and when the system crystallizes, some of the IPMMA chains are trapped between poly(ethylene oxide) crystalline lamellae, leaving IPMMA chains in interlamellar zones close to amorphous poly(ethylene oxide) chains.

Our results indicate that the molecular weight of the components strongly influences the miscibility of poly(ethylene oxide) and isotactic poly(methyl methacrylate) in their blends in the melt and, consequently, in the amorphous phase when PEO is crystallized. These conclusions are in agreement with results we have obtained from growth rate measurements, from melting point depressions, and from the long periods obtained by SAXS for these blends which will be published elsewhere.[38]

In recent work by Martuscelli et al.[8] the system poly(ethylene oxide)/isotactic poly(methyl methacrylate) was found to be incompatible by SAXS and DSC. However, it must be pointed out that this conclusion has been obtained for blends in which the molecular weight of PEO was relatively low (M_n = 20 000) and this polymer was blended with an IPMMA sample with molecular weight of 132 000. It is also interesting to quote recent works on PEO/APMMA which show incompatibility, in opposition to previous claims.[18,39] Privalko et al.[39] have found no changes in crystallinity, T_m or T_g, in mixtures of PEO (M_n = 2000 and M_n = 125 000) with APMMA (M_n = 500 000), and only when the concentration of PEO is less than 20%, is the system compatible. By using low molecular weight PEO (M = 8500) with APMMA (M_n = 46 800) segregation has been found at certain compositions[18] from inverse gas chromatography studies.

An obvious yet important conclusion can be drawn. Before establishing the compatibility or incompatibility of blends, a more systematic analysis of the influence of molecular weight should be carried out. As demonstrated in this study, careful attention should be paid to the molecular weight effect on the compatibility of polymers in their blends. Blends whose components are considered incompatible could have a "window of compatibility" affected by the molecular weight of the components, in addition to other factors like composition and thermal treatment.

In summary, the compatibility of components in the melt state and in the amorphous phase of blends of poly(ethylene oxide) and isotactic poly(methyl methacrylate) is dependent on the molecular weight of the components as observed by differential scanning calorimetry and solid-state ^{13}C NMR techniques. Solid-state NMR appears to be a very useful technique to establish degrees of intermixing in solid polymeric blends, particularly in the case of crystalline/amorphous blends whose T_m's and T_g's may overlap.

Acknowledgment. We thank F. C. Schilling (AT&T Bell Laboratories) for helpful discussions.

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Registry No. PEO, 25322-68-3; IPMMA, 25188-98-1.