BUTTERWORTH
HEINEMANN

Polymer Vol. 36 No. 6, pp. 1147–1155, 1995

0032-3861/95/$10.00+0.00

Blends of poly(ethylene oxide)/poly(methyl methacrylate). An i.r. and n.m.r. study

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(Received 28 July 1994; revised 23 September 1994)

I.r. and high-resolution solid-state ^{13}C n.m.r. spectra, as well as proton relaxation times T_1^{H} and $T_{1\rho}^{\mathrm{H}}$ of poly(ethylene oxide) (PEO)/atactic poly(methyl methacrylate) (a-PMMA) blends in the solid state, with PEO weight fractions of 10, 30, 50 and 70% were measured. Infra-red spectra of pure PEO with various molecular weights were also measured. The measurements indicate that no large changes in the content of the *ttt* conformational structure of PEO with blending occur. In the blends containing 30% PEO or less, only a negligible amount of crystalline PEO has been found. From the T_1^{H} and $T_{1\rho}^{\mathrm{H}}$ relaxation times it follows that all the blends studied are completely homogeneous on the scale of 20–70 nm; at the same time at least part of the PMMA and PEO chains are intimately mixed in the amorphous phase with the average size of the PMMA domains being below 6 nm, T_1^{H} values and ^{13}C n.m.r. linewidths indicate changes in the mobility of polymer segments with blending.

(Keywords: poly(ethylene oxide); poly(methyl methacrylate); blends)

INTRODUCTION

A lot of attention has been devoted in recent years to the characterization of polymer blends. One of the interesting questions in blend characterization is the degree of phase separation and microstructure changes induced by blending. Spectroscopic methods are particularly useful in such investigations. In our study we used i.r. and solid-state n.m.r. spectroscopy for the characterization of poly(ethylene oxide)/atactic poly(methyl methacrylate) (PEO/a-PMMA) blends with varying composition. The PEO/a-PMMA blend is a complex system consisting of semicrystalline (PEO) and amorphous (PMMA) components. Numerous investigations on the compatibility of the PEO/PMMA system have been carried out. Studies of crystallization kinetics showed that the crystallization process of PEO is affected by blending with PMMA, the effect depending on the molecular weight and tacticity of the PMMA[1–5]. PEO melting point depression was observed with increasing PMMA content and a negative interaction parameter was calculated[6–8]. A single glass transition temperature (T_g) was reported in the d.s.c. measurement for mixtures of PEO with a-PMMA or syndiotactic PMMA (s-PMMA), while two T_gs were detected in a mixture with isotactic PMMA (i-PMMA)[2,9,10]. These results indicate that the PEO/PMMA system is miscible in the amorphous phase, with the exception of a highly isotactic PMMA component. Evidence for the miscibility in PEO/a-PMMA blends was also given in a study of relaxation dynamics using measurements of i.r. dichroism and birefringence[9]. Miscibility of the two polymers is also in agreement with theoretical calculations[2,11–13]. Nevertheless, there are also papers indicating that some phase separation in the amorphous phase may occur, especially at low PEO concentrations[14–16].

Besides the miscibility of the PEO/PMMA blends, considerable attention has also been paid to the phase and supramolecular structure below the melting point of PEO. Optical microscopy shows no evidence of large domain segregation of the non-crystallizable component in intraspherulitic regions or in interspherulitic contact zones[2]. This suggests that the amorphous material is present in interfibrillar and/or interlamellar zones of PEO crystals. From small-angle X-ray scattering (SAXS) measurements it was concluded that amorphous a- or s-PMMA is incorporated between the crystalline PEO lamellae, thus increasing the long period, whereas i-PMMA is rejected to the interfibrillar PEO spherulite region[2,7,10,17,18]. A comparison of the small-angle neutron scattering and SAXS measurements supports the idea that there exists an interfacial region at the surface of the PEO crystal from which the amorphous PMMA is excluded[17]. Dielectrical measurements lead to a similar conclusion[19,20]. These results support the existing general consensus that in the PEO/PMMA system below the PEO melting point, the amorphous phase is homogeneous with a- and s-PMMA, while with i-PMMA the amorphous system is phase separated. Thus for the PEO/a-PMMA blend, a two-phase system is assumed, consisting of PEO crystalline lamellae separated by amorphous layers containing PMMA and amorphous PEO.

The interaction between PEO and PMMA is generally

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*To whom correspondence should be addressed reported to be very weak, possibly on the order of van der Waals type interactions[2,21]. Little is known up to now about the exact nature of this interaction. Specific interactions between the carbonyl carbon atoms of PMMA and the oxygen atoms of PEO were suggested[21]. It was concluded from i.r. spectra that the interaction with PMMA forces PEO to adopt the planar zigzag conformation[21,22]. This conclusion is based on the observation of strong intensity changes of some bands in i.r. spectra with blending which in references 21 and 22 were ascribed to conformational changes of PEO molecules.

Surprisingly only a few investigations on PEO/PMMA blends used n.m.r. spectroscopy although solid-state n.m.r. spectroscopy is very useful for the characterization of heterogeneous polymeric systems. Evidence of miscibility of the PEO/a-PMMA blend was obtained from the measurement of ^{13}C n.m.r. spectra and carbon T_1 relaxation of PEO in the melt and supercooled melt state[23]. Chain dynamics was studied by means of the transverse magnetic relaxation of protons in a system PEO/deuterated-PMMA with low molecular weight components[24]. Marco *et al.*[25] studied PEO/i-PMMA blends by a combination of d.s.c. and high-resolution solid-state ^{13}C n.m.r. spectroscopy. From the measurements of the proton spin-lattice relaxation time in the rotating frame, $T_{1\rho}^{\mathrm{H}}$, they detected partial miscibility of both components, depending on the molecular weight of PMMA.

Contrary to the PEO/PMMA blends, both pure PMMA and pure PEO have been extensively studied by solid-state n.m.r.[26]. In the ^{13}C CP/MAS/DD (cross-polarization, magic angle spinning, dipolar decoupling) n.m.r. spectra of PEO at room temperature the PEO band consists of two components, a narrow and a broad one[27–29]. These components were assigned to the amorphous and crystalline phases, respectively[28,29]. The unusual broadness of the band corresponding to the crystalline phase was ascribed to the competition between molecular motion and decoupling, a mechanism described by Rothwell and Waugh[30]. Moreover the PEO crystalline phase exhibits a very short $T_{1\rho}^{\mathrm{H}}$ relaxation time at room temperature and thus for its efficient detection in the ^{13}C CP/MAS/DD n.m.r. spectra, a contact time on the order of 100 μs must be used[28]. On the other hand, the $T_{1\rho}^{\mathrm{H}}$ relaxation time of the amorphous phase of PEO is much longer and the line exhibits moderate linewidth. The difference in relaxation times can be used for selective observation of the closely spaced signals of the crystalline and the amorphous phases.

EXPERIMENTAL

For the preparation of the PEO/a-PMMA blends PEO produced by BDH Chemicals (UK) with $M_w = 5 \times 10^6$, and PMMA produced by Röhm (Darmstadt, Germany) with $M_w = 3 \times 10^6$, were used. The PMMA sample was characterized by n.m.r. as containing 10% isotactic, 40% heterotactic and 50% syndiotactic triads. The blends were prepared by mixing the components in an extruder at 195°C for 12 min (PEO/PMMA weight ratios: 70/30, 50/50, 30/70, 10/90). Besides the i.r. and n.m.r. measurements, the degree of crystallinity of the blends as well as of the pure PEO sample was also characterized by wide-angle X-ray scattering (WAXS) measurements.

I.r. spectra of the blends and of the PMMA sample were measured, after grinding the samples in an agate mortar, in KBr pellets. The pellets were also measured at −145°C in a RIIC low temperature cell.

For the measurements of the i.r. spectra of pure PEO the following samples with various molecular weights were used: poly(ethylene glycol) 2000 (Fluka), 1000 (Merck), PEO 10^5 (Aldrich), 3×10^5 and 5×10^6 (BDH Chemicals). The solutions (1% w/v in $CHCl_3$) of the pure PEO samples of various molecular weights were evaporated at room temperature on KBr windows; further they were heat treated in a metal desiccator at 85°C for 15 min, followed by 24 h at 50°C. Besides the normal measurement, the samples were also measured in a position tilted by 55° with respect to the incident beam. The PEO powder samples were measured in KBr pellets; for diffusion reflection measurements they were mixed with KBr powder.

I.r. spectra were measured on a Perkin– Elmer 580 B spectrometer connected on-line with a multichannel analyzer (Tracor TN 4000) and on a *FT*i.r. spectrometer (Bruker IFS 88).

The solid-state n.m.r. spectra were measured on a Bruker MSL 200 spectrometer at 50.3 MHz (^{13}C) and 200 MHz (^{1}H). The rotating-frame spin-lattice relaxation time for protons, $T_{1\rho}^{\mathrm{H}}$, was measured indirectly from the ^{13}C CP/MAS/DD n.m.r. spectra. The experimental scheme with a variable spin-lock time after the proton signal excitation followed by constant contact time was used. The contact time was set either to 100 μs (suitable for the PEO crystalline phase detection) or to 1 ms (suitable for the detection of the amorphous PEO and PMMA). The proton spin-locking field in frequency units was 60 kHz, the same value was used for decoupling. The MAS frequency was 4 kHz, recycle delay 3 s; 1600–3000 spectra were accumulated. The spectra were externally referenced to the signal of the carbonyl carbon of glycine ($\delta = 176.0$ ppm) by sample replacement.

The non-selective proton spin-lattice relaxation times T_1^{H} were measured with static samples using the inversion–recovery pulse sequence (180°–τ–90°). In these measurements 16 spectra were accumulated with a recycle delay of 5 s (PMMA and PEO/PMMA blends) and 20 s (PEO).

WAXS diffractograms were obtained with a HZG/4A diffractometer. The diffracted radiation was recorded by means of a proportional counter.

RESULTS AND DISCUSSION

I.r. measurements

First we have investigated the intensity changes of i.r. bands of PEO upon annealing, assumed to correspond to the concentration changes of *ttt* conformational structures[21,22]. We measured spectra of PEO with various molecular weights in KBr pellets, in mixtures with KBr powder (by diffusion reflection) and in the form of thin films prepared by evaporation from the PEO solutions in $CHCl_3$ on KBr windows. Both in the KBr pellets and in the KBr mixtures, where no preference for the orientation direction of the polymer should occur, for all molecular weights we obtained practically the same i.r. spectra, corresponding to the usual *tgt* conformation of the chains[31]. On the other hand, in the spectra of PEO films evaporated from solution on the surface of KBr windows we observed intensity changes of some bands

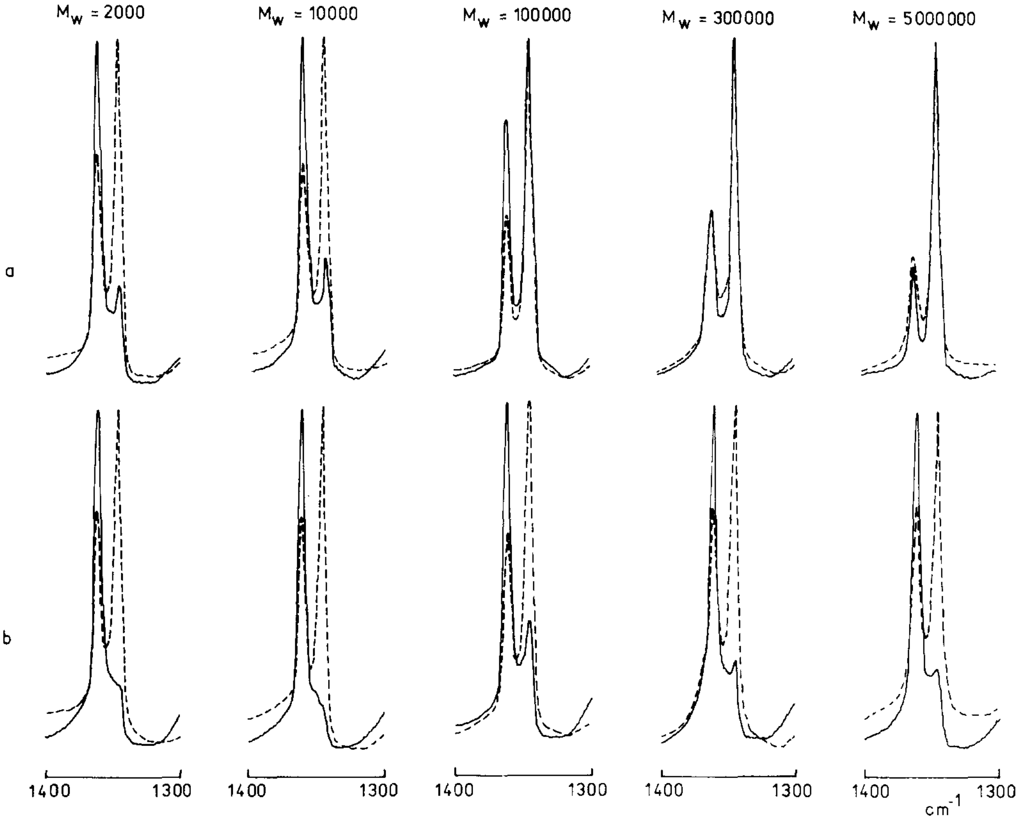

Figure 1 I.r. bands of PEO with various molecular weights: (a) samples evaporated at room temperature on KBr windows; (b) the same samples after heat treatment. (——) Normal position; (– – –) tilted position of the sample

similar to those found in references 21 and 22. Examples of such changes are given in *Figure 1* for the bands at 1343 and 1362 cm^{-1}. According to reference 32 these bands correspond to the transition dipole moment orientations parallel and perpendicular with respect to the direction of the chain, respectively. From *Figure 1* it can be seen that the absorbance ratio A_{1343}/A_{1362} of the bands measured with the beam perpendicular to the plane of the window increases in the direction of increasing molecular weight and decreases on heat treatment of the samples. With the samples measured in a tilted position the values of the absorbance ratio A_{1343}/A_{1362} strongly increased.

It follows from these results that the PEO chains have a tendency to assume perpendicular orientation to the surface of the KBr windows. This result agrees well with the finding of Davison[33], who made a dichroic measurement of the crystalline PEO samples and found that with PEO crystallized between NaCl windows, the polymer chains can assume an orientation normal with respect to the plane of the sample. After crystallization at room temperature, the orientation is better for the shorter polymer chains, and it is highly improved by the heat treatment of the samples. As in references 21 and 22 the orientation effects were neglected; the assumption about the presence of relatively high concentrations of *ttt* conformational structures based on the increase of the absorbance ratio A_{1343}/A_{1362} is not well-founded.

Shimomura *et al.*[34] were able to obtain, under specific conditions of preparation, solution-grown crystals of PEO giving i.r. spectra in which some of the A_2 symmetry bands are shifted to higher frequencies compared with the spectra of PEO samples prepared in the usual way. Such shifts were not found in the i.r. spectra of our samples prepared under the conditions described in the Experimental section.

Further we have investigated the i.r. spectra of the PEO/a-PMMA blends. The difference spectra of PEO obtained by subtracting the spectrum of PMMA are given in *Figure 2.* We can see that the PEO spectrum from the PEO/PMMA 70/30 blend is very similar to the spectrum of pure PEO with a high degree of crystallinity. In the difference spectrum of the PEO/PMMA 50/50 blend, slight changes can be seen, whereas in the spectra of the blends with a higher content of PMMA, some of the PEO bands disappear (e.g. 1362, 1343, 1061, 530 and 510 cm^{-1}), new bands appear (e.g. 1352 and 1300 cm^{-1}) and other bands show a broadening or frequency shifts. The difference spectra of the 30/70 and 10/90 PEO/PMMA blends resemble very closely the spectrum of non-crystalline PEO as found in the melt[35].

The measurement of i.r. spectra at −145°C of the pure PEO has shown that some weak additional bands appear in the regions 1440–1470, 1345–1380, 910–935 and 810–870 cm^{-1} corresponding to the presence of a small amount of *ttt* rotational isomers in the folding of the PEO chains in the crystalline regions[36]. As we have observed the same additional bands also in the low-temperature spectra of the PEO/PMMA 50/50 blend (having still a relatively high degree of crystallinity), it is apparent that the small amount of *ttt* isomer present in the crystalline part of PEO does not change during the preparation of the PEO/PMMA blends in an extruder.

In a large frequency range of the spectra of the blends, the absorption of the PEO component prevails; also, as already mentioned, the degree of crystallinity of PEO

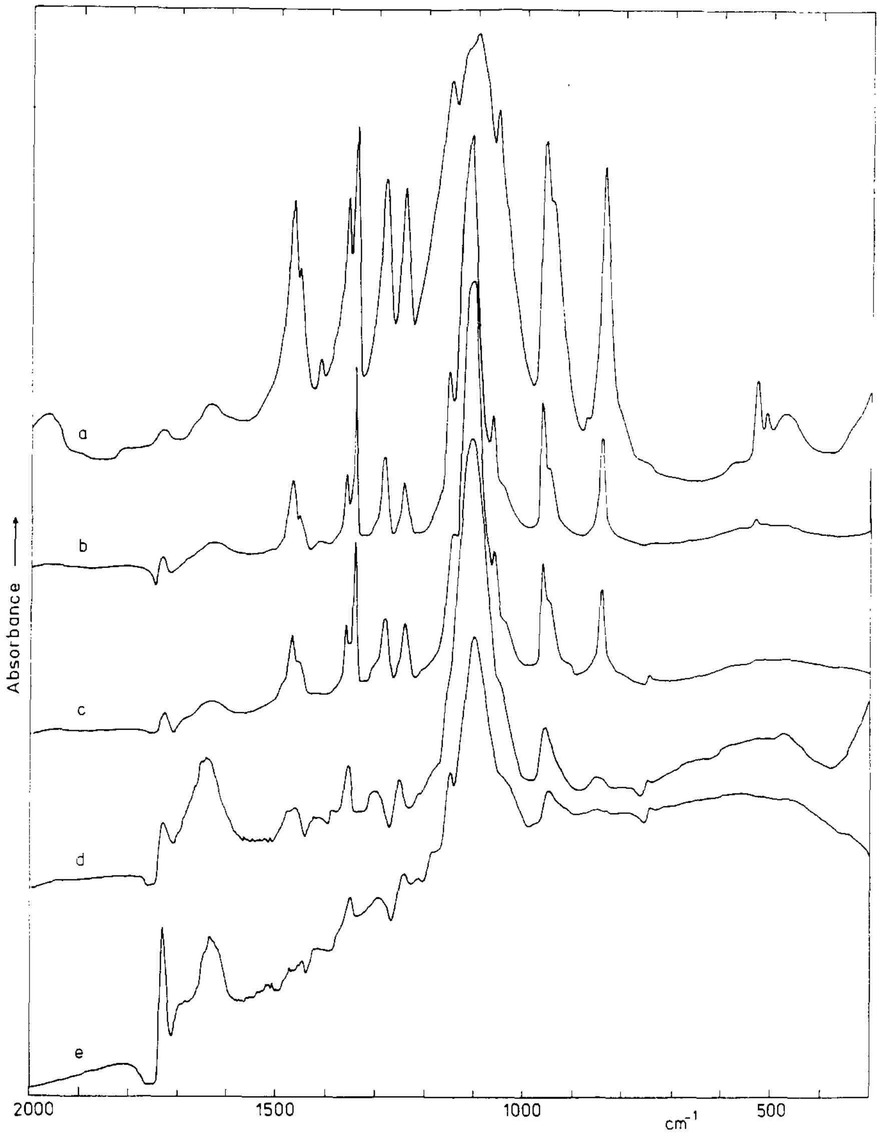

Figure 2 I.r. spectrum of PEO and difference spectra of PEO in PEO/PMMA blends with the spectrum of PMMA subtracted: (a) pure PEO; PEO/PMMA blends with weight ratios (b) 70/30, (c) 50/50, (d) 30/70, (e) 10/90

changes with blending. As a result, the difference spectra of the PMMA component cannot be reliably extracted from the spectra of the blends. Nevertheless, the i.r. spectra of PMMA do not seem to change considerably with blending.

N.m.r. measurements

A typical ^{13}C CP/MAS/DD n.m.r. spectrum of the PEO/a-PMMA blend, with an assignment of individual resonances, is given in *Figure 3*. This spectrum was measured with a contact time of 1 ms, thus predominantly detecting the PEO signal from the amorphous region. In the ^{13}C CP/MAS/DD n.m.r. spectra of the blends, only small changes in the lineshape or position of the PMMA bands in comparison with the spectrum of pure PMMA occurred. The largest effect was observed in the lineshape of the PMMA α-CH$_3$ carbon (*Figure 4*). The linewidth gradually decreased up to 30% PEO content but at higher PEO concentration the lineshape did not further change. Some small line narrowing of other PMMA resonances was also apparent. It is difficult to interpret this lineshape change without a thorough study and some support from other methods. Nevertheless, the interpretation of this lineshape change as caused by intermolecular PEO shielding can be probably ruled out because it is hard to believe that it could cause a detectable line narrowing. Although the lineshape of the α-CH$_3$ carbons is very sensitive to the geometrical structure of the PMMA chain backbone[37,38], structural changes probably do not account for this effect as no signs of possible changes in PMMA conformation were observed in the i.r. spectra. The most plausible explanation for the observed line narrowing seems to be an increase in PMMA backbone mobility. A strong dependence of the linewidth of PMMA signals on PEO content in PEO/PMMA blends in the melt has previously been observed in ^{13}C n.m.r. spectra[23]. Changes in the mobility of polymer segments in the blend are also indicated by proton T_1^H values (see below).

Pronounced changes in the PEO lineshape with increasing content of PMMA in the blend were observed (*Figure 5*). In the spectrum of the PEO/PMMA 70/30 blend measured with 100 μs contact time, the broad band corresponding to the crystalline phase dominates, while

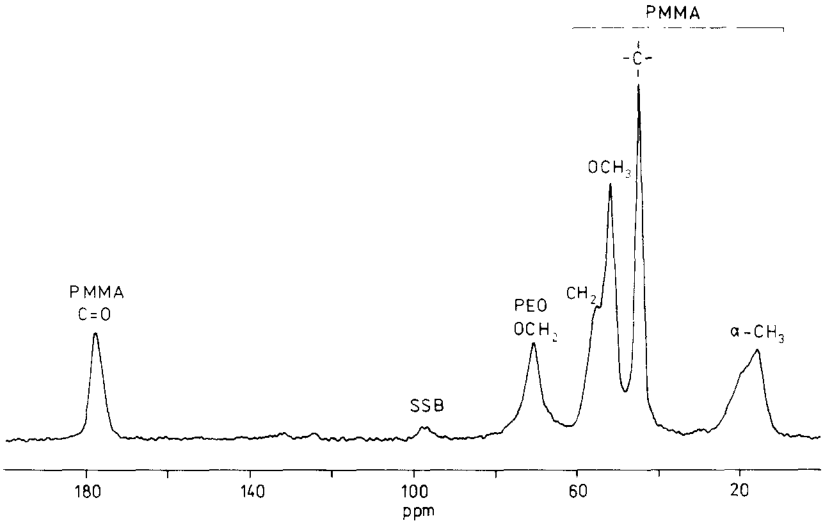

Figure 3 ^{13}C CP/MAS/DD n.m.r. spectrum of the PEO/PMMA 50/50 blend. Contact time 1 ms. SSB denotes spinning sideband

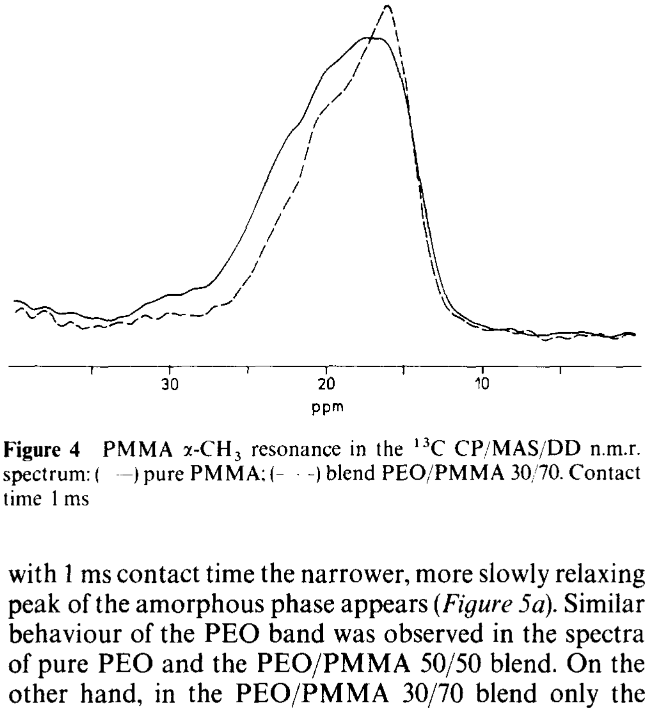

Figure 4 PMMA α-CH_3 resonance in the ^{13}C CP/MAS/DD n.m.r. spectrum: (——) pure PMMA; (- - -) blend PEO/PMMA 30/70. Contact time 1 ms

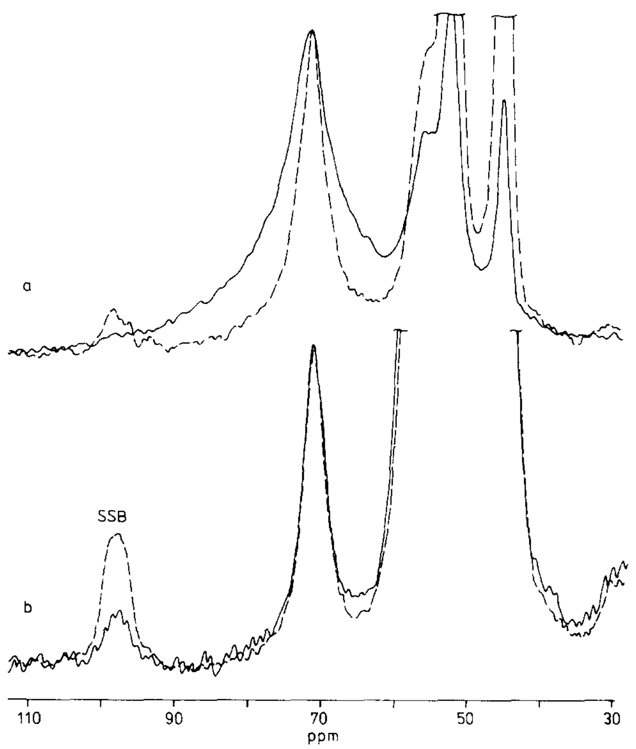

Figure 5 Region of PEO resonance in the ^{13}C CP/MAS/DD n.m.r. spectra: (a) blend PEO/PMMA 70/30; (b) blend PEO/PMMA 10/90. (——) Contact time 100 μs; (– – –) contact time 1 ms

with 1 ms contact time the narrower, more slowly relaxing peak of the amorphous phase appears (*Figure 5a*). Similar behaviour of the PEO band was observed in the spectra of pure PEO and the PEO/PMMA 50/50 blend. On the other hand, in the PEO/PMMA 30/70 blend only the narrow peak could be seen with both the 100 μs and 1 ms contact times. With 1 ms contact time the peak had a higher intensity than with the 100 μs contact time. The same was observed in the spectra of the PEO/PMMA 10/90 blend (*Figure 5b*). This can obviously be explained by the absence of the crystalline phase in the blend with a PEO content of $\leqslant 30\%$. The absence of the crystalline phase in samples with low PEO content is consistent with our i.r. (see above) and X-ray (*Table 1*) measurements, and also with the results of other studies[11,14].

In order to obtain more information about the phase structure in the studied samples, we measured the proton spin-lattice relaxation time T_1^H and the proton spin-lattice relaxation time in the rotating frame $T_{1\rho}^H$. Due to the transport of magnetization between dissimilar components caused by dipolar interactions (so called spin-diffusion), such measurements can provide information about domain sizes in heterogeneous systems[26].

In non-selective T_1^H relaxation measurements a single exponential recovery of the proton magnetization was observed for each sample (*Figure 6*); the fitted values of the relaxation times are given in *Table 1*. This indicates that spin-diffusion is fast enough to equilibrate the relaxation times for all protons and the studied samples are completely homogeneous on a T_1^H relaxation timescale. Here we implicitly assume that the T_1^H relaxation times in the various components of the blend differ sufficiently and can be in principle resolved. This is certainly true in the blends with semicrystalline PEO as the relaxation times T_1^C of the amorphous and crystalline PEO differ by almost two orders of magnitude[28] and the T_1^H values for the pure semicrystalline PEO and pure

Table 1 Degree of crystallinity and T_1^H and $T_{1\rho}^H$ n.m.r. relaxation times of the studied samples

PEO/PMMA	c^a (%)	T_1^H (s)	PMMA $T_{1\rho}^{H\,b}$ (ms)	PEO short $T_{1\rho}^{H\,c}$ (ms)	PEO long $T_{1\rho}^{H\,d}$ (ms)
0/100	–	0.47	15.8	–	–
10/90	0	0.50	10.0	One component 1.2–2.1	Two components 0.7–1.3 (70–90%) 3.5–8.8 (10–30%)
30/70	~5^e	0.45	7.0		
50/50	68	0.67	7.0	Two components 0.1–0.3 (50–70%) 0.7–2.2 (30–50%)	
70/30	77	1.08	6.6		
100/0	74	3.36	-		

[a] Weight crystallinity of PEO calculated from WAXS crystallinity determination

[b] Average relaxation time determined from the carbonyl, methoxy (partially overlapped with the methylene band), quaternary and α-methyl bands of PMMA

[c] Range of PEO relaxation time values determined from measurements with contact time 50 μs (see text)

[d] Range of PEO relaxation time values determined from measurements with contact time 1 ms (see text)

[e] Only very small traces of crystalline reflections that could not be evaluated were seen in X-ray patterns. The crystalline phase content was estimated to be ~5%. Almost no traces of crystalline phase bands were observed in i.r. spectra

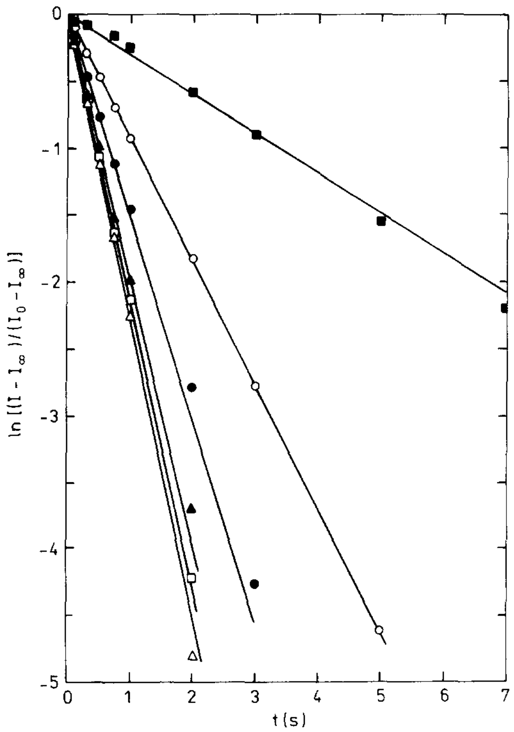

Figure 6 Non-selective inversion recovery T_1 relaxation data for the ^{1}H magnetization in (■) pure PEO, (□) pure PMMA and PEO/PMMA blends with weight ratios (▲) 10/90, (△) 30/70, (●) 50/50, (○) 70/30. Normalized intensities were calculated using an I_∞ value determined by averaging several long t values. Solid lines are the best fits obtained from raw inversion recovery data using three adjustable parameters (I_∞, I_0, T_1)

PMMA are considerably different (*Table 1*). In principle, this might not be true in blends consisting of amorphous PEO and PMMA.

From the n.m.r. relaxation measurements the average domain sizes can be estimated using the formula for the maximum diffusive path length[39]:

$$L = (6DT_i)^{1/2} \tag{1}$$

where D is the spin-diffusion coefficient and T_i is either T_1^H or $T_{1\rho}^H$ according to the relaxation experiment. For the spin-diffusion coefficient a value of $8 \times 10^{-16}\,\mathrm{m^2\,s^{-1}}$ has recently been found in rigid PMMA/polystyrene block copolymers[40]. For the spin-diffusion coefficient in mobile amorphous PEO a lower value can be expected. A value of the order of $10^{-16}\,\mathrm{m^2\,s^{-1}}$ is probably a reasonable estimate. Using the measured T_1^H values and the spin-diffusion coefficient $D = 10^{-16}$–$8 \times 10^{-16}\,\mathrm{m^2\,s^{-1}}$ we obtained from equation (1) $L \simeq 20$–70 nm. Therefore, if heterogeneities are present in the studied blends, their linear dimensions are < 20–70 nm. In particular, this also holds for the size of the crystalline and amorphous domains in PEO.

Theoretically, the averaged relaxation rate $(T_1^H)^{-1}$ of a homogeneous blend can be calculated using the formula:

$$(T_1^H)^{-1} = (N_A/N)(T_{1A}^H)^{-1} + (N_B/N)(T_{1B}^H)^{-1} \tag{2}$$

where $(T_{1A}^H)^{-1}$ and $(T_{1B}^H)^{-1}$ are the relaxation rates of the pure components, N_A and N_B are the numbers of protons per mole of the components and $N = N_A + N_B$. It is clear that equation (2) cannot be used for the PEO/PMMA 10/90 and 30/70 blends, as they contain only negligible amounts of crystalline PEO. It can be used, however, for the PEO/PMMA 70/30 and 50/50 blends, where the WAXS measurements indicate approximately the same degree of crystallinity as in pure PEO. The calculated values for T_1^H using equation (2) are 1.25 and 0.86 s for the PEO/PMMA 70/30 and 50/50 blends, respectively. The calculated values are significantly higher than the experimentally determined values given in *Table 1*. When we used a model where in PMMA only the α-methyl motion provides a relaxation site[39], the discrepancy between the measured and calculated (2.29 and 1.87 s for the PEO/PMMA 70/30 and 50/50 blends, respectively) T_1^H values was even larger. The differences between measured and calculated T_1^H values of the PEO/PMMA blends indicate that an implicit assumption of equation (2), i.e. that the T_1^H values of the components are not changed by blending, is not fulfilled. Thus in these blends the molecular motions of PEO and/or PMMA in the amorphous phase are most probably affected by blending. The effect of blending on the relaxation time T_1^H is similar to the effect of increasing the temperature because we observed that heating leads to a decrease of T_1^H values. This is in agreement with the PMMA lineshape changes observed in ^{13}C CP/MAS/DD spectra which indicated increased PMMA mobility in the blends.

Plots of the $T_{1\rho}^H$ decays for the magnetization of the quaternary carbon in PMMA for blends of various composition are given in *Figure 7*. The decay plots for other PMMA carbons were very similar. The PMMA $T_{1\rho}^H$

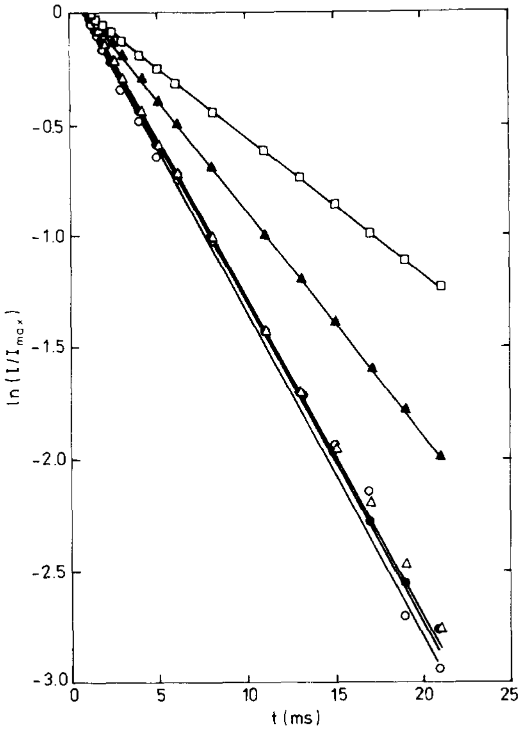

Figure 7 $T_{1\rho}^{H}$ relaxation decays for the magnetization of the quaternary PMMA carbon in (□) pure PMMA and PEO/PMMA blends with weight ratios (▲) 10/90, (△) 30/70, (●) 50/50, (○) 70/30. Contact time 1 ms, spin-locking field in frequency units 60 kHz. Solid lines are fits assuming one relaxation time

decays of all peaks could be very well described by a single exponential function for all blend compositions. The fitted $T_{1\rho}^{H}$ values are given in *Table 1*. The variations of the $T_{1\rho}^{H}$ value between various PMMA peaks in one sample were within ±0.2 ms. With some peaks we could observe some marginal deviations from strict exponentiality for long relaxation times, but they were very small and attempts to decompose the magnetization decay into more than one component gave no consistent results, either among different peaks of one sample or when comparing various samples.

From *Figure 7* and *Table 1* one can immediately see that the PMMA relaxation time $T_{1\rho}^{H}$ is strongly affected by the presence of PEO. The $T_{1\rho}^{H}$ value seems to gradually change below 30% PEO content, consistent with the gradual change of the α-CH_3 resonance lineshape. This is probably caused by a change in the composition of the mixed phase in this range of PEO concentrations; with >30% PEO content it does not considerably change further and the extraneous PEO forms the crystalline phase. The effect of PEO on PMMA $T_{1\rho}^{H}$ relaxation can be caused either by fast spin diffusion between PEO and PMMA in the blend (the $T_{1\rho}^{H}$ relaxation of PEO is faster than that of PMMA, see *Table 1*), or by a change in PMMA chain dynamics. In both cases the blend components in the amorphous phase must be in close contact. The situation is similar to that observed in PEO/i-PMMA blends[25] for i-PMMA molecular weight below 10^6. On the other hand, in the blend of PEO with i-PMMA of molecular weight 1.4×10^6, both components appeared as immiscible on the basis of $T_{1\rho}^{H}$ data[25]. Because the molecular weight of the a-PMMA in our systems was even higher (3×10^6), our results support the idea that a-PMMA is more miscible with PEO than i-PMMA.

These observations lead to the conclusion that in all studied blends PMMA is relatively homogeneously spread in the mixed phase, without large concentration fluctuations or phase separation with phases differing considerably in composition. As no component corresponding to pure PMMA was observed in $T_{1\rho}^{H}$ relaxation decays, the upper limit for the size of the PMMA domains can be estimated from equation (1). Using the value of the spin-diffusion coefficient $D = 8 \times 10^{-16}\,m^2\,s^{-1}$ and the intrinsic PMMA $T_{1\rho}^{H}$ relaxation time (15.8 ms), and taking into account that in the on-resonance $T_{1\rho}^{H}$ experiment[41], the spin-diffusion coefficient D is scaled by a factor of 1/2, we obtained the maximum average domain size of PMMA as ~6 nm. This is the upper limit for the size of the pure rigid PMMA domains.

The $T_{1\rho}^{H}$ relaxation of PEO is more complicated. In all studied samples the PEO relaxation was non-exponential. Typical PEO magnetization decays are given in *Figure 8* for pure PEO and for the PEO/PMMA 10/90 blend. These decays were evaluated from the spectra measured with 1 ms contact time, so preferentially amorphous PEO was detected. All decays could be well fitted assuming two relaxation times. Numerical results of the fits are given in *Table 1*. The relative amounts of the two components given in *Table 1* in parentheses are only illustrative and they cannot be directly related to the phase structure of the samples. The value of the longer component was rather difficult to determine, due to its low intensity. It is clear that this non-exponentiality cannot be attributed just to the presence of the crystalline phase, as it was observed also in the samples with a negligible degree of crystallinity. Further we measured the relaxation behaviour in the region of very short relaxation times, with contact time 50 μs, to detect also the crystalline phase. Typical PEO decays for pure PEO

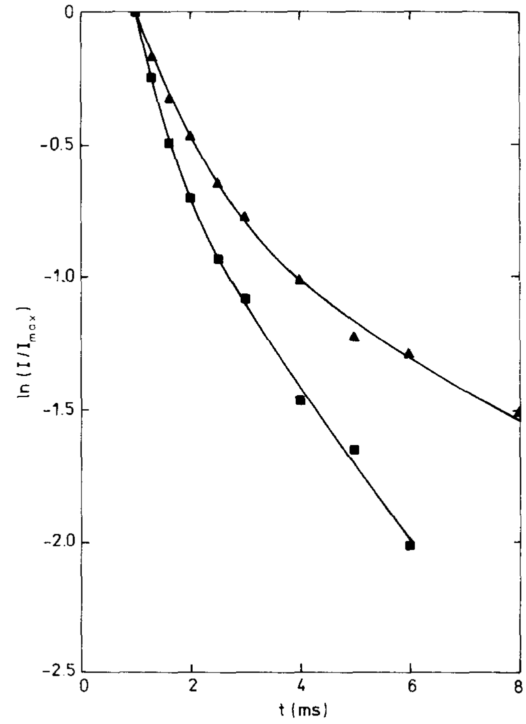

Figure 8 $T_{1\rho}^{H}$ relaxation decays for the PEO magnetization in (■) pure PEO and (▲) PEO/PMMA 10/90 blend. Contact time 1 ms, spin-locking field in frequency units 60 kHz. Solid lines are fits assuming two relaxation times

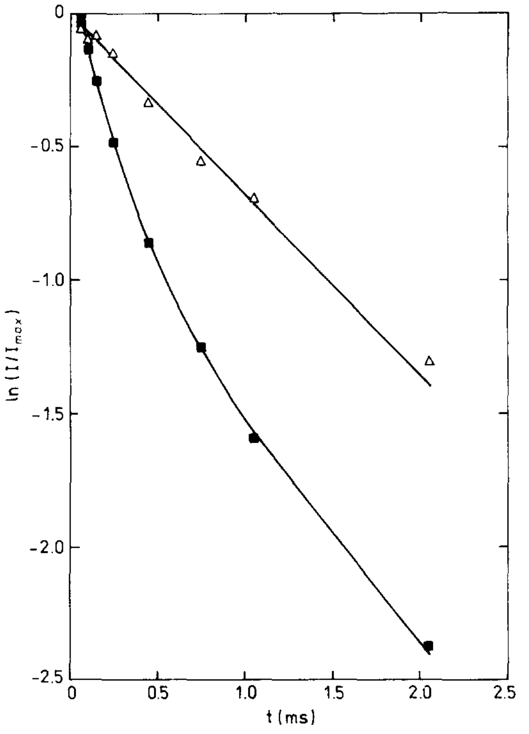

Figure 9 $T_{1\rho}^{H}$ relaxation decays for the PEO magnetization in (■) pure PEO and (△) PEO/PMMA 30/70 blend. Contact time 50 μs, spin-locking field in frequency units 60 kHz. Solid lines are fits assuming one (blend PEO/PMMA 30/70) and two (pure PEO) relaxation times

and the blend PEO/PMMA 30/70 are in *Figure 9*. These measurements revealed another very fast-relaxing component in samples with high crystallinity (pure PEO, blends PEO/PMMA 70/30, 50/50). In the samples with negligible crystalline phase content this component was absent. Numerical results of the fits assuming one or two components are given in *Table 1*.

Thus we can see that the $T_{1\rho}^{H}$ relaxation in pure PEO shows at least three resolvable components. Although the presence of various relaxation components does not automatically mean the presence of corresponding phases[42], it is very tempting to assign the three detected components in pure PEO to the crystalline, amorphous and interphase regions. As already mentioned in the Introduction, the existence of a disordered and probably relatively immobile interfacial region on the surface of the PEO crystals in PEO/PMMA blends has been reported[17,19,20]. In the non-crystalline blends a possible explanation for the two-component-like behaviour of PEO relaxation could be the presence of PEO in the mixed phase with PMMA, in addition to a small amount of pure PEO, or an incomplete averaging of the $T_{1\rho}^{H}$ relaxation due to relatively large PEO domains[42]. In the blends we may also expect an effect of PEO mobility changes on the $T_{1\rho}^{H}$ relaxation. A slowing down of motion of PEO segments in PEO/a-PMMA blends in the melt and supercooled melt state caused by the interaction with PMMA has been reported[23] and also our results indicate that some mobility changes do occur with blending. In the semicrystalline blends all the above-mentioned effects are expected to be present. Thus the detailed analysis of the influence of PMMA on PEO relaxation would require reliable decomposition of the magnetization decays into multiple components and their exact interpretation. Such a study was not done due to the rather low signal-to-noise ratio of the ^{13}C CP/MAS/DD n.m.r. spectra and difficulties with simultaneous detection of the crystalline and amorphous PEO phases.

CONCLUSIONS

The i.r. spectra showed that the pronounced intensity changes of some bands in i.r. spectra of PEO mixed with PMMA reported by some authors are probably caused by the orientation of PEO chains during sample preparation rather than by a large increase in the content of *ttt* conformational structures due to the interaction with PMMA. Nevertheless, PMMA tends to block the PEO crystallization, especially at low PEO concentrations, thus a slight increase in the content of the *ttt* conformational structures due to the higher content of the amorphous phase is possible. Absence of the ordered crystalline phase in samples with low PEO content was confirmed by i.r., n.m.r. and WAXS measurements. T_1^{H} relaxation data show that all studied samples are completely homogeneous on a scale of 20–70 nm. T_1^{H} values together with ^{13}C n.m.r. linewidths indicate changes in the motions of polymer segments in the blends as compared with pure polymers. From $T_{1\rho}^{H}$ relaxation measurements it follows that at least part of the a-PMMA and PEO chains are intimately mixed in the amorphous phase, with the upper limit for the average dimensions of the pure rigid PMMA domains being ~6 nm. A similar estimate of the maximum size of the PEO domains was not made because of the complicated PEO relaxation behaviour. Thus the presence of PEO-rich amorphous domains cannot be excluded.

ACKNOWLEDGEMENTS

We are indebted to F. Szöcs and K. Miklešová from the Polymer Institute, Slovak Academy of Sciences, Bratislava, Slovak Republic for kindly providing the blend samples. We are also indebted to J. Baldrian of this Institute for the WAXS measurements.

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