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Fourier-Transform Infrared and Calorimetric Studies about the Influence of Tacticity of Poly (methyl methacrylate) on the Compatibility with Poly(ethylene oxide)

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Calorimetric study in conjunction with Fourier-transform infrared (FTIR) spectroscopic study was carried out on the blends of poly(ethylene oxide) (PEO) with isotactic, atactic and syndiotactic poly(methyl methacrylate) (*i*-, *a*-, and *s*-PMMA). From the differential scanning calorimetric (DSC) measurements, the three types of blends show a depression of the melting temperatures. This indicates that PEO is compatible with *i*-, *a*- and *s*-PMMA. But the largest melting point depressions of PEO are always found in the blends with *s*-PMMA. For PEO/*a*-PMMA and PEO/*s*-PMMA, the degree of crystallinity as a function of composition deviates substantially from that of the ideal blend in which no interaction between the components exists. The FTIR spectra of all three types of blends are recorded. In order to observe the microstructural changes of PEO in blends, we analyzed the spectra using digital weighted subtraction and addition techniques. It was concluded that the microstructures of PEO are strongly perturbed by the PMMA's. Among these blends PEO microstructure in PEO/*s*-PMMA blends is most greatly influenced. It indicates that the blending is most preferred with *s*-PMMA than *a*- and *i*-PMMA. It can be explained on the basis of the molecular structure of PMMA's.

Introduction

Recently a growing interest has been taken in the compatible polymer blend systems consisting of a crystallizable component and an amorphous one.^{1,6}

One of the most frequently studied polymer pairs is crystalline poly (ethylene oxide) (PEO)/amorphous atactic poly(methyl methacrylate) (*a*-PMMA) system.^{7,21} The PEO/*a*-PMMA blends are compatible in the molten state.⁷ The various properties of PEO are strongly perturbed by the presence of *a*-PMMA which acts as a diluent for the crystallizable PEO. The PEO in blends shows the unique morphology,^{13,18} the depression of spherulite growth rate,^{10,13,19} the melting point depression,^{8,15} and the changes of microstructures with increasing contents of *a*-PMMA.

In addition to the blend compositions, several authors^{22,25} have recently shown that a change in tacticity of a blend component may influence the blend compatibility. From these studies, it was revealed that the compatibility, the melting behaviour, the glass transition temperature and the transition behavior are strongly dependent on the tacticity. There are many possible explanations for these phenomena. With

the Flory equation of state, Vorenkamp *et al.*²⁴ showed that the free volume contribution is one of the principal reasons for the difference in phase behavior. There may be other explanations; the difference in flexibility, the difference in conformation, the radius of gyration in the various tactic forms of PMMA, and the strength of the exchange interactions. However the influence of tacticity of PMMA on the compatibility with PEO has not been studied in detail.²¹

In this paper, the influence of tacticity of PMMA on the compatibility of PEO/PMMA blends has been studied with differential scanning calorimetry (DSC) and Fourier-transform infrared (FTIR) spectroscopy. We used the degree of melting point depression to study the differences in the interaction of PEO with PMMA's with different tacticity. The melting point depressions are taken as an indicative for the strength of the binary interactions.^{1,4,26} The larger melting point depressions led to the conclusion that the binary polymer-polymer interaction is stronger in blends. Although the melting point depressions show the strength of the binary interaction, it does not reveal anything about the nature of this interaction. Coleman *et al.*²⁷ suggested that FTIR spectroscopy offers the considerable potentiality for studying the

Table 1. Characteristics of PEO and PMMA Polymers used^a

	$M_w \times 10^{-5}$	Contents of Triads (%)		
		I	H	S
PEO	1.00	—	—	—
<i>i</i> -PMMA	2.50	95	1	4
<i>a</i> -PMMA	1.54	5	35	60
<i>s</i> -PMMA	1.00	1	23	76

^aI: isotacticity, H: heterotacticity, S: syndiotacticity.

compatibility of polymer blends. With its inherent sensitivity and computational facilities, it offers the information for the specific interactions between the individual polymer chains, and for the changes in the conformation.^{14,17,27-30}

The main object of present work consists in the study for the influence of the tacticity of PMMA on the compatibility with PEO as well as on the changes of the molecular microstructures of PEO. Specially we have an interest in the influence of the tacticity on the changes of the conformation of PEO chains in the blends. The details will be described in the text.

Experimental

Materials. The polymers, PEO and PMMA's, used in this study are the commodities of Polysciences Inc., Washington, Pa. USA. Molecular weight distributions of the polymers were determined by gel permeation chromatography in tetrahydrofuran at 25 °C using polystyrene as a calibration standard. The characteristics of the polymers are listed in Table 1. The tacticities of the PMMA samples were measured for five percent solutions of the polymers in chloroform-d at 25 °C by F.T.-¹H n.m.r. spectroscopy with a Varian FT 80A instrument.

Preparation of Samples. In our study, samples of pure PEO and the blends with PMMA ranging from 90% to 10% PEO by weight were prepared by solution casting, with chloroform as the solvent. For the DSC measurements, samples were prepared in the following way: the first step in the solution blending process was to make individual 3 g/100 ml solutions of the respective polymers in chloroform followed by stirring for 6 hrs. These solutions were subsequently blended in the proper proportions and stirred for 24 hrs. Thin films of pure PEO, PMMA's, and their blends were prepared by casting the above solutions on a glass plate at room temperature. The solvent was slowly evaporated at 50 °C under stream of air. The resulting films were subjected to further drying under vacuum at 70 °C for 48 hrs and cooled to room temperature within 3 min. Then in order to eliminate kinetic effects, the samples were kept at room temperature for a week to ensure complete crystallization.

For the FTIR study, samples were prepared as follows: blending process is the same as above; but the concentration of the solution is 1 g/100 ml; aliquots of the solutions of 0.075 ml were homogeneously spread with a micropipette on KBr pellets maintained at 50 °C, and the complete removal of the last trace of the solvent was achieved by heating in vacuum at 60 °C for 24 hrs; then the samples were subjected to further drying at 80 °C for 15 min and cooled to room temperature within 3 min. The films and pellets were sufficiently thin so that the band intensities are within the absorbance

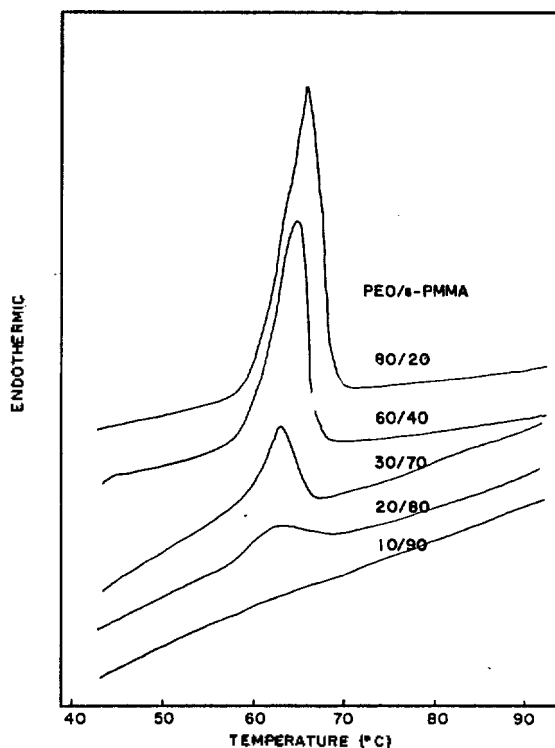


Figure 1. Thermograms of PEO/*s*-PMMA blends obtained by DSC at a heating rate of 10 °C/min. The composition of PEO/*s*-PMMA is expressed by parts in weight.

range for which the Beer-Lambert law is obeyed. The above procedure led to an average film thickness of about 5 μm.

Measurement. The DSC measurements were made by using a Perkin-Elmer differential scanning calorimeter (Model DSC-4) equipped with a TADS computer. All measurements were calibrated with ultrapure indium (mp 153.6 °C). A scanning rate of 10 °C/min was always used.

For T_m (melting temperature) studies, the sample of 5.00 mg was used. The T_m was determined by thermograms obtained for the samples without any previous treatment and three runs are always made. T_m (error ± 1 °C) was taken as the temperature corresponding to the maximum of the melting endotherm.

The degree of crystallinity, χ_c , was calculated from the endothermic area by the following equation:

$$\chi_c = \Delta H_{fus} / \Delta H_{fus}^0$$

where ΔH_{fus}^0 , the heat of fusion of 100% crystalline PEO, is taken as 51 cal/g¹⁴, and ΔH_{fus} is the heat of fusion for the sample, and is obtained from the endothermic area of the melting endotherm. Large amount of samples (≈ 10 mg) were used for the determination of ΔH_{fus} in order to avoid errors inherent in weighing small amount of samples (error ± 1%).

Infrared spectra were obtained on a Nicolet MX-10 FTIR instrument. Sixty four scans at a resolution of 2 cm⁻¹ were analyses. Although the samples slightly differ in their thickness, this does not affect the data and the derived conclusions.

Results

Melting Behavior. Figure 1 shows the representative

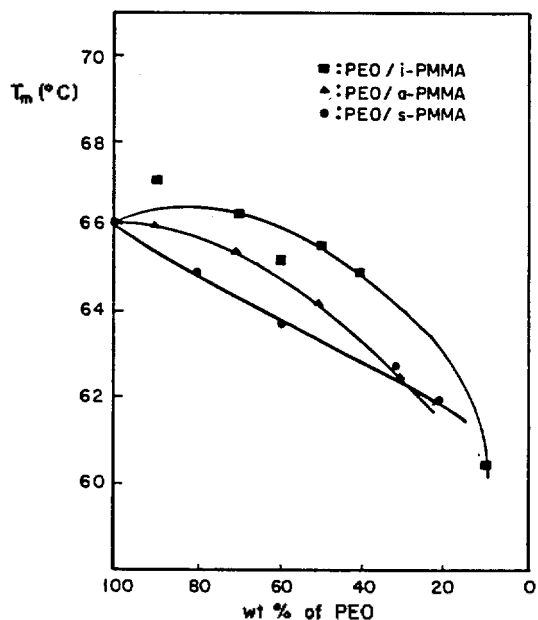


Figure 2. Melting points measured for PEO/PMMA (*i*, *a* and *s*) blends as a function of PEO concentration (weight percent). The heating rate: 10°C/min.

DSC thermograms of PEO/*s*-PMMA blends measured at a heating rate of 10°C/min. Each type of blends show a melting endotherm with a single melting point. In the case of PEO/*s*-PMMA, PEO melting endotherms appear up to 80 wt% *s*-PMMA, and disappear at higher contents of *s*-PMMA (see Figure 1). Similar phenomena were observed for the PEO/*a*-PMMA. For the blends containing *i*-PMMA, however, the melting endotherms appear up to its 90 wt% of *i*-PMMA. In Figure 2 the melting points (T_m) for all the three types of blends, crystallized at room temperature for a week, are presented as a function of the weight percent of PEO. One notes that the melting temperatures of PEO in the PEO/*s*-PMMA are always lower than those of PEO/*a*-PMMA and PEO/*i*-PMMA at the same compositions. The blends containing 10% and 20% *i*-PMMA, the melting points are higher than pure PEO. When some polymers are blended with other polymers, in fact, rather than disrupting crystallinity, it often appears that crystallinity is enhanced.³¹ Although we didn't performed X-ray analyses, these results can indicate that the addition of *i*-PMMA to PEO seems to lead to more complete crystallization of PEO at these compositions. However, T_m decreases generally with increasing PMMA's. Among the three types of blends PEO/*s*-PMMA show the most marked T_m depression. Although these observed melting points may not be the equilibrium melting temperatures, from these melting point depressions one can notice that favorable interactions exist between the two components in PEO/PMMA's, and that the interactions are most strong in PEO/*s*-PMMA.

Figure 3 shows the degree of crystallinity (χ_c) vs. PEO content of the three types of blends. All the three types of blends show that crystallinity decreases with increasing PMMA's contents. The dashed line represents the expected crystallinity of an ideal blend of PEO/PMMA in which no interaction exists between PEO and PMMA's. The degrees of the deviations from this dashed line are dependent on the blend compositions and the tacticity of PMMA. This

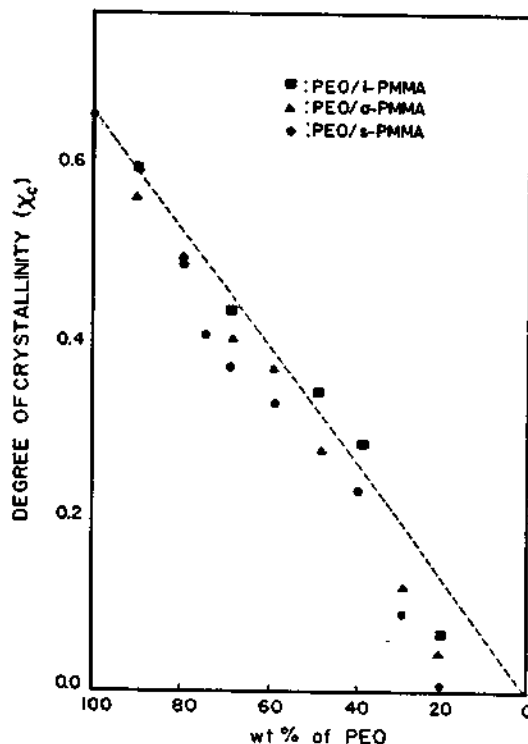


Figure 3. Degree of crystallinity obtained for PEO/PMMA (*i*, *a* and *s*) blends as a function of PEO concentration. The samples are crystallized for a week at room temperature.

deviation is most marked for blends containing *s*-PMMA. The χ_c values of PEO/*i*-PMMA blends are almost equal to the dashed line values up to blends containing 70 wt% *i*-PMMA.

In a large number of studies on the blends of crystalline/amorphous polymers the T_m of the crystalline component has been observed to decrease as the concentration of the non-crystalline (amorphous) component increases. This phenomenon bears a close similarity to the melting point depression observed in the crystalline polymer-diluent systems.¹ Several mechanisms have been proposed regarding the melting point depression.³²⁻³⁴ It has been suggested that the morphological effects such as the size and imperfection of the crystal are responsible for the lowering of the melting point.¹ An alternative explanation is the thermodynamic effect of mixing.³²⁻³⁴

Judging from the higher T_m and χ_c of PEO/*i*-PMMA blends than PEO/*a*-PMMA and PEO/*s*-PMMA (see Figures 2 and 3) PEO seems to be less influenced by *i*-PMMA than *a*- and *s*-PMMA. That is, *a*- and *s*-PMMA are more compatible with PEO.

FTIR Study. The melting point depressions only indicate the strength of the binary interactions, and do not show anything about the nature of the interactions.²⁵

The FTIR studies of polymer blends show the nature of the chemical interactions between polymer chains which are responsible for the apparent compatibility in a specific range of compositions.^{25,27-29} Thus the vibrational spectroscopic techniques have been used to follow the microstructural changes of polymer chain in blends.^{14,27}

All the three types of blends show a few general features: the spectra of the blends show the band broadening with in-

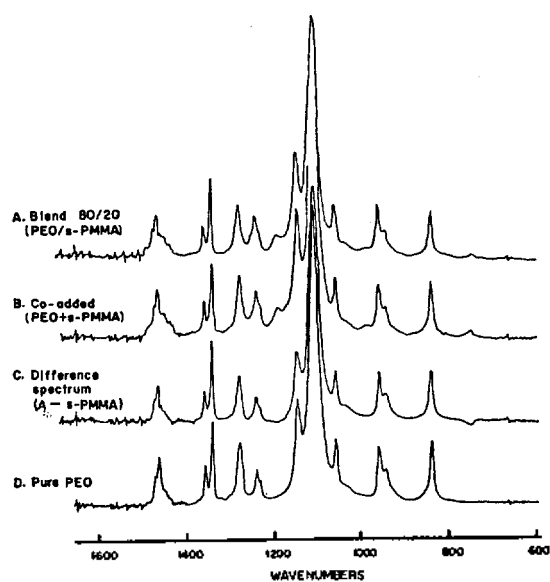


Figure 4. FTIR spectra in the range of 700-1600 cm^{-1} . (A) Experimental spectrum of PEO/*s*-PMMA 80/20 blend; (B) co-added spectrum of PEO/*s*-PMMA 80/20 blend; (C) difference spectrum, *i.e.*, obtained from spectrum A by subtracting weighted *s*-PMMA spectrum D in Figure 5; (D) pure PEO.

creasing PMMA contents. The spectral perturbations occur mainly near 1340-1360 cm^{-1} (CH_2 wagging) and 800-1000 cm^{-1} (coupled C-O stretching, CH_2 rocking, and C-C stretching). The degree of spectral perturbations depends on the blend compositions and tacticity of PMMA.

In order to obtain the information about the specific interaction between the individual polymer chains and the changes in the conformation of PEO, it is instructive to employ the digital subtraction or addition techniques.²⁷ We selected the band at 1728 cm^{-1} of *s*-PMMA and *a*-PMMA in PEO/*s*-PMMA and PEO/*a*-PMMA blends, respectively, and 1732 cm^{-1} of *i*-PMMA in PEO/*i*-PMMA blend since the absorption of PEO in these regions is negligible in comparison with those of PMMA's.

FTIR Spectra of 80 / 20 PEO / *s*-PMMA Blend

In Figure 4 are shown the FTIR spectra of the samples in the range of 700-1600 cm^{-1} : spectrum D is for pure PEO, and A is for 80/20 PEO/*s*-PMMA blend (crystallized for three days to complete crystallization). Spectrum B was obtained by a weighted addition technique from the pure PEO spectrum D and the pure *s*-PMMA [shown in Figure 5(D)]. The spectrum C was obtained by subtracting weighted *s*-PMMA spectrum from that of blend (A) by a digital subtraction technique. By comparing A and B in Figure 4, it is apparent that the experimental spectrum of the blend (A) is almost identical to that of the synthesized spectrum (B). It is well known that in the incompatible binary blend system the weighted absorbance addition of the spectra of the two pure components is identical to the spectrum of the blend.²⁷ Therefore we conclude that PEO and *s*-PMMA are less compatible in this composition of PEO/*s*-PMMA (80/20). The difference spectrum C, which was obtained from spectrum A by subtracting the weighted *s*-PMMA spectrum [Figure 5(D)], is almost identical to the spectrum of pure PEO (D). There are no spectral changes of PEO in the blend. This indicates that in this composition of PEO/*s*-PMMA (80/20) a

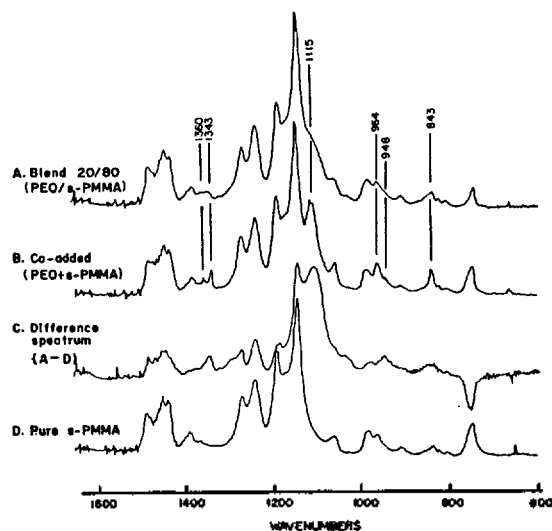


Figure 5. FTIR spectra in the range of 700-1600 cm^{-1} . (A) Experimental spectrum of PEO/*s*-PMMA 20/80 blend; (B) co-added spectrum PEO/*s*-PMMA of 20/80 blend; (C) difference spectrum, *i.e.*, the weighted *s*-PMMA spectrum was subtracted from the blend spectrum A; (D) pure *s*-PMMA.

distinct chemical interaction does not exist between the chains of the one polymer and those of the other.

The spectra of PEO/*a*-PMMA (80/20) and PEO/*i*-PMMA (80/20) were also obtained in this study, although are not shown here. We obtained the same results as in PEO/*s*-PMMA (80/20) (Figure 4), *i.e.*, both *a*-PMMA and *i*-PMMA are also incompatible with PEO in this composition, and the conformational changes of PEO do not exist.

FTIR Spectra of 20 / 80 PEO / *s*-PMMA Blend

Figure 5 shows the results of a 20/80 PEO/*s*-PMMA blend (crystallized for three days). It is clear that the experimental spectrum of the blend A is apparently different from the synthesized spectrum B which was obtained by weighted addition of spectrum D for pure *s*-PMMA and spectrum D for pure PEO in Figure 4. In particular, bands at 843, 948, 964, 1115, 1343, and 1360 cm^{-1} are not matched in the spectra A and B. They are considerably stronger in the synthesized spectrum (B) than in that of the blend (A). Particularly, the absence of the 1115, 1343 and 1360 cm^{-1} bands is remarkable in A while they are distinct in B. If the polymers are compatible, there are considerable differences between the experimental infrared spectrum obtained from the blend and that synthesized by addition of the absorbance spectra of the pure components.²⁷ It is apparent that the difference spectrum (C) obtained by subtracting D from A is quite different from the PEO spectrum (D) in Figure 4, while the two are expected to be identical for a incompatible blend. These differences are derived from the changes in the conformation as well as chemical interactions resulting in band shifts and band broadening.²⁷ From this point of view, we believe that the 20/80 PEO/*s*-PMMA is a compatible blend.

Difference Spectra of PEO / PMMA Blends

The PEO chain in crystalline state has been found to contain seven $\text{CH}_2\text{CH}_2\text{O}$ units in two helical turns per fiber identity period 19.3 Å. The internal rotations about the O- CH_2 , CH_2 - CH_2 and CH_2 -O bonds yield the *trans*, *gauche*, and *trans* form, respectively, and yield the resultant conformation

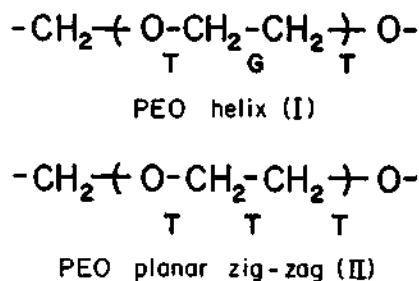


Figure 6. PEO conformers: (I) helix (TGT); (II) planar zig-zag form (TTT).

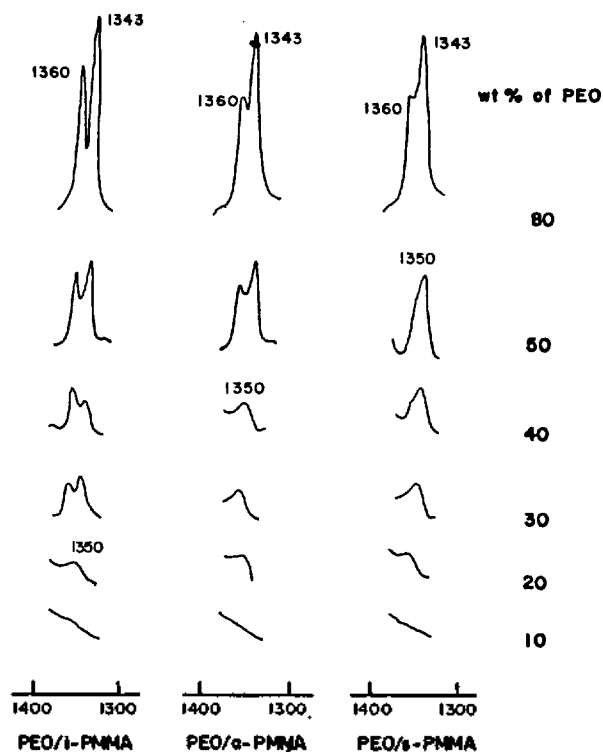


Figure 7. Difference spectra of PEO in PEO/PMMA blends in the 1300-1400 cm^{-1} region. The spectra for the blends with different tacticities of PMMA are shown as a function of PEO concentration (weight percent).

TGT. But upon blending, the PEO takes preferentially a planar zig-zag structure (TTT).¹⁷ These are shown in Figure 6 as conformers I and II, respectively. Detailed normal-coordinate analysis was carried out on a large number of conformers of molecules of PEO.³³

On the basis of normal vibrational analysis, the vibrational bands of the crystalline PEO are well understood: the bands at 1343 and 1360 cm^{-1} correspond to CH_2 wagging motion; the 948 and 964 cm^{-1} bands correspond to CH_2 rocking; the band at 843 cm^{-1} to the mixed motion of CH_2 rocking and COC deformation. It was known that the 1343 and 1360 cm^{-1} doublet bands and the 948 and 964 cm^{-1} doublet bands are crystalline bands, however, in molten state the two doublets turn to two singlet at 1350 and 952 cm^{-1} , respectively.¹⁴

In Figure 7 are shown the FTIR difference spectra of PEO (PEO/PMMA's blends spectra minus PMMA's spectra) in the range of 1300-1400 cm^{-1} for the three types of

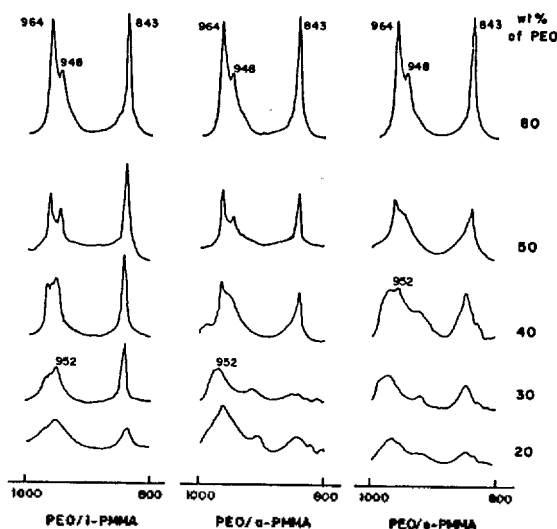


Figure 8. Difference spectra of PEO in the PEO/PMMA blends in the 800-1000 cm^{-1} . The spectra of the blends with different tacticities of PMMA are shown as a function of PEO concentration (weight percent).

blends crystallized for three hours at room temperature. It is clear that the split peaks of crystalline bands at 1343 and 1360 cm^{-1} are reduced into an amorphous band at 1350 cm^{-1} with increasing α -PMMA and s -PMMA contents. This is construed as the decrease of crystallinity and the changes of conformation* of PEO. However, in the case of PEO/ i -PMMA the split peaks are not replaced by the 1350 cm^{-1} band up to blend composition 30/70. In the PEO/ s -PMMA blends, there is a growing tendency to the reduction of crystalline split bands into single amorphous band (see Figure 7).

Figure 8 shows the FTIR difference spectra of PEO in the region 800-1000 cm^{-1} for the three types of blends crystallized for three hours at room temperature. The crystalline band at 948 and 964 cm^{-1} is reduced to the amorphous 952 cm^{-1} which is due to the GT-TG conformation of the $\text{CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_2$ group.¹⁴ Among the three types of blends, PEO/ s -PMMA shows the tendency for reducing to the 952 cm^{-1} band most quickly for the same composition.

The spectral changes of PEO (Figures 4,5,7,8) indicate the conformational changes upon blending. It is not feasible to register the conformation where optimum interaction might be attained between the different polymers and to obtain a complete register of the interacting units. It can be expected, however, that PEO chain conformations are most influenced by the presence of s -PMMA compared with that in the pure PEO crystal. But in the blends containing i -PMMA, the chain conformations of PEO are less influenced by the presence of i -PMMA.

Crystallization behavior of PEO/ i -PMMA is also different from that of PEO/ α -PMMA or PEO/ s -PMMA. For example, in the case of the blends containing 70 wt% i -PMMA, no further spectroscopic changes occur after three hours. However, for the same composition PEO/ α -PMMA and PEO/ s -PMMA show the spectroscopic changes, indicating that crystallization continues to take place. All the facts mentioned above indicate that PEO/ s -PMMA blends are more compatible compared with PEO/ α -PMMA and PEO/ i -PMMA.

Discussion

From the DSC experiments we derived the conclusion that PEO is more compatible with *s*-PMMA than *a*-PMMA or *i*-PMMA. This result is consistent with that obtained by the spectroscopic technique. Consequently the compatibility, chain conformation, and crystallization behavior of PEO/PMMA blends are strongly influenced by the composition and the configuration of PMMA's.

The marked differences in the interaction of PEO with the *i*-PMMA and *s*-PMMA might be due to the different configurations of these PMMA's. Rao *et al.*¹⁷ considered for *s*-PMMA and *i*-PMMA a planar zig-zag and a 3/1 helix structure, respectively. Using the atomic charge idea, they predicted that the *i*-PMMA is more compatible with the PEO than *s*-PMMA. Their conclusion disagree with our experimental results. Rao *et al.*, however, used the 3/1 helix model for *i*-PMMA in their theory in contrast to the experimental fact that the *i*-PMMA does not take the 3/1 helix form.³⁵ Thus, their conclusion is hardly acceptable.

We made mentioned of the reasons for the difference in phase behavior in introduction section. There may be many possible explanations. Among the many reasons, we suppose that the difference in conformation plays an important role.

In the following, our view on the compatibility of PEO/PMMA's is described. It is well known that the *i*-PMMA takes a 5/1 helix form.³⁵ In 5/1 helix model the -CH₂ groups and the side-chain ester-groups are nearly coplanar. The ester groups are packed in the spaces between the turns of the skeletal chain and obliged to orient inwards. Thus it becomes less accessible to intermolecular interaction with PEO. This situation is quite different for the case of *s*-PMMA with PEO, where the *s*-PMMA takes the planar zig-zag form, as a results the interaction with PEO becomes easier since the PEO also preferentially takes a planar zig-zag form upon blending. Thus *s*-PMMA is more compatible with PEO than *a*- and *i*-PMMA.

Other explanations may be possible for the compatibility difference of the tactic PMMA's with PEO. For example, Silvestre *et al.*²² considered that the difference is due to the free volume and thermal expansivity difference of the tactic PMMA's. But, their conclusion is not yet conclusive since it has not been confirmed experimentally, yet.

A great deal of study is needed to understand the specific interaction between PEO and PMMA of different tacticity in order to understand the details of the difference in mixing behavior.

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