Probing the structure of polymer blends by vibrational spectroscopy: the case of poly(ethylene oxide) and poly(methyl methacrylate) blends*

G. Ramana Rao†, C. Castiglioni, M. Gussoni and G. Zerbi
Dipartimento di Chimica Industriale e Ingegneria Chimica Giulio Natta, Politecnico di Milano, 20133 Milano, Italy

and E. Martuscelli
Istituto di Ricerche su Technologia dei Polimeri e Reologia del CNR Arco Felice, Napoli, Italy
(*Received 3 April 1984; revised 30 June 1984*)

The blends of poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) are prepared in the form of thin films from solution casting. The Fourier transform infrared spectra of the blends are recorded in the spectral range 4000–400 cm^{-1}. The spectra are analysed using various recent techniques of vibrational spectroscopy. It is concluded that upon blending PEO takes preferentially a planar zig-zag structure. Furthermore the intermolecular interactions between the molecules of PEO and PMMA in blends are very weak and their compatibility as blends is more 'physical' than 'chemical'. Further, on the basis of the atomic charges transferred from model molecules it is seen that the blending is preferred with isotactic PMMA when compared to syndiotactic PMMA.

(Keywords: polymer blends; vibrational spectroscopy; poly(ethylene oxide); poly(methyl methacrylate); intermolecular interactions)

INTRODUCTION

The determination of the microstructure of polymer blends is, at present, one of the most essential steps in understanding the relationship between molecular structure and macroscopic physical properties of this important class of new materials. While the measurement of overall macroscopic physical properties is simple, the determination of the molecular structure is not easy as these systems lack periodicity and symmetry of any type. This underlines the need for the development of new theoretical, as well as experimental, techniques. Vibrational spectroscopy has, generally, been used on a correlative basis for understanding the general features of the chemical structure of these systems. However, a detailed analysis in terms of the molecular structure has seldom been carried out.

The blends of poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) are becoming a matter of study and the results so far presented from optical microscopy[1] and small and wide angle X-ray scattering[2] do not give sufficient information on the system. Nothing is known of the nature of intermolecular interactions and the shape adopted by the molecules of PEO and PMMA in the blends. It is worthwhile to apply the methods of modern vibrational spectroscopy such as symmetry analysis, intensity sepctroscopy, difference spectroscopy, factor analysis and least-squares curve-fitting in order to gain some insight into the microstructure of this material.

Using the various methods listed above we come to the conclusion that upon formation of the blend, within a certain range of concentrations, the planar zig-zag form of PEO, originally helical, is the one involved in the interaction. Moreover PMMA does not interact with specific directional forces at specific sites, but is only interacting through very weak van der Waals type interactions. Based on these results we must conclude that the compatibility of PEO and PMMA in the solid is only 'physical' since 'chemical' interactions are non-existent. The reasons for such statements will be discussed in this paper.

EXPERIMENTAL

The origin and the physical properties of the materials used were given in *Table 1* of a paper by Martuscelli *et al.*[2] Samples were prepared as cast films, from a solution of $CHCl_3$, on a KBr disc maintained at 50°C. The solvent was removed under vacuum at 70°C for 3–4 h. Then the samples were heated at 80°C for 15 min and annealed at 55°C for 6 h to allow for crystallization. The blends investigated were made by taking PEO and PMMA in the ratio of 10:1, 10:2, 10:3, 10:4, 10:5 and a few other intermediate compositions by weight. Thin films of individual components were also prepared and annealed under the same conditions.

Fourier transform infra-red spectra, in the range 4000–400 cm^{-1}, were recorded with Nicolet FTIR 7199 dual

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* Supported by CNR, Programmi Finalizzati Chimica Fine Secondaria

† ICTP Fellow, on leave of absence from the Kakatiya University, Warangal-506 009 (A.P.), India

0032-3861/85/060811-10$03.00

beam spectrometer equipped with liquid nitrogen-cooled 'Deuterated Triglycine Sulphate (DTGS) detector. The resolution adopted was 1 cm^{-1}. Each spectrum is a result of the co-addition of 32 scans. All data processing was done on the computer of the spectrometer using the programs available in the software. The samples differ in their thickness; this does not affect the processing of the data and the conclusions. The spectra of the blends analysed are those after annealing; however to know the effect of temperature we also recorded the spectra of PEO, PMMA and a blend (82% PEO and 18% PMMA) before and after annealing.

Table 1 Factor analysis of PEO/PMMA blends in various spectral regions

S. no.	PEO:PMMA w/w)	Eigen value	RE* × 10^4	IND* × 10^5
(a) 3100–2650 cm^{-1}				
1	10:2	97.15707	211.23231	132.020
2	0:1	2.70311	54.09178	60.102
3	10:5	0.12606	20.78268	51.957
4	10:4	0.00866	17.89338	178.934
5	10:1	0.00510	—	—
(b) 1800–1300 cm^{-1}				
1	1:0	84.97332	363.36634	145.347
2	0:1	12.37499	170.55255	106.595
3	10:5	2.53685	40.29069	44.767
4	10:2	0.07917	26.37109	65.928
5	10:4	0.02160	21.01548	210.155
6	10:1	0.01005	—	—
(c) 1000–500 cm^{-1}				
1	1:0	91.24459	277.40163	110.961
2	10:5	8.41243	61.38299	38.364
3	0:1	0.28181	29.92912	33.255
4	10:1	0.04547	18.56155	46.404
5	10:4	0.01290	10.93304	109.330
6	10:2	0.00272	—	—

* RE and IND are defined in Ref 5

GENERAL OBSERVATIONS ON THE INFRA-RED SPECTRA

At first, a few general observations can be made on the infra-red spectra.

(1) The spectra of the blends are dominated by the spectrum of PEO since its concentration is higher than that of PMMA. However, the spectra of the blends are different from that of annealed PEO in a few spectral ranges.

(2) The spectral perturbations which will be shown to be relevant to our analysis occur mainly near 1350 cm^{-1} (CH_2 wagging), 1240 cm^{-1} (CH_2 twisting) and 1200 to 900 cm^{-1} (coupled C–O stretching, CH_2 rocking and C–C stretching).

(3) All the bands which show perturbations belong to PEO. The spectral perturbations of PMMA are hardly seen due to its small concentration and overlapping by intrinsically strong PEO bands.

(4) The spectrum of PEO before and after annealing is different mainly in the regions mentioned above (*Figure 1*) whereas that of PMMA remains unchanged (*Figure 2*).

(5) The spectrum of the blend (PEO 82%, PMMA 18%) also changes with annealing (3 h) in the same spectral ranges (*Figure 4*).

The interpretation of the above spectral changes in terms of the formation of a blend or of some new structures is not possible from simple correlation studies. Hence we use factor analysis and least-squares curve-fitting in an attempt to solve the problem.

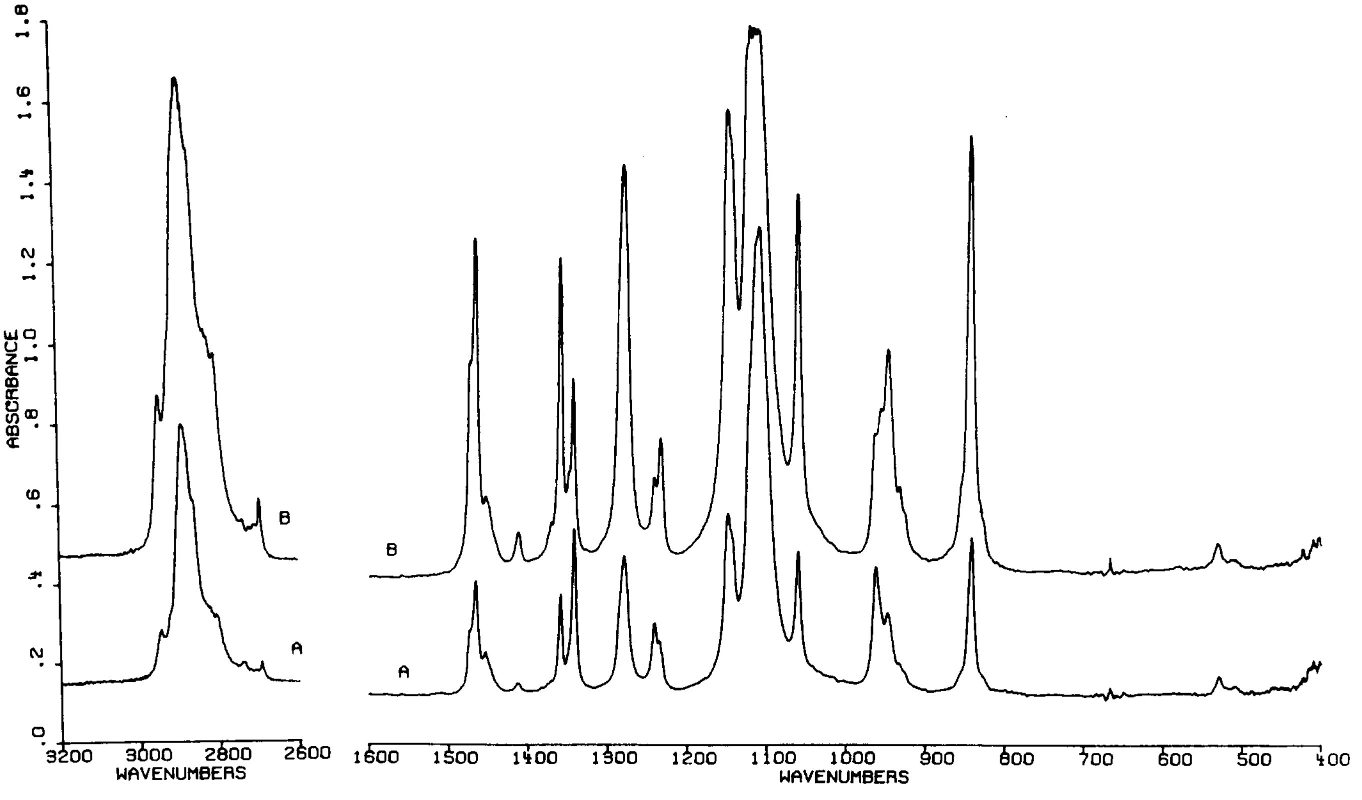

Figure 1 Infrared spectrum of PEO (thickness is different) (A) Before thermal treatment; (B) after thermal treatment

SPECTROSCOPIC ANALYSIS

The analysis of the spectra was made in various steps as discussed in the following:

Factor analysis

The first relevant information that is required is to know whether PEO and PMMA interact to form a 'blend' considered as a complex with optical properties which are different from those of the starting materials. One way to get this information is to perform 'factor analysis'. It is a statistical process by means of which the number of linearly independent components present in a composite system could be found. The details of calculations have already appeared in the literature[3,4]. In essence, one diagonalizes the covariance matrix which is obtained by pre-multiplying the absorbance matrix with its transpose. The resulting eigenvalues[5,6] or eigenvectors[7] can be used to arrive at the number of independent components. This technique was already applied to the case of a polymer blend[8]. The application of factor analysis to vibrational spectra is not free from difficulties and must be applied

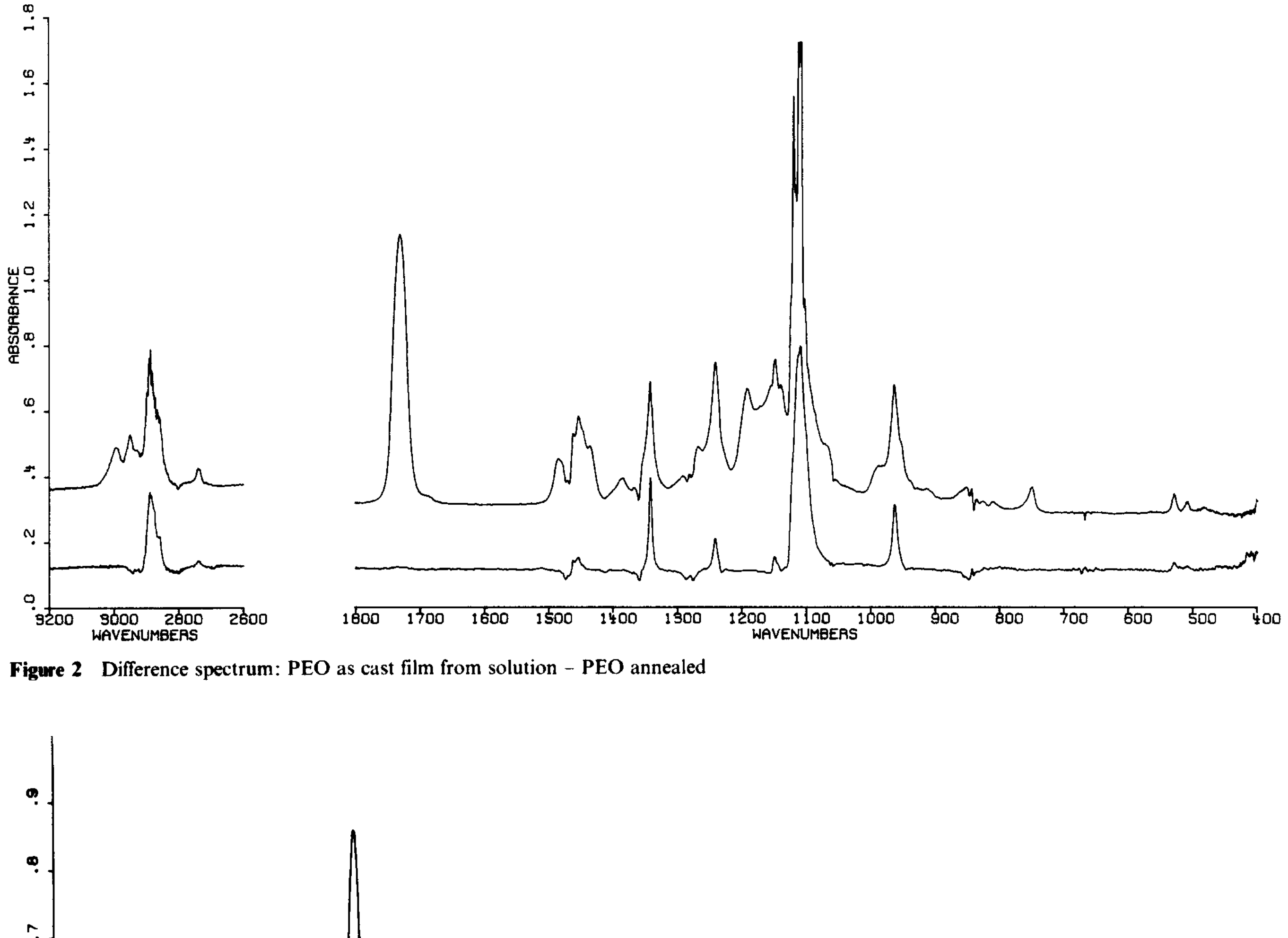

Figure 2 Difference spectrum: PEO as cast film from solution – PEO annealed

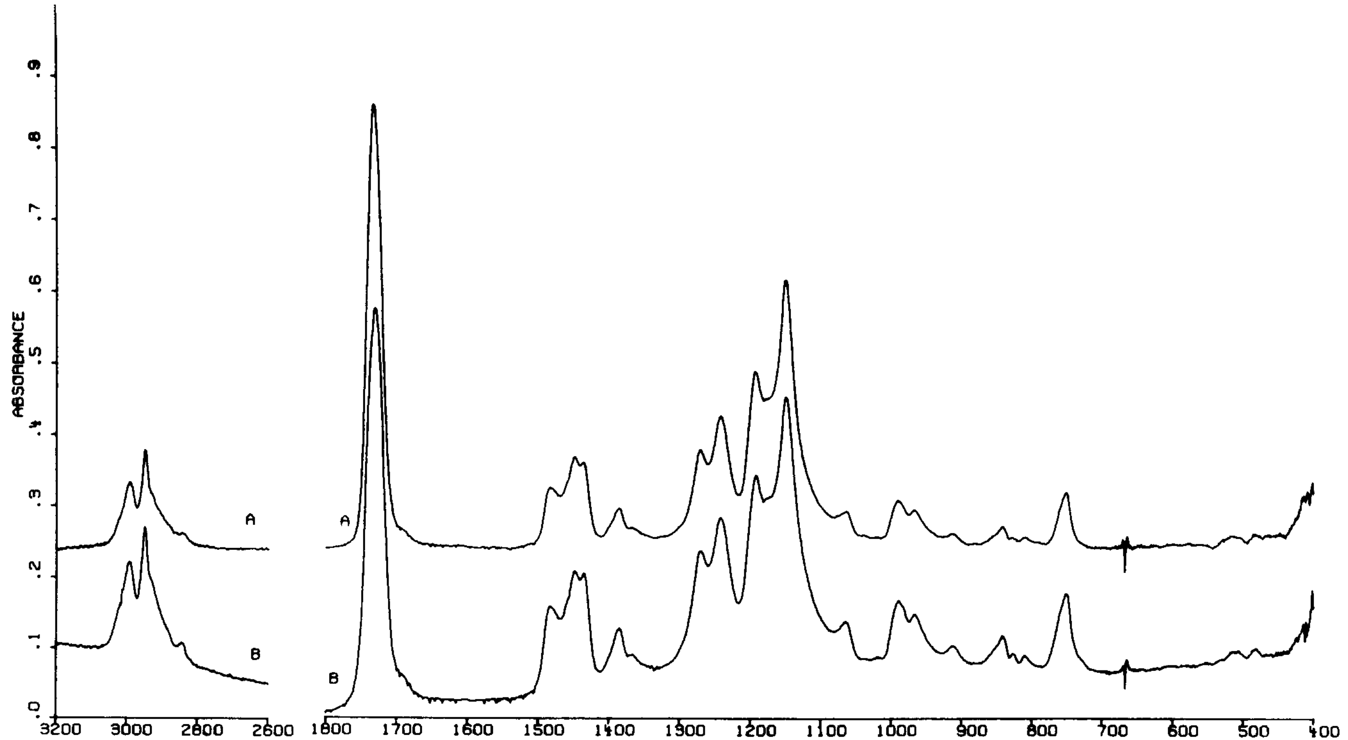

Figure 3 Infrared spectrum of PMMA (thickness is different). (A) Before thermal treatment; (B) after thermal treatment

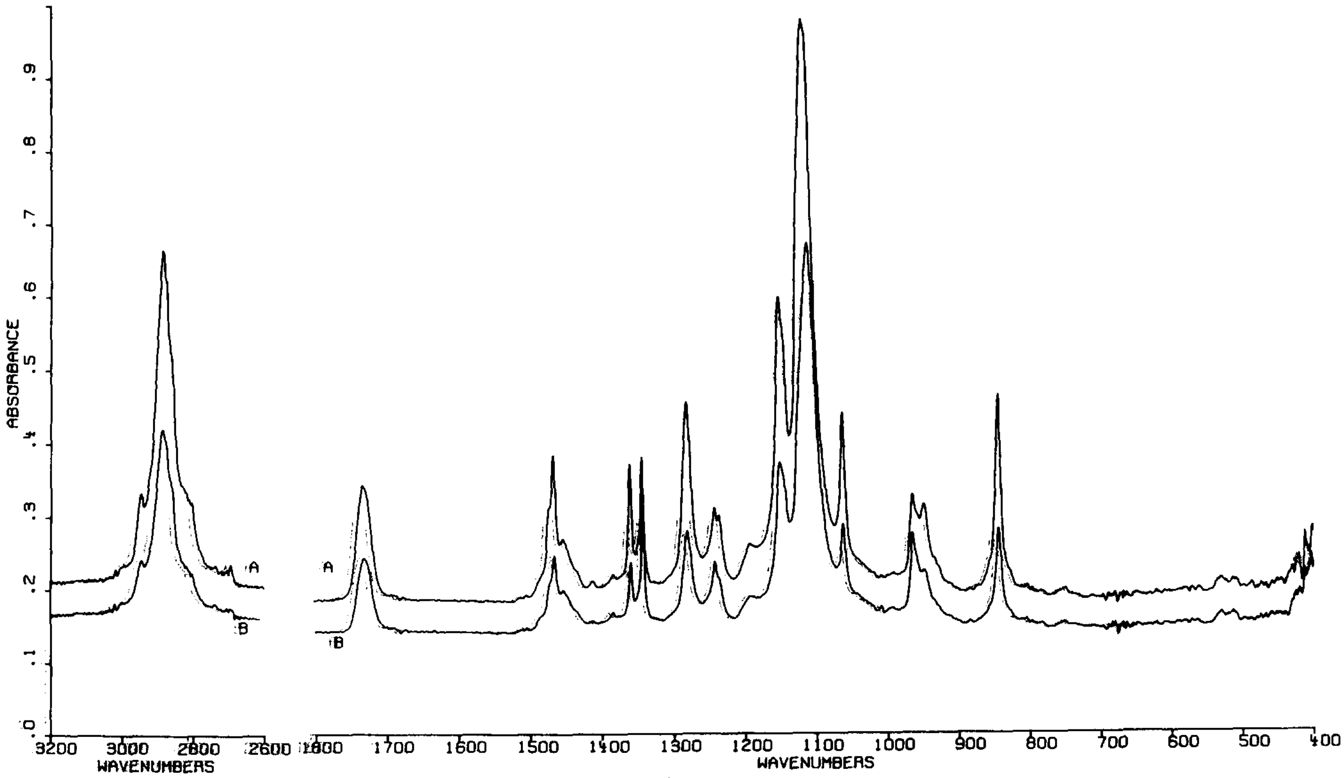

Figure 4 Infrared spectrum of a blend (82% PEO and 18 PMMA; same film). (A) Before thermal treatment; (B) after thermal treatment

Table 2 Eigenvectors in the spectral range 1000–500 cm^{-1}

PEO:PMMA	I	II	III	IV	V
0:1	0.336116	0.598690	0.726041	0.019886	0.032607
10:1	0.443620	−0.420646	0.124141	−0.433211	0.650518
10:2	0.453947	−0.546698	0.266542	0.107766	−0.272559
10:5	0.526988	0.404663	−0.553868	−0.421273	−0.272559
10:4	0.454358	0.044671	−0.282199	0.789206	0.298460

with caution. Some of the problems have recently been pointed out and discussed[9].

The factor analysis is performed in the spectral ranges 3100–2650, 1800–1300 and 1000–500 cm^{-1}. The results using the indicator function (IND)[5] are shown in *Table 1*. In all the three cases IND reaches a minimum at the number of components corresponding to three, indicating the presence of three linearly independent components. To check this result we have made data reconstruction[7] using the eigenvectors in the range 1000–500 cm^{-1}. The eigenvectors are shown in *Table 2*. The reconstructed and experimental spectra agree very well when the first three eigenvectors derived from the 1000–500 cm^{-1} range are used. The agreement is perfect in this frequency range and is quite acceptable throughout the whole spectrum. One of the experimental spectra and its reconstructed counterpart are shown in *Figure 5*.

Least-squares curve-fitting

If the blend is not formed it must be possible to reconstruct the spectrum of the mixture as a linear combination of the spectra of PEO and PMMA. If, instead, the blend is formed or some other kind of structure has evolved because of mixing, the linear combination of the spectra of PEO and PMMA will not be sufficient to reproduce the observed spectra. Hence we tried the least-squares curve-fitting method[9–11] on the blends using the spectra of annealed PEO and PMMA as standards. We observe that the reconstructed spectra do not agree with experimental ones indicating the presence of a third component. The spectrum of the third component has been obtained as difference from 10:1 blend. This is used as the spectrum of the third 'component' in the least-squares method. The least-squares coefficients are shown in *Table 3*. One of the reconstructed spectra along with its experimental counterpart is shown in *Figure 6*. The agreement is very acceptable.

Thus both factor analysis and least-squares method give the same number of independent components. This is expected due to the equivalence of the two methods as shown in our earlier paper[9]. One of the components can be immediately identified as PEO which is dominant in concentration. The second component is very likely to be 'unreacted PMMA'. The third could be either the 'complex' between PEO and PMMA or a new structure, induced by thermal treatment, in PEO and further influenced by PMMA (the opposite is unlikely since we do not observe any spectral changes in PMMA on annealing). It has been noted earlier that the absorption of PMMA in the blends is masked by strong absorption of PEO making it impossible to visualize the spectral perturbations of PMMA on blending. If the spectrum of

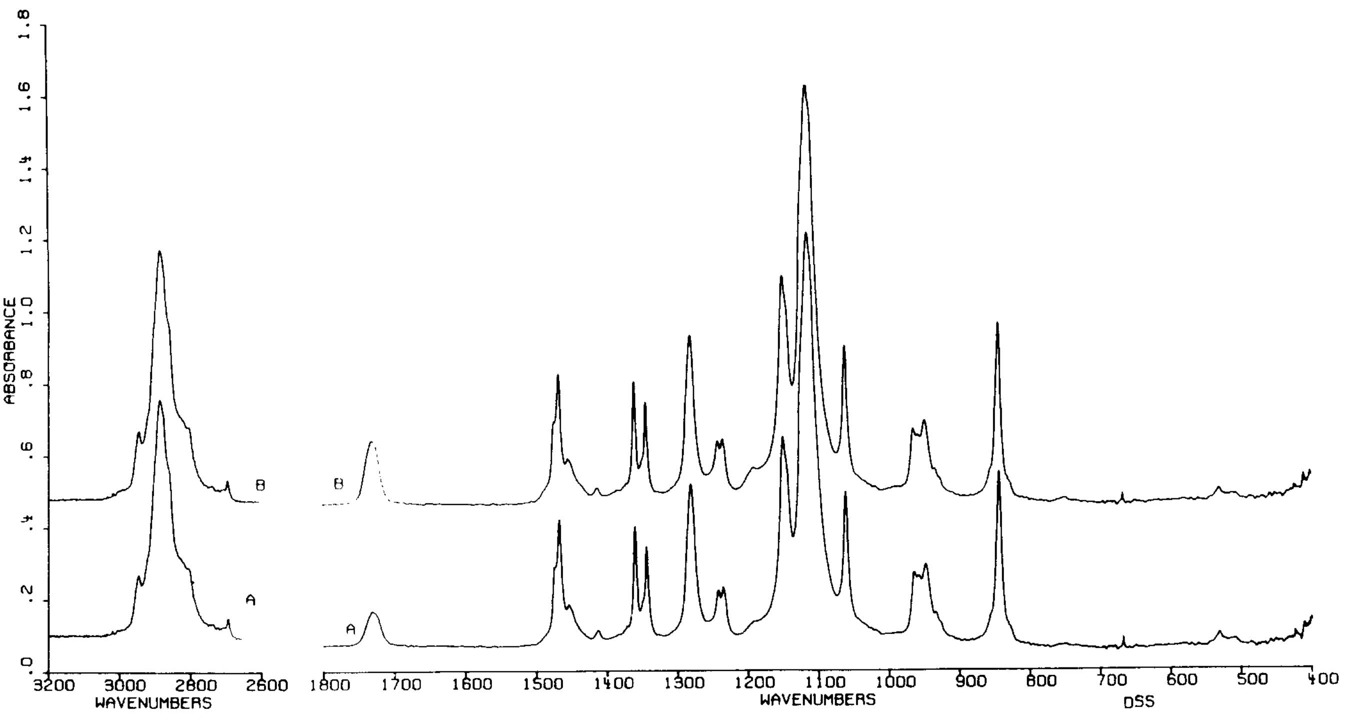

Figure 5 Experimental and calculated spectra of 10:1 blend. (A) Experimental; (B) calculated using eigenvectors

Table 3 Least-squares ciefficients in the spectral range 3100–2650 cm^{-1}

PEO:PMMA	PEO	PMMA	Difference spectrum from 10:1 blend
10:1	0.5021	0.3480	0.9999
10:2	0.5705	0.2063	0.7396
10:5	0.3092	0.4940	0.7821
10:4	0.3888	0.3035	0.7821

PEO could be subtracted from those of the blends it may be possible to see the spectral perturbations undergone by PMMA in the blends. We also expect to see the spectrum of PEO that has taken part in blending. It is to this end we now turn to the difference spectroscopy.

Difference spectroscopy

It is known that the method of spectral stripping[12] can be used in order to remove the spectrum of a component from the spectrum of a composite system. The method requires the presence of a characteristic band of the component in the spectrum of the composite system in a spectral range where the absorptions due to other components do not appear. In the case of the compounds studied in this work the band at 844 cm^{-1} serves this purpose as the absorption of PMMA in this region is negligible in comparison with that of PEO.

We have applied difference spectroscopy to two cases. First we subtract the spectrum of pure annealed PEL from the spectrum of PEO before annealing (spectrum A – spectrum B of *Figure 1*). Indeed one can follow a regular evolution of the spectrum, with annealing time as if PEO, as prepared from solution, were a mixture of two components (or two structures). One may speak of a starting more 'amorphous' polymer which evolves towards a more crystalline polymer. On the other hand one may also think of the starting materials as a mixture of two 'structures' which evolves towards a more stable one.

The spectrum of PEO after annealing is identical to the one reported by the Japanese school[9] and interpreted in terms of a helical structure whose factor group is isomorphous with the point group D(4π/7).

The difference spectrum reveals the existence of a very simple structure, with well defined bands, which are not easily ascribed to a highly distorted and coiled up 'amorphous' chain. It is rather more reasonable to think that another chain structure may be formed immediately upon casting the film together with the helical one. Upon heating, the concentration of the D(4π/7) chain increases and dominates at the expenses of the other seemingly less stable structure.

The spectral changes which are relevant to our analysis are the following:

(i) The doublet at 1358 and 1342 cm^{-1} (CH_2 wagging) before subtraction becomes a singlet at 1342 cm^{-1} whereas that at 1411 cm^{-1} disappears completely.

(ii) The strong band at 1280 cm^{-1} (CH_2 twisting) is not found in the difference spectrum.

(iii) The doublet at 1235 and 1241 cm^{-1} (CH_2 twisting) appears as a singlet with a peak at 1241 cm^{-1}.

(iv) The strong band at 1145 cm^{-1} disappears while a strong residual absorption is still found at 1105 cm^{-1}, below the very strong original doublet at 1116 and 1105 cm^{-1}.

(v) The sharp peak at 1060 cm^{-1} disappears.

(vi) The triplet centred near 950 cm^{-1} evolves into a sharp singlet at 962 cm^{-1}.

The simplification of the spectrum indicates that the molecular structure of the less stable modification has a more symmetric overall shape. This will be tested by the application of group theory.

We then apply difference spectroscopy in the case of the blend and remove from the spectrum of PMMA+PEO

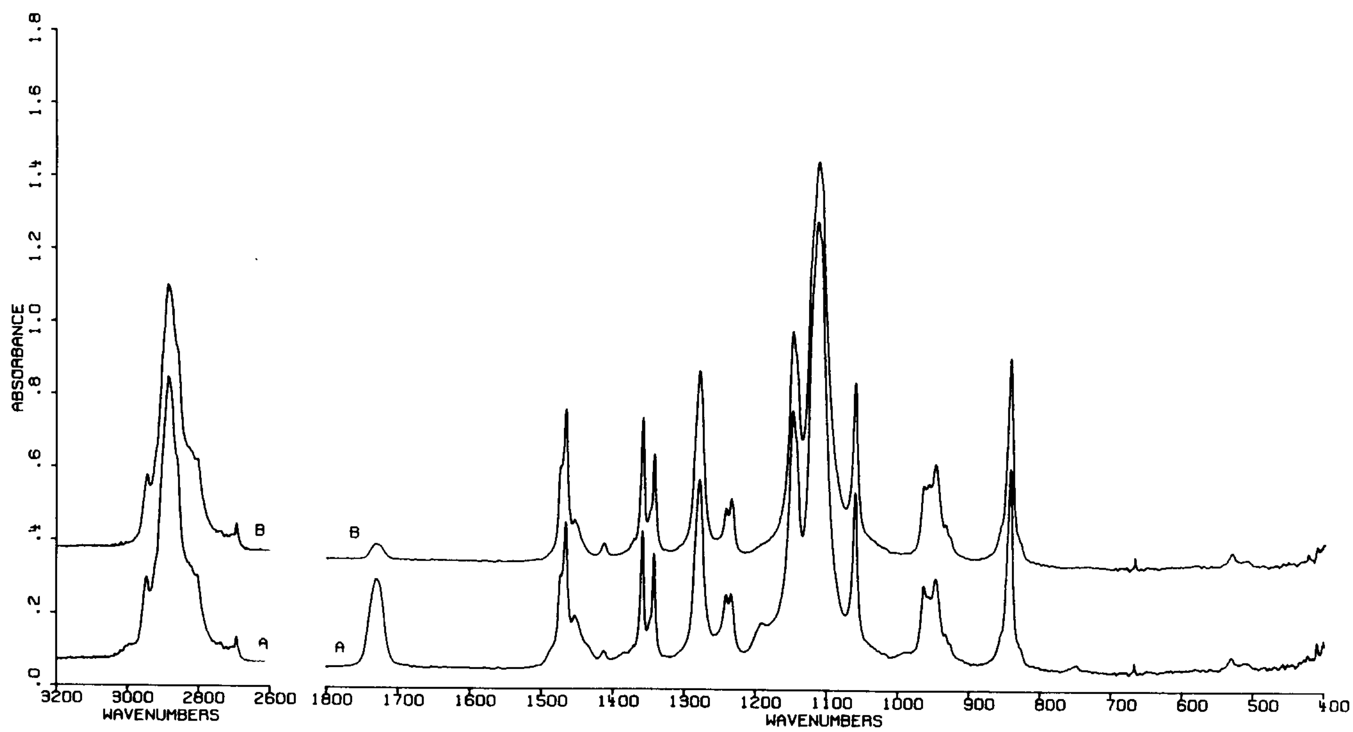

Figure 6 Experimental and calculated spectra of 10:2 blend. (A) Experimental; (B) calculated using least-squares method

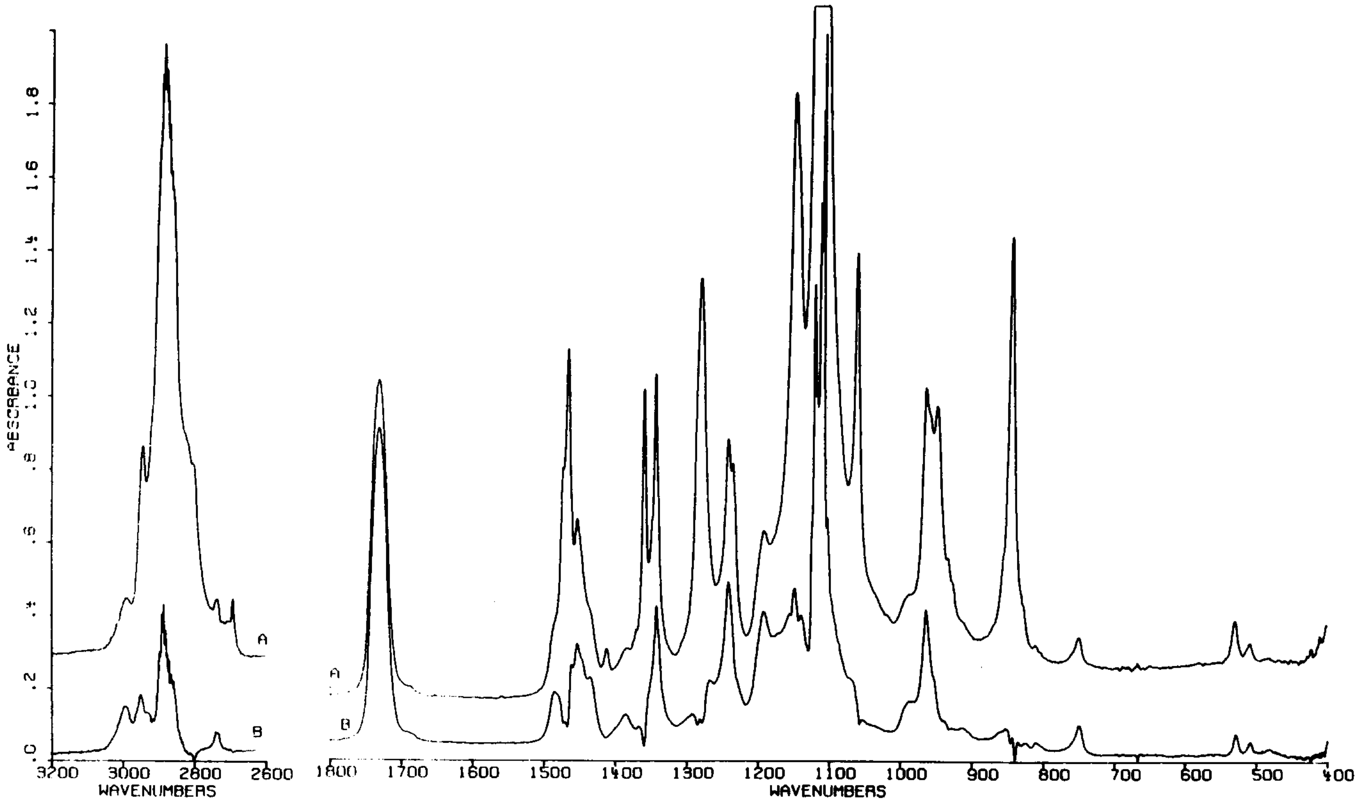

Figure 7 Infrared spectra of 10:3 blend. (A) Experimental; (B) difference spectrum after subtracting PEO using the band at 844 cm^{-1}

(3:10) the spectrum of PEO obtained in the same annealing conditions.

We are left with a spectrum which is made up by the spectrum of PMMA, seemingly unperturbed, and the spectrum of the material identical to that obtained in *Figure 3*.

One is then led to conclude that the addition of PMMA and thermal treatment has generated a material with a larger amount of 'the simpler' structure which has yet to be identified.

Regarding PMMA, it is difficult to observe in *Figure 7* spectral changes that might have taken place in it on blending with PEO. As an example we show in *Figure 7* a section of the difference spectra blown up for sake of clarity. From *Figure 8* it is clear that the spectrum of PMMA remains practically unchanged except for 1 or

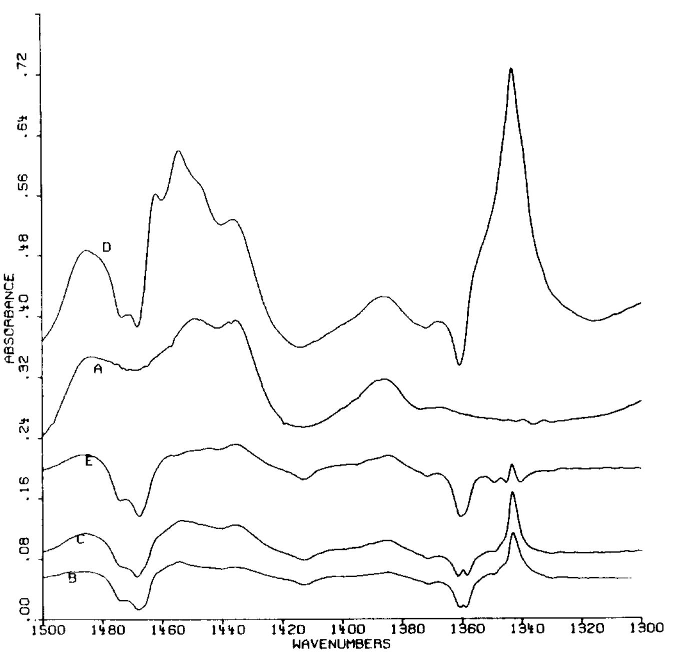

Figure 8 Blown up spectra in the range 1500–1300 cm^{-1}. (A) PMMA after annealing; (B) 10:1 blend difference spectrum; (C) 10:2 blend difference spectrum; (D) 10:3 blend difference spectrum; (E) 10:4 blend difference spectrum

2 cm^{-1} shifts of a few bands. One can then conclude that the intermolecular interactions of PMMA with PEO, if any, must be very weak.

Group theory

The suggestion from the difference spectrum that PEO takes another more symmetrical conformation implies that the helical structure of PEO has evolved into a planar zig-zag structure. Group theoretical analysis needs to be carried out in order to check the point group of the molecule and the corresponding selection rules.

The structure of the starting PEO has been studied first by Miyazawa *et al.*[13] by infra-red and later by Tadokoro *et al.*[14,15] using infra-red and X-ray diffraction. PEO takes up a helical structure with 7 chemical units in 2 turns (7/2 helix). the same authors point out the chain of PEO is flexible and could adopt other conformations including the planar zig-zag one[15]. The line group of the one dimensional crystal of PEO with 7/2 structure is isomorphous with the point group D(4π/7). The structure of the irreducible representation and the corresponding spectroscopic activities are the following:

$\phi = 0°$ 10 A_1 Raman active, and 9 A_2 infra-red active with parallel polarization.

$\phi = 103°$ 20 doubly degenerate E_1 modes active both in Raman and infra-red with perpendicular polarization.

$\phi = 206°$ 21 E_2 Only Raman active. Generally E_2 modes are difficult to be observed[16].

From the symmetry coordinates which are built for the point group D(4π/7) we consider only those which are related to the absorption bands observed in the spectrum of PEO and are related to the absorption bands observed in the spectrum of PEO and are pure, i.e. uncoupled with other modes, namely:

CH_2 wagging: 1411 (E_1), 1358 (E_1), 1342 (A_2)
CH_2 twisting: 1278 (E_1), 1234 (E_1), 1240 (A_2)

The C–O stretching, C–C stretching and CH_2 rocking modes are coupled with one another and account for the bands observed at 1103 (A_2), 958 (A_2), 1147 (E_1), 1116 (E_1), 1066 (E_1), 947 (E_1) and 844 (E_1).*

The vibrational assignments listed above are derived from normal coordinate analysis done by Yokoyama *et al.*[14] on the basis of a simplified valence force field.

For a planar zig-zag chain the line group is isomorphous with the point group D_{2h} and the structure of the irreducible representation is the following:

6 A_g (Raman) + 4 B_{1g} (Raman) + 5 B_{2g} (Raman) + 3 B_{3g} (Raman) + 4 A_u (inactive) + 5 B_{1u} (infra-red with parallel polarization) + 5 B_{2u} (infra-red with perpendicular polarization) + 6 B_{3u} (infra-red with perpendicular polarization).

With such a symmetry, in infra-red, we expect to find one CH_2 twisting mode (B_{2u}) and two CH_2 wagging modes (B_{1u} and B_{3u}). Moreover the number of C–O stretching and CH_2 rocking modes decreases from D(4π/7) to D_{2h}. Hence if PEO, after blending, takes a planar conformation we expect to find a simpler spectrum with fewer bands compared to the 7/2 helix.

Indeed, from the difference spectrum we observe only one CH_2 twisting at 1241 cm^{-1} while the others have disappeared (observation (ii) and (iii)). Moreover the whole frequency range of C–O stretching, C–C stretching and CH_2 rocking has been simplified. As to the CH_2 wagging, the number of bands expected for D_{2h} symmetry is two, while only one is observed. The fact that one band is missing may be ascribed to an intrinsically weak mode or to an accidental degeneracy of the two waggings at 1342 cm^{-1}. Examination of the corresponding symmetry coordinates show that the oxygen atom between the CH_2 groups may decouple the wagging vibrations thus giving rise to an accidental degeneracy (*Figure 9*).

Thus symmetry considerations on the basis of group theory strongly support the existence of a planar zig-zag conformation for PEO upon casting from solution and upon blending. Such planar conformation may occur as segments within a long chain originally completely helical or the entire chain may take the planar conformation and cluster into domains. On the other hand planar segments cannot be too short if optical selction rules have to be satisifed as clearly as we find for this case. If the planar segments are embedded in a helical structure we must speak of 'local symmetry' and 'local selection rules'. When Born's cyclic conditions are fulfilled (i.e. when the selection rules for an infinite chan can be applied) depends on the extent of intramolecular coupling.

The first relevant conclusion is that upon blending, PMMA forces the molecule of PEO to be preferentially coplanar. The third component whose existence was suggested by factor analysis and least-squares procedures is then identified in the planar zig-zag structures. Whether the forcing of coplanarity is induced by preferential strong interactions with PMMA or whether is only a physical sterical encumbrance has yet to be analysed.

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*The frequencies listed here are taken from Ref. 14 and may differ slightly from those read from our spectra

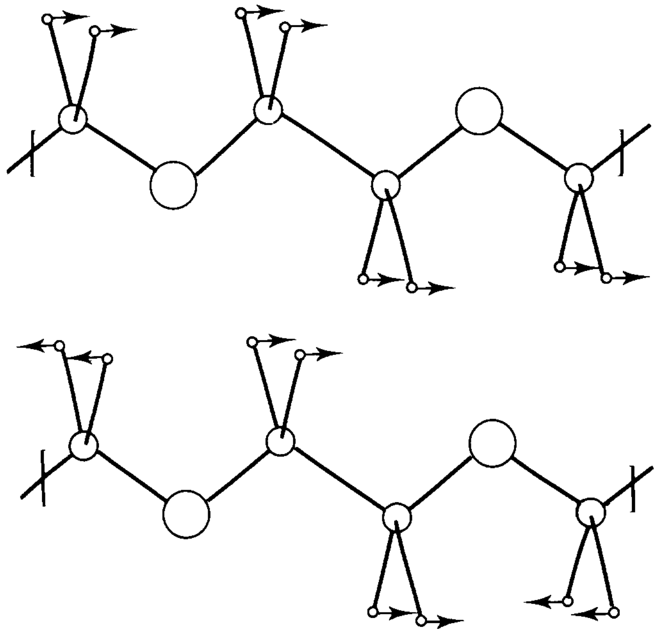

Figure 9 Shape of infrared active wagging modes of CH_2 groups of PEO in planar zig-zag conformation

Use of atomic charges from intensity spectroscopy for the study of intermolecular interactions

The intermolecular interactions depend on the electronic charge distribution in the molecules. The study of integrated infra-red intensities of small model molecules has allowed us to determine 'experimental' atomic charges and charge fluxes for several kinds of molecules[17]. These charges nicely compare with those calculated by sophisticated quantum mechanical methods[18] and correlate well with electronegativities of atoms, bond lengths and bond force constants[19]. With such charges it has been possible to predict which hydrogen atoms are able to form weak or strong hydrogen bonds[20] and which atoms in a polyatomic molecule can act as proton donor or acceptor[21]. The sites and strengths of intermolecular interactions nicely fit the experimental ones[21,22]. Hence we have tried to use the information derived from intensity spectroscopy as small molecules to understand the possible intermolecular interactions in blends studied in this work.

In order that PEO and PMMA can form blends of 'chemical' type there must exist sites in the molecule with excess $(-\Delta q)$ or deficit $(+\Delta q)$ of negative charge. From molecular models it has been shown that to make a complex of sizeable bond strength (a few kcal mole^{-1}) Δq should at least be $\sim 0.2e$ if the two interacting atoms are separated by a distance equal to the sum of their van der Waals radii (2-3 Å)[21].

In the case of PEO (*Figure 12a*), using the results from simpler ethers[23], the oxygen atoms should have the following charges: $\Delta q(O_1)=\Delta q(O_2)\simeq -0.3e$. Moreover there should be no sites with strong localization of positive charge as the hydrogen atoms of CH_2 groups, for ethers, are even more weakly positively charged than the hydrogen atoms of n-alkanes[17,24] which are known not to form 'chemical' complexes[20,21]. Hence PEO can act as proton acceptor, but not as proton donor in 'chemical' blends.

In PMMA there are sites with localized negative charge; in analogy with ethers and ketones[23] $\Delta q(O_1)=\Delta q(O_2)\simeq -0.3e$ (*Figure 12b*). Also in PMMA there should not be any strongly positive hydrogen atom; the hydrogens of CH_2 and $(CH_3)_1$ are similar to those of n-alkanes and the hydrogens of $(CH_3)_2$ should be even less positive being similar to those of ethers. However, C_3 atom in sp^2 hybridization could be strongly positive $(\Delta q=0.45e)$. In the case of formaldehyde[25], where the carbon atom is less positive, there is some evidence[26] that formaldehyde forms molecular complexes acting as proton donor at the site of the carbon atom. Hence PMMA can act both as a proton acceptor through the negative oxygens and as a proton donor through the positive carbonyl carbon atom.

The simultaneous occurrence of both negative and positive sites demands that the structures of interacting molecules be such as to bring the oxygens of PEO into the vicinity of carbonyl carbon atoms of PMMA in order to form a chemical blend. This may be sterically possible.

While the structure of PEO is known either as a helix or as a planar zig-zag as seen in this work, the structure of PMMA is instead less clear. From the value of T_g reported in Ref. 2, the sample we studied seems to be atactic. In general the atactic PMMA can be considered as a block copolymer with iso- and syndiotactic structures[27]. For the sake of convenience of discussion let us consider the isotactic and syndiotactic PMMA separately.

Syndiotactic PMMA should have a planar zig-zag structure as in the case of many other syndiotactic vinyl polymers[28]. Its repeat distance can be estimated to be approximately 4.8 Å. It is seen from *Figure 11a* that a sterically preferred interaction could occur if the planar zig-zag form of PEO brings its oxygen atoms closer to the

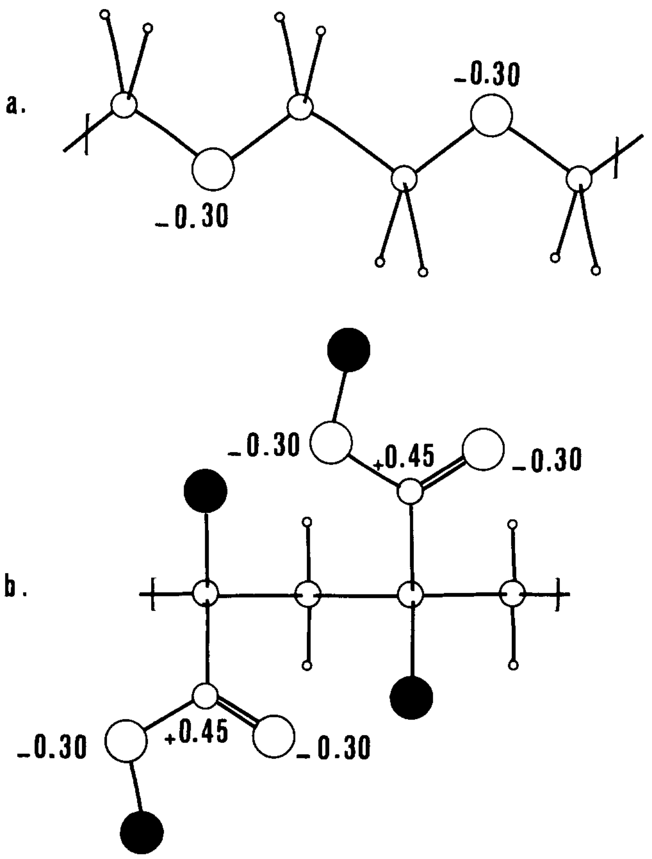

Figure 10 Atomic charges in PEO and PMMA (approximate as taken from model molecules). (A) PEO; (B) PMMA

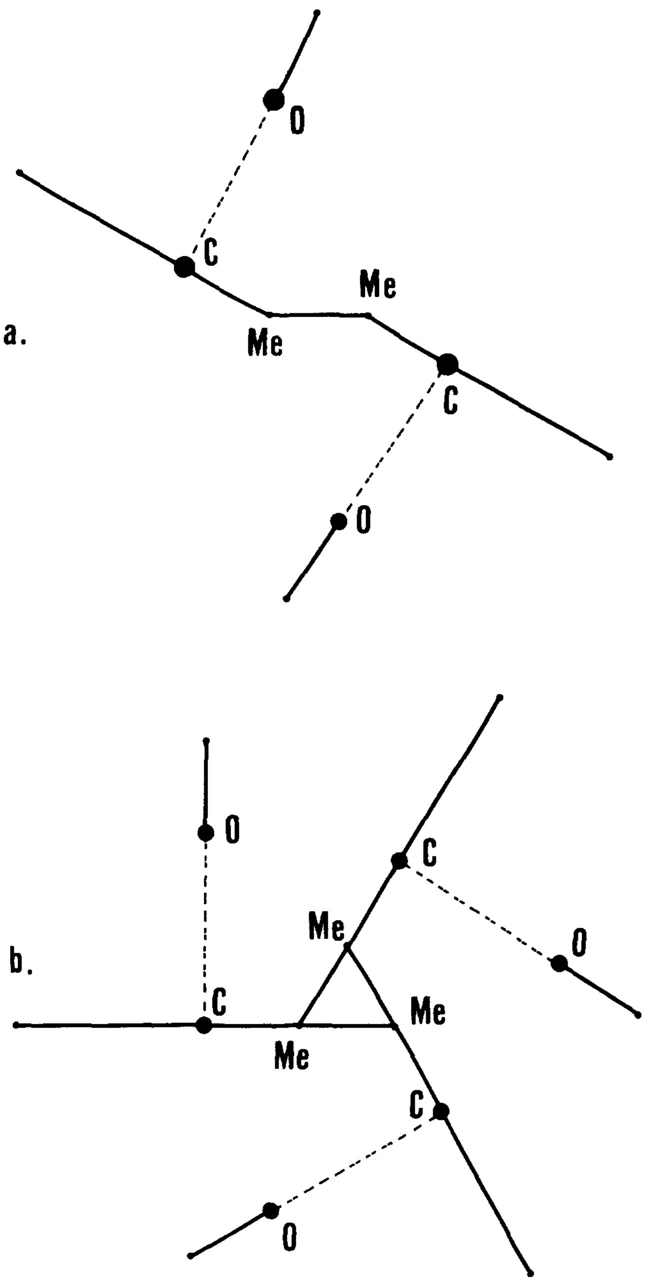

Figure 11 Sketch of the approach of planar zig-zag PEO. (A) Towards syndiotactic PMMA; (B) towards isotactic PMMA

carbonyl carbon atoms of PMMA along the Y-axis in the YZ-plane. Since the estimated repeat distance of trans planar PEO is approximately 7.0 Å, the mismatch is fairly large and prevents every oxygen atom of PEO interacting with every carbonyl carbon atom of PMMA in the syndiotactic structure. Some periodicity of interaction may occur only at longer distances. Accepting the estimated repeat distances of 4.8 Å for PMMA and 7.0 Å for PEO, every fifth oxygen atom of PEO interacts with every seventh carbonyl carbon atom of PMMA that are on the same side of the chains. Independently from the exact periodicity, if the interactions occur, they take place at a few sites at a large distance one from the other.

If we consider the isotactic PMMA it must take up helical structure of the type 3/1 (*Figure 11b*) as in other isotactic vinyl polymers[28]. The repeat distance as measured for other 3/1 helices is approximately 6.5 Å. In this case there is almost a 1:1 correspondence between the repeat distances of isotactic PMMA and planar PEO thus offering more sites for interaction. If this is the case, in the ideal situation, isotactic PMMA interacts with three planar PEO chains since there are three channels around the three-fold helix.

Using the atomic charge, as discussed before, one can estimate that even in both the ideal isotactic and syndiotactic cases there cannot be a strong 'chemical' interaction between PMMA and PEO since the attractive forces between the negatively charged oxygen atoms of PEO and positively charged carbonyl carbon atoms of PMMA are weakened by the repulsive forces offered by the negatively charged oxygen atoms of PMMA. In conclusion, the electronic charge distribution of PEO and PMMA do not allow them to form strong blends through strong intermolecular forces. Due to the occurrence of both attractive and repulsive forces having their origin in the carbonyl group the interaction must be very weak and quite possibly of the magnitude of van der Waals type. This accounts for the almost unchanged spectra of PMMA on blending with PEO.

DISCUSSION

The systematic use of the various theoretical and experimental methods previously discussed in this paper has allowed us to gain a deeper understanding of the structure of PEO/PMMA 'blends'. Factor analysis and least-squares curve-fitting have indicated the existence of a third component which could be the result of formation of the blend or a structural change in the starting material. Difference spectroscopy has allowed us to bring up the spectrum of the third component which is a more symmetric form of PEO. Selection rules based on group theory have lead to the conclusion that this new form of PEO is planar zig-zag. This planar structure is also formed in mixture when the polymer is prepared as cast film from solution.

The use of 'experimental' atomic charges derived from vibrational intensities of small molecules gave an idea of the sites of intermolecular interactions and their magnitude. Thus PEO and PMMA will always form 'blends' with weak interactions approaching those of van der Waals type. The compatibility of PEO/PMMA is more 'physical' than 'chemical'. Since, ideally, PMMA can have a isotactic or syndiotactic structure the interactions seem to be preferred with the isotactic structure. Indeed due to the approximate matching of the repeat distances the number of sites of interactions is larger than in the syndiotactic structure. Further, each chain of isotactic PMMA can interact with three chains of PEO compared to two in syndiotactic PMMA.

In reality PMMA, often, is mostly atactic. The determination of tacticity of PMMA has been carried out mainly with n.m.r. spectroscopy[27,29]. From infra-red very little is known on the possibility of judging the microtacticity of our samples. Schneider *et al.*[30] suggest that an infra-red band at 753 cm^{-1} is characteristic of the isotactic structure. We do observe this band in the spectrum of PMMA used in our experiments thus suggesting a predominantly isotactic structure. However, the glass transition temperature reported as 100°C–110°C in Ref. 2 characterizes a predominantly atactic material[27].

For an atactic PMMA considered mostly as a copolymer os iso- and syndio- structures the interactions discussed for the case of perfect iso- and syndio- structures will only take place on small segments embedded in an irregular environment. During the annealing process of our samples the chains of PEO and PMMA, because of the thermal energy provided, gain enough mobility to uncoil and to move such as to make the 'blending' process easier. It is impossible to decide, in such a complex structure, whether the blending takes place on the isotactic or syndiotactic segments.

CONCLUSION

From this analysis a suggestion relevant to material science can be offered, namely, since PMMA with predominant iso- or syndiotactic structure can be synthesized, blends of two types could be prepared with PEO. In principle both blends could be formed, but that with isotactic PMMA should be relatively more stable and more compatible. Moreover, the physical properties of the two kinds of blends should be strongly different because the arrangement of the polymer chains in the material is drastically different. New experiments are needed along these lines.

ACKNOWLEDGEMENT

One of the authors (GRR) is grateful to 'The International Centre for Theoretical Physics (ICTP)', Trieste, Italy, for a grant under the programme 'The ICTP Programme for Training and Research in Italian Laboratories', which made his stay in Italy possible and undertake this work.

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