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Blends and Complexes of Poly(monomethyl itaconate) with Polybases Poly(*N*,*N*-dimethylacrylamide) and Poly(ethyloxazoline). Association and Thermal Behavior[†]

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ABSTRACT: This paper reports on the interpolymer complex formation and polymer blends between poly(monomethyl itaconate) (PMMI) and two polymer acceptors poly(*N*,*N*-dimethylacrylamide) (PDMA) and poly(ethyloxazoline) (PEOX). We have found that the formation or inhibition of interpolymer complexes for these systems strongly depends upon the solvent medium. The stoichiometry of the complexes prepared from methanol solutions has been calculated from elemental analysis, resulting in a stoichiometry near a 1:1 ratio. Specific interactions of PMMI/PDMA and PMMI/PEOX complexes and blends have been characterized by FTIR. Strong hydrogen bonding for complexes and blends has been found. Finally, a calorimetric and thermogravimetric study of the complexes and blends has been performed in a wide temperature range.

Introduction

In the development of new polymer materials blending is one of the ways that has received large interest in the last years. Most of the miscible blends reported concern polymer pairs that establish intermolecular specific interactions. Probably, the most extended type of specific interaction responsible for polymer−polymer miscibility is hydrogen bonding. In fact, the introduction of small amounts of complementary groups in the components of the blend is accepted as an adequate method for polymer−polymer compatibilization.

When a large number of intermolecular interactions are present, highly associated materials can be obtained. Usually, they are named interpolymers or polymer−polymer complexes. Polymer−polymer complexes are frequently obtained by mixing a polyacid with a polybase using a common solvent. Depending on the extension of interpolymer association (usually controlled by concentration, temperature, and the chemical structure of the solvent and polymers) a precipitate can be formed. Most of the interpolymer complexes have been studied in water solutions, because they can be considered as models for interactions between biological macromolecules. A large number of works related to polymer−polymer complexation has been published, and some excellent reviews are devoted to the subject.[1,2] Usually, precipitation in these systems is attributed to the cooperative effect of specific interactions leading to large sequences of associated groups. This picture has been questioned by Wang and Morawetz[3] and Yang et al.[4] on the basis of the experimental results obtained for homopolymer/copolymer systems. In these systems the number of specific interactions could be controlled by altering the copolymer composition. Nevertheless, recent results in the same type of system[5,6] seem to agree with a theoretical model based on large sequences of hydrogen bonding developed by Iliopoulos and Audebert.[7]

The association and properties in the solid state of that kind of material are much less studied. Our research group is interested in the study of polymer blends and complexes formed by poly(monoitaconates) and polybases. Poly(mono itaconates) are strong donor polymers obtained by polymerization of monomers derived from the partial esterification of itaconic acid (a diacid obtained from natural sources). In this paper we present a study of association of the first member of this family, the poly(monomethyl itaconate) (PMMI) with two typical polybases: poly(*N*,*N*-dimethylacrylamide) (PDMA) and poly(ethyloxazoline) (PEOX). Both polymers are isomers that contain amide groups in their chemical structures. As will be presented, the specific interactions in these systems strongly depend on the solvent used for the mixture. These specific interactions will be quantitatively characterized by FTIR spectroscopy. The thermal behaviors of the obtained materials have been also studied.

Experimental Part

Poly(*N*,*N*-dimethylacrylamide) (PDMA) was bulk polymerized at 60 °C with 0.5% azobis(isobutyronitrile) (AIBN) as initiator under a N_2 atmosphere. The monomer was supplied by Aldrich Chemical Co. and was used without further purification. The molar mass of the polymer was measured viscometrically in an Ubbelohde type viscometer in methanol, at 25 °C, using the following equation:[8]

$$[\eta] = 1.75 \times 10^{-4} M_{\mathrm{v}}^{0.68}\ (\mathrm{dL/g})$$

which leads to the value $M_{\mathrm{v}} = 2.9 \times 10^5$ g/mol.

Poly(ethyloxazoline) (PEOX) is a Polysciences product and was purified by solution−precipitation in the methyl ethyl ketone/hexane pair. According to the supplier the molar mass of the sample is $M_{\mathrm{w}} = 50\,000$ g/mol.

Monomethyl itaconate was obtained by esterification of itaconic acid with methanol, using acetyl chloride as catalyst, according to a method previously described.[9] The monomer was characterized by FTIR, ^{1}H-NMR, and ^{13}C-NMR. The poly(monomethyl itaconate) was obtained by free radical bulk polymerization using 0.3% AIBN as initiator under a N_2 atmosphere at 80 °C. The polymer was characterized by light scattering in methanol solution, at 25.0 °C. The obtained molar mass was 130 000 g/mol.

The complexes were prepared by mixing methanolic solutions (2% wt/v) of both polymers, adding the PMMI solution on the PDMA or PEOX one. After 4 days, to assure equilibrium conditions, the precipitate was separated by centrifuga-

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[†] To Claude Strazielle, his memory will always remain with us.

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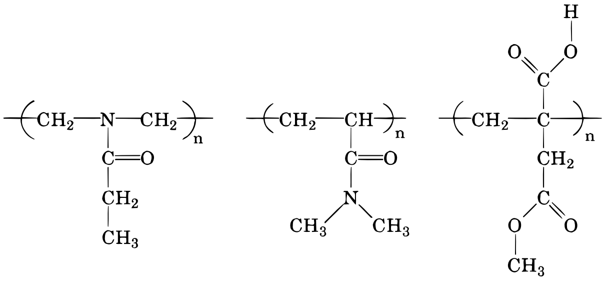

PEOX PDMA PMMI

Figure 1. Chemical structures of poly(ethyloxazoline) (PEOX), poly(*N*,*N*′-dimethylacrylamide) (PDMA) and poly(monomethyl itaconate) (PMMI).

tion, washed with methanol, and dried under vacuum for 3 days, at 65 °C, to assure total elimination of residual solvent. The blends were prepared by mixing 2% wt/v solutions of both components, using DMF as the solvent for the PMMI/PDMA pair and ethylene glycol for PMMI/PEOX. The solvent was evaporated on Petri dishes, at 60 °C, under vacuum, and the cast films were kept under vacuum to assure total removal of residual solvent. The strong acceptor character of DMF makes very difficult its total removal from the samples. Therefore, special care during this process has to be taken. We have found that when the samples are placed in a vacuum chamber, for 24 h, with a small amount of methanol, DMF is completely removed. It seems that methanol replaces the DMF in the sample. Finally, the methanol is removed according the above treatment. The total removal of DMF has been checked by infrared spectroscopy, using one of the vibration modes of DMF placed at 698 cm^{-1}, since this band does not overlap any of the other bands of the polymers used in this paper.

The elemental analysis of the complexes was done using a Perkin-Elmer 2400CHN elemental analyzer, the sample weight being about 2 mg in all cases. The thermal behavior of blends and complexes was studied with a Mettler TA4000 DSC and a Mettler TG50 thermobalance. The weight of the samples was about 8 mg in all cases and the scan speed was 10 °C/min under a nitrogen atmosphere (200 mL/min).

Infrared spectra of blends and complexes were recorded on a Nicolet-520 Fourier transform infrared spectrophotometer (FTIR). Spectra were taken with a resolution of 2 cm^{-1} and were averaged over 150 scans. In the case of blends, the samples were prepared by directly casting the solutions on KBr pellets. This process was done under vacuum at a temperature of 60 °C. In the case of complexes, purified samples still swollen with methanol were compressed between KBr pellets. The resulting films were dried under vacuum.

Experimental Results

The addition of a PMMI methanolic solution to a PDMA or PEOX one forthwith leads to a precipitate formation. The phenomenon is observed even in very dilute solutions ($\approx$0.05% wt/v). Precipitation in such systems is generally attributed to cooperative hydorgen bonding between components, yielding insoluble species, which are termed polymer−polymer or interpolymer complexes. The chemical structures of both components (Figure 1) support this hypothesis, and besides, the obtained precipitate is no longer soluble in the solvent from which it is obtained. Thus, we are dealing with a strong associated material, as will be confirmed by infrared spectroscopy.

The yield and the kinetics of the interpolymer complex formation are generally influenced by several factors, such as solvent medium, ionic strength, temperature, etc.[1,2] One of the most important factors is the solvent medium in which the process takes place. The solvent may play a decisive role on the complex formation, because depending on its chemical structure it may compete with the polymeric chains in interacting with donor or acceptors sites. Accordingly, a study about the complexing capacity of these two polymer pairs in different common solvents has been performed. The results are summarized in Table 1.

Table 1. Complexing Ability of Some Common Solvents of PMMI, PDMA, and PEOX, Starting from a Solution with a Concentration of 2% wt/v

solvent	PMMI/PDMA	PMMI/PEOX
water	no	yes
DMSO	no	no
N,*N*-dimethylacetamide	no	no
N-methylformamide	no	no
N,*N*-dimethylformamide	no	no
methanol	yes	yes
ethylene glycol	yes	no

The results shown in this table fairly display that solvent medium dramatically influences the complexation behavior of our systems. When solvents with a strong basic character are employed, such as DMSO or amides, the solvent competes favorably with PDMA. Taking into account that small molecules have more mobility than the polymer chains, these last ones block the acid sites of PMMI for PDMA or PEOX, inhibiting the formation of the interpolymer complex. When we use solvents with a weaker donor or acceptor character or a strong ability for self-association, such as methanol, the acid−base interaction between PMMI and PDMA or PEOX chains are favored, leading to the formation of a interpolymer complex that forms a precipitate.

In other solvent media (water or ethylene glycol) complexation is observed for one system but not for the other. The case of water solutions is of special interest due to the large number of polymer−polymer complexes studied in this medium.[1,2] In this solvent no complex formation is observed for the PMMI/PDMA pair. This behavior is associated with the acid−base dissociation equilibria of the polyacid in aqueous media, that reduces the carboxylic groups available for the cooperative interaction responsible for the complex formation. Thus, if a small amount of a strong acid (such as HCl) is added to the mixture, a white precipitate readily appears. The formation of PMMI/PEOX complexes in pure water suggests a higher hydrophobic character in PEOX than in PDMA. In fact a lower critical solution behavior has been found for PEOX but not for PDMA.[10] In the same way, the behavior observed in ethylene glycol is probably due to differences in its solvating power over the two acceptor polymers.

According to these results, in the case of the PMMI/PDMA and PMMI/PEOX systems it is possible to obtain, depending on the experimental conditions, interpolymer complexes and blends. Materials with a composition imposed by the interactions in the system will be named complexes, as those obtained from methanol solutions. On the contrary, the materials prepared by solvent casting from solutions based in solvents with a strong acceptor character that prevents polymer−polymer association will be named blends. We will analyze some of the characteristics of both kinds of materials.

The study of the PMMI/PDMA and PMMI/PEOX complexes has been always performed using samples obtained from methanol solutions. The choice of this solvent is due to its high complexing character and the ease with which it can be removed from the precipitates.

PMMI/PDMA blends were prepared by casting from DMF solutions, because this method leads to clear films and miscible systems. Surprisingly, the same method applied to PMMI/PEOX blends results in opaque films

Table 2. Yields and Elemental Compositions of PMMI/PDMA and PMMI/PEOX Complexes Botained from 2% wt/v Methanol Solutions, for Several Compositions of the Feed Mixture

feed comp		PMMI/PDMA		PMMI/PEOX	
PMMI (wt %)	PMMI (mol %)	PMMI (mol %)	yield (wt %)	PMMI (mol %)	yield (wt %)
20	14.7	51.8	25	47.4	18
40	31.4	53.2	54	50.2	52
60	50.8	53.6	83	53.3	82
80	73.3	60	65	59.3	61

and immiscible blends. This is good evidence of the influence of the solvent on miscibility behavior ($\Delta\chi$ effect[11]). In order to prepare PMMI/PEOX miscible blends by solvent casting, ethylene glycol was employed (solvent with a complexing character for PMMI/PDMA pair). Consequently, the analysis of both types of blends are not directly comparable.

Complex Stoichiometry. Generally, the composition of interpolymer complexes corresponds to a simple ratio of the monomer units of the components,[1,2] although it may be dependent on feed composition in the preparation process.[4,12] There are several methods to determine the complex stoichiometry. In our system, elemental analysis is an appropriate tool because PDMA and PEOX have a nitrogen atom in both monomeric units, while in PMMI this chemical element is not present. In Table 2 are reported the results obtained by elemental analysis of the PMMI/PDMA and PMMI/PEOX complexes prepared from methanolic solutions (2% wt/v) at different feed compositions. The obtained results show a close correlation to 1:1 stoichiometry for almost all compositions. Only when the feed composition is rich in PMMI is a slight deviation leading to a 3:2 composition observed.

To simplify the understanding of the following discussion, we will denote the complexes by referring to their feed composition. However, it must be remembered that besides this nomenclature all of them have almost the same composition, very close to the blends with 60% of PMMI.

The observed 1:1 stoichiometry for most of the PMMI/PDMA and PMMI/PEOX complexes agrees with the results obtained for other similar polymer systems such as poly(4-hydroxystyrene)/poly(*N*,*N*-dimethylacrylamide),[12] poly(monomethyl itaconate)/poly(*N*-vinyl-2-pyrrolidone),[13] and poly(monoethyl itaconate)/poly(*N*-vinyl-2-pyrrolidone).[9] This preferred stoichiometry is confirmed if we analyze the evolution of the yield of complex formation (regarding the total weight of the two polymers) as a function of feed composition for constant total concentration (Table 2). We can see that the maximum yield in both systems is reached for compositions with 60% (wt/wt) PMMI, corresponding to a 1:1 ratio in molar repetitive units.

Specific Interactions. According to the chemical structures of the polymers involved in the interpolymer complexation process (Figure 1), it may be expected that an extensive hydrogen bonding between both components (involving carboxyl and amide groups) will be the origin of the interpolymer complexes. In the last years Fourier transform infrared spectroscopy (FTIR) became one of the most powerful tools in the identification and quantitative analysis of hydrogen bonding in polymers. We have performed a study of the main characteristics in the infrared spectra of complexes and blends prepared for these systems.

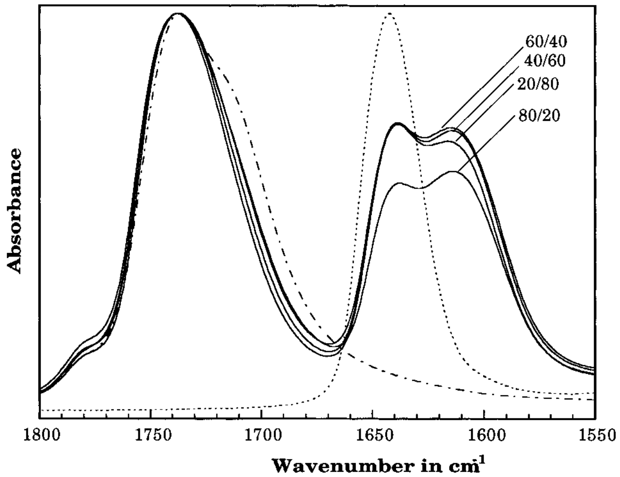

Figure 2. Autoscaled infrared spectra in the 1550−1800 cm^{-1} region for PDMA (- - -), PMMI (-•-) and PMMI/PDMA complexes with different feed compositions (wt/wt).

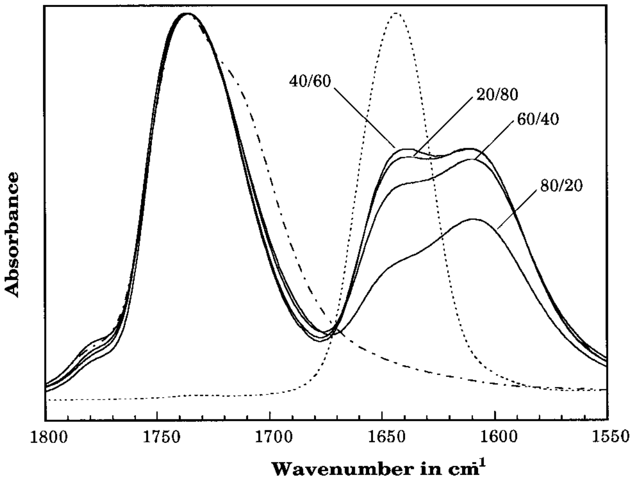

Figure 3. Autoscaled infrared spectra in the 1550−1800 cm^{-1} region for PEOX (- - -), PMMI (-•-) and PMMI/PEOX complexes with different feed compositions (wt/wt).

The groups involved in the hypothetical hydrogen bonding must be the hydroxyl placed in the carboxyl group of PMMI and the carbonyl placed in the pendant group of PDMA or PEOX. The carbonyl stretching region for pure components is displayed in Figures 2 and 3. This is a quite complicated spectral region in PMMI for several reasons. First, this polymer shows two different carbonyl groups on its monomer unit: those corresponding to ester and those corresponding to acid. It is well-known that polyacids tend to self-associate by formation of dimers, splitting their carbonyl stretching bands.[14] Moreover, in PMMI we can expect hydrogen bonding between hydroxyl and ester carbonyl groups. Finally, poly(mono itaconates) tend to form some anhydrides during the polymerization process,[15] these anhydrides are manifested by bands at 1781 and 1859 cm^{-1}, respectively. Accordingly, PMMI shows a wide carbonyl band.

PDMA and PEOX present two principal bands in this region, located at 1642 and 1643 cm^{-1}, respectively. These bands correspond to the amide I mode in both polymers. The amide I band is a composed spectral mode, but the largest contribution corresponds to the carbonyl stretching in the amide group. In the future these bands will be referred to as the carbonyl stretching band in both polymers. Fortunately, these are single bands and only a slight overlapping takes place between

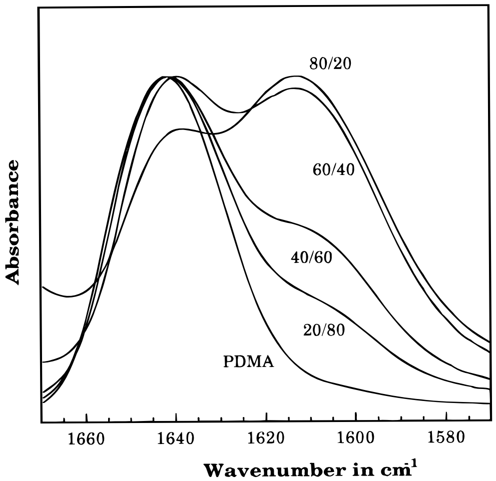

Figure 4. Autoscaled infrared spectra in the 1570−1670 cm^{-1} region for PDMA and PMMI/PDMA blends with different compositions (wt/wt).

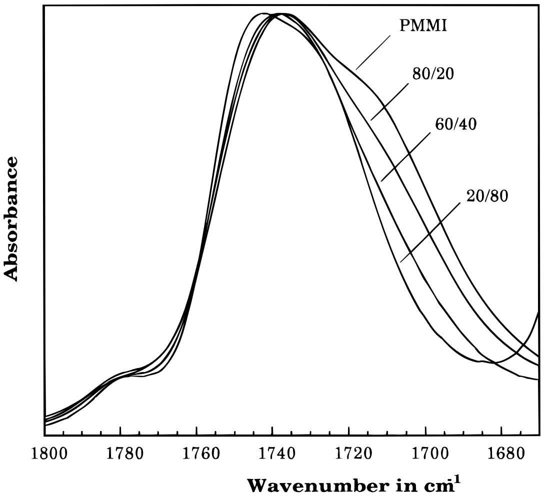

Figure 5. Autoscaled infrared spectra in the 1800−1670 cm^{-1} region for PMMI and PMMI/PDMA blends with different compositions (wt/wt).

PMMI and PDMA or PEOX carbonyl bands, allowing a quantitative analysis of hydrogen bonding in the complexes and blends.

Figures 2 and 3 show the carbonyl stretching region for PMMI/PDMA and PMMI/PEOX complexes with different feed compositions. Spectral inspection evidences that in both cases a new band is present at lower wavenumbers. This band is placed at around 1609 cm^{-1} and can be attributed to PDMA and PEOX hydrogen-bonded carbonyl groups. We must point out that the spectra of the complexes show bands whose relative intensities are close, in agreement with a similar complex composition for different feed ratios. Hydrogen bonding also influences the carbonyl stretching band of PMMI in complexes. In Figures 2 and 3 a clear decrease in the contributions placed at lower wavenumbers in the band can be observed. This effect seems to be a consequence of the replacement of carboxyl−carboxyl interactions by carboxyl−amide in the complexes. Similar results have been reported by Lichkus et al.[16] for poly(ethylene-*co*-methacrylic acid)/PEOX blends.

As we have previously reported, some solvents can prevent the complex formation, which makes it possible to prepare PMMI/PDMA blends of different compositions. Figures 4 and 5 show the infrared spectra in the carbonyl stretching region for blends prepared from DMF solutions. Again, a band at 1609 cm^{-1}, corresponding to hydrogen-bonded PDMA appears (Figure 4). The relative intensity of this band clearly depends on polymer blend composition. Thus, as the PMMI content of the blend increases, the relative intensity of the associated PDMA band (lower wavenumber) is higher than the nonassociated PDMA one (higher wavenumber). In fact, as the percentage of PMMI in the blend increases there are more hydroxyl groups available to hydrogen bonding with PDMA carbonyl ones. In the same way, the lower wavenumber contribution in the carbonyl stretching band of PMMI decreases as the content of PDMA increases (see Figure 5).

For PMMI/PEOX blends obtained from ethylene glycol solutions similar results are obtained; i.e. a new band placed at lower wavenumbers and with a relative intensity depending on blend composition is observed.

The percentage of PDMA and PEOX carbonyl groups associated and nonassociated in blends and complexes can be determined by using spectral curve fitting methods. Special caution must be taken in the fitting procedure because the final results can be affected by the partial overlapping of the bands previously reported. Thus, the contributions at higher wavenumbers in the amide I bands of PEOX and PDMA closer to the PMMI carbonyl band have been excluded for the fitting. The Gaussian line shape function was employed in the fitting procedure. This line shape function allows a good fitting for the carbonyl bands in the pure components as well as in the blends and complexes.

In Tables 3−6 the obtained results for the spectral fitting of the carbonyl stretching bands of PDMA and PEOX in complexes and blends are shown.

From the calculated values of the absorbance of the associated (A_A) and nonassociated (A_F) contributions it is possible to determine the fraction of nonassociated carbonyl groups f_{CO}^{F}:

$$f_{CO}^{F} = \frac{A_F}{A_F + \frac{\epsilon_F}{\epsilon_A} A_A} \qquad (1)$$

The procedure requires the ratio of molar absorption coefficients of both spectral contributions (ϵ_F/ϵ_A). The relative spectral contributions of the associated and nonassociated carbonyl groups in our systems depend strongly on temperature. This behavior can be used in the evaluation of the ratio of molar absorption coefficients.[17,18] In particular, we have observed that the total area of the carbonyl stretching bands of PDMA an PEOX remains roughly constant as a function of temperature. Then, we can consider that the molar absorption coefficients for the associated and nonassociated contributions are similar and $\epsilon_F/\epsilon_A = 1$. The fraction of nonassociated carbonyl groups calculated for blends and complexes according to eq 1, are included in Tables 2−5.

The evolution of f_{CO}^{F} as a function of the composition for complexes and blends is displayed in Figure 6. All blends studied in this paper show in both systems a similar behavior. The association in the system increases the higher the content in PMMI, according with the presence of a larger number of carboxyl groups available for hydrogen bonding. In this figure the real composition of the complexes is plotted, determined by their elemental analysis (Table 2). This procedure allows a direct comparison with the blends. An interesting result for both systems is the coincidence in the degree of association between the complexes and the

Table 3. General Results Obtained for the Curve Fittings Performed on the Carbonyl Band in the Case of PMMI/PDMA Complexes

	free carbonyl band			associated carbonyl band			
PMMI feed (wt %)	wavenumber (cm^{-1})	width (cm^{-1})	rel area (%)	wavenumber (cm^{-1})	width (cm^{-1})	rel area (%)	f^{F}_{CO}
20	1642	28	36.5	1610	42	63.5	0.37
40	1642	28	35.9	1609	42	64.1	0.36
60	1642	28	35.7	1609	42	64.3	0.36
80	1642	28	33.5	1609	42	66.5	0.34

Table 4. General Results Obtained for the Curve Fittings Performed on the Carbonyl Band in the Case of PMMI/PEOX Complexes

	free carbonyl band			associated carbonyl band			
PMMI feed (wt%)	wavenumber (cm^{-1})	width (cm^{-1})	rel area (%)	wavenumber (cm^{-1})	width (cm^{-1})	rel area (%)	f^{E}_{CO}
20	1648	35	29.8	1608	56	70.2	0.30
40	1648	35	30.9	1608	59	69.1	0.31
60	1649	35	27.8	1608	56	72.2	0.28
80	1650	35	23.4	1608	56	76.6	0.23

Table 5. General Results Obtained for the Curve Fittings Performed on the Carbonyl Band in the Case of PMMI/PDMA Blends

	free carbonyl band			associated carbonyl band			
PMMI feed (wt %)	wavenumber (cm^{-1})	width (cm^{-1})	rel area (%)	wavenumber (cm^{-1})	width (cm^{-1})	rel area (%)	f^{E}_{CO}
0	1642	30					1
20	1642	29	78.4	1610	39	21.6	0.78
40	1642	28	55.9	1609	39	44.1	0.56
60	1642	28	39.0	1609	39	61.0	0.39
80	1642	28	33.5	1609	39	66.5	0.34

Table 6. General Results Obtained for the Curve Fittings Performed on the Carbonyl Band in the Case of PMMI/PEOX Blends

	free carbonyl band			associated carbonyl band			
PMMI feed (wt %)	wavenumber (cm^{-1})	width (cm^{-1})	rel area (%)	wavenumber (cm^{-1})	width (cm^{-1})	rel area (%)	f^{F}_{CO}
0	1643	37					1
20	1645	37	76.5	1609	56	23.5	0.77
40	1648	36	47.0	1609	56	53.0	0.47
60	1649	35	27.9	1609	56	72.1	0.28
80	1651	35	19.9	1608	56	80.1	0.20

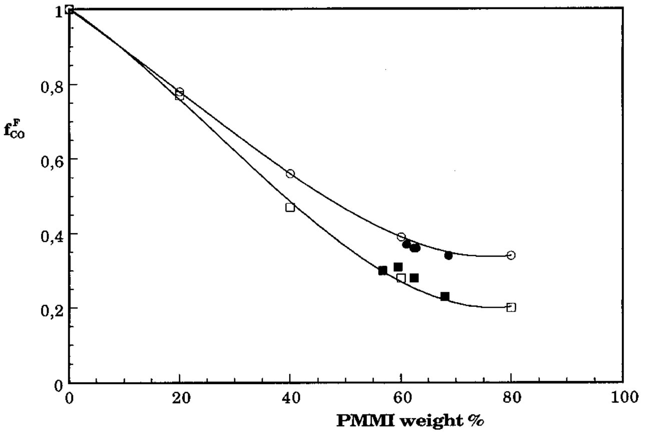

Figure 6. Fraction of nonassociated carbonyl groups of PDMA and PEOX for complexes and blends as a function of the composition: PMMI/PDMA blends (○); PMMI/PEOX blends (□); PMMI/PDMA complexes (●); PMMI/PEOX complexes (■).

blends. It seems that, independently of feed compositions, the association in the complexes reaches the maximum degree allowed for the system.

According to the results plotted in Figure 6, PEOX exhibits a greater ability than PDMA for hydrogen bonding with PMMI, in blends as well as in complexes. Regarding the fitting results in Tables 2−5, the shift between associated and nonassociated PDMA carbonyl bands is about 33 and ≈40 cm^{-1} for PEOX. This shift is assumed to be correlated with the strength of the implicated specific interactions. In this way, our results also suggest a higher strength in the PMMI/PEOX system than in the PMMI−PDMA one.

These data deserve an additional comment. In this case the infrared spectra only allow us to detect the hydroxyl−carbonyl interactions. In the amide groups of PEOX and PDMA, there are nitrogen atoms that also are potential proton acceptors. The influence of them on the total balance of the interactions is very hard to point. It seems that the PEOX carbonyl groups are more accessible than the PDMA ones, but the total balance of the carbonyl−amide interactions may be very similar in both cases.

For the hydrogen-bonding characterization of our systems a second spectral zone of interest is that of hydroxyl stretching. In this region, PMMI shows the characteristic typical spectrum of a self-associated polyacid: a wide band with practical absence of any free hydroxyl contributions (typically around 3500 cm^{-1}) and a maximum at 3200 cm^{-1}. In our blends and complexes significant modifications in this spectral region are not observed. This behavior suggests that the hydrogen bond strength in PMMI self-association is similar to PMMI/PEOX and PMMI/PDMA inter-association. In this way, the replacement of specific interactions keeps the overall shape of the hydroxyl stretching region.

In conclusion, infrared spectra of PMMI/PDMA and PMMI/PEOX complexes and blends evidence strong intermolecular hydrogen bonding in these systems.

Thermal Behavior. Usually, polymer blends and complexes exhibit a thermal behavior quite different from that of their pure components. The DSC curves

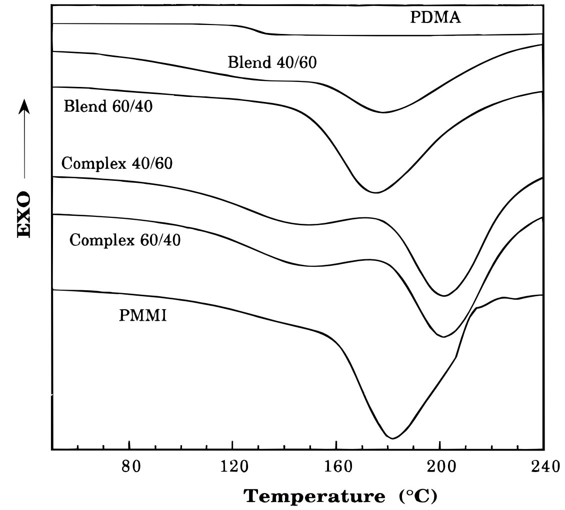

Figure 7. DSC curves for PMMI, PDMA, and different PMMI/PDMA complexes and blends.

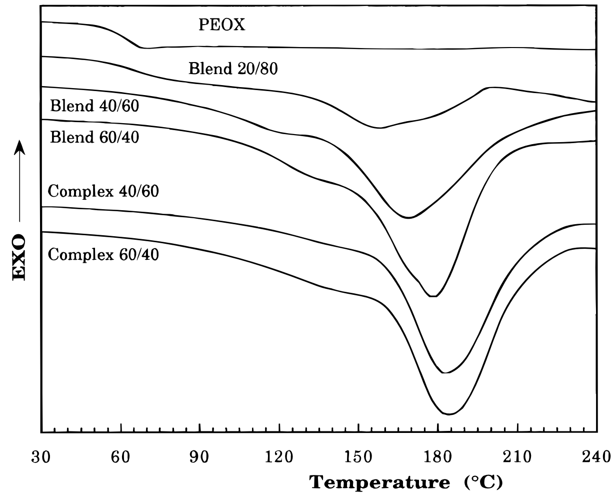

Figure 8. DSC curves for PEOX and different PMMI/PDMA complexes and blends.

corresponding to PMMI/PDMA blends and complexes are plotted in Figure 7. Figure 8 contains the same data for the PMMI/PEOX system.

One of the most striking facts in pure PMMI is the absence of any specific heat jump corresponding to its glass transition. This is a common characteristic for most poly(monoalkyl itaconates).[19] PMMI shows a low degradation temperature with a wide endothermic peak ($\approx$154 °C). This endothermic peak makes difficult the thermal study of the blends and complexes. PDMA and PEOX are very stable polymers that do not show any thermal degradation up to 400 and 380 °C, respectively. Both polymers show a clear T_g placed at 130 °C for PDMA and 61 °C for PEOX.

In the thermograms of the complexes it is not possible to find any specific heat jump corresponding to a glass transition process. A similar behavior is found in PMMI/PDMA blends. On the contrary, in the 20:80 PMMI/PEOX blend a well-defined glass transition temperature at 66 °C is detected. Considering that PEOX is the component with a lower T_g, this result suggests that probably for the rest of the systems the glass transitions are masked by the wide endothermic peak previously reported for PMMI. In fact, it is usual to find high T_g temperatures in blends with strong specific interactions, because they act like physical cross-linking.

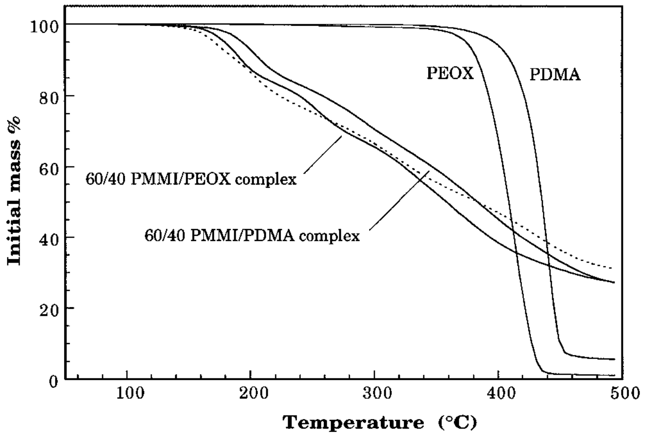

Figure 9. Thermogravimetric curves for PEOX, PDMA, and PMMI (dashed curve) and two PMMI/PEOX and PMMI/PDMA complexes with the same feed composition (wt/wt).

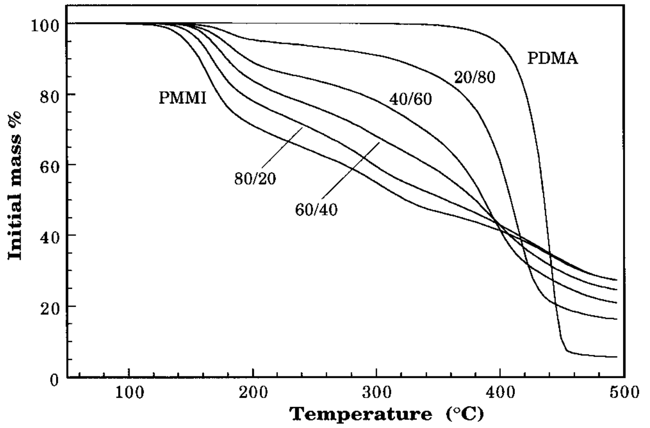

Figure 10. Thermogravimetric curves for PMMI, PDMA, and different PMMI/PDMA (wt/wt) blends.

Another remarkable fact is that the location of the endothermic peak depends on the composition and the type of sample: complexes or blends. This fact is clearly shown in Figures 7 and 8. It must be remembered that both complexes have a similar composition, which is very close to a blend of 60:40. In other words, the thermal degradation of the complexes and blends takes place in a different way than the simple addition of the thermal degradation behavior of single components. In order to confirm this behavior a thermogravimetric study of these systems has been performed.

The thermogravimetric behavior of the PMMI/PDMA and PMMI/PEOX complexes is displayed in Figure 9. The most remarkable fact is the increase in the onset of the thermal degradation temperature for these samples. The values of the degradation onset temperature for the studied polymers are measured with a precision of ±1 deg. While PMMI shows an onset of thermal degradation at about 154 °C, for PMMI/PDMA complexes it is placed between 180 and 185 °C, and for PMMI/PEOX complexes between 169 and 171 °C.

For PMMI/PDMA blends, the thermogravimetric curves (Figure 10) show a composition dependent onset of thermal degradation. We found that as the PMMI content in the blend increases, the onset temperature decreases. For PMMI/PDMA blends with a composition 20:80 the onset of thermal degradation reaches its higher value, 162 °C, lower than the values reached in the case of polycomplexes.

In PMMI/PEOX blends the degradation onset temperatures also depend on composition. Now, an increase is also observed until 60:40 blend composition. For higher contents in PEOX the degradation onset temperatures decrease, and even lower temperatures than that corresponding to pure PMMI are observed.

The reported data suggest that the thermal degradation behavior is mainly controlled by the hydrogen bonding in the system. According to previous studies, the first degradative process in polyacids is anhydride formation[20,21] in particular in PMMI. This process involves the hydroxyl placed into carboxyl groups of PMMI. In the complexes or blends, a large number of hydroxyl groups are strongly hydrogen bonded to PDMA or PEOX. For these groups the first step before the anhydride formation must be the break of hydrogen bonds. Thus, as the extension of hydrogen bonding is more important in a particular sample, its break is more difficult and requires more thermal energy. In fact, the complexes exhibit higher onset temperatures than the blends, which probably could be related to a more compact distribution (cooperative effect) of the hydrogen bonds, and in PMMI/PDMA blends higher onsets are observed as the association in the system increases (higher contents in PDMA). The degradative behavior of pure PMMI deserves a special comment. The samples prepared from DMF solutions (thermogravimetric curves of which are is shown in Figure 10) have a degradation onset temperature much lower than those prepared from methanol or ethyleneglycol solutions. In our opinion this discrepancy could be due to the different association degrees of both samples. Specifically, a lower degree of self-association of the PMMI samples prepared from DMF (strong acceptor) is expected. Nevertheless, we can not exclude the possible influence of nonvolatile solvent impurities in casted samples. However, infrared spectra obtained from ethanol or DMF in PMMI-casted samples do not show relevant differences.

Another important factor to take into account is the particular glass transition of the system. A lower glass transition temperature allows greater motion in the system, favoring the contacts for anhydride formation and also the breaking of specific interactions. Unfortunately, we do not have data about T_g in these systems. Nevertheless, PDMA is a polymer with a notably higher T_g ($\approx$60 °C) than PEOX. According to the general behavior in hydrogen-bonded blends and complexes, higher glass transition temperatures can be expected for PMMI/PDMA systems than for PMMI/PEOX ones. And in fact, the first complexes exhibit higher degradation onset temperatures. On the other hand, the 80:20 PMMI/PEOX blend is the only system with a detectable glass transition (66 °C). Just in this system we have found degradation onset temperatures lower than those in pure PMMI.

Conclusions

The above experimental results show that poly(monomethyl itaconate) establishes strong specific interactions via hydrogen bonding with poly(*N*,*N*-dimethylacrylamide) and poly(ethyloxazoline). Depending on the solvent medium we can obtain polymer blends or polymer−polymer complexes with a stoichiometry close to 1:1.

According to our spectroscopic study, the specific interactions between chains are of the same type, for complexes as well as for blends: hydrogen bonds between hydroxyl placed in carboxyl groups of PMMI and carbonyl groups placed in the lateral pendant groups of PDMA and PEOX. In both systems, the number, kind, and position of the bands for complexes and blends are similar. We can conclude that the strengths of the interactions are identical.

The fundamental difference between these two types of materials must be in the way that the specific interactions are distributed. For interpolymer complexes the cooperative effect must be strong and originate a compact network that excludes the solvent molecules, leading to precipitation. Blends are obtained in a solvent medium that competes favorably with PDMA or PEOX for hydrogen bonding, limiting the scope and extension of specific interactions between chains. As evaporation vanishes the solvent molecules, the polymer chains progressively increase its specific interactions. Obviously, the end point of this process is reached in a viscous medium that constrains the mobility of the polymer chains and, so, the cooperative effect. The material retains the feed composition.

The thermal behavior of these systems seems to be also controlled by hydrogen bonding. In particular, the onset temperatures for thermal degradation in complexes and blends are in general higher that those corresponding to the pure PMMI. Thermal degraation in PMMI starts by anhydride formation involving carboxyl groups, it seems that hydrogen bonding involving a considerable number of such groups, retards the process.

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