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FTIR Study of Hydrogen Bonding of Blends of Poly(mono *n*-alkyl itaconates) with Poly(*N*,*N*-dimethylacrylamide) and Poly(ethyloxazoline)

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ABSTRACT: This paper reports a FTIR study of blends of poly(mono *n*-alkyl itaconates) with poly(*N*,*N*-dimethylacrylamide) (PDMA) and poly(ethyloxazoline) (PEOX). Strong hydrogen bonding has been found, and both polybases have shown similar acceptor strengths. The extent of the interassociation has been estimated by spectral curve fitting of the polybase carbonyl band. The solvent medium employed to cast the sample has been shown to have a negligible influence on the interassociation degree attained in the blend, whenever casting did not lead to phase-separated blends due to the $\Delta\chi$ effect. Results show that the interaction degree in blends with PEOX does not depend on the length of the poly(monoalkyl itaconate) side group, while an interassociating ability loss is observed in blends with PDMA as the side group size of the polyacid increases. This different behavior is attributed to the greater interspacing between vicinal carbonyl groups in PEOX. In any case, this band shows conformational sensitivity and reflects the conformational changes that the polymer is forced to adopt as the steric hindrances present in the medium (due to the bulky side groups of the polyacids) increase.

Introduction

Polymer blending is an alternative to obtain new polymeric materials, being thus a subject of widespread theoretical and practical interest. From a thermodynamic point of view, a negative free energy of mixing is necessary in order to achieve miscibility. According to theoretical models developed for polymer blends,[1−3] there are three contributions to ΔG^{m}: the combinatorial energy of mixing, the "free-volume" effect, arising from the mismatch of the equation-of-state parameters, and the intermolecular interaction. The first term is small for high molar mass polymers, and the free volume-term is positive. Therefore, an exothermic polymer−polymer interaction of sufficient magnitude is a prerequisite for miscibility.

Since the dispersive force of interaction between molecules leads to a positive contribution to the heat of mixing, the so called "specific interactions", which give a negative contribution, are the driving force for miscibility in most polymer blends. In many industrial polymer blends or solutions hydrogen bonding is present. Its understanding may provide us with new insight into the mechanisms responsible for miscibility. The magnitude of the hydrogen-bonding contribution to the heat of mixing depends on its strength and on the number of bonds. Both facts depend on the chemical structure of the groups that interact and the relative distance and molecular orientation of the involved groups.

Here, we present the results of the quantitative characterization by FTIR spectroscopy of the extent of the interassociation in blends of poly(mono-*n*-alkyl itaconates) with poly(*N*,*N*-dimethylacrylamide) (PDMA) and poly(ethyloxazoline) (PEOX). The poly(mono-*n*-alkyl itaconates) employed are polyacids with different side chain lengths, while the donor group remains unchanged. PDMA and PEOX are two typical polybases that contain amide groups in their chemical structures. These two polymers are isomers and have similar acceptor strengths.[4] So, we are dealing with blends of polyacids with polybases, which usually lead to miscible systems stabilized through hydrogen bonding.[4−6] We are interested in studying the relationship between stereocomplementarity and associative behavior for these systems.

Experimental Part

Poly(*N*,*N*-dimethylacrylamide) (PDMA) was bulk polymerized at 60 °C with 0.5% azobis(isobutyronitrile) (AIBN) as initiator under 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 a Ubbelohde type viscometer in methanol at 25 °C, using the relation[7]

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

which leads to a viscosity-average molar mass of 2.9×10^5 g/mol.

Poly(ethyloxazoline) (PEOX) is a Polysciences product, and was purified by solution−precipitation in the methyl ethyl ketone/*n*-hexane pair. According to the supplier, the weight-average molar mass of the sample is 50 000 g/mol.

Mono-*n*-alkyl itaconates were obtained by the esterification of itaconic acid with the corresponding alcohol, using acetyl chloride as catalyst, according to a method previously described.[8] The monomers were characterized by FTIR, ^{1}H-NMR, and ^{13}C-NMR. The poly(mono-*n*-alkyl itaconates) used in this study, poly(monomethyl itaconate) PMMI, poly(monoethyl itaconate) PMEI, poly(monobutyl itaconate) PMBuI, poly(monohexyl itaconate) PMHeI, poly(monodecyl itaconate) PMDeI, and poly(monododecyl itaconate) PMDoI, were obtained by free radical bulk polymerization using 0.3% AIBN as initiator under N_2 atmosphere at 60 or 80 °C, depending on the melting temperature of the monomer. The polymers were characterized by laser light scattering in methanol or tetrahydrofuran solutions, at 25.0 °C. Laser light scattering measurements were carried out, at 25,0 °C, with a modified FICA 42000 light scattering photometer, where both light source and optical block of the incident beam were substituted by a He−Ne laser (Spectra Physics, Model 157) which emits at $\lambda = 632.8$ nm, with a power of 3 mW. The instrument was calibrated using benzene, for which the Raleigh ratios is known. Polymer

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Table 1. Weight-Average Molar Masses and Specific Refractive Index Increments of the Poly(mono-*n*-alkyl itaconates) Calculated by Laser Light Scattering in Methanol

polymer	M_w	d*n*/d*c* ($cm^3 \cdot g^{-1}$)
PMMI	1.3×10^5	0.144
PMEI	2.5×10^5	0.130
PMBuI	3.5×10^5	0.139
PMHeI	3.9×10^5	0.142
PMDeI	1.1×10^5	0.137
PMDoI	9.2×10^4	0.135

solutions and solvent were clarified by centrifugation for 2 h in a Sorvell preparative ultracentrifuge at 14 000 cycles/min. The refractive index increment, d*n*/d*c*, was measured in a Brice-Phoenix differential refractometer, Model BP-2000, previously calibrated with solutions of highly purified KCl solutions. Refractive indices were measured, at 25.0 °C and 632.8 nm, with an Abbé refractometer, previously calibrated with several liquids in which the refractive index was known. The obtained weight-average molar masses of the different homopolymers are summarized in Table 1.

The blends were obtained by solvent casting from solutions with a total concentration of 2% w/v. The medium conditions that lead to homogeneous solutions from which blends can be obtained are discussed in a previous paper.[9] Chosen solvents were DMF (PMMI/PDMA system), ethylene glycol (PMMI/PEOX system), methanol (blends with PMEI, PMBuI and PMHeI), butanol (blends with PMDeI), and pentanol (blends with PMDoI). In all cases the solvent was cast at 50 °C.

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 100 scans. Blend samples were prepared on KBr pellets, using the following procedure. First, the polymer solution was cast in a petri dish at 50 °C under vacuum if necessary. When the system reached a gellike state, it was spreaded between two KBr pellets in order to obtain a film of homogeneous thickness. Immediately, the upper pellet was removed and the sample was vacuum dried at 65 °C for 72 h. The absorbance of all the studied samples was within the absorbance range in which the Lambert−Beer law is obeyed.

The least-squares fittings of the spectral bands were performed with the program PeakFit 3.0. The number of peaks and their approximate position were previously investigated using derivation techniques.

Experimental Results

Specific Interactions. The chemical structure of the polymers (Figure 1) supports the posibility of formation of hydrogen bonds between carboxylic acid and amide groups, that should lead to miscible blends. Fourier transform infrared spectroscopy is one of the most advantageous techniques for the identification and quantitative analysis of the groups linked by hydrogen bonds in polymers. A study of the major characteristics of the infrared spectra of these systems has been performed in this work.

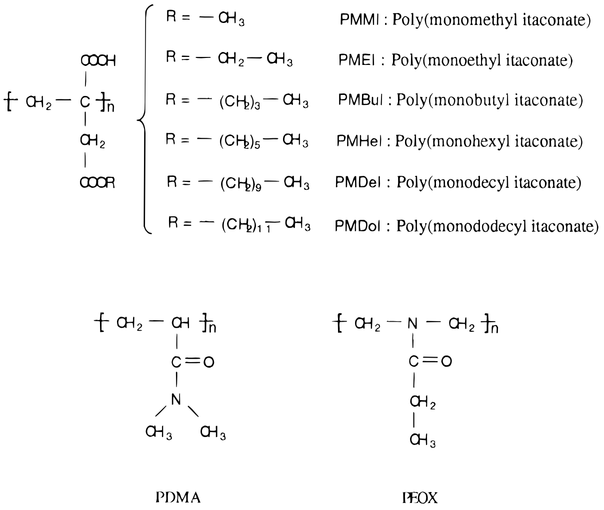


Figure 1. Chemical structures of the poly(mono-*n*-alkyl itaconates) and the polybases studied in the present work.

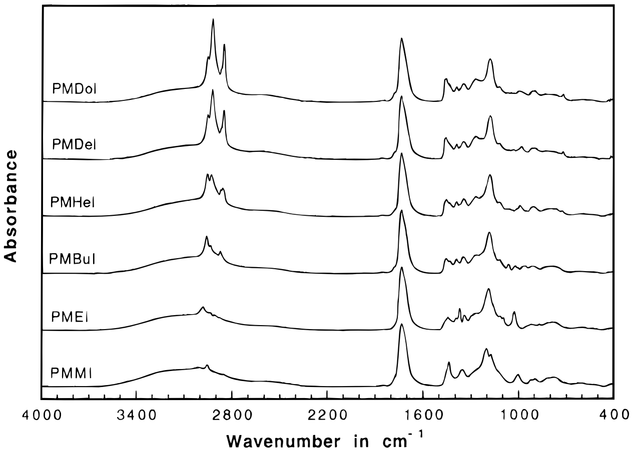


Figure 2. Autoscaled infrared spectra of PMMI, PMEI, PMBuI, PMHeI, PMDeI, and PMDoI.

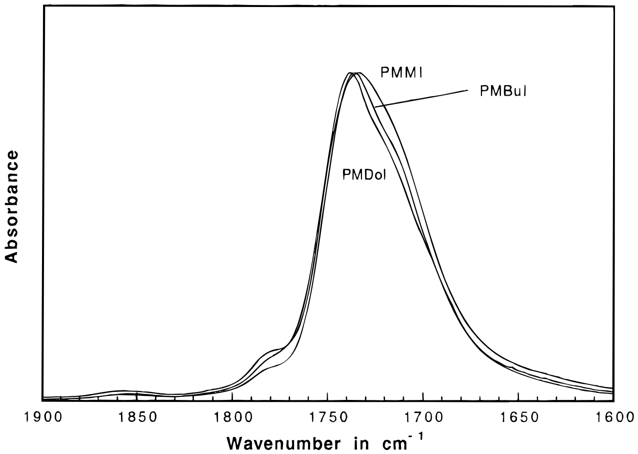


Figure 3. Autoscaled carbonyl stretching bands for PMMI, PMBuI, and PMDoI.

Figure 2 shows the autoscaled spectra of the pure poly(mono *n*-alkyl itaconates). Because their chemical structure includes a carboxylic acid and a ester group in each repetitive unit, we are dealing with self-associated polymers. The most interesting spectral regions will be the carbonyl and the hydroxyl stretching bands. Figure 3 shows the carbonyl stretching region for PMMI, PMBuI, and PMDoI, which presents a rather complex profile due to the overlapping of several bands. It is interesting to describe its major features in order to understand the modifications observed upon blending. Reported spectral data for methacrylic acid[5] indicate that ester group contribution occurs at about 1735 cm^{-1}. The carboxylic acid group can exist nonassociated (band at about 1750 cm^{-1}), but most of it tends to be associated, in the form of carboxylic acid dimers (band at about 1700 cm^{-1}).[5] The spectra show that as the side group size of the poly(mono-*n*-alkyl itaconate) increases, the relative absorption due to carboxylic acid dimers decreases. Finally, it has been reported that poly(mono-*n*-alkyl itaconates) tend to form anhydrides of different structure during the polymerization process.[10,11] Their

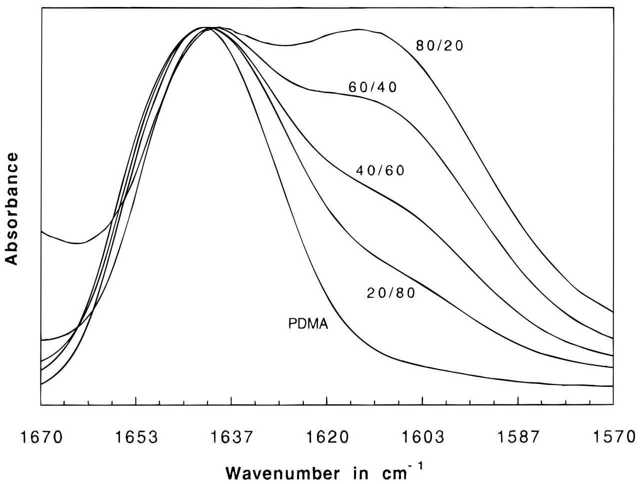


Figure 4. Autoscaled carbonyl stretching bands for PDMA and PMEI/PDMA blends with different composition.

only distinguishable contributions occur at about 1780 and 1850 cm^{-1}.

The hydroxyl stretching region band shows the typical shape for self-associated polyacids: a very wide band in which the contribution due to free hydroxyl groups is barely observable (should occur at about 3500 cm^{-1}) and a maximum at 3200 cm^{-1}. Because carboxylic acid dimer absorptions[5] occur at 3100 cm^{-1}, the spectra indicate that most of the carboxylic acid groups are in the form of dimers. Another characteristic feature in this region is the wide band with lower intensity at 2610 cm^{-1}. This band is attributed to overtones and/or combination of the O—H and O||||H stretching band modes.

PDMA and PEOX are polymers containing tertiary amide groups in the chemical structure of their respective repetitive unit (Figure 1); this group can act as a hydrogen bond acceptor when blending with a hydrogen bond donor. There are two possible hydrogen bond acceptor sites in the polymers: the carbonyl group and the nitrogen atom. Studies performed in model compounds[12,13] have shown that almost all the association takes place with the carbonyl group, as the formation of hydrogen bonds with the nitrogen atom is negligible. The amide groups in PDMA and PEOX give bands at 1642 and 1643 cm^{-1}, respectively. This absorption band is called Amide I, and is a composed mode with contribution of the C═O and C—N stretching modes,[14] with a larger weight for the first one. Due to this fact, this peak occurs at lower wavenumbers than expected for a pure carbonyl peak, and is well resolved in the case of the poly(mono-*n*-alkyl itaconates). We will refer this peak as the carbonyl band of PEOX or PDMA.

Figure 4 shows the carbonyl stretching region for PMEI/PDMA blends, obtained from methanol solutions. Spectral inspection shows the presence of a new band at the lower wavenumbers. This band is present at about 1610 cm^{-1} and can be assigned to PDMA hydrogen-bonded carbonyl groups. Its relative intensity depends on composition: as the PMEI content in the blend increases, the intensity of the associated PDMA band relative to the nonassociated one becomes higher. Figure 5 shows the PMEI carbonyl band region for the same system. In this case, imcreasing the content of PDMA produces a steady loss of the relative intensity of the contribution located at about 1700 cm^{-1}. These results suggest that blending breaks the carboxylic acid dimers and permits hydrogen bond formation between the carboxylic acid and the amide groups. This behavior matches qualitatively that obtained by our research group in PMMI/PDMA blends[4] and by Lichkus et al. in poly(ethylene-*co*-methacrylic acid)/PEOX blends.[5]

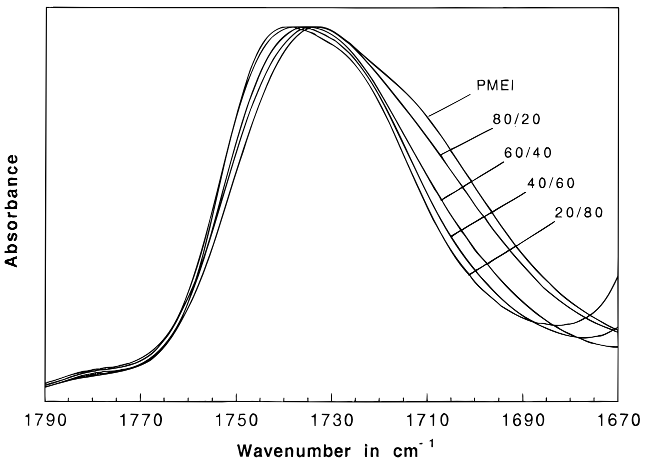


Figure 5. Autoscaled carbonyl stretching bands for PMEI and PMEI/PDMA blends with different composition.

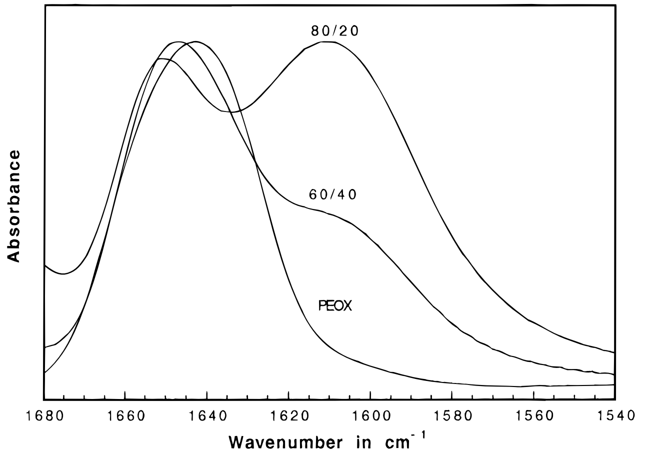


Figure 6. Autoscaled carbonyl stretching bands for PEOX and PMDoI/PEOX blends with different composition.

Similar results were obtained for blends of PMEI/PEOX. Again, addition of PMEI results in a new band around 1610 cm^{-1}, with a intensity dependent on composition. The behavior of the 1700 cm^{-1} band is similar to that of PMEI/PDMA blends. Thus, the infrared results suggest that the mechanisms responsible for miscibility in PMEI/PEOX and PMEI/PDMA blends are very similar. Furthermore, the spectral shifts observed in both cases are similar. Considering the relation between spectral shift and bond strength,[16] it suggests a similar bond strength in both cases.

In the other systems studied, the qualitative results resemble those obtained for blends containing PMEI. The carbonyl spectrum region of PEOX in PMDoI/PEOX blends again occurs at about 1610 cm^{-1} (Figure 6). In this system, the shifting of the PEOX nonassociated carbonyl band to higher wavenumbers as the content of PMDoI in the blend increases is readily noticeable. This is not an apparent effect (due to the overlapping of the neighboring band), because overlapping with the PEOX carbonyl associated band would shift the nonassociated band to lower wavenumbers.

Figure 7 shows the hydroxyl stretching spectral region for PMMI/PDMA blends. No remarkable changes are noticeable in the shape of this region. This situation is typical of systems in which the strength of the new

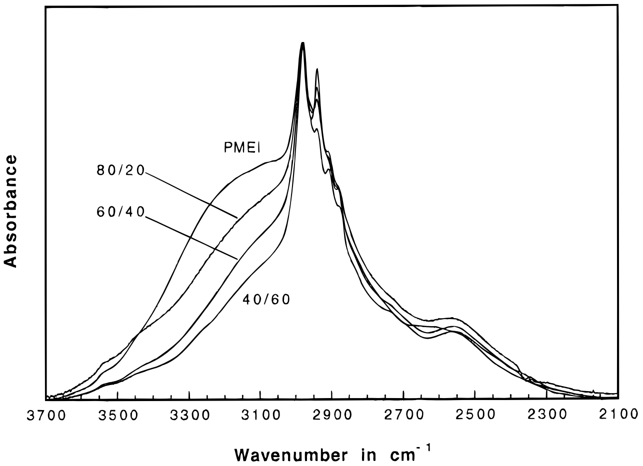


Figure 7. Autoscaled hydroxyl stretching bands for PDMA and PMMI/PDMA blends with different composition.

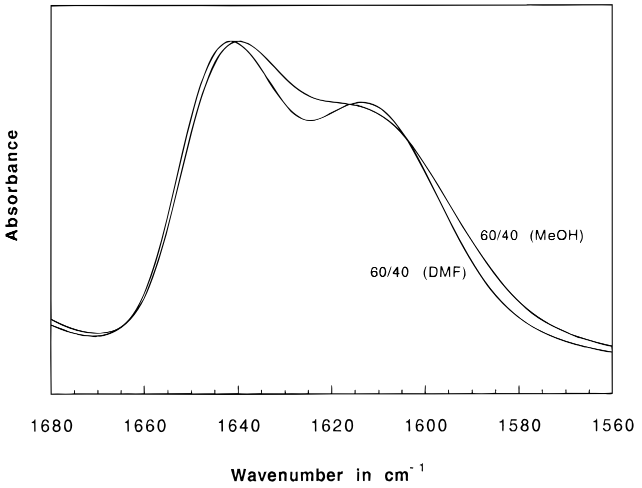


Figure 8. Autoscaled carbonyl stretching bands for PDMA and PMEI/PDMA blends of 60/40 w/w composition obtained from methanol and DMF solutions.

and the replaced bonds are similar. The spectra in this region for the other blends studied show a similar overall behavior.

Finally, it must be pointed out that the use of strong donor or acceptor solvents to obtain the samples might have a relevant influence on the degree of mixing. PMMI/PDMA blends have been cast from DMF solutions. This solvent contains an amide group and thus can compete with the polybase as hydrogen bond acceptor. Since PMEI/PDMA blends can be obtained from DMF or methanol solutions, we have obtained the spectra for that system cast from both solvents (Figure 8). The carbonyl stretching region in both cases shows a similar profile, suggesting a minor influence of the solvent on the interassociation degree attained in the blend. Only a slight difference in the width of the associated band is observed, probably due to a different distribution of bonding distances and angles between carboxylic acids and amide groups. On the other hand, casting poly(mono-*n*-alkyl itaconate)/PEOX mixtures from DMF solutions results in phase-separated films, as confirmed by DSC and FTIR. Such a phenomenon has been attributed to the $\Delta\chi$ effect,[15] in which the solvent is capable of displacing the polybase from the polyacid, probably due to solvent–polymer interactions stronger than the polymer–polymer ones.

Spectral Curve Fitting. The percentage of PDMA and PEOX carbonyl groups associated and nonassociated can be determined by using spectral curve fitting methods. In order to avoid errors due to the arbitrary choice of baseline (zero absorbance), wings have been excluded for the fitting. Because the Gaussian line shape function gives a good fitting for the pure components as well as for the blends, it was employed in the fitting procedure.

In any case, it is advisable to use some criteria in order to avoid artifacts in the fitting procedure. With this aim, a derivation of spectra obtained from samples with compositions closer to the stoichiometric one has been performed. Derivation increases spectral resolution, but when it is performed on overlapping bands with different widths, it also results in the increase of the relative intensity of the narrower band. This can be easily proved by deriving twice the mathematical equation for a Gaussian profile and calculating the absorbance ratio at the maximum for two hypothetical overlapping peaks (1 and 2)

$$\frac{(A_0'')_1}{(A_0'')_2} = \frac{(A_0)_1}{(A_0)_2}\left[\frac{(\Delta X_{1/2})_2}{(\Delta X_{1/2})_1}\right]^2 \qquad (1)$$

where A_0 is the intensity at the peak maximum, A_0'' is the intensity at the peak maximum for the second derivative, $\Delta X_{1/2}$ is the half-height width of the band, and the subscripts 1 and 2 are referred to each of the overlapping peaks. Thus, second derivatives of overlapping bands with similar relative intensities but different half-height widths (as is the case for the spectra of the blends studied with compositions close to the stoichiometric one) will give a more accurate position for the narrower band than for the wider one, because side wings of the first one may modify the profile of the second one to a larger extent.

Figure 9 displays the amide I band and its second derivative for the systems PMEI/PDMA and PMEI/PEOX with 60/40 w/w composition. As stated before, spectral derivation seems to increase the relative intensity of the narrower band. Table 2 shows the free carbonyl band position obtained from the derivatives of some of the spectra of the blends studied. These values have been set on the spectral curve fitting calculations, but such procedure has not given good fitting. In our opinion, the slight asymmetry observed for the amide I band, even in the pure polymers, causes the shift of the maximum values. This fitting procedure has been discarded.

When spectral curve fitting methods are used, the reliability of the results depends mainly on the resolution of the overlapping bands. Fortunately, the carbonyl stretching region of PEOX and PDMA for the blends studied in this work is fairly well resolved, with two clearly distinguishable components (see Figure 4, 6, or 8). The observed resolution increases with the length of the side group of the poly(mono-*n*-alkyl itaconate). This is probably due to the narrowing of the overlapping bands: we are always dealing with the same interacting groups, and for this reason peak positions should remain almost unchanged. To diminish errors associated with the arbitrary choice of baseline, spectral fitting has been performed initially on the blends with composition closer to the stoichiometric for each system. The half-height width thus obtained for the bonded carbonyl band has been fixed in the fittings of the spectra in which this band shows low relative intensity. Tables 3 and 4 show the spectral fitting results obtained for the carbonyl stretching bands of PDMA and PEOX. As can be seen,

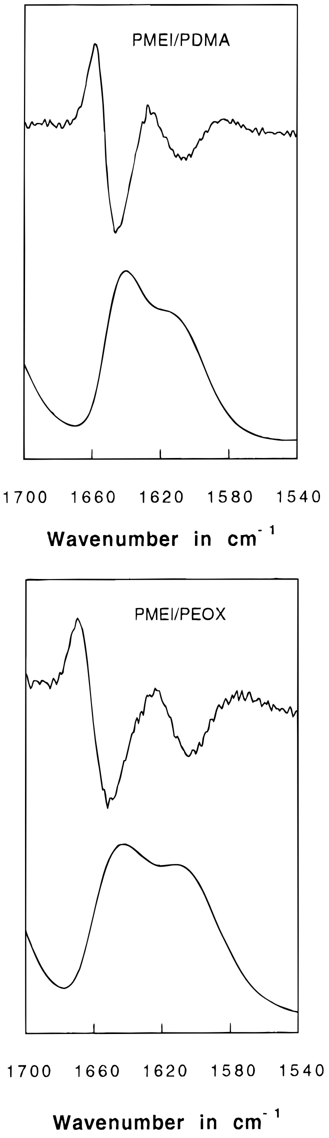


Figure 9. Autoscaled carbonyl stretching bands for PMEI/PDMA (top) and PMEI/PEOX (bottom) blends of 60/40 w/w composition and their second derivatives.

values for the position of the free carbonyl band display the same qualitative behavior as those obtained with derivative techniques, but differences are not negligible. From the calculated values of the absorbance of the associated and nonassociated contributions it is possible to determine the fraction of nonassociated carbonyl groups f_{CO}^F:

$$f_{CO}^F = \frac{A_F}{A_F + \frac{\epsilon_F}{\epsilon_A} A_A} \qquad (2)$$

The procedure requires the ratio of molar absorption coefficients of both spectral contributions (ϵ_F/ϵ_A). The value for the systems under study has been reported in a previous work[4] and is equal to 1.0.

Table 2. Nonassociated Carbonyl Band Positions in PDMA, PEOX, and Some Blends Obtained by Spectral Derivation

			free carbonyl band location (cm^{-1})	
poly(monoalkyl itaconate)	wt %	mol %	blends with PDMA	blends with PEOX
none			1642	1641
PMMI	60	50.8	1644	1650
PMEI	60	48.5	1645	1650
PMBuI	60	44.4	1647	
PMHeI	60	41.0		1652
PMDeI	80	59.5	1648	1653
PMDoI	80	57.1	1648	1651

Table 3. Curve-Fitting Results for PDMA Carbonyl Stretching Bands

		free C=O band			bonded C=O band			
wt %	mol %	wave-number (cm^{-1})	width (cm^{-1})	rel area	wave-number (cm^{-1})	width (cm^{-1})	rel area	f_F
				PMMI/PDMA				
0	0	1642	30	100				1
20	14.7	1642	29	81.3	1610	40	18.7	0.81
40	31.4	1643	28	53.8	1611	40	46.2	0.53
60	50.8	1643	26	35.8	1610	40	64.2	0.36
80	73.4	1644	26	27.6	1611	42	72.4	0.28
				PMEI/PDMA				
20	13.6	1642	30	81.1	1611	44	18.9	0.81
40	29.5	1643	29	53.7	1611	44	46.3	0.54
60	48.5	1643	27	37.9	1611	44	62.1	0.38
80	71.5	1644	27	31.3	1611	44	68.7	0.31
				PMBuI/PDMA				
20	11.7	1643	29	85.3	1612	44	14.7	0.85
40	26.2	1644	28	54.9	1611	44	45.1	0.55
60	44.4	1644	26	40.0	1613	44	60.0	0.40
80	68.1	1645	26	33.1	1612	44	66.9	0.33
				PMHeI/PDMA				
20	10.4	1643	30	87.1	1612	44	12.9	0.87
40	23.6	1644	29	54.9	1612	44	45.1	0.55
60	41.0	1644	26	43.0	1612	44	57.0	0.43
80	64.9	1645	26	37.0	1612	44	63.0	0.37
				PMDeI/PDMA				
20	8.4	1642	30	92.7	1610	38	7.3	0.93
40	19.6	1643	27	70.8	1610	38	29.2	0.71
60	35.5	1644	26	53.2	1611	38	46.8	0.53
80	59.5	1645	26	42.7	1611	38	57.3	0.43
90	76.7	1645	25	39.4	1611	38	60.6	0.39
				PMDoI/PDM				
20	7.7	1642	29	91.0	1611	38	9.0	0.91
40	18.1	1643	27	74.7	1611	38	25.3	0.75
60	33.3	1644	26	53.3	1611	38	46.7	0.53
80	57.1	1645	26	43.2	1611	38	56.8	0.43
90	74.9	1646	26	41.1	1611	38	58.9	0.41

Figures 10 and 11 show the free carbonyl fraction against the blend composition for different systems with PEOX and with PDMA respectively. The experimental points fit a curved line that tends to a maximum interassociation extent lower than 100% of associated carbonyl groups. This is a typical characteristic of polymer chains interassociated by hydrogen bonds, in which interconectivity, with the relative orientation effects that implies, prevents the system from getting higher interassociation extents.[17] As can be seen, in systems with PEOX (Figure 10), the interassociation extent for a given composition does not depend on the size of the poly(mono-*n*-alkyl itaconate) side group. However, in blends with PDMA (Figure 11), it seems to be a slight but steadily interassociation loss as the size of the poly(mono-*n*-alkyl itaconate) side group increases. Thus, the system PMDoI/PDMA shows a maximum interassociation extent about 15% lower than that for the system PMMI/PDMA. This difference can not be attributed to different steric hindrance around the acceptor groups in PDMA and PEOX. Both polymers have the acceptor group at the same distance from the polymeric chain, and the chemical groups surrounding them do not seem to be responsible for the different steric hindrance. Moreover, according to the measured

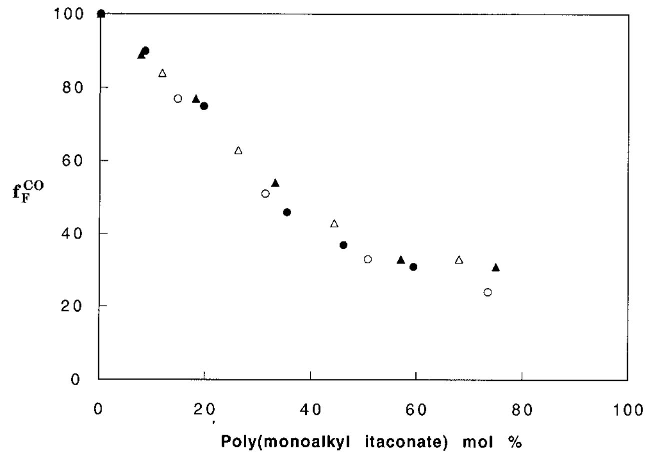


Figure 10. Nonassociated PEOX carbonyl groups ratio vs composition for the (○) PMMI/PEOX, (△) PMBuI/PEOX, (●) PMDeI/PEOX, and (▲) PMDoI/PEOX blends.

Table 4. Curve-Fitting Results for PEOX Carbonyl Stretching Bands

		free C=O band			bonded C=O band			
wt %	mol %	wave-number (cm^{-1})	width (cm^{-1})	rel area	wave-number (cm^{-1})	width (cm^{-1})	rel area	f_F
			PMMI/PEOX					
0	0	1643	37	100				1.0
20	14.7	1645	37	77.1	1608	52	22.9	0.77
40	31.4	1647	37	50.9	1608	52	49.1	0.51
60	50.8	1649	37	32.6	1608	52	67.4	0.33
80	73.4	1652	37	23.8	1608	54	76.2	0.24
			PMEI/PEOX					
20	13.6	1645	37	81.3	1606	52	18.7	0.81
40	29.5	1647	37	56.3	1607	52	43.7	0.56
60	48.5	1648	37	40.6	1607	52	59.4	0.41
80	71.5	1650	37	29.8	1607	54	70.2	0.30
			PMBuI/PEOX					
20	11.7	1645	37	84.2	1607	50	15.8	0.84
40	26.2	1646	36	62.7	1608	50	37.3	0.63
60	44.4	1649	36	42.8	1608	50	57.2	0.43
80	68.1	1651	36	32.6	1608	52	67.4	0.33
			PMHeI/PEOX					
20	10.4	1645	37	85.5	1607	50	14.5	0.86
40	23.6	1646	37	64.9	1607	50	35.1	0.65
60	41.0	1649	35	44.3	1608	50	55.7	0.44
80	64.9	1652	34	31.8	1608	52	68.2	0.32
			PMDeI/PEOX					
20	8.4	1646	36	89.7	1609	50	10.3	0.90
40	19.6	1647	35	75.1	1609	50	24.9	0.75
60	35.5	1650	32	45.7	1610	50	54.3	0.46
70	46.1	1651	30	36.9	1610	50	63.1	0.37
80	59.5	1653	30	30.8	1609	50	69.2	0.31
			PMDoI/PEOX					
20	7.7	1645	36	89.1	1609	50	10.9	0.89
40	18.1	1647	35	76.7	1609	50	23.3	0.77
60	33.3	1649	33	54.4	1610	50	45.6	0.54
70	43.7	1653	31	32.9	1609	50	67.1	0.33
80	57.1	1654	30	30.8	1610	50	69.2	0.31

spectral shifts, both carbonyl groups have similar acceptor strengths and in fact show similar interassociation extents when blending with poly(mono *n*-alkyl itaconates) of small side groups. The different behavior of both polybases with respect to the poly(mono-*n*-alkyl itaconate) side group size can be attributed to the different interspacing between neighboring interacting sites in the polybases. In PDMA, there are four covalent bonds between two vicinal carbonyl groups, while in PEOX there are five. This circumstance gives more degrees of freedom to the PEOX chain and so a higher ability to adopt the required conformation that leads to the formation of as many hydrogen bonds as possible when the steric hindrances present in the medium increase.

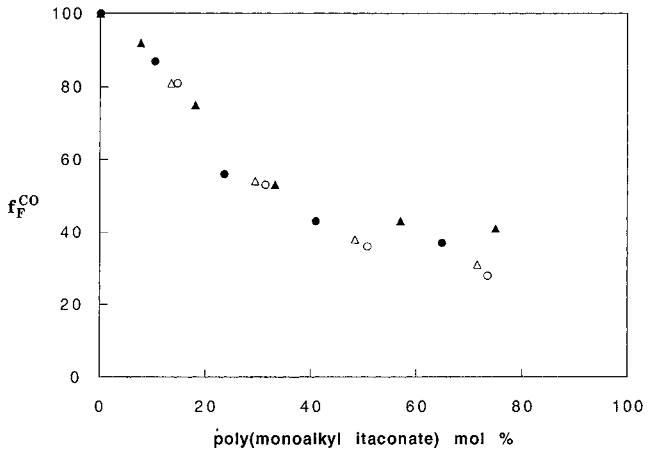


Figure 11. Nonassociated PDMA carbonyl groups ratio vs. composition for the (○) PMMI/PDMA, (△) PMEI/PDMA, (●) PMHeI/PDMA, and (▲) PMDoI/PDMA blends.

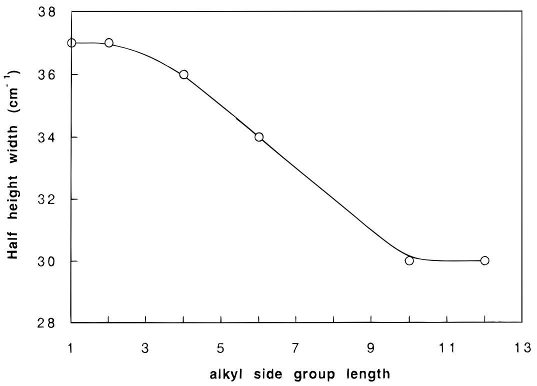
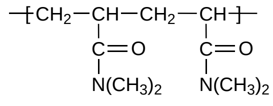
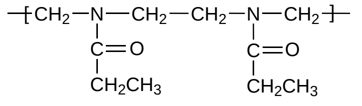


Figure 12. Half-height width for the PEOX free carbonyl band of blends of stoichiometric composition vs the length of the side alkyl group.


$$-\!\!\left[CH_2-\underset{\substack{|\\ C=O\\ |\\ N(CH_3)_2}}{CH}-CH_2-\underset{\substack{|\\ C=O\\ |\\ N(CH_3)_2}}{CH}\right]\!\!-$$

PDMA


$$-\!\!\left[CH_2-\underset{\substack{|\\ C=O\\ |\\ CH_2CH_3}}{N}-CH_2-CH_2-\underset{\substack{|\\ C=O\\ |\\ CH_2CH_3}}{N}-CH_2\right]\!\!-$$

PEOX

In a previous work,[9] it has been observed that the complexes that form these systems dissolve when heated. The temperature at which the complex dissolved was determined through turbidimetric measurements, and it was found that as the side group size of the poly(mono-*n*-alkyl itaconate) increases, the relative stability of the interpolymer complexes with PEOX increases as compared to that of the complexes with PDMA. Now the FTIR results explain that behavior.

A final remark, in relation to the previously stated adaptability of the PEOX chain, concerns the width of its free carbonyl band. When a polymer is mixed, the form of any infrared band can change due to environmental or conformational changes related to blending.[18] The amide group in PEOX is directly linked to the polymeric chain, and it is expected to show some conformational sensitivity for this absorption band. Figure 12 shows the half-height width of the PEOX free carbonyl band as a function of the alkyl side group length of the poly(mono-*n*-alkyl itaconate) for blends of stoichiometric composition. The PEOX free carbonyl band narrows as the poly(mono-*n*-alkyl itaconate) side group size increases. Narrower bands are typical of systems with higher structural regularity. It seems that blending with poly(mono-*n*-alkyl itaconates) of a bulky side group forces the PEOX chain to adopt a more regular and probably constrained conformation.

Conclusions

This work presents a FTIR study of the specific interactions when poly(mono-*n*-alkyl itaconate)s are blended with poly(ethyloxazoline) and poly(*N*,*N*-dimethylacrylamide). Hydrogen bonding occurs between carboxylic acid groups of poly(mono-*n*-alkyl itaconate)s and carbonyl groups of PDMA and PEOX. Infrared results suggest too similar strengths in hydrogen bonds with PDMA or with PEOX.

Some of the systems have been cast from solvents of a different chemical nature, and it has no substantial differences in the association extent reached by the systems has been observed. However, if the donor or acceptor ability of the solvent is high enough, casting can yield to phase-separated blends ($\Delta\chi$ effect[15]). Thus, casting from DMF solutions leads to phase-separated mixtures in poly(monoalkyl itaconate)/PEOX, but not in poly(mono-*n*-alkyl itaconate)/PDMA systems. This result suggests that hydrogen bonds with PDMA would be at least slightly stronger than bonds with PEOX. Phase-separated mixtures have been also obtained in many of the studied systems cast from pyridine or acetic acid.

Derivative techniques have been employed to obtain the free carbonyl band position. However, second derivatives presented asymmetric profiles, and the peak positions obtained did not lead to good quality fits. So, derivation techniques do not seem to be an accurate tool to obtain peak positions in these systems.

Curve fitting results show that blends of PMMI with PEOX or PDMA present the same interassociation extents. Blending with poly(mono-*n*-alkyl itaconate)s of a larger side group gives a steady loss of the interassociating ability of PDMA, not observed in blends with PEOX. This difference has been attributed to the larger interspacing between neighboring carbonyl groups in PEOX, resulting in higher chain conformational freedom degrees. There would be necessary higher steric hindrances in the medium to begin breaking hydrogen bonds with the PEOX chain. This result supports one explanation of the solution complexation behavior for these systems: it was observed that the relative intensity of the complexes poly(mono-*n*-alkyl itaconate)/PEOX compared to that of the complexes with PDMA increases with the side group length of the poly(mono-*n*-alkyl itaconate). Finally, the PEOX chain seems to be forced to adopt more regular and constrained conformations as the steric hindrances in the medium increase, as reflected by the variation of its free carbonyl band width.

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