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Study of the solvent role on complexation in systems poly(mono *n*-alkyl itaconate)/tertiary polyamide

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This paper reports a study of the solvent role on complexation in systems composed by a polyacid and a polybase. Complexation has been found in water, *n*-alcohols, ethers and acetone, depending on the chosen polymer pair and temperature. The temperature at which the transition from a biphasic system to homogeneous solution occurs, has been employed as a measure of the relative stability of the complex. In general, complexes with bulky side groups are less stable than those with small ones. The influence of solvophobic and hydrophobic interactions has been discussed. The stability of complexes in ethers shows a marked dependence on the aliphatic character of the polymeric system, showing a complexing character similar to that of *n*-alcohols for the polymer systems with lower aliphatic character. Acetone is the most complexing solvent, probably due to its lower competing ability. Finally, it has been found that the relative stability of complexes with poly(ethyloxazoline) (compared with those with poly(*N,N*-dimethylacrylamide)) increases with the size of the side group of the poly(mono *n*-alkyl itaconate). © 1997 Elsevier Science Ltd.

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INTRODUCTION

Interpolymer complexation through cooperative hydrogen bonding is a phenomenon usually found in solutions containing a polyacid and a polybase[1-3]. The study of cooperative interactions in solution is a subject of great interest, since this type of force controls many biological processes, and can yield highly interassociated materials suitable for use as drug release vehicles[4-7].

One of the most important factors governing interpolymer complexation is the solvent medium. In organic solvents, complexation depends mainly on the overall interaction balance[2]. Since hydrogen bonding is the stronger interacting force in these systems, strong donor or acceptor solvents (such as amides, sulfoxides, organic acids, etc.) can prevent complexation, owing to their competing ability with the interacting sites in the polymers. But, in solvents with weaker competing ability (such as alcohols, ethers, ketones, etc.), complexation can occur depending on the complexing character of the solvent and solvophobic interactions. Only a few works deal with the role of the solvent in these cases[1,2,8,9], and this work attempts to give insight into this subject. Complexation between poly(mono *n*-alkyl itaconate)s (with alkyl side groups ranging from methyl to dodecyl) and the tertiary polyamides poly(*N,N*-dimethylacrylamide) (PDMA) and poly(ethyloxazoline) (PEOX) has been studied. The poly(mono *n*-alkyl itaconate)s are polyacids with different side chain lengths, while the donor group remains unchanged. Thus, the major difference between them with regard to their complexation behaviour

should be their solvophilic character. Nevertheless, steric hindrances arising from the size of the side groups of the poly(mono *n*-alkyl itaconate) may influence complexation behaviour. PDMA and PEOX are two polybases with isomeric repetitive units that contain an amide group: known to be potential hydrogen bond acceptor group. Moreover, both polymers show similar acceptor strength, with no steric hindrances around the accepting sites, and thus show similar accepting abilities. However, PEOX shows stronger hydrophobic interactions than PDMA, that could result in an additional stabilisation of complexes in an aqueous medium.

The temperature at which the transition from a homogeneous to a heterogeneous solution occurs has been measured in water, *n*-alcohols, ethers and acetones. Its value is related to the complex stability, and has been employed to discuss the complexation behaviour in these systems.

EXPERIMENTAL

Poly(*N,N*-dimethylacrylamide) (PDMA) was bulk polymerised at 60°C with 0.5% azobis(isobutyronitrile) (AIBN) as initiator under an N₂ 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[10]:

$$[\eta] = 1.75 \cdot 10^{-4} M_v^{0.68} \text{ (dl g}^{-1})$$

giving a value $M_v = 2.9 \cdot 10^5$ g mol^{-1}.

PEOX is a Polysciences product, and was purified by solution-precipitation in the methyl ethyl ketone/*n*-hexane

Table 1 Molar masses of the poly(mono *n*-alkyl itaconate)s employed

Polymer	M_w (g mol^{-1})
PMMI	$1.3 \cdot 10^5$
PMEI	$2.5 \cdot 10^5$
PMPrI	$2.0 \cdot 10^5$
PMBuI	$3.5 \cdot 10^5$
PMPeI	$1.7 \cdot 10^5$
PMHeI	$3.9 \cdot 10^5$
PMDeI	$1.1 \cdot 10^5$
PMDoI	$9.2 \cdot 10^4$

pair. According to the supplier the molar mass of the sample is $M_w = 50\,000$ g mol^{-1}.

Mono *n*-alkyl itaconates were obtained by the esterification of itaconic acid with the corresponding *n*-alcohols, using acetyl chloride as catalyst, according to a method previously described[11,12]. The monomers were characterised by *FT*i.r., ^{1}H n.m.r. and ^{13}C n.m.r. The poly(mono *n*-alkyl itaconate)s used in this study, i.e. poly(monomethyl itaconate) PMMI, poly(monoethyl itaconate) PMEI, poly(monopropyl itaconate) PMPrI, poly(monobutyl itaconate) PMBuI, poly(monopentyl itaconate) PMPeI, poly(monohexyl itaconate) PMHeI, poly(monodecyl itaconate) PMDeI, and poly(monodedecyl itaconate) PMDoI, were obtained by free radical bulk polymerisation using 0.3% AIBN as initiator under N$_2$ atmosphere at 60 or 80°C, depending on the melting temperature of the corresponding monomer. The polymers were characterised by light scattering in methanol or tetrahydrofurane solutions at 25.0°C. The molar masses obtained are summarised in *Table 1*.

Turbidimetry has been employed to measure the temperature at which phase separation occurs for the different systems studied in this paper (T_s). Solvent media were distilled water and analytical grade methanol, ethanol,

n-propanol, *n*-butanol, THF, *p*-dioxane and acetone. The T_s values were averaged between two consecutive runs (cooling and heating), at a rate of 1°C min^{-1}. Typical differences between the values obtained in both runs are about 2 and 4°C in *n*-alcohols and ethers, respectively. Stoichiometric ratios of the polymers were used and the total polymer concentration was 1% wt/v.

Viscometric measurements were performed in *n*-pentanol solutions at 20°C, with a total polymer concentration of 0.5 g dl^{-1}, in a Ubbelohde type viscometer.

RESULTS

According to the chemical structures of the polymers (*Figure 1*), hydrogen bonding is expected to occur between carboxylic acid groups of poly(mono *n*-alkyl itaconate)s and amide groups of PDMA or PEOX. There are two possible interacting sites in PDMA and PEOX: the nitrogen atom and the carbonyl group. Studies performed on model compounds[13,14] have proved that hydrogen bonding with the carbonyl group is stronger, while interassociation with the nitrogen atom is negligible. Such interactions were verified by our research group[15,16] by means of *FT*i.r.

The addition of a poly(mono *n*-alkyl itaconate) solution to PDMA or PEOX, in organic solvents with complexing character (such as alcohols, ethers or ketones), yields a biphasic or a homogeneous solution, depending on the chosen solvent, polymeric system and temperature. Complexation was observed in methanol solutions when the polyacids employed were poly(acrylic acid)[7,17] or poly(methacrylic acid)[18]. Precipitation in those systems has been attributed to cooperative hydrogen bonding between the polymer chains, yielding insoluble species, called polymer–polymer or interpolymer complexes.

Heating can break the interpolymer complex. This process is reversible, and cooling leads again to a precipitate, at temperatures close to the one obtained in
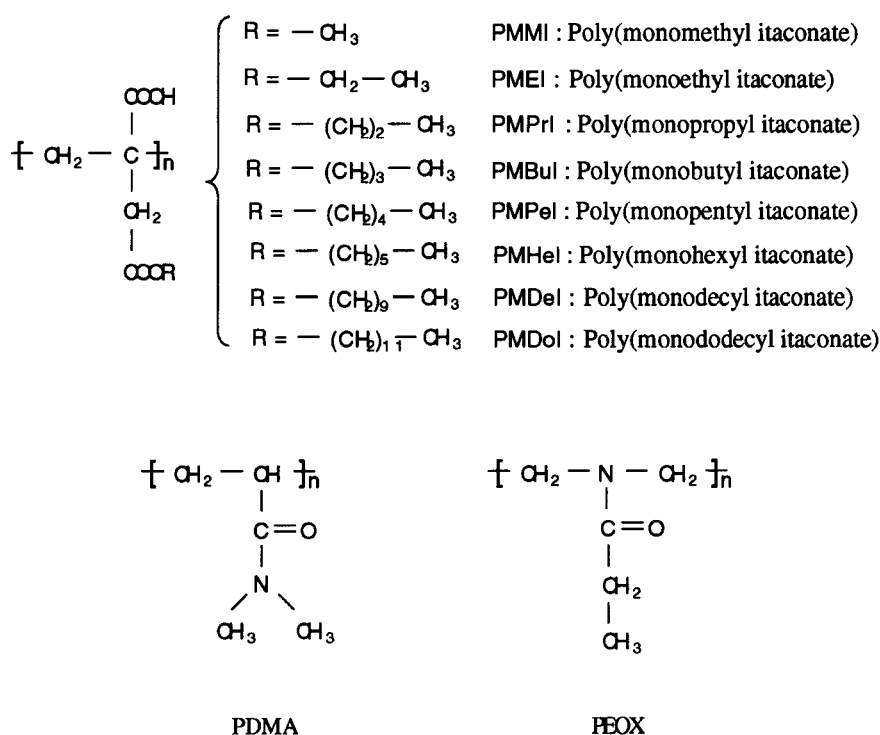
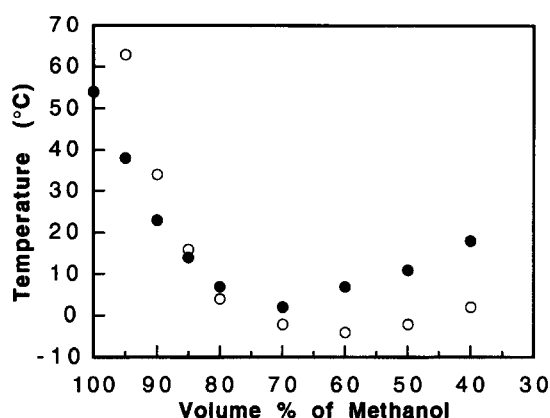**Figure 1** Chemical structures of the studied polymers

Figure 2 T_s values for the PMMI/PDMA (O) and PMMI/PEOX (●) systems in methanol/water mixtures as a function of the volume percentage of methanol

the heating run. In this case, heating weakens interchain association, and favours solvent–polymer interactions. The phase separation temperature of the system can be used as a measure of the relative stability of the complex for comparative purposes.

When feed composition was stoichiometric, stoichiometric precipitate compositions were found in all cases. Thus, the complexation mechanism is expected to be always the same. Results were classified according to the class of solvents studied: water, n-alcohols, ethers or ketones.

Water

PMMI is the only poly(mono n-alkyl itaconate) soluble in water, and its aqueous solutions with PDMA and PEOX have been studied. PEOX is known to show a higher number of hydrophobic interactions than PDMA: LCST behaviour has been observed in PEOX aqueous solutions at about 60°C, while PDMA solutions remain homogeneous. In the PMMI/PEOX system, precipitation has been observed at 25°C, whereas the PMMI/PDMA solution is homogeneous. This difference can be attributed to more hydrophobic interactions in the first system. The PMMI/PDMA system precipitates when heated to about 50°C. This can be attributed to the increase in the number of hydrophobic interactions with temperature, suggesting that they may also play an important role. The study of the phase separation temperature in media of different hydrophobic character can give an insight into the role of hydrophobic interactions. *Figure 2* shows T_s values measured in methanol/water solutions of different composition, where UCST behaviour has been found in all cases. When the medium is rich in

methanol, hydrophobic interactions are low, and water addition causes a significant decrease of the complex stability. Thus, water acts as a complexation inhibitor, probably due to its high ability to solvate the polar groups involved in complexation. Water is a strong solvent and its bonding strength with the polymer interacting sites is similar to that between the complexed polymers. Nevertheless, as the water content in the medium increases, its effect on the complex stability reverses, due to hydrophobic interactions between the aliphatic polymer chains. Addition of water causes a greater stability loss in complexes with PDMA, and the curve minimum occurs in media richer in water. This situation confirms that hydrophobic interactions are higher in systems with PEOX than with PDMA.

n-*Alcohols*

Phase separation temperatures have been measured in methanol, ethanol, n-propanol and n-butanol. Complexation with PEOX or PDMA has been observed in all cases even in dilute solutions (total polymer concentration 0.02% wt). This is a typical behaviour in hydrogen bonded complexes due to the cooperative nature of the interaction, even though some systems do not fit this general trend[2]. *Table 2* shows the transition temperature between a homogeneous solution and a biphasic system. Squares with no data correspond to systems in which the poly(mono n-alkyl itaconate) is insoluble. Results are briefly discussed in the following paragraphs.

Methanolic systems with PMMI exhibit a phase separation temperature much higher than the others in that solvent. This can be attributed to the stronger donor ability of PMMI, as shown in poly(mono n-alkyl itaconate)/poly(vinyl-pyridine) blends[19,20]. The other poly(mono n-alkyl itaconate)/polybase systems show similar T_s values. Finally, complexes with PDMA are more stable than those with PEOX when the side group of the poly(mono n-alkyl itaconate) is small. However, complexes with PEOX become more stable as the side group size of the polyacid increases.

Solutions in ethanol, n-propanol and n-butanol show T_s values higher than in methanol. As in methanol solutions, the relative stability of complexes with PEOX increases with the length of the side group of the poly(mono n-alkyl itaconate).

Figure 3 displays the phase separation temperature against the side chain length of the poly(mono n-alkyl itaconate) in n-butanol solutions. In complexes with PDMA, T_s decreases linearly as the side chain length of the poly(mono n-alkyl itaconate) increases. This behaviour could be due to an increase of the steric hindrances or to the

Table 2 T_s values for systems of stoichiometric composition in n-alcohols

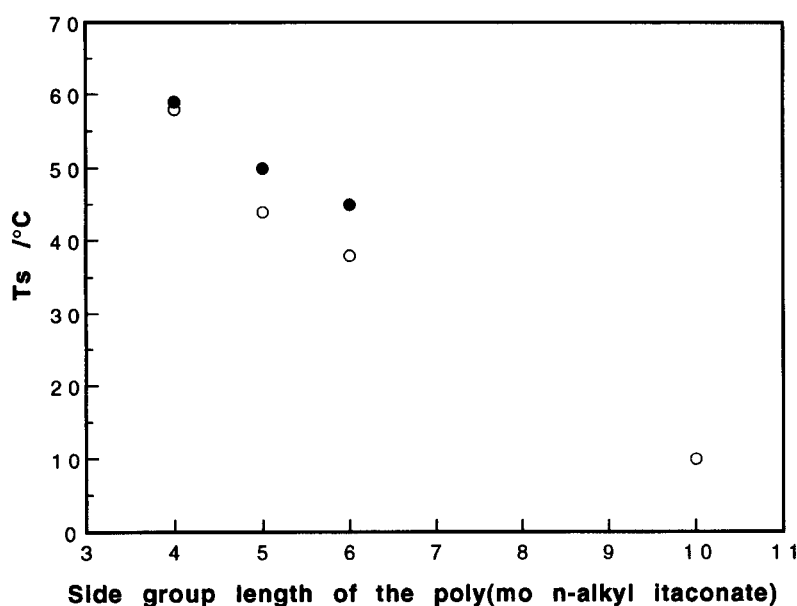|	T_s (°C) in methanol		T_s (°C) in ethanol		T_s (°C) in n-propanol		T_s (°C) in n-butanol	
	/PDMA	/PEOX	/PDMA	/PEOX	/PDMA	/PEOX	/PDMA	/PEOX
PMMI/	>65	54	–	–	–	–	–	–
PMEI/	35	26	>78	78	–	–	–	–
PMPrI/	15	16	60	60	58	61	–	–
PMBuI/	21	18	64	63	56	58	58	59
PMPeI/	11	18	54	58	42	49	44	50
PMHeI/	10	21	48	56	40	49	38	45
PMDeI/	–	–	–	–	–	–	11	<−20
PMDoI/	–	–	–	–	–	–	–	–

Figure 3 T_s values in butanol as a function of the side group length of poly(mono n-alkyl itaconate) for systems with PDMA (O) and with PEOX (●)

variation of the solvophobic interactions. Complexes with PEOX should show similar trends due to the similar acceptor strength of both polybases. Nevertheless, solutions containing PEOX and poly(mono n-alkyl itaconate)s with bulky side groups behave unexpectedly: system PMDeI/PDMA forms complexes at 11°C in n-butanol, but system PMDeI/PEOX does not show complexation even at temperatures as low as −20°C. Similarly, system PMDoI/PDMA complexes at 23°C in n-pentanol, while a homogeneous solution is again observed at −20°C in the PMDoI/PEOX system. Such behaviour can be attributed to the difference in molar masses between PEOX and PDMA: if polymers do not attain a critical chain lengths, complexation does not occur. Assuming a typical polydispersivity value of 2, the PEOX sample employed in this work would have a polymerisation degree of about 250, and the PMDeI and PMDoI intaconates of about 200. These values are close to the critical chain length of about 200 for the POE chain in the poly(acrylic acid)/poly(ethylene oxide) system reported by Ikawa et al.[21]. Thus, the most reasonable explanation for the absence of complexation in PMDeI/PEOX and PMDoI/PEOX systems in n-alcohols is that these systems do not reach the critical chain length required for complexation.

We would like to add a final consideration concerning polycomplex structure. Iliopoulos et al.[22,23] have proposed a complexation model that supposes the formation of 'sequences of uninterrupted bonds' longer than certain 'critical lengths'. These sequences would be complexed while shorter ones would not, adopting the form of loops. As stated previously, PEOX does not form precipitated complexes with PMDeI or PMDoI: however, according to the mentioned model, if those polymers had complexable sequences in their chains, those would link to each other, resulting in a solution viscosity different from the ideal behaviour. Viscosity measurements have been performed in n-pentanol for the PMDoI/PEOX system at 20°C, where complexation was expected. The specific viscosity of the system follows the additive behaviour, indicating the absence of interpolymer interactions. According to the model, this result implies that loops in complexes of the PMDoI/PEOX system (obtainable using longer polymer chains), could be very long, because our polymer samples

have not shown 'complexable sequences'. The formation of precipitated complexes with loops as long as those is difficult to understand, and we conclude that the previous model is not suitable to explain complexation in these systems. More likely, complexation seems to occur when the chains are long enough to form the required number of bonds that lead to the precipitated complex, irrespective of whether the bonds are formed in the vicinal sites or not. If not, complexation is not observed. The model of Iliopoulos et al. has been criticised in other works arguing that the formation of 'long uninterrupted sequences' would be restrained by large steric hindrances[24,25].

Water and n-alcohols are protic solvents, and now their complexing ability can be compared. Tsuchida et al.[1,8] studied the complexation in this class of solvents for the poly(methacrylic acid)/poly(vinylpyrrolidone) system. On the basis of the polymer concentration at which the polymer complex solution shows 50% transmittance, C_T, it was proposed that, for a given class of solvents, the complexing character of the solvent increases as C_T decreases. According to their results, complexation would be favoured as the solvent polarity increases. This behaviour was attributed to an increase of the hydrogen bonding ability between solvent molecules with the dielectric constant of the solvent, resulting in a decrease of the interaction forces between solute and solvent[1]. Nevertheless, Tsuchida et al. measured C_T only in methanol, ethanol and water. The first two points are very close to each other, while the last one must have a significative contribution due to hydrophobic interactions, as PVP possesses a large aliphatic surface. We have checked these results in our systems. *Figure 4* displays the T_s values obtained in methanol, ethanol, n-propanol and n-butanol solutions of systems containing PMBuI and PMHeI. As can be seen, in ethanol, n-propanol and n-butanol, T_s varies only slightly with solvent polarity. This result seems reasonable considering that the major factor governing interpolymer complexation in organic solvents is the overall interactions balance. Anyway, the general trend observed in these n-alcohols is a decrease of T_s (and thus, a reduction of the complexation impairing ability) with the solvent polarity. Solvophobic interactions may cause this behaviour: the polymeric systems studied possess a high aliphatic
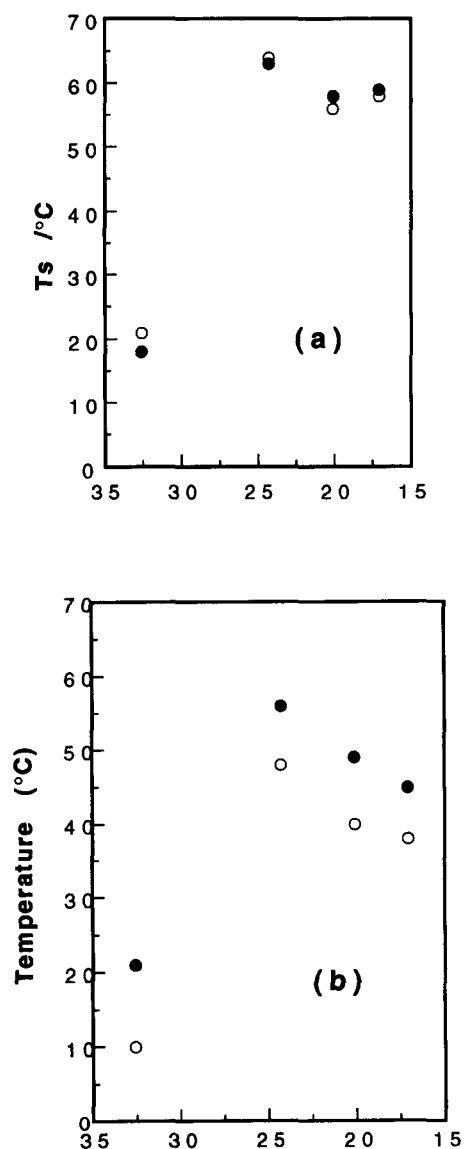
Figure 4 T_s values for the systems (a) PMBuI/PDMA (○) and PMBuI/PEOX (●) and (b) PMeI/PDMA (○) and PMHeI/PEOX (●) as a function of the solvent dielectric constant (methanol, ethanol, *n*-propanol and *n*-butanol)

character, and those interactions will be higher in polar *n*-alcohols. Moreover, T_s shows a higher slope in systems with PMHeI. As PMHeI is more aliphatic than PMBuI, it seems logical that there should be a larger reduction in solvophobic interactions in the first polymer as the aliphatic character of the solvent increases.

The phase separation temperature obtained in methanol is much lower than expected, taking into account the trend shown by the other *n*-alcohols. Strong solvent–polymer interactions must be assumed to explain this deviation, that may be due to a higher solvating ability of the solvent. Thus, the overall behaviour of protic solvents can be summarised as follows. *n*-Alcohols (apart from methanol) show a similar complexing ability. Differences between them can be explained by solvophobic interactions. Methanol shows a higher ability to impair complexation. Finally, complexation in water depends strongly on hydrophobic interactions. If these are not high, water shows an impairing ability even greater than *n*-alcohols (as in the PMMI/PDMA system).

Ethers

Of the solvents with this chemical functionality, tetrahydrofurane and *p*-dioxane have been chosen owing to the wide range of poly(mono *n*-alkyl itaconate)s that dissolve. Similarly to *n*-alcohols, complexation has been found even in dilute solutions (0.02% wt/v). *Table 3* shows the values obtained for T_s. This parameter shows a marked dependence on the alkyl side group of the poly(mono *n*-alkyl itaconate), which is stronger in THF than in *p*-dioxane. As for the *n*-alcohols, the relative stability of complexes with PEOX compared with those with PDMA increases with the side group size of the poly(mono *n*-alkyl itaconate).

Ketones

The only poly(mono *n*-alkyl itaconate) soluble in this medium is PMHeI. Its complexes with PEOX or PDMA are not broken below the boiling temperature of the solvent (56°C). The higher stability of complexes with PMHeI in this solvent can be attributed to its lower competing ability.

Recalling all the above data, further insight into the impairing ability of the solvents can be obtained. *Figure 5* shows the T_s values in several systems with PEOX, using ethers and *n*-alcohols as solvents. The following trends are observed: the complexing ability of ethers shows a marked dependence on the aliphatic character of the polymeric system. *n*-Alcohols also show dependence, more noticeable as the aliphatic character of the solvent increases. Thus, in the polymeric systems with lower aliphatic character, ethers and *n*-alcohols (methanol is an exception) show similar complexing abilities. Moreover, if data were extrapolated to the region of less aliphatic systems, THF would show the higher complexing ability. On the other hand, in the region of systems with high aliphatic character, THF would become the solvent with higher impairing power.

Table 3 T_s values for systems of stoichiometric composition in ethers

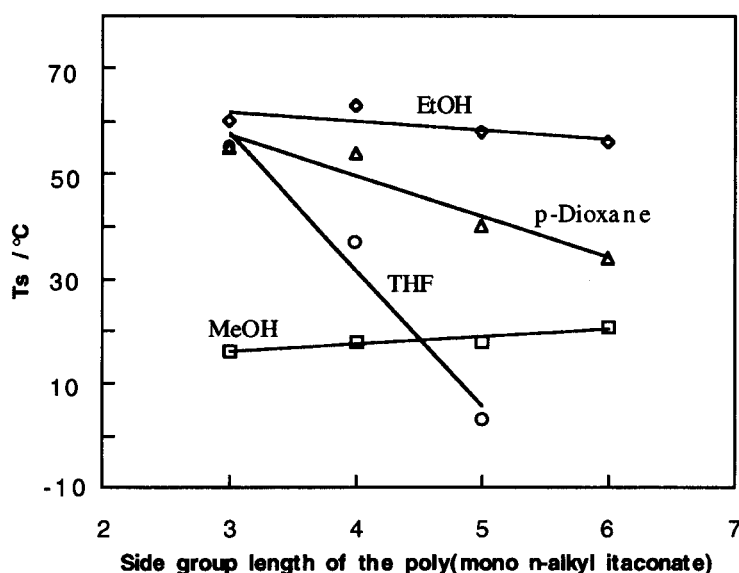|	T_s (°C) in THF		T_s (°C) in dioxane	
	/PDMA	/PEOX	/PDMA	/PEOX
PMMI/	–	–	–	–
PMEI/	–	–	–	–
PMPrI/	>65	55	>101	55
PMBuI/	>65	37	96	54
PMPeI/	65	3	68	40
PMHeI/	35	<−20	51	34
PMDeI	<−20	<−20	<12	<12
PMDoI/	<−20	<−20	<12	<12

Figure 5 T_s values obtained for the PMPrI/PEOX, PMBuI/PEOX, PMPeI/PEOX and PMHEI/PEOX systems as a function of poly(mono *n*-alkyl itaconate) side group length in methanol (□), ethanol (◇), *p*-dioxane (△) and THF (○)

Finally, it has been shown that the relative stability of complexes with PEOX, compared with those with PDMA, increases with the size of the side group of the poly(mono *n*-alkyl itaconate). An explanation for this behaviour was given in a previous paper. It was shown that, for a given composition, poly(mono *n*-alkyl itaconate)/PEOX systems reach the same interassociation extent irrespective of the side group size of the polyacid. However, in systems with PDMA, a steady loss in the interassociation ability with the length of the side group of the polyacid was found. This fact must result in an additional stability loss of the complex. From a structural point of view, such behaviour was attributed to the different nature of the polymeric chains of PDMA and PEOX. As can be seen, there are four covalent bonds between two vicinal groups in PDMA, while there are five in PEOX. This confers on the PEOX chain a higher ability to adopt a suitable conformation without breaking hydrogen bonds when the steric hindrances around the donor sites (due to the side groups of the poly(mono *n*-alkyl itaconate)) increase.

CONCLUSIONS

Experimental results show that poly(mono *n*-alkyl itaconate)s form intermacromolecular complexes with PDMA or PEOX when solvents of complexing character are employed. The measurement of phase separation temperature has been shown to be an adequate tool for the qualitative study of the stability of the complexes.

In general, it has been found that as the size of the side group of the poly(mono *n*-alkyl itaconate) increases, its complexes show lower stability. Within the *n*-alcohols, methanol shows an exceptional ability to impair interpolymer complexation. The other *n*-alcohols show a similar complexing character, and differences found between them can be explained in terms of the solvophobic interactions. Addition of water to methanol solutions has been found to cause a large reduction of the complex stability, indicating a high complexation inhibiting character for the water molecules. However, hydrophobic interactions also play an important role in this solvent, stabilising additionally the interpolymer complex. Thus, the PMMI/PDMA system

does not complex in aqueous medium, while the PMMI/PEOX system does, owing to its higher hydrophobic interactions.

The stability of complexes in ethers shows a marked dependence on the aliphatic character of the polymeric system. These solvents show a complexing character similar to that of *n*-alcohols for polymer systems with lower aliphatic character, but their complexation impairing ability is higher for systems with bulky aliphatic groups. Acetone is the most complexing solvent, probably owing to its lower competing ability.

Finally, it has been found that the relative stability of complexes with PEOX (compared with those with PDMA), increases with the size of the side group of the poly(mono *n*-alkyl itaconate). This behaviour agrees with a previous finding. In complexes with PDMA, it was reported[16] that the interassociating ability decreased as the side group size of the polyacid increased, while complexes with PEOX showed no dependence. From a structural point of view, such behaviour was attributed to the different nature of the polymeric chains of PDMA and PEOX: there are four covalent bonds between two vicinal groups in PDMA, while there are five in PEOX. This would confer on the PEOX chain a higher ability to adopt a suitable conformation without breaking hydrogen bonds when the steric hindrances around the donor sites increase.

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