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Polymer Cosolvent System

6. Effect of the Ortho Substitution on Poly(Phenyl Methacrylate)s in Tetrahydrofuran Water Mixtures

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Summary

Both preferential adsorption coefficient λ and intrinsic viscosity [η] for poly(di-o-alkylphenyl methacrylates)/Tetrahydrofuran (THF)/water have been determined. The results are discussed in relation to the steric effect of the ortho-substituent groups on the aromatic ring.

INTRODUCTION

Most of the investigations (STRAZIELLE, et al., 1961; DONDOS, et al, 1969; LANGE, 1965; COWIE, et al., 1972) on polymer cosolvent systems involve the measurements of the selective adsorption coefficient by the polymer of either of the non-solvents.

Selective adsorption by a polymer is considerably influenced by different factors (DONDOS, et al., 1970; MUNK, et al., 1978; KATIME, et al., 1974; GARGALLO, et al., 1984); the most important of these are: temperature, the nature of the liquids, polymer molecular weight, the thermodynamic nature of the solvents and of the mixture itself, the composition of the binary mixture, and the nature of the chemical structure of the polymer.

There are no exhaustive results dealing with the chemical structure of the polymer on the preferential adsorption (KATIME, et al., 1985). Particularly interesting seems to be the effect of the steric hindrance of the side group on the preferential adsorption.

We have previously measured the preferential adsorption coefficient λ of certain polymers with bulky side groups, i.e., polystyrene (PS), poly(4-tert-butylstyrene) (PTBS), poly(phenyl methacrylate) (PPh), poly(4-tert-butylphenyl methacrylate) (PBPh) and poly[4-(1,1,3,3-tetramethylbutyl)phenyl methacrylate] (POPh) in tetrahydrofuran (THF)/water (RADIC, et al., 1982). The behaviour of these polymers is very similar; water is preferentially adsorbed by the polymer at low water content in the solvent mixture. There is enhancement of the polymer solubility, and the solvent mixture is thermodynamically a better solvent than any of its components. Moreover, viscosity is higher in the mixed solvent than in the pure solvent. This cosolvent effect is explained by preferential adsorption

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of one of the components of the liquid mixture (RADIC, et al., 1982; GARGALLO, et al., 1984). A qualitative correlation between λ values and the rigidity factor σ ($\sigma=\langle r^2\rangle_0^{1/2}/\langle r^2\rangle_{0f}^{1/2}$) is found in these systems, i.e., λ decreases when σ increases.

In order to investigate the effect of ortho-substituents in polymers with aromatic bulky side groups on the preferential adsorption we have determined the λ coefficient by Differential Refractometry and Equilibrium Dialysis in poly(phenyl methacrylate) and its dimethyl and diisopropyl ortho derivatives. We also report the viscometric behaviour of these polymers in THF/water.

EXPERIMENTAL

Poly(phenyl methacrylate) (poly[1-(phenyloxycarbonyl)-1-methylethylene])(PPh), poly(2,6-dimethylphenyl methacrylate) (poly[1-(2,6-dimethylphenyloxycarbonyl)-1-methylethylene] (PDMPh), and poly(2,6-diisopropylphenyl methacrylate)(poly[1-2,6-diisopropyloxycarbonyl)-1-methylethylene]) (PDPPh) were prepared by radical polymerization at 50°C, under vacuum, in the homogeneous benzene phase and in the presence of 2,2'-azoisobutyronitrile.

Mixtures of THF/water were made by volume. The viscosities of dilute solutions were measured at 25°C by using a Desreux-Bischoff dilution viscometer. Both shear-rate and kinetic-energy corrections were unnecessary. The values of η_{sp}/c were plotted against concentration and extrapolated to zero concentration, in agreement with the classical Huggins and Kraemer equations.

Equilibrium Dialysis experiments were carried out in a dializer with a total volume of about 15 ml. The semipermeable cellophane membrane was conditioned in each of the solvent mixtures before using. Dialytic equilibrium was obtained in 6 h. (RADIC, et al., 1981). The preferential adsorption coefficient λ was determined by using the refractometric data and the relation

$$\lambda = (dn/dc)_\mu - (dn/dc)_k/(dn/dk),$$

where $(dn/dc)_k$ is the polymer refractive index increment in the solvent mixture, dn/dk is the variation of the refractive index of solvent mixture as a function of volumetric composition and $(dn/dc)_\mu$ the polymer solution refractive index increment after establishing equilibrium dialysis. Number average molecular weight $\overline{M}_n$ and weight average molecular weight $\overline{M}_w$ of the samples were determined by membrane osmometry and GPC respectively. The polymolecularity of the samples ($\overline{M}_w/\overline{M}_n$) was 1.3-1.4.

RESULTS AND DISCUSSION

Fig. 1 shows the variation of the preferential adsorption coefficient λ for PPh, PDMPh and PDPPh, in THF/water mixtures at 25°C for fractions of similar molecular weight (see Table 1). As can be seen, the variation of the λ coefficient with ν_2, the molar fraction of water, shows a minimum with an inversion

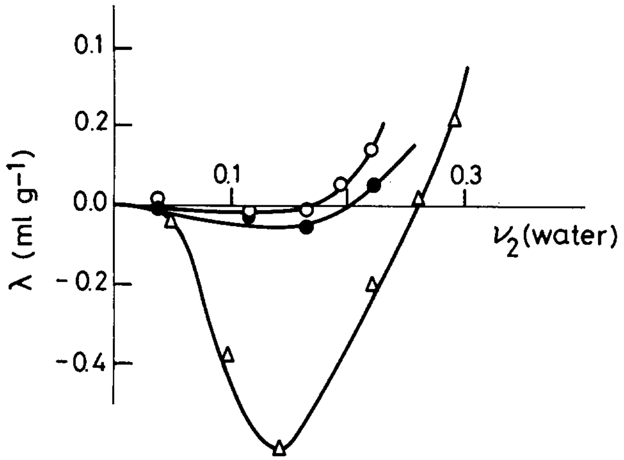


Fig. 1. Variation of the preferential adsorption as a function of solvent composition (Δ) PPh (GARGALLO, et al., 1984); (●) PDMPh; (O) PDPPh.

point ($\lambda = 0$) at $\nu_2 = 0.25$ for PPh (GARGALLO, et al., 1984). PDMPh seems to present a very slight preferential adsorption (<0.02 ml g^{-1}). But for PDPPh preferential adsorption was not observed in the composition range studied, considering experimental error.

This behaviour could be explained taking into account the presence of 2-6 substituents on the side aromatic ring of the polymer chain. They should give rise to a bigger difficulty for the adsorption of water molecules by the PDMPh; the preferential adsorption disappears for PDPPh as a consequence of the steric hindrance of the two isopropyl groups in ortho position. The effects are known of ortho-substituents on reactivities and ceiling temperatures of 2,6-substituted phenyl methacrylate monomers, as well as on the tacticities and thermal stabilities of the corresponding polymers (T.OTSU, et al., 1980).

The importance of specific interactions in the preferential adsorption phenomenon has been studied by different authors (KATIME, et al., 1977; RADIC, et al., 1982). According to these previous results, it is difficult to explain the water adsorption by specific interactions between polymer and water, because of the similar behaviour of polar and non-polar polymers. However, if the specific interactions between polar groups (carbonyl groups) and water were important, the ortho-substituent would overlap the carbonyl groups of the ester, and the preferential adsorption of water (the polar component of the mixture) would diminish.The effect of the overlapping of the carbonyl groups by side chains has been recently reported by Katime et al.(1985) in the case of PMMA and its derivatives.

On the other hand, in the case of poly(methacrylates) with para-substituted aromatic rings on the lateral chain, the preferential adsorption behaviour is quite similar in the sense that λ diminishes when the rigidity factor and the volume of the side groups increase (GARGALLO, et al., 1984); in all cases, however, there is a strong water adsorption.

When considering the preferential adsorption, one can imagine three different models for the physical image of this phenomenon (GARGALLO, et al., 1982). One model considers the preferential sorption to be located only in the first solvation layer, but not in the total volume of the coil. Furthermore, sorption is uniform along the chain.

Experimental evidence has been reported, which does not yet provide a clear support for this model, but the results may be interpreted as an indication for the location of adsorption in a polymer coil (GARGALLO, et al., 1982). According to this model, the preferential adsorption behaviour would be different if the rigidity of the chain and the steric hindrance increased.

The viscometric behaviour of aromatic polymethacrylates in THF/water, i.e., poly(4-tert-butylphenyl methacrylate) and poly[4-(1,1,3,3-tetramethylbuthyl)phenyl methacrylate], shows that water enhances the solubility of these polymers. The intrinsic viscosity was taken as a measurement of the solubility (GARGALLO, et al., 1984).

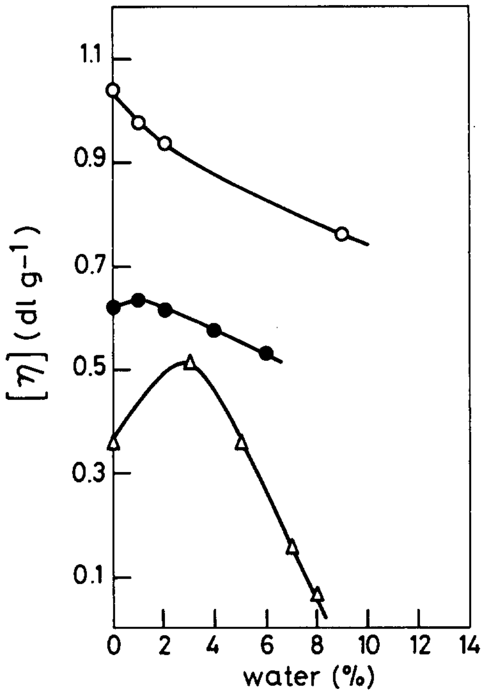


Fig. 2. Variation of the intrinsic viscosity [η], as a function of the solvent composition, (Δ) PPh, $\overline{M}_w$: 92.000; (●) PDMPh, $\overline{M}_w$: 260.000 and (o) PDPPh, $\overline{M}_w$: 403.000; in the THF/water mixtures.

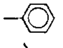
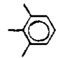
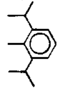
Fig. 2 shows the viscometric behaviour of PPh, PDMPh and PDPPh in THF/water mixtures. We can see that the intrinsic viscosity [η] plotted as a function of the binary solvent composition is completely different. In this figure we have selected three samples of very different molecular weight in order to illustrate that even for high molecular weight, in the case of ortho substituted polymers, the cosolvent effect disappears.

It is interesting to note that in the case of poly(2,6-diisopropylphenyl methacrylate), the cosolvent effect disappears in this mixture. This result shows an anomalous behaviour, if we compare these systems with the para-substituted aromatic polymer, i.e.,PBPh and POPh (RADIC, et al., 1982).

Finally, this comparative study would indicate that the cosolvent effect decreases or disappears when the preferential adsorption λ is very small or is not observed.

Table 1 summarizes the values of the preferential adsorption coefficient at the composition where the adsorption is maximum (minimum of the curve), as well as the molar volume, the structure of the side group, and the average molecular weight of the samples. The amount of water adsorbed by the polymer decreases as the molar volume (V) and the number of carbon atoms (n) of the side chain increase. Fig. 3 shows a linear dependence of inversion composition $\nu_2(\lambda=0)$ on V and n. From this figure we can see that equisolvation ($\lambda=0$) is reached at lower water composition as the volume of the side group increases. These results may indicate that the size and nature of the side group would play an important role in the adsorption of the polar component of the mixture.

TABLE 1. Preferential adsorption coefficient, λ, composition of the inversion point ($\lambda = 0$), molar volume of the side group, weight average molecular weight $\bar{M}_w$, structure of the side group, and rigidity factor σ.

polymer	$\nu_2(\lambda=0)$ % v/v	λ min ml mg^{-1}	Molar volume of side group (cm^3)	n	$\bar{M}_w \times 10^{-5}$	side group	$\sigma = \frac{\langle r^2\rangle_o^{1/2}}{\langle r^2\rangle_{of}^{1/2}}$
PPh	0.26	-0.60	0.933	6	2.47		2.45
PDMPh	0.21	-0.05	1.016	8	2.60		2.83
PDPPh	0.17	<-0.01(~0.0)	1.040	12	2.44		3.46

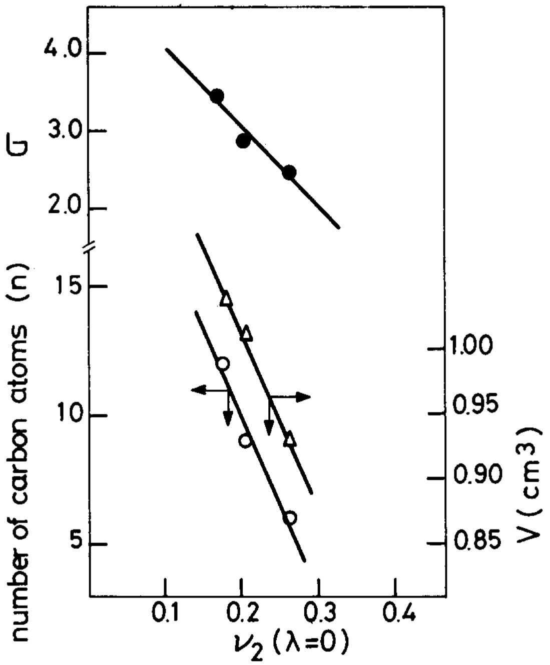


Fig. 3. Dependence of the inversion composition $\nu_2(\lambda=0)$ of the preferential adsorption on the number of carbon atoms (o) and molar volume (Δ) of the side group and with the rigidity factor (●).

Fig. 3 also shows a linear relationship between the composition of the inversion point and the rigidity factor, σ. These results agree with the others which support the model of preferential adsorption, which considers that the adsorption is along the chain.

Therefore, according to our experimental results, we think that one of the main factors which would condition the cosolvent effect could be the preferential adsorption of one of the solvents of the binary mixture. Apparently the relative preferential adsorption decreases by the introduction of the orthosubstituents in the following order: PPh>PDMPh>PDPPh.

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