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4. Influence of Nature and Size of the Lateral Group in the Preferential Solvation of Aromatic Polymethacrylates in Tetrahydrofuran/Water

Ligia Gargallo, Hernán Ríos and Deodato Radic

Laboratorio de Físico Química Molecular. Faculted de Química Pontificia Universidad Católica de Chile, Casilla 114-D, Santiago, Chile

Summary

The preferential adsorption parameter λ of poly(phenyl methacrylate), poly[4-(1,1,3,3- tetramethylbutyl) phenyl methacrylate] and poly(4-tert-butyl styrene) in the mixture THF/water has been determined by exclusion chromatography (GPC) and differential refractometry and dialysis equilibrium (DR). The general behaviour of the polymers studied in this mixture is very similar, water is preferentially adsorbed by the polymer at low water content. The results are discussed in relation to the rigidity of the macromolecular chains and the hydrophobic degree of the substituent group in the aromatic ring.

INTRODUCTION

It is well known that the behaviour of polymer solutions in binary solvents is influenced considerably by the thermodynamic nature of the solvents and of the mixture itself (DONDOS, et al., 1970; MUNK, et al., 1978; GARGALLO, et al., 1980). The thermodynamic properties of the mixture seems to play an important rol in the solvating process of polymeric solutes. Tetrahydrofuran (THF/water is an interesting mixture because THF is one of the most common good solvents for poly(methacrylate)s and water is a non-solvent for these polymers. The mixture is strongly non-ideal. At 298.15 K the excess enthalpy curve is S-shaped, with a zero value near 0.4 mole fraction of water (ERVA, 1955; NAKAYAMA, et al., 1973; GLEW, et al., 1973). The excess Gibbs free energy is positive (SINGER, et al., 1969) and the excess entropy and volume are negative over the whole mole fraction range (SINGER, et al., 1969; MATOUS, et al., 1972; MORCOM, et al., 1970). However, there are fairly large discrepancies between the published excess enthalpy results. In previous paper (VIRA, et al., 1974; RADIC, et al., 1982) it has been reported the enhancement of the polymer solubility when a non-solvent is mixed with a solvent. Particularly this mixture show a cosolvency and preferential adsorption effect in poly(4-tert-butylphenyl methacrylate) (PBPh) and polystyrene (PS). In both system water is preferentially adsorbed by these polymers (RADIC, et al., 1982).

One of the most accepted models to explain the preferential adsorption is that which consider that preferential adsorption is located only in the first solvation layer, but not in the total volume of the coil, and that is uniform along the chain (GARGALLO, et al., 1982). According with this model, the preferential adsorption behaviour would be different if the rigidity of the chain and the steric hindrance increase. To take into account the effect of the structure in the preferential adsorption we have determined the λ coefficient by exclusion chromatography (GPC) and differential refractometry and dialysis equilibrium (DR) in poly(phenyl methacrylate)(PPh), poly[4-(1,1,3,3-tetramethylbutyl)phenyl methacrylate] (POPh) and poly(4-tert-butyl styrene)(PTBST) in the mixture THF/water and to compare these polymers with polystyrene (PS) and poly (4-tert-butylphenyl methacrylate) (PBPh) previously reported (RADIC, et al., 1982).

EXPERIMENTAL

The polymers used in this study were commercial polystyrene and poly(4-tert-butylstyrene). Poly(phenyl methacrylate), poly(4-tert-butylphenyl methacrylate) and poly[4-(1,1,3,3-tetramethylbutyl)phenyl methacrylate] were prepared by radical polymerization as it was described in previous papers (GARGALLO, et al., 1977; OJEDA, et al., 1980). All the samples have similar molecular weight.

Exclusion chromatography was performed in a Perkin Elmer High Performance Liquid Chromatograph (HPLC) equipped with a 6000 psi pump, a Perkin Elmer differential refractometer LC-25, an injector of 175 µl, and Shodex A805/S column (molecular weight range 10^4-$5\cdot10^6$). Samples were eluted with the mixture tetrahydrofuran-water of the corresponding composition. The flow rate was always 1 ml/min.

Mixture of THF/water were made by volume. The polymer solutions were prepared inmediately before injection, using solvent mixtures from the solvent reservoir.

Equilibrium dialysis experiments were carried out in a dialyzer with a total volume of about 15 ml. The semipermeable cellophane membrane was conditioned in each of the solvent mixtures before use. Dialytic equilibrium was obtained in 6 h. (RADIC, et al., 1981).

RESULTS AND DISCUSSION

The preferential adsorption coefficient λ for THF/water/PPh, THF/water/POPh and THF/water/PTBST systems was determined by using the refractometric data and the classical relation:

$$dn/dk\cdot\lambda = (dn/dc)_\mu - (dn/dc)_k \qquad (1)$$

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 $(dn/dc)_\mu$ i.e. the polymer refractive index increment after establishing dialysis equilibrium.

The experimental determination of preferential adsorption parameter λ has been performed also by exclusion chromatography. This is another procedure which is a good and fast technique for the determination of λ. The frequent presence of vacant peaks in gel permeation chromatograms is a known experimental fact when working with mixed solvents (SLAIS, et al., 1974; BEREK, et al., 1976) what is the result of the differences in composition between the solvated polymer and the rest of the solvent. An increase in the composition of one of the components of the mixed solvents in the vicinity of the polymer coil leads to a decrease of the composition of this component in the rest of the solvent, as BEREK, et al., (1976), pointed out.

By this way the preferential adsorption parameter λ can be defined as the difference in volume fraction of the component which is adsorbed with respect to the polymer concentration, in the "dialyzed" solvent at infinite dilution (BEREK, et al., 1976). In a ternary system solvent(1)-solvent(2)-polymer(3), the expression for λ would be

$$\lambda = \frac{d\nu_1}{dC_3} = \frac{d\nu_2}{dC_3} \qquad (2)$$

where ν_i is the mol fraction of solvent i, and C_3 is the polymer concentration in g/ml.

In order to relate in a quantitative form the size of the vacant peak with the preferential adsorption parameter λ, before injecting any polymer, a THF solution of known concentration in a given eluent mixture was injected. The height of the THF peak h_1 was related to the difference in the volume fraction of water ($\Delta\ \gamma_H°$) between the mixture and the above THF solution injected. The injection of polymer solution will provoke a vacant THF peak which height is h_2, and can be related to change in volume fraction of water $\Delta\ \gamma_H$ because of the preferential adsorption and therefore,

$$\frac{\Delta\ \gamma_H}{h_2} = \frac{\Delta\ \gamma_H°}{h_1} \qquad (3)$$

Taking into account equation (2) and replacing the differential by increments and introducing in this equation the $\Delta\ \gamma_H$ value given by equation (3), the expression for λ is

$$\lambda = \frac{\Delta\ \gamma_H°}{C_3}\ \frac{h_2}{h_1} \qquad (4)$$

The results obtained from the different chromatograms performed for the different polymers in the THF/water mixture are summarized in Table 1 and 2, where the value of λ has been obtained from equation (4).

Table 1. Preferential solvation parameter λ determined by exclusion chromatography for three ternary systems: PPh/THF/water, PBPh/THF/water and POPh/THF/water.

ν_{THF}	$\Delta\ \gamma_H° \times 10^3$	$C_3 \times 10^3$ g/ml	h_1 (mm)	h_2 (mm)	λ
THF/WATER/PPH					
0.92	0.72	3.5	5.0	6.0	- 0.24
0.86	1.41	4.0	4.0	7.0	- 0.62
0.81	0.60	3.2	2.0	5.5	- 0.515
0.74	1.90*	25.0	76.0	1.0	0.001
THF/WATER/PBPH					
0.95	0.40	3.0	1.0	6	- 0.08
0.90	1.00	4.5	8.0	7.5	- 0.208
0.86	1.40	2.5	9.0	5.5	- 0.34
0.78	1.70	3.0	12.0	6.0	- 0.283
0.71	1.60*	3.0	36.0	6.0	0.088
THF/WATER/POPH					
0.95	0.30	4.5	7.0	7.5	- 0.07
0.86	0.90	3.0	5.0	6.0	- 0.38
0.83	1.50	5.2	11.5	8.0	- 0.20
0.80	1.26	6.0	38.0	9.0	- 0.05

(*) The pure component injected was water.

Table 2. Preferential solvation parameter, determined by exclusion chromatography for PS/THF/water and PTBST/THF/water.

ν_{THF}	$\Delta\ \gamma_H° \times 10^3$	$C_3 \times 10^3$ g/ml	h_1 (mm)	h_2 (mm)	λ
THF/WATER/PS					
0.95	0.62	6.0	85	9.0	- 0.011
0.90	5.0	5.0	28	8.0	- 0.079
0.86	3.50	3.5	34	6.0	- 0.100
0.78	15.00	15.0	68	7.0	- 0.018
THF/WATER/PTBST					
0.95	0.40	8.0	13	8	- 0.031
0.90	0.90	8.5	24	9	- 0.039
0.81	0.60	8.2	14	9.5	- 0.049
0.74	1.90*	8.0	40	8.5	- 0.050

(*) The pure component injected was water.

Table 3 summarized the λ values obtained by differential refractometry and dialysis equilibrium for PPh, POPh and PTBST.

Table 3. Preferential adsorption coefficient λ, determined by DR and the composition of the mixture, for PPh, POPh and PTBST.

Polymer	ν_2 (mol fraction)	λ ml g^{-1}
PPh	0.050	- 0.04
	0.100	- 0.38
	0.140	- 0.62
	0.220	- 0.20
	0.290	0.22
POPh	0.050	- 0.15
	0.100	- 0.36
	0.140	0.39
	0.190	- 0.09
	0.220	0.07
	0.240	0.14
PTBST	0.040	- 0.040
	0.078	- 0.095
	0.140	- 0.035
	0.205	- 0.050
	0.220	- 0.015
	0.265	0.050

Fig. 1 show the variation of the preferential adsorption coefficient λ for PPh and POPh, in THF/water mixtures at 25°C determined by differential refractometry and dialysis equilibrium and by exclusion chromatography. In the same figure, the variation of λ coefficient for PBPh in the same mixture taken from the literature (RADIC, et al., 1982) is shown.

As can be seen in Figs. 1 and 2 the variation of the λ coefficient with γ_2 the molar fraction of water show a minimum with an inversion point (λ= 0) at ν_2= 0.25 for PPh; ν_2= 0.26 for PBPh; ν_2= 0.26 for POPh; ν_2= 0.23 for PS and ν_2= 0.25 for PTBST.

These figures show the same trend for the results obtained from GPC and dialysis equilibrium.

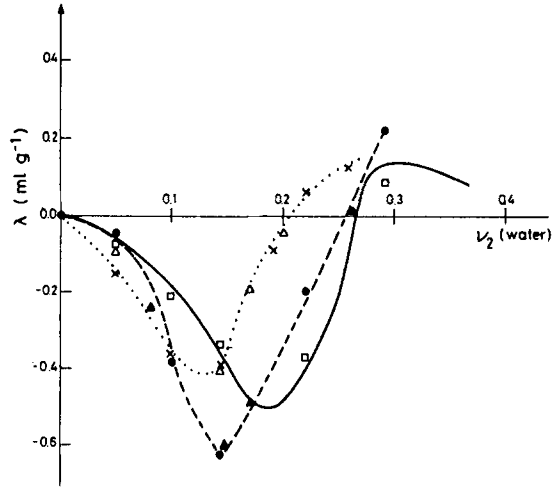


Fig. 1
Variation of the preferential adsorption coefficient as a function of solvent composition: ---PPh (●, DR; ▲, GPC); — PBPh (—, DR from RADIC, et al., 1982; □, GPC); ···POPh (X, DR; Δ, GPC).

The results show a good agreement between the two techniques. It is interesting to note that the agreement between GPC and dialysis equilibrium is good throughout all the composition range, showing that GPC techniques is a good experimental procedure to determine the preferential adsorption behaviour of polymer in binary systems.

The general behaviour of the polymers studied in the THF/water mixture, is very similar i.e. water is preferentially adsorbed by the polymer at low water content of the solvent mixture, as it has been previously reported (RADIC, et al., 1982).

It can be seen that the variation of λ in these systems is rather different, and that the amount of the adsorbed water by the polymer decreases with the increasing in the substitution degree in the aromtic ring, i.e. the sequence of the λ values in the minimum of the curve are PPh>PBPh>>POPh.

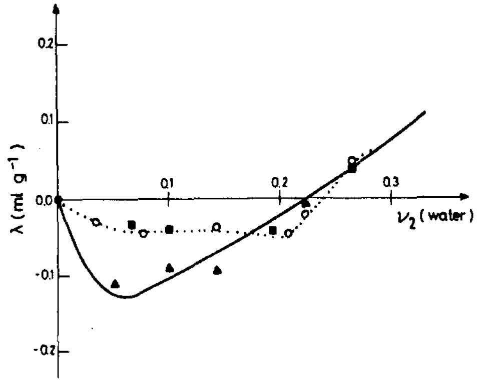


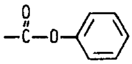
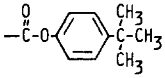
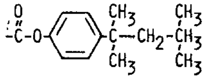
Fig. 2
Variation of the preferential adsorption coefficient as a function of solvent composition: —— PS (—, DR from RADIC, et al., 1982; ▲ GPC); ··· PTBST (o, DR; ■, GPC).

Similar results are obtained in the case of PS and PTBST (λ values are PS>PTBST). Fig. 2 show the variation of λ for these systems in THF/ water mixture, at 25°C determined by exclusion chromatography and (DR). The plot for PS determined by DR, has been taken from the literature (RADIC, et al., 1982). As in the case of poly(methacrylate)s mentioned above, there is a decreasing in the λ values when the aromatic ring have alkyl groups as substituents. This behaviour can be explained taken into account at least two factors. In fact if the model accepted to explain the preferential adsorption is that which consider that this phenomenon occurs along the polymer chain, the rigidity of the macromolecule must influence the amount of the adsorbed solvent, what can be observed in Table 4, where the rigidity factor ($\sigma = \langle r^2_0\rangle^{1/2}/\langle r^2_{0f}\rangle^{1/2}$) for the different poly(methacrylate)s and the value of the preferential adsorption coefficient in the maximum adsorption (minimum of the curve) is compared. On the other hand, the presence of hydrophobic substituents in the aromatic ring of the polymer chain, should provoke a bigger difficulty for the adsorption of water molecules by the polymer, and therefore the decreasing of the amount of adsorbed water could be explained also as a consequence of this effect.

Although the main factors which would govern the preferential adsorption of one solvent by a polymer in a binary mixture is matter of discussion, the results of this work would show that the nature and size of the side group, the rigidity of the chain and the hydrophobic interaction play an important rol in this phenomenon.

In the case of PS and PTBST the behaviour is similar to that of methacrylates, the explanation is similar, although according with the literature (KATIME, et al., 1973), the rigidity factor of substituted polystyrenes is quite similar. Perhaps in these systems the main factor which would condition the preferential adsorption would be the hydrophobic interaction.

Table 4. λ values in the maximum adsorption, rigidity factor σ and the structures of the side groups of poly (methacrylate)s.

Polymer	λ(min) ml g^{-1}	$\sigma = \frac{\langle r_0^2 \rangle^{1/2}}{\langle r_{of}^2 \rangle^{1/2}}$	Side group
PPH	0.62	2.75[a]	
PBPH	0.50	2.90[b]	
POPH	0.44	3.36[c]	

[a] Hadjichristidis, et al., 1972 ; [b] Gargallo, et al., 1977; [c] Ojeda, et al., 1980.

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