

Preferential adsorption behaviour of several vinyl polymers in poly(ethylene glycol)(1)/THF(2)

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SUMMARY

The preferential sorption coefficient in the ternary systems vinyl polymers (3)/ Poly (ethylene glycol) (1)/THF(2) has been determined in dilute solutions by dialysis equilibrium differential refractometry at 633 nm and 298 K. A series of vinyl polymers of different side groups (Polystyrene, Poly (p-iodostyrene), Poly (n-vinyl carbazole), Poly (vinyl chloride) and Poly (methyl methacrylate)) has been studied.

The results indicate that polymer side group play a fundamental role in the solvation behaviours of vinyl polymers. The characteristics of the polymer side group influences the kind and intensity of the polymer-binary solvent interactions and so, the rest of solution properties of these systems.

INTRODUCTION

When a mixture of two liquids is employed as a solvent for polymers, its solvent power is usually quite different from the averaged solvent power of the two pure solvent components. Such solutions also exhibit preferential adsorption of one component onto polymer and this phenomena seems to be a general property. This adsorption phenomenon is due to the difference in affinity of each solvent with regards to the polymer, and leads to composition variations of the mixed solvent in the vicinity of the macromolecular coil. The preferential solvation is affected by several factors such as: temperature, nature of the solvents, polymer molecular weight, thermodynamic nature of the solvents and of the mixture, binary mixture composition and polymer structure. The influence of these parameters has been studied by Katime et al. (1982,1975) and Vira

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et al. (1974) in non polar polymers like polystyrene (PS). Katime et al. (1985) have also study this phenomena in a family of polars polymers like polymethacrylates.

In the present work, we are going to study the preferential solvation phenomena that take place in the systems constituted by a vinyl polymer dissolved in poly (ethylene glycol) (1)/ Tetrahydrofuran (2) binary mixtures. We have studied the behaviour of five different vinyl polymers: Poly(p-iodostyrene) (IPS), Poly(n-vinyl carbazole) (PNVK), Poly(vinyl chloride) (PVC), Poly(methyl methacrylate) (PMMA) and Polystyrene (PS).

Our ternary systems are constituted by two polymers (one of very low molecular weight) and one organic solvent. One of the polymers in the ternary systems is always the poly (ethylene glycol) of 2000 g/mol and this oligomer acts like a solvent in the dialysis process.

The study has been carried out in order to determine the influence of the side group of the polymer chain on the solution behaviour of the polymer. We have used dialysis equilibrium differential refractometry as the main technique in order to analyze the preferential adsorption of one of the solvents forming the binary mixture to the polymer chain.

EXPERIMENTAL PART

All the solvents used have been purified following the standard methods (RIDDICK, BUNGER 1970; PERRIN, ARMAREGO 1988). Special precautions were assumed to avoid peroxides formation in tetrahydrofuran.

Poly(vinyl carbazole) was prepared via radical polymerization at 323 K using benzene as solvent and 2,2'-azobis(isobutyronitrile) (AIBN) as initiator. The commercial monomer (Fluka) was previously purified via Plesch method (1973) consisting on several recrystallizations in methanol, followed by vacuum drying until constant weight. The polymer obtained was subjected to fractional precipitation using benzene/methanol as solvent/precipitant pair in order to obtain polydispersities lower than 1.3.

Poly(ethylene glycol) and Poly(vinyl chloride) were from Fluka. Poly(ethylene glycol) commercial specifications indicated a molecular weight around 2,000 g/mol and a polydispersity lower than 1.17. Poly(vinyl chloride) was characterized via Gel permeation chromatography (GPC), giving an approximate molecular weight of 45,000 g/mol with a polydispersity lower than 1.15.

Polystyrene was synthesized from commercial monomer (Fluka) via anionic polymerization. The monomer was previously purified by distillation under reduced pressure. The polymer was then fractionated using benzene/methanol as solvent/precipitant pair in order to obtain polydispersities lower than 1.02.

Poly(p-iodostyrene) was obtained by iodation of polystyrene with Iodine and Iodic acid, using nitrobenzene as solvent (BRAUN et al. 1962). Poly(methyl methacrylate) was also synthesized from the monomer as described elsewhere (KATIME et al. 1988).

Dialysis technique was developed as explained elsewhere (KATIME et al. 1979) using bronze dialyzers with a total volume of about 15 ml. The membranes used for the dialysis equilibrium are commercial semipermeable cellophane or regenerated cellulose. Membranes are conditioned in each of the solvent binary mixtures. The dialytic equilibrium is normally obtained in five or six hours. Differential refractometry measures were performed at $298.0 \pm 0,1$ K using Brice-Phoenix BP-2000V differential refractometer. The radiation source was a 0.5 mW He-Ne laser, and the used wavelength was the one corresponding to red (633 nm). Aqueous solutions of sodium chloride at 298 K were used for the calibration of the differential refractometer.

In our notation, the indices 1 and 2 will be used for the two components of the binary mixture and index 3 for vinyl polymers.

Solvent mixtures were prepared by weighing appropriate volumes of THF and PEG, and the composition is reported as a volume fraction before mixing. The different vinyl polymers solutions were prepared by dissolving a known amount of vinyl polymer in the binary mixture in a volumetric flask.

Preferential adsorption coefficient, λ_1 , was calculated by differential refractometry of dialysis equilibrium and interferometry using the equation (ZIVNY et al. 1967):

$$\lambda_1 = \frac{\left(\frac{dn}{dc}\right)_\mu - \left(\frac{dn}{dc}\right)_k}{\frac{dn}{d\phi_1}}$$

where $(dn/dc)_\mu$ is the specific refractive index of the polymer in the mixed solvent at constant chemical potential of the components, $(dn/dc)_k$ is the specific refractive index increment of the polymer measured directly in the mixed solvent of composition ϕ_1 and $dn/d\phi_1$ is the variation in the refractive index of the binary solvent mixture with composition.

RESULTS AND DISCUSSION

In Figures 1 and 2 are represented the coefficients of preferential adsorption, λ_1 , as a function of the binary mixture composition for the five studied polymers. The solvent composition is given as volume fraction of solvent 1 (PEG) in the binary mixture PEG(1)/THF(2) and is represented as ϕ_1 . So, we are representing in those plots the amount in which Poly(ethylene glycol) is preferentially adsorbed to the polymer chain with respect to the other solvent of the binary mixture (THF).

Looking at those figures, we can conclude that THF is preferentially adsorbed to the polymer chain (negative λ_1 values) in the zone of small ϕ_1 values (when the binary mixture is in fact a dilute solution of PEG in THF). This can be explained if we take into account that THF behaves as a good solvent of Poly(ethylene glycol), solvating Poly(ethylene glycol) molecules and avoiding Poly(ethylene glycol)-polymer interactions. In other words, there is a competition between THF and the polymer molecules to interact with Poly(ethylene glycol), being the THF-PEG more favoured at this stage. As ϕ_1 increased, PEG(1)/THF(2) becomes grater and THF cannot solvate Poly(ethylene glycol) molecules as intensively as with small ϕ_1 values, allowing Poly(ethylene glycol)-polymer interactions. Increasing ϕ_1 , this tendency can even lead to a preferential solvation of Poly(ethylene glycol) on the polymer chain, as occurs with Poly(vinyl chloride), Poly(vinyl carbazole) and Poly(methyl methacrylate).

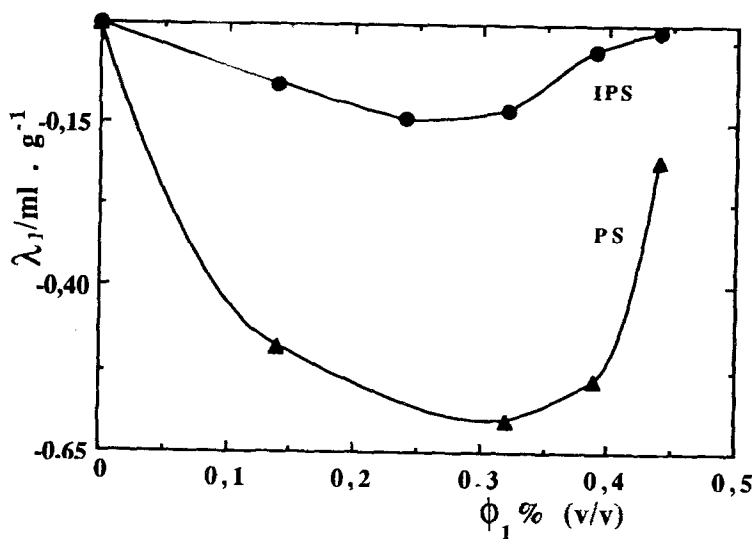


Figure 1. Preferential sorption coefficient, λ_1 , as a function of volume fraction of PEG for Polystyrene and Poly(p-iodostyrene)

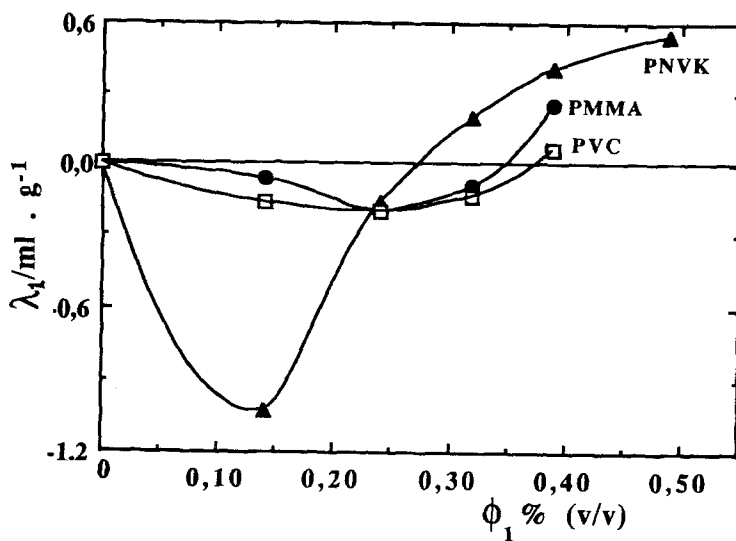


Figure 2. Preferential sorption coefficient, λ_1 , as a function of volume fraction of PEG for Poly(n-vinyl carbazole), Poly(methyl methacrylate) and Poly(vinyl chloride)

Comparing the five systems studied in this paper, we must point out that the polymers with halogenated side groups (Poly(vinyl chloride) and Poly(p-iodostyrene)) show lower λ_1 values. It is a remarkable fact the great difference between Polystyrene and Poly(p-iodostyrene) behaviours. The decrease in THF preferential solvation from Polystyrene to Poly(p-iodostyrene) systems can be explained considering the negative charge area produced by an halogen atom like iodine or chlorine. This negative area enhances Poly(ethylene glycol)-polymer interaction provided the Poly(ethylene glycol) structure proposed by H. Tadokoro (1984). In this structure (Fig. 3), Poly(ethylene glycol) forms an helix with the oxygen atoms in the inside and the methylene groups in the outside of the structure, making easier the interaction of partially negative charged areas.

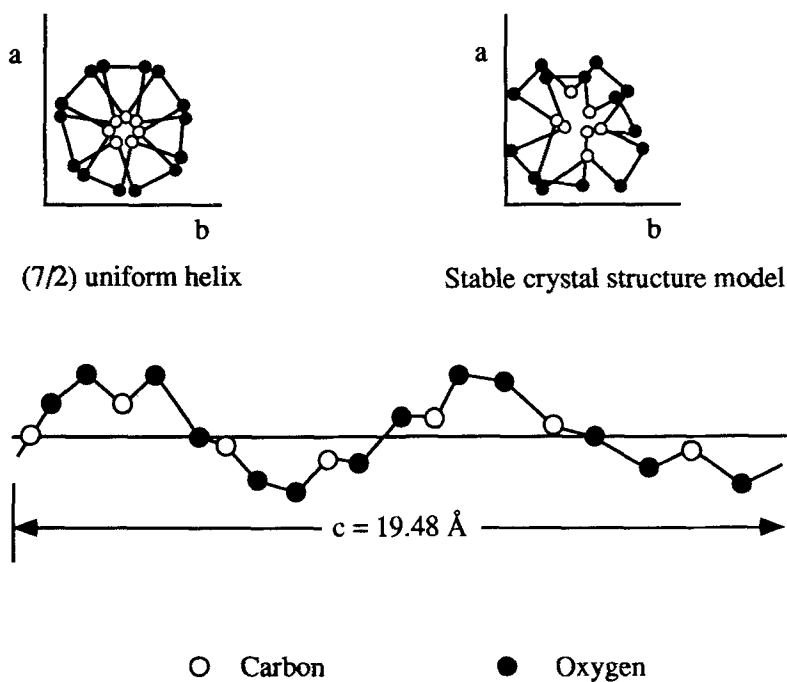


Figure 3. Molecular structure of Poly(ethylene glycol) from H. Tadokoro(1984).

With respect to Poly(vinyl carbazole), we can observe high preferential adsorption coefficient values, not only for Poly(ethylene glycol) (positive values) but for THF as well. This results indicate that preferential adsorption of either THF or Poly(ethylene glycol) is highly favoured, which can be explained on the basis of the existence of an easily polarizable aromatic side group in the polymer chain. The Poly(methyl methacrylate) case is similar, because although there is not an aromatic group, we can find either positive (α -methylene) or negative (carbonyl) groups in the lateral substituent of the polymer chain. So, THF and Poly(ethylene glycol) molecules have a way to interact with the polymer and, depending on the conditions derived from the PEG(1)/THF(2) relative concentration, both preferential solvations can occur.

Summarizing all the above explained, the analysis of the results obtained for these systems shows that the chemical composition of the polymer side group plays a fundamental role in the solution behaviour of vinyl polymers. The characteristics of the polymer side group influences the kind and intensity of the polymer-solvent interactions and so the rest of solution properties of these systems.

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