# Viscometric and preferential adsorption behaviour of poly(4-tert-butylphenyl methacrylate) in tetrahydrofuran/chloroform

**Deodato Radic and Ligia Gargallo**
*Departamento de Físico Química, Instituto de Ciencias Químicas, Pontificia Universidad Católica de Chile, Casilla* 114-D, *Santiago, Chile*
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The viscometric behaviour of poly(4-tert-butylphenyl methacrylate) in the solvent mixture tetrahydrofuran/chloroform has been investigated. There is qualitative agreement between variations in $[\eta]$ and predictions from the Dondos and Patterson theory. The role of the preferential adsorption of one of the solvents on the polymer was considered. The experimental adsorption coefficients $\lambda^*$ are discussed in this particular mixture where $G^E < 0$. In this binary solvent rthe $k\theta$ values of the polymer are similar in the three different mixed solvent compositions studied.

## INTRODUCTION

The viscosimetric behaviour of polymers in binary solvents has been studied in a series of papers[1-5], using polar and non-polar polymers. Interesting phenomena such as cosolvency[6-8], preferential adsorption[8-10], and variations in unperturbed dimensions[11,12] have been observed.

The intrinsic viscosity, $[\eta]$, of polymers in mixed solvents depends on the interactions among the components of the mixture. Dondos and Patterson[1] have found a good qualitative relation between $\Delta[\eta]$ and $G^E$, the excess free energy of the solvent mixture, where $\Delta[\eta]$ is the difference between $[\eta]$ for the polymer in the solvent mixture and an 'average $[\eta]$' at the same solvent composition which lies on the straight line joining the values of $[\eta]$ in the pure solvents. In a mixed solvent with $G^E > 0$, $\Delta[\eta]$ should be positive. However, when $G^E > 0$, there is a certain incompatibility between the molecules of components 1 and 2, and the dissolution of the polymer occurs due to preferential contacts in the ternary system[2,7]. Dondos and Patterson[1] have stated that the sign and magnitude of $\chi_{12}$ must be considered as a guide to possible cosolvency. When $\chi_{12}$ is relatively large and positive for a mixture of two non-solvents, they may act as cosolvents for the polymer[9,13].

When $G^E > 0$ and the predicted intrinsic viscosity is much higher than the experimental $[\eta]$ it might be possible to explain the discrepancy between theory and experiment in terms of preferential adsorption of one of the solvents on the polymer coil, according to Pouchly *et al.*[14].

The effect of allowing for adsorption is always to reduce the intrinsic viscosity in the respective Pouchly equations. However, in systems where $G^E < 0$, the predicted $[\eta]$, is low and would be further lowered by allowing for adsorption. When a mixture exhibits $G^E < 0$, it is difficult to imagine preferential adsorption, because of the strong interaction between the components of the mixture.

This paper deals with the viscometric and preferential adsorption behaviour of poly(4-tert-butylphenyl methacrylate) (PBPh) in tetrahydrofuran–chloroform. This mixture has been recently studied, and the $G^E < 0$[15].

## EXPERIMENTAL

This study was carried on with five fractions of poly(4-tert-butylphenyl methacrylate) (PBPh), prepared by free radical polymerization at 50°C in benzene solution (20% w/w) using $\alpha,\alpha'$-azobisisobutyronitrile ($5 \times 10^{-3}$–1.0% w/w)[16]. The monomer preparation was described previously[16]. The weight-average molecular weights $\bar{M}_w$ were determined by light scattering in cyclohexane solution at 25°C as described previously[16]. The weight-average molecular weights of the fractions used were: A, 2 040 000; B, 880 000; C, 170 000; D, 70 000 and E, 50 000.

Viscosities were measured at $25^\circ \pm 0.02^\circ$C using a Desreux–Bischoff dilution viscometer[17].

Equilibrium dialysis experiments were carried out in a dialyser 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.

The refractive index increments of the polymer solutions were measured at 25°C using a Brice–Phoenix Differential Refractometer, BP 2000.

## RESULTS AND DISCUSSION

*Figure 1* gives the viscometric behaviour of the five PBPh fractions in the tetrahydrofuran/chloroform mixture; $[\eta]$ values are lower than the weighted mean values of the viscosities measured in pure solvents. In this case, the $[\eta]$ values in tetrahydrofuran and in chloroform are similar. Both are good solvents and with the same thermodynamic power for poly(4-tert-butylphenyl methacrylate).

The viscosimetric behaviour agrees with the Dondos and Patterson theory[1]. The THF/chloroform system has $G^E < 0$, i.e. the interaction parameter $\chi_{12}$ is negative; this implies a specific interaction between molecules of both

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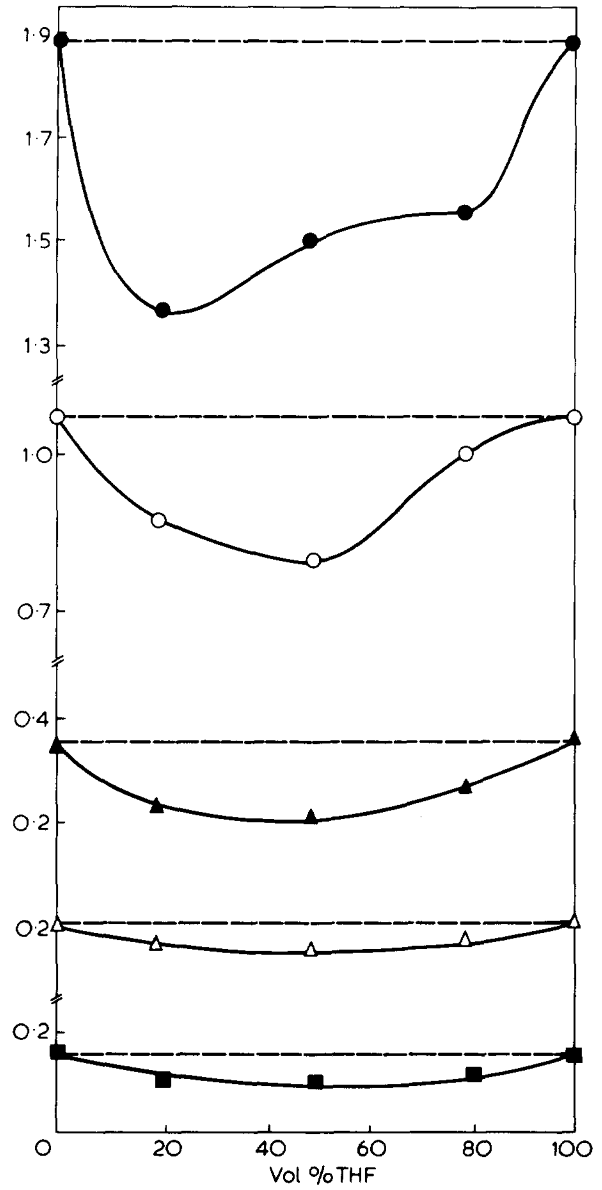

*Figure 1* Variation of the intrinsic viscosities [η] with mixed solvent composition in the ternary system PBPh/THF/chloroform for five fractions studied: A (●); B (○); C (▲); D (△) and E (■)

constituents. The difference in the intrinsic viscosity, Δ[η], for PBPh/THF/CHCl$_3$, was calculated from the following expression, proposed by Dondos *et al.*[1]:

$$\Delta[\eta] = \frac{1.02\bar{v}\varphi_0 M}{N_0} \frac{G^E(\varphi_2^0}{VRT} \qquad (1)$$

where $\varphi_0$ is the Flory constant; $\bar{v}$ is the polymer specific volume; $N_0$ is Avogadro's number; $\varphi_2^0$ is the volume fraction of 2 in the mixed solvent; $V$ is the unit volume of the mixed solvent; and $M$ is the molecular weight of the polymer.

*Figure 2* shows the calculated function Δ[η] from equation (1) for $G^E$ data[15] for THF/chloroform. The calculated Δ[η] has the correct sign, but there is a large quantitative discrepancy in the experimental intrinsic viscosity.

Several polymers[12,18,19] exhibit a conformational parameter $K_\theta$ which can change, depending on the thermodynamic characteristics of the binary solvent. $K_\theta$ is associated with the mean square unperturbed dimensions $\langle r_0^2\rangle^{1/2}$ of a chain with molecular weight $M$ by the equation:

$$K_\theta = \varphi_0(\langle r^2\rangle_0/M)^{3/2} \qquad (2)$$

Values for PBPh in three THF/CHCl$_3$ mixtures were estimated using the semiempirical Stockmayer–Fixman method[20]. *Figure 3* shows the Stockmayer–Fixman diagram. In this figure, the $K_\theta$ value does not change with the binary solvent composition: (20:80); (50:50) and (80:20) v/v THF/chloroform. It seems reasonable for a binary solvent in which $G^E < 0$ and where both the constituents are good

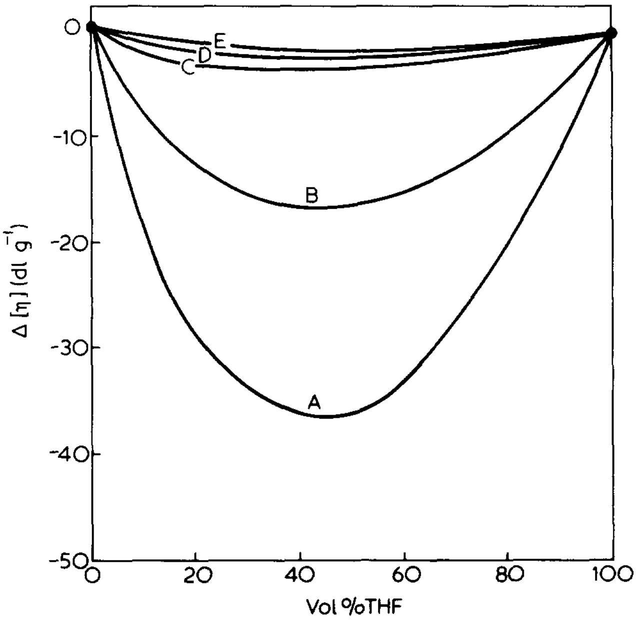

*Figure 2* Variation of the Δ[η] calculated from equation (1) for $G^E$ data[15] for tetrahydrofuran/chloroform in function of the mixed solvent composition

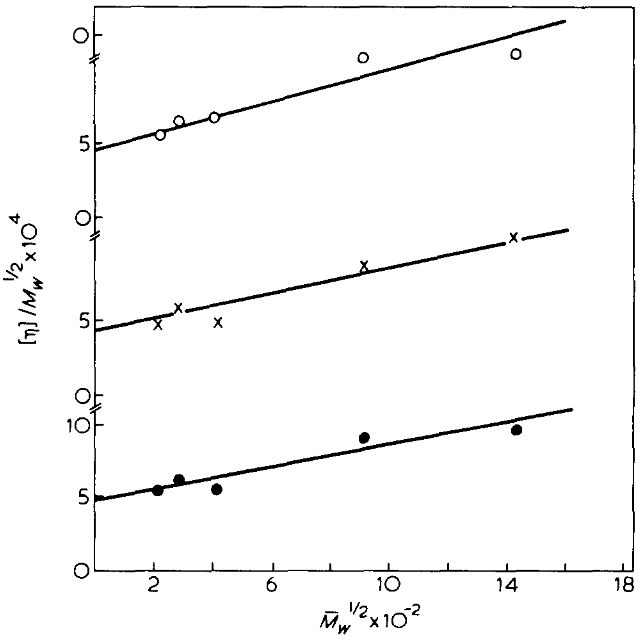

*Figure 3* Stockmayer–Fixman plot for poly(4-tert-butylphenyl methacrylate) in the mixed solvent THF/chloroform: ○, 80:20 v/v; X, 50:50 v/v; ●, 20:80 v/v at 25°

*Table 1* Preferential solvation parameter for tetrahydrofuran–chloroform–poly(4-tert-butylphenyl methacrylate) determined from dialysis equilibrium at various mixture compositions

| Vol % THF | $(dn/dc)_\mu$ | $(dn/dc)_k$ | $(dn/dk)$ | $\lambda^*$ (ml g$^{-1}$) |
|---|---|---|---|---|
| 10 | 0.107 | 0.110 | 0.018 | −0.169 |
| 30 | 0.100 | 0.120 | 0.032 | −0.625 |
| 50 | 0.129 | 0.130 | 0.037 | −0.013 |
| 70 | 0.206 | 0.133 | 0.130 | +0.562 |
| 90 | 0.266 | 0.164 | 0.675 | +0.150 |

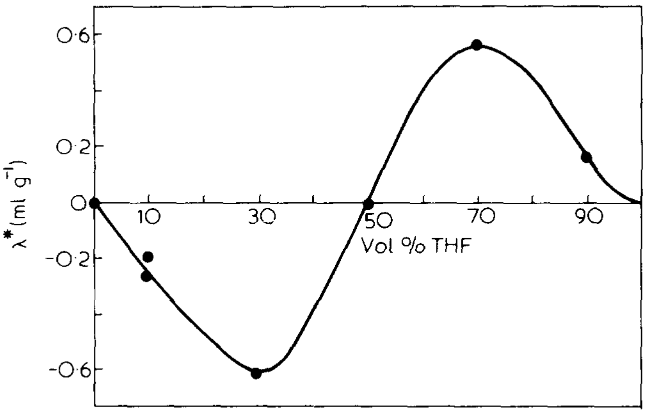

*Figure 4* Dependence of the preferential adsorption parameter $\lambda^*$ on mixed solvent composition for the ternary system PBPh/THF/chloroform

solvents and have the same solvent power for the polymer, that the preferential adsorption should be excluded as an important factor. However, preferential adsorption is a general phenomenon when a polymer is in a binary solvent[21]. To ascertain whether or not preferential adsorption was a significant factor in the present system the preferential adsorption coefficient $\lambda^*$ was determined from the relation[22]:

$$\lambda^* = \frac{(dn/dc)_\mu - (dn/dc)_k}{(dn/dk)} \tag{3}$$

where $(dn/dc)_k$ is the polymer refractive index increment in the solvent mixture; $dn/dk$ is the variation in refractive index of the solvent mixture as a function of volumetric composition and $(dn/dc)_\mu$ is the increment in solution refractive index after the establishment of dialysis equilibrium.

Values of $\lambda^*$ calculated from equation (3) and the variations in refractive index for all solvent compositions, are summarized in *Table 1*, and also shown in *Figure 4*. The results obtained indicate a preferential adsorption of chloroform and tetrahydrofuran of the same magnitude with an inversion point $\lambda^* = 0$ at 50:50 v/v tetrahydrofuran/chloroform. This behaviour implies that the inversion point represents conditions favouring the formation of the maximum number of (1–2–3) contacts in the system. As either (1–3) or (2–3) contacts are energetically similar (same solvent power for the polymer), the phenomenon would seem to be governed by entropic factors rather than energetic factors.

This phenomenon should not be seen only from the point of view of the adsorbed solvent–polymer interactions but must be considered with respect to what happens inside the solution. This implies that at least two independent processes would contribute to the overall interaction: (i) the preferential adsorption of a solvent by the polymeric chain; and (ii) the change in composition of the binary mixture. Process (i) may be unfavourable thermodynamically ($\Delta G_1 > 0$) but process (ii) may be favourable ($\Delta G_2 < 0$), making the whole process favourable ($\Delta G_{total} = \Delta G_1 + \Delta G_2 < 0$). This would explain the preferential adsorption of a polymer on a binary solvent with $\Delta G^E < 0$.

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## REFERENCES

1 Dondos, A. and Patterson, D. *J. Polym. Sci. (A-2)* 1969, **7**, 209
2 Radic, D., Boys, D. and Gargallo, L. *Polymer* 1977, **18**, 121
3 Munk, P., Abijaoude, M. T. and Halbrook, M. E. *J. Polym. Sci. (Polym. Phys. Edn)* 1978, **16**, 105
4 Maillols, H., Bardet, L. and Gromb, S. *Eur. Polym. J.* 1978, **14**, 1015
5 Spychaj, T., Lath, D. and Berek, D. *Polymer* 1979, **20**, 437
6 Deb, P. C., Prasad, J. and Chatterjee, S. P. *Makromol. Chem.* 1977, **178**, 1455
7 Gargallo, L., Radic, D. and Katime, I. *Eur. Polym. J.* 1980, **16**, 383
8 Cowie, J. M. G. and McCrindle, J. T. *Eur. Polym. J.* 1972, **8**, 1325
9 Dondos, A. and Benoît, H. *J. Polym. Sci. (Polym. Phys. Edn)* 1977, **15**, 137
10 Dondos, A. *Eur. Polym. J.* 1976, **12**, 435
11 Vira, F., Viras, K., Aroni, F. and Dondos, A. *Eur. Polym. J.* 1974, **10**, 891
12 Gargallo, L. *Colloid Polym. Sci.* 1975, **253**, 288
13 Sarkar, D. K. and Palit, S. R. *J. Polym. Sci. (C)* 1970, **30**, 69
14 Pouchly, J., Zivny, A. and Solc, K. *J. Polym. Sci. (C)* 1968, **23**, 245
15 Oswal, S. L. and Deshpande, D. D. *Indian J. Chem.* (A) 1978, 16, 9, 798
16 Gargallo, L., Niezette, J. and Desreux, V. *Bull. Soc. Roy. Sci., Liège* 1977, **1-2**, 82
17 Desreux, V. and Bischoff, J. *Bull. Soc. Chim. Belg.* 1950, **59**, 93
18 Dondos, A. and Benoit, H. *Macromolecules* 1973, **6**, 242
19 Dondos, A., Rempp, D. and Benoit, H. *J. Polym. Sci. (C)* 1970, **30**, 9
20 Stockmayer, W. H. and Fixman, M. *J. Polym. Sci. (C)* 1963, **1**, 137
21 Cowie, J. M. G. *Pure Appl. Chem.* 1970, **23**, 355
22 Katime, I. and Strazielle, C. *Makromol. Chem.* 1977, **178**, 2295