Behaviour of diphilic copolymers in solution: case of *p*-tert-butyl phenyl methacrylate–vinyl pyrrolidone

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Properties of dilute solutions of vinyl pyrrolidone-*p*-tert-butyl phenyl methacrylate in binary solvents have been investigated through viscosity measurements. A diphilic characteristic for these copolymers of various compositions in two binary solvents, (a) benzene/methanol (a cross-selective solvent) and (b) benzene/chloroform (with a common solvent chloroform) is reported. We also report data obtained for homopolymers in the same binary solvents. Eskin and Korotkine's equations have been applied to these systems. Unusual behaviour, found in benzene/methanol, is discussed.

INTRODUCTION

Eskin and Korotkina have used the term diphilic for copolymers consisting of components which differ markedly in their selective solubilities[1]. The properties of diphilic copolymers in solution have been studied mostly by the manner in which their viscometric behaviour changes with the composition of a mixed solvent[2,3,4].

Copolymers containing styrene and vinyl pyrrolidone were shown to present a diphilic effect in the binary solvent methyl ethyl ketone–isopropyl alcohol[1].

In this paper we report the diphilic characteristics of *p*-tert-butyl phenyl methacrylate–vinyl pyrrolidone copolymers of various compositions, in two binary solvents: benzene/methanol (a cross-selective solvent) and benzene/chloroform (with a common solvent, chloroform). We also report data obtained for the homopolymers in the same binary solvents.

EXPERIMENTAL

Copolymers of *p*-tert-butyl phenyl methacrylate and vinyl pyrrolidone of different compositions were obtained by standard free copolymerization in benzene at 50°C using AIBN as thermal initiator, at different feed ratios. Their compositions were determined by i.r. spectroscopy; the i.r. spectra of mixtures of the corresponding homopolymers at known compositions were used as standards[5].

Poly(*p*-tert-butyl phenyl methacrylate), PMBPh, was obtained by free radical polymerization in benzene solution using AIBN as initiator[6].

Poly(vinyl pyrrolidone), PVP, was obtained by fractionation from a commercial* sample[7].

Characteristics of the copolymers and homopolymers studied are shown in *Table 1*. The number-average molecular weights, $\bar{M}_n$, were determined using a Hewlett–Packard 502 high speed membrane osmometer. Methanol and chloroform (Merck p.a.) were used without treatment. Benzene (Merck p.a.) was dried and distilled before using.

Viscosity measurements were performed with a Desreux and Bischoff dilution viscosimeter[8].

RESULTS AND DISCUSSION

The viscometric behaviour of poly(*p*-tert-butyl phenyl methacrylate) (PMBPh) and poly(vinyl pyrrolidone) (PVP), homopolymers and the copolymers is shown in *Figures 1* and *2*, in the binary solvents benzene/methanol and benzene/chloroform.

Figures 1 and *2* show the dependence of the intrinsic viscosity $[\eta]$ of PMBPh and PVP and copolymers on the composition of the mixed solvents. The CO–6 copolymer with a large vinyl pyrrolidone content is insoluble in benzene/methanol, and therefore was not studied in this binary solvent.

The change in binary solvent composition has different effects on the intrinsic viscosity value $[\eta]$ and consequently on the coil dimensions in solution. $[\eta]$ is related to the coefficient α of swelling of the macromolecule[9] by the equation:

$$[\eta] = [\eta]_\theta \alpha^3 = K_\theta M^{1/2} \alpha^3 \tag{1}$$

where $[\eta]_\theta$ is the intrinsic viscosity in a θ solvent and K_θ

Table 1 Composition and number-average molecular weights of *p*-tert-butyl phenyl methacrylate and vinyl pyrrolidone homopolymers and copolymers

Polymer	x_A *	$\bar{M}_n \times 10^{-5}$
PMBPh	0.000	7.90
CO–1	0.395	4.94
CO–5	0.662	1.93
CO–6	0.855	0.65
PVP	1.000	3.60

* x_A is the mole fraction of vinyl pyrrolidone in the copolymer

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* General Biochemicals Laboratory Park, Chagrin Falls, Ainio 44022, Chile. Lot 85899. Control, 2100A.

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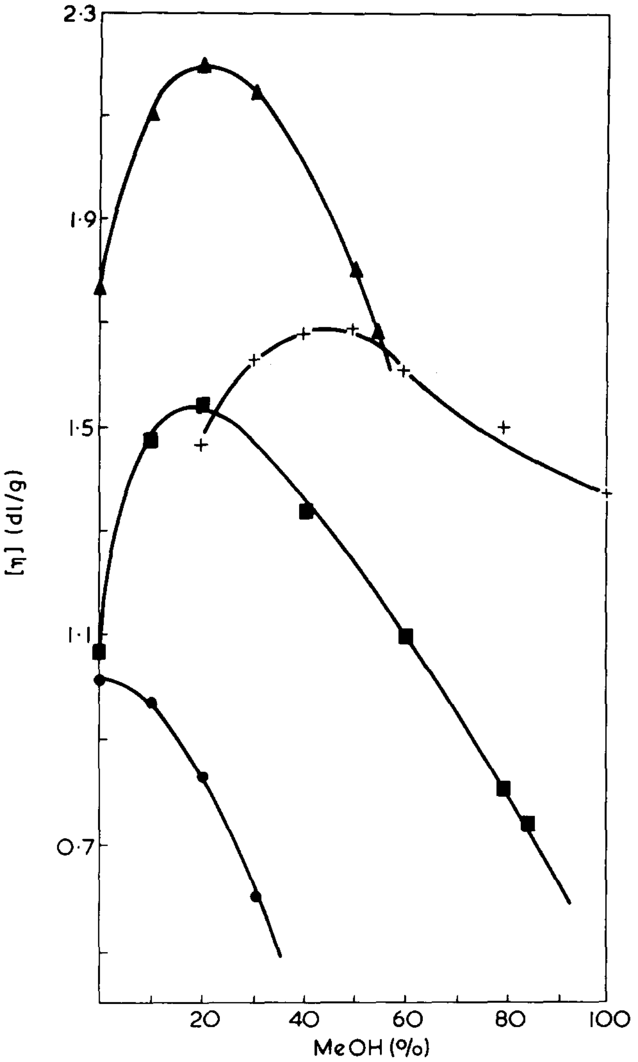

Figure 1 Intrinsic viscosities [η] of PMBPh (●), PVP (+) and copolymer solutions (▲, CO–1; ■, CO–5) depending on the composition of the mixed solvent benzene/methanol at 25°C

should be a constant for a given polymer.

Taking the composition of the mixed solvent as the methanol or chloroform volume fraction ϕ_1, it follows that:

$$\frac{d[\eta]}{d\phi_1} = 3K_\theta M^{1/2}\alpha^2 \frac{d\alpha}{d\phi_1} \qquad (2)$$

The quantity $d[\eta]/d\phi_1$ for all the copolymers studied was calculated from the slope of the curves in *Figures 1* and *2*.

In order to analyse the effect of the binary solvent composition (ϕ_1) on the coil dimensions[9], we used the equation obtained by Eskin and Korotkina[1]:

$$3\alpha^2\frac{d\alpha}{dn_1} = 4\left(\frac{3}{2\pi b^2}\right)^{3/2}\frac{V_s N^{1/2}}{N_A}[\chi_A(\chi_{2A} - \chi_{1A}) - \chi_B(\chi_{1B} - \chi_{2B}) - (2n_1 - 1)\chi_{12}] \qquad (3)$$

In this equation χ_A and χ_B are the mole fractions of A and B links in the copolymer; n_1 and n_2 are the mole fractions of the components of the mixed solvent; χ_{12} characterizes the interaction between the latter† and V_s is the molar volume of the solvent.

This equation was derived from Fixman's equation[10] which relates the coefficient of swelling of the macromolecule to the value of the statistical parameter Z ($\alpha^3 = 1 + 2Z$). This parameter Z is determined by the number of interactions between segments of the macromolecule per unit volume. Its magnitude depends on the chain flexibility (the length of the segment, b), its contour length (number of segments, N) and the excluded volume of the segment ν_0^c in the solution[11]:

$$Z = \left(\frac{3}{2\pi b^2}\right)^{3/2} \nu_0^c N^{1/2}$$

Taking into account the total number of interactions in the coil, the contribution of the interactions of any particular type depends on the copolymer composition. The excluded volume for the different types of interaction between segments in the copolymer may be expressed in terms of the molar volume of the solvent V_s and the corresponding parameters of interaction between the segments and the solvent molecules and between each other; we thus obtain equation (3). The behaviour of a copolymer in a binary solvent is determined for a given value of n_1 and χ_A by a set of five parameters χ_{1A}, χ_{2A}, χ_{1B}, χ_{2B} and χ_{12}.

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† The volume fraction ϕ_1 of a component in the mixed solvent differs from its mole fraction n_1 by a factor which does not depend on χ_A or χ_B.

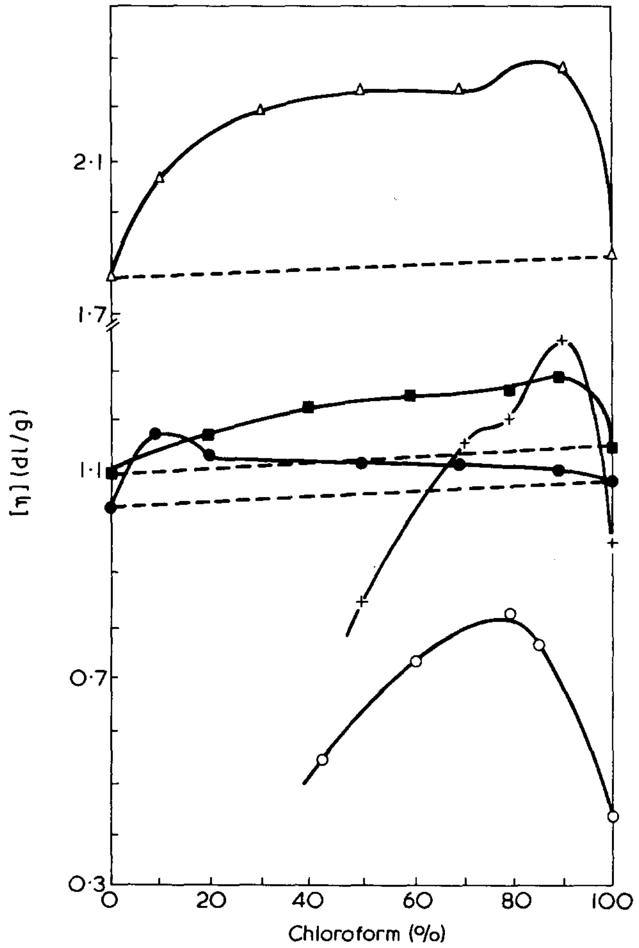

Figure 2 Intrinsic viscosities [η] of PMBPh (●), PVP (+) and copolymer solutions (△, CO–1; ■, CO–5; ○, CO–6) depending on the composition of the mixed solvent benzene/chloroform

Since $N^{1/2} \sim M^{1/2}$ and using equation (2) we find that the quantity $(1/M)\mathrm{d}[\eta]/\mathrm{d}\phi_1$ is proportional to the contents of the square brackets in equation (3). *Figure 3* is a plot of $(1/M)\mathrm{d}[\eta]/\mathrm{d}\phi_1$ for the copolymers studied as a function of their composition (vinyl pyrrolidone fraction, χ_A). We have found a linear dependence on χ_A as predicted by equation (3). For given compositions of mixed solvents (ϕ_1 = volume fraction) there exist copolymer compositions at which $\mathrm{d}[\eta]/\mathrm{d}\phi_1 = \mathrm{d}\alpha/\mathrm{d}\phi_1 = 0$. The copolymer chains would not change conformation with the composition of the mixed solvent. The dimensions of the copolymer coils or the different interactions in the system do not imply variations in the empirical function α. That is, depending on the ratio of the binary solvent components, there is a copolymer which has a specific ratio of vinyl pyrrolidone (VP) and tert-butyl phenyl methacrylate (MBPh) units which fulfills this condition.

Table 2 summarizes thc ϕ_1 values and the copolymer composition χ_A which would fulfil the condition $\mathrm{d}[\eta]/\mathrm{d}\phi_1 = 0$, as well as the vinyl pyrrolidone-*p*-tert-butyl phenyl methacrylate ratio which would give these compositions.

It is noteworthy that in the binary solvent benzene/chloroform only one copolymer composition exists at which $\mathrm{d}[\eta]/\mathrm{d}\phi_1 = \mathrm{d}\alpha/\mathrm{d}\phi_1 = 0$ for different ϕ_1 values.

Imposing the condition $\mathrm{d}\alpha/\mathrm{d}\phi_1 = 0$, equation (3) gives:

$$\chi_A(\chi_{2A} - \chi_{1A}) - \chi_B(\chi_{1B} - \chi_{2B}) = (2n_1 - 1)\chi_{12} \quad (4)$$

For a solvent composition $n_1 = 1/2$ it is possible to determine the following ratio from the composition at which $\mathrm{d}\alpha/\mathrm{d}\phi_1 = 0$:

$$\frac{\chi_{2A} - \chi_{1A}}{\chi_{1B} - \chi_{2B}} = \frac{\chi_B}{\chi_A} \quad (5)$$

This ratio characterizes the difference in the selective solubility of the components of the copolymer in a given pair of liquids of low molecular weight[1].

From *Figure 3* we can see that when $n_1 = 1/2$ ($\phi_1 = 0.53$ and $\phi_1 = 0.42$) $\chi_A = 0.65$ and $\chi_A = 0.2$ for benzene/methanol and benzene/chloroform, respectively, for these mixtures under the conditions $\mathrm{d}\alpha/\mathrm{d}\phi_1 = 0$.

Since $\chi_A + \chi_B = 1$, we obtain $\chi_{2A} - \chi_{1A}/\chi_{1B} - \chi_{2B} = 0.54$ and 4, respectively, in the two binary solvents.

Thus, the relative difference in the selective solubility of PMBPh, and PVP for the binary solvent benzene/methanol is <1 and is >1 for benzene/chloroform, if the selective solubility of the polymer for the given pair of solvents is

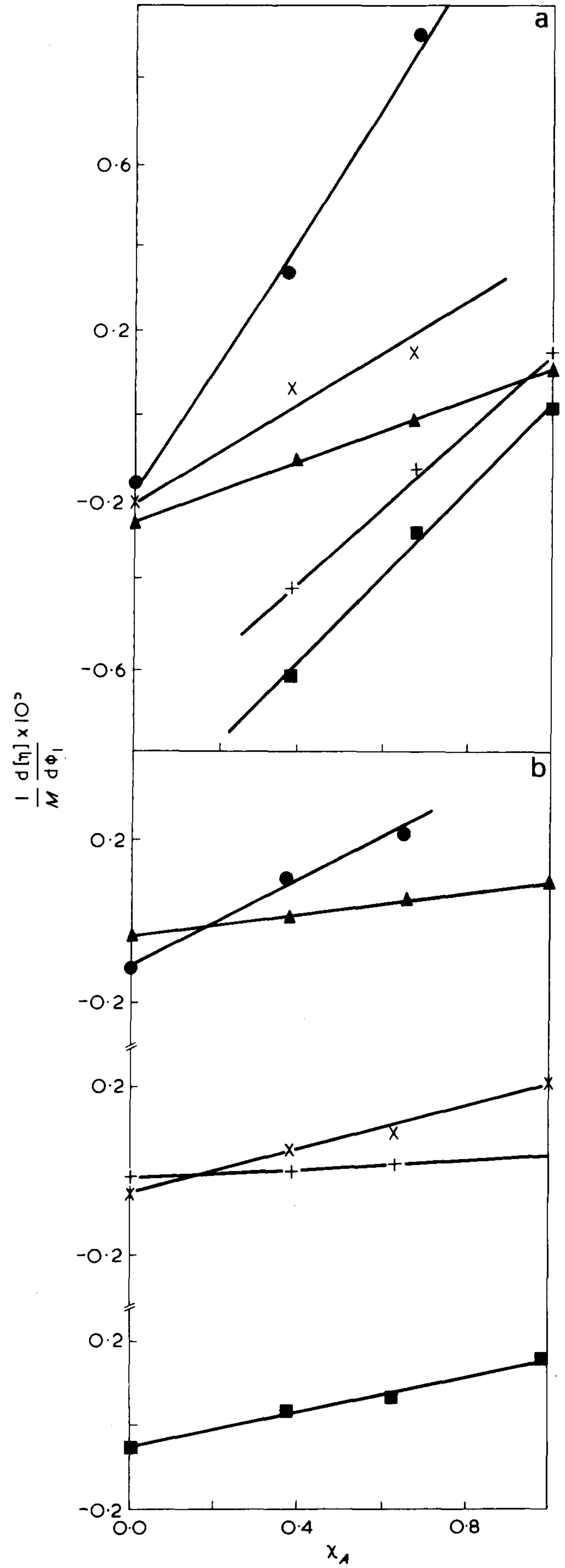

Figure 3 Dependence of $(1/M)\,\mathrm{d}[\eta]/\mathrm{d}\phi_1$ on the composition (χ_A) of copolymers for several compositions of the mixed solvent: (a) benzene/methanol ϕ_1: ●, 0.10; x, 0.30; ▲, 0.50; +, 0.53; ■, 0.60; and (b) benzene/chloroform ϕ_1 values ●, 0.10; x, 0.30;▲, 0.50; ■, 0.60; +, 0.70

Table 2 ϕ_1 values, the copolymer composition χ_A for which $\mathrm{d}[\eta]/\mathrm{d}\phi_1 = 0$ and the ratio of the copolymer composition

Binary solvent	ϕ_1	$\chi_A(\mathrm{d}[\eta]/\mathrm{d}\phi_1=0)$	Ratio VP/MBPh
Benzene/methanol	0.10	0.12	1:7
	0.30	0.34	1:2
	0.50	0.68	2:1
	0.53	0.82	5:1
	0.60	0.98	49:1
Benzene/chloroform	0.10	0.20	1:4
	0.30	0.20	1:4
	0.50	0.20	1:4
	0.60	0.20	1:4
	0.70	0.20	1:4

Table 3 ϕ_1 and n_1 values of the binary solvent composition and the value of the ratio $\chi_{2A} - \chi_{1A}/\chi_{12}$

Binary solvent	ϕ_1(MeOH)	n_1	$\chi_{2A} - \chi_{1A}/\chi_{12}$
Benzene/methanol	0.10	0.091	0.542
	0.30	0.279	0.471
	0.34	0.355	−1.690
	0.40	0.376	−2.834
	0.44	0.409	−0.894
	0.50	0.474	1.955
	0.53	0.500	0.000
	0.60	0.576	0.161
Binary solvent	**ϕ_1($CHCl_3$)**	**n_1**	**$\chi_{2A} - \chi_{1A}/\chi_{12}$**
Benzene/chloroform	0.10	0.158	0.534
	0.30	0.421	0.124
	0.50	0.626	−0.971
	0.60	0.715	−0.335
	0.70	0.797	−0.463

characterized by the difference in the thermodynamic parameters ($\chi_{2P} - \chi_{1P}$). This difference can be described in terms of χ_{12} from equation (4).

Table 3 shows the different values for ϕ_1, n_1 and $\chi_{2A} - \chi_{1A}/\chi_{12}$ parameters for the two binary solvents studied.

Figure 4 shows $\chi_{2A} - \chi_{1A}/\chi_{12}$ as a function of the binary solvent composition n_1 of the mixture which is solvent for the poly(vinyl pyrrolidone) (Polymer *A*), methanol and chloroform.

The ratio $(\chi_{2A} - \chi_{1A})/\chi_{12}$ varies only slightly with the composition of the mixed solvent for the benzene/chloroform mixture. On the contrary, for the benzene/methanol binary solvent, this ratio changes strongly with the composition of the mixed solvent. This behaviour can be explained by a variation of the values of α and $[\eta]$ arising from selective adsorption by the macromolecule of one component of the mixture which has not been taken into account[12] and can change the K_θ value. Another effect may be the 'segregated conformations' originating from strong repulsions between chemically dissimilar sequences of the same molecule[13]. We have found in preliminary works that the K_θ value for these copolymers is solvent dependent in benzene/chloroform, but not in benzene/methanol where K_θ does not change significantly[14].

In conclusion, for the benzene/methanol binary solvent, the copolymer behaviour can be explained through an effect on the value of α.

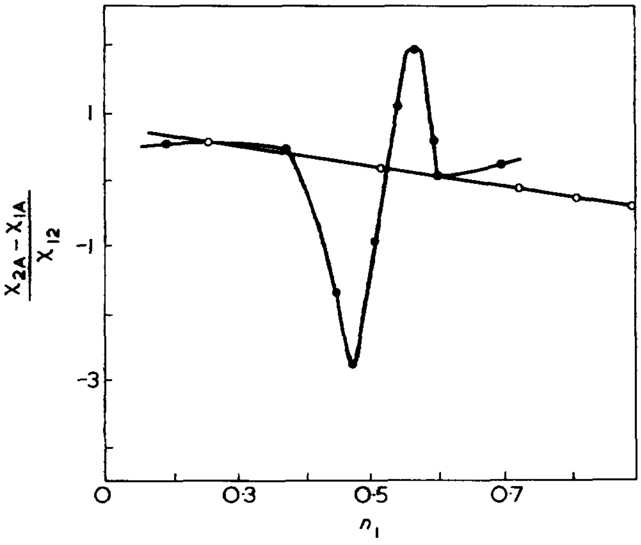

Figure 4 $\chi_{2A} - \chi_{1A}/\chi_{12}$ ratio as a function of the binary solvent composition n_1 of the solvent mixture for PVP (Polymer A), methanol and chloroform. ●, Benzene–methanol; ○, benzene–chloroform

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