Cosolvency, coil expansion and dimensions of PMMA in mixed solvents

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Limiting viscosity numbers ($[\eta]$) and Schulz–Blaschke constants (k_s) of PMMA samples (differing in molecular weight) have been determined at 25°C (as a function of mixed solvent composition) for the following mixtures: acetonitrile + 1-butanol, acetonitrile + pentyl acetate, and 1-chlorobutane + pentyl acetate. The first two mixtures are powerful cosolvents of PMMA and the third one is a 'co-nonsolvent' of the polymer. The samples are predominantly heterotactic. Their k_s values at θ indicate some association tendency of the polymer. Unperturbed dimensions and coil expansion coefficients have been obtained from $[\eta]$, as a function of solvent mixture composition. All the pure liquids are poor or non-solvents of PMMA (at 25°C), but the cosolvent pairs behave as very good solvents for the polymer. The mechanism of such cosolvency is analysed in terms of the different molecular interactions present in these systems.

(Keywords: poly(methyl methacrylate); cosolvency; viscosity; coil expansion; dimensions)

INTRODUCTION

A number of liquid mixtures are known to act as cosolvents of poly(methyl methacrylate) (PMMA)[1-4]. Their cosolvency has been demonstrated by studying temperatures of phase separation[1-4]. The synergistic action of cosolvents influences not only the solubility of the polymer, but also its hydrodynamic and thermodynamic properties. One of the properties of interest in the study of cosolvency is intrinsic viscosity, $[\eta]$.

For PMMA, the intrinsic viscosity has been reported in cosolvent mixtures containing CCl_4, i.e. CCl_4 + methanol (MeOH)[5,6], ethanol (EtOH)[5], 1-propanol (PrOH)[5], 1-butanol (BuOH)[5], 1-chlorobutane (ClBu)[4], and acetonitrile (MeCN)[7], and in MeCN + MeOH[7]. We have also reported the intrinsic viscosity of PMMA in the cosolvent mixture MeCN + ClBu[8]. This last system is a powerful cosolvent which means that liquid mixing produces a large cosolvency effect (a sharp decrease in critical solution temperature[3] and a large increase in $[\eta]$[8]). The other cosolvents of PMMA for which $[\eta]$ has been reported, have a cosolvency effect weaker than the one for this system.

Acetonitrile forms powerful cosolvents for PMMA not only with ClBu, but also with other liquids having a wide variety of chemical groups[2]. In the present work we report measurements of solution viscosity in the powerful cosolvents formed by acetonitrile with an alcohol, BuOH, and with an ester, pentyl acetate (PAc). The opposite effect to cosolvency has been reported for PMMA in a mixture of ClBu + PAc[9]. In this system, the cloud point temperature was found to be higher in certain mixtures than in the pure liquids[9]. Here, we shall study the solution viscosity of PMMA in this ClBu + PAc 'cononsolvent', and compare it with the behaviour in the cosolvent mixtures.

EXPERIMENTAL

Polymer. The PMMA samples are monodisperse Monopol standards supplied by Dr T. G. Croucher (Polymer Laboratories Ltd., Shrewsbury, England). They are of the type described before[10].

The tacticity of these samples has been determined by ^{1}H n.m.r.[10] The mean triad content of samples A through E is 6% *iso*, 51% *hetero*, 43% *syndio*. They are, thus, more heterotactic than conventional atactic PMMA[10].

The molecular weights of the samples, determined by us using light scattering[8] in EtAc, at 25°C, are:

$$M_w(\text{sample}).10^{-3} = 73.4(A); \quad 87.5(B); \quad 124(C); \quad 189(D);$$
$$232(E); \quad 654(F)$$

Their polydispersity, $M_w/M_n \leqslant 1.1$, has been determined by the supplier using g.p.c.

Solvents. MeCN, PAc, BuOH, and ClBu (from Carlo Erba RPE); EtAc (from Riedel de Haën p.a.) were distilled before use.

Viscometry. Viscosity has been measured at 25°C in modified Ubbelohde viscometers which had previously been calibrated. Precision in efflux times was 0.1 s and temperature was controlled to ± 0.05°C. Liquid mixtures

were prepared by weighing. Polymer solutions were obtained by successively diluting an initial PMMA solution whose concentration, c, never exceeded $1 \times 10^{-2}\,\text{g cm}^{-3}$. Viscosities were calculated applying corrections of kinetic energy (always less than 2%) and of density ($<1\%$).

Intrinsic viscosity has been determined by means of the Schulz–Blaschke extrapolation[29]:

$$\eta_{sp}/c = [\eta] + k_s[\eta]\eta_{sp} \qquad (1)$$

Extrapolations of Huggins (η_{sp}/c *versus* c) and of Kraemer ($\ln\eta_r/c$ *versus* c) have been also used. They lead to slightly different values of $[\eta]$ (0–2% difference). In all three extrapolation methods deviations from linearity appear at a given value of concentration, c', which is located in the range 0.6–1% (w/v)[11]. The values of $[\eta]$ and k_s have been obtained by linear regression of the data corresponding to $c < c'$.

RESULTS AND DISCUSSION

Viscosity results

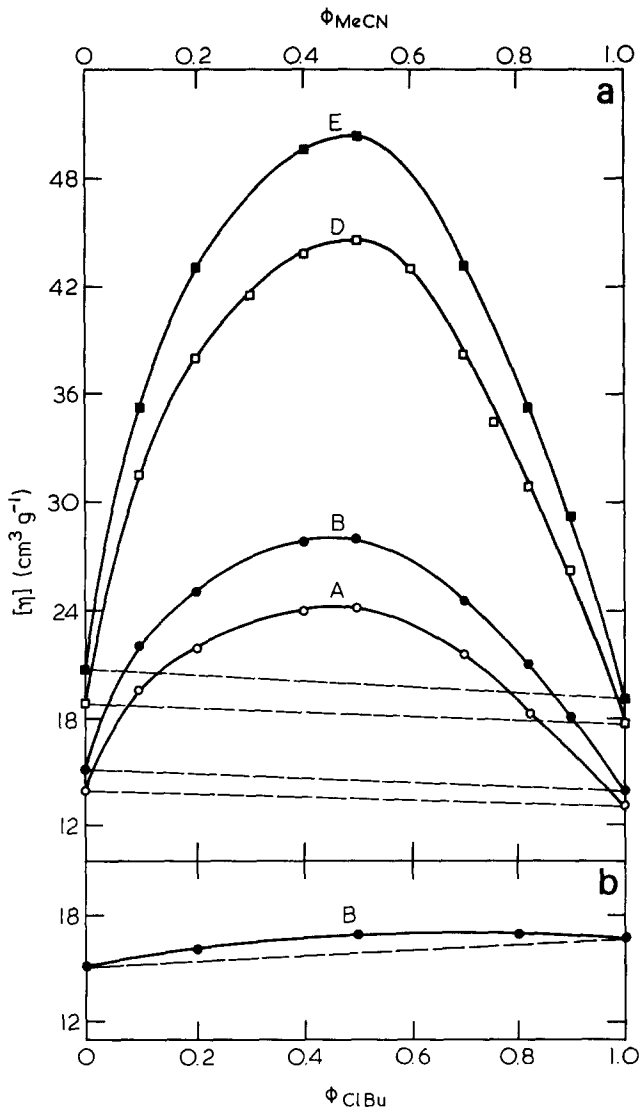In *Figures 1* and *2* we show the results for intrinsic

Figure 1 Intrinsic viscosity of PMMA in the mixtures MeCN + PAc (a), and ClBu + PAc (b), as a function of MeCN (a) and ClBu (b) volume fractions, respectively. Samples: (O) A; (●) B; (□) D; (■) E
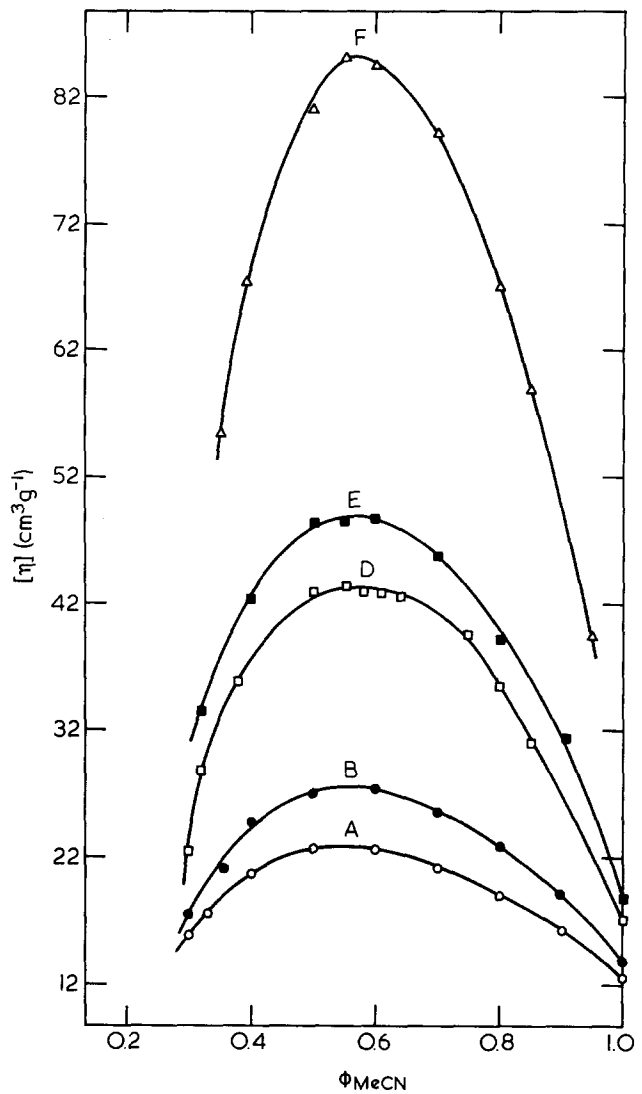

Figure 2 Intrinsic viscosity of PMMA in the mixture MeCN + BuOH, as a function of MeCN volume fraction. Samples: (O) A; (●) B; (□) D; (■) E; (△) F

viscosity of the PMMA samples as a function of liquid mixture composition, expressed by means of volume fraction, ϕ. *Figure 1a* is for the mixture MeCN + PAc, *Figure 1b* for ClBu + PAc, and *Figure 2* for MeCN + BuOH.

The sample of highest molecular weight (sample F) is not soluble in any of the pure liquids. The other samples can be dissolved in pure MeCN, pure PAc, or pure ClBu, but not in pure BuOH. Hence, MeCN, PAc, and ClBu can be termed as poor solvents and BuOH as a nonsolvent for our PMMA at 25°C. Mixing MeCN with PAc, or mixing MeCN with BuOH greatly increases solubility (sample F is soluble in the mixtures), and produces a large increase in $[\eta]$. The intrinsic viscosity reaches values in the cosolvent mixtures MeCN + PAc and MeCN + BuOH which, for some samples, is more than twice its value in the pure liquids MeCN or PAc. This large increase of $[\eta]$ in the cosolvents contrasts with the approximate constancy of $[\eta]$ in the ClBu + PAc mixture. In *Table 1* we show the values of $[\eta]$ in the pure liquids and in the mixtures at the composition where the intrinsic viscosity is maximum. Our previous results for the MeCN + ClBu pair[8] are also included for comparison.

The increase of intrinsic viscosity in a mixed solvent

Table 1 Intrinsic viscosity of PMMA in pure liquids and in mixtures at the composition of maximum $[\eta]$

					$[\eta]$ $(cm^3\ g^{-1})$			
Sample	$M_w \times 10^{-3}$	MeCN	PAc	ClBu	MeCN + PAc $\phi_{MeCN} = 0.50$	MeCN + BuOH $\phi_{MeCN} = 0.55$	PAc + ClBu $\phi_{ClBu} = 0.50$	MeCN + ClBu $\phi_{MeCN} = 0.40$
A	73.4	13.1	13.9	15.1	24.2	22.8	15.3	28.3*
B	87.5	13.9	15.1	16.5	28.0	27.4	16.9	–
C	124	15.5	17.0	17.6	–	–	–	41.6*
D	189	17.8	18.8	21.1	44.6	43.3	21.3	54.9*
E	232	19.1	20.7	23.4	50.4	48.8	23.7	63.3*
F	654	n.s.	n.s.	n.s.	–	85.1	n.s.	–

* From reference 8
n.s. = Not soluble

Table 2 Thermodynamic properties of the liquid mixtures used as cosolvents of PMMA. Excess Gibbs function, G^E, and excess entropy, S^E, of the binary mixtures at equimolar composition (temperature = 25°C)

Cosolvent mixture	G^E $(J\ mol^{-1})$	S^E $(J\ mol^{-1}\ K^{-1})$
MeCN + BuOH[13]	1044	3.70
MeCN + PAc[13]	646	−0.58
MeCN + ClBu[14]	1032	–

over its weighted mean value in the pure liquids is usually expressed as:

$$\Delta[\eta] = [\eta] - [\eta]_1\phi_1 - [\eta]_2\phi_2 \qquad (2)$$

where $[\eta]_1$ and $[\eta]_2$ refer to values in the pure liquids 1 and 2, and $[\eta]$ refers to the value in the mixture. This increase in $[\eta]$ has been attributed to the existence of unfavourable interactions between the two liquids[12]. For a given molecular weight, $\Delta[\eta]$ is usually taken to be proportional to the excess Gibbs function of the mixture: $\Delta[\eta](\phi) \sim G^E(\phi)/RT^{12}$. The values of G^E for our cosolvent mixtures[13,14] at equimolecular composition, and 25°C, are given in *Table 2*. These G^E's allow for a qualitative interpretation of the relative values of $\Delta[\eta]$ in the three systems. $\Delta[\eta]$ is larger in MeCN + ClBu than in MeCN + PAc because interactions yield a larger G^E in the former liquid mixture (see the 'Cosolvency and Interactions' section below). In the MeCN + BuOH pair it is not possible to obtain $\Delta[\eta]$ from pure liquid values because the extreme $\phi_{MeCN} = 0$ is inaccessible. The values of G^E (equimolar) in the MeCN + BuOH and MeCN + ClBu mixtures are practically equal, but BuOH is a much worse solvent for PMMA than ClBu. Hence, $[\eta]$ should reach a lower value in MeCN + BuOH than in MeCN + ClBu (*Table 1*).

We can compare the increase in $[\eta]$ produced by solvent mixing at a constant 25°C with that produced by raising the temperature in pure MeCN. This comparison has been established already for the cosolvent mixture MeCN + ClBu[15]. Since MeCN is a bad solvent for PMMA at 25°C, the temperature increases $[\eta]$ in pure MeCN[15]. The same increase in $[\eta]$ experienced by sample D in pure MeCN in going from 25°C to 45°C[15] is reached at 25°C by adding just 9% PAc, or 8% BuOH (6% in the case of ClBu[15]). Mixing cosolvents is thus much more effective in expanding the polymer coil than increasing temperature.

As can be seen in *Figure 1b*, the behaviour of $[\eta]$ in the mixture ClBu + PAc is very different from that in cosolvents. $\Delta[\eta]$ in the mixture ClBu + PAc is extremely small.

However, it is detectable and positive. The sign of $\Delta[\eta]$ seems to be in contradiction with the cononsolvent character attributed to this mixture by cloud point studies[9]. The clue to this apparent inconsistency may be the different range of concentrations in which $[\eta]$ and cloud point temperatures, T_p, are determined. T_p values higher in the mixtures than in the pure liquids (cononsolvency) were detected with solutions of $c \geqslant 1 \times 10^{-2}$ g cm^{-3},[9] while $[\eta]$ is here determined using solutions in the range $c \leqslant 6 \times 10^{-3}$ g cm^{-3} (see Experimental section). It is possible that the cononsolvent effect manifests itself only above a minimum concentration, and is thus not seen in $[\eta]$, which is an infinite dilution property.

The results of η_{sp}/c at finite concentrations tend to support this idea. *Figure 3a* shows results of η_{sp}/c at three different concentrations: $c = 0$ ($\eta_{sp}/c = [\eta]$, extrapolated value), $c = 4 \times 10^{-3}$ g cm^{-3}, and $c = 6 \times 10^{-3}$ g cm^{-3}. The broken lines drawn are the linear interpolation of η_{sp}/c between the two pure liquids. We can see that the increment $\Delta(\eta_{sp}/c)$ with respect to this line is positive at $c = 0$ but vanishes as c grows. *Figure 3b* shows results of η_{sp}/c in the cosolvent mixture MeCN + PAc for the same concentrations of *Figure 3a*. We can see that contrary to the mixture ClBu + PAc, in the cosolvent MeCN + PAc, $\Delta(\eta_{sp}/c)$ has a slight growth with increasing concentration. The decrease of $\Delta(\eta_{sp}/c)$ with increasing c is thus peculiar to the cononsolvent system and opposite to what happens in the cosolvent one.

G^E of the ClBu + PAc pair is not known, but it had been argued that it might be negative in order to explain the T_p results[9]. The cohesive energy densities of both liquid components are almost equal, so that the value of G^E should be very small unless some specific effects are present. If G^E is small, its effect could be easily offset by other interactions dependent on polymer concentration.

In order to analyse what the influence of concentration on this system may be, we can use thermodynamic theory. The magnitude of interest is the potential of total solvent sorption by the polymer coils, π, or, more specifically, its increment over the weighted mean in the pure liquids, $\Delta\pi$. In general the expression for $\Delta\pi$ is complex, but we can take the usual single liquid approximation, which reads[16]:

$$\Delta\pi = (RTc^2\bar{v}_3^2/V_1)\phi_1\phi_2[\chi_{12} - 2\chi_T(1 - \bar{v}_3 c)] \qquad (3)$$

Here, 1 and 2 designate the liquids in the mixture, χ_{12} is their mutual interaction parameter, χ_T the ternary interaction parameter (equation (3) implies χ_T independent of c), $\bar{v}_3$ is the partial specific volume of the polymer, and V_1 the molar volume of liquid 1. The experimental findings

Figure 5 Schulz–Blaschke constant for PMMA in the mixture MeCN + BuOH as a function of MeCN volume fraction. Samples: (O) A; (●) B; (□) D; (■) E; (△) F
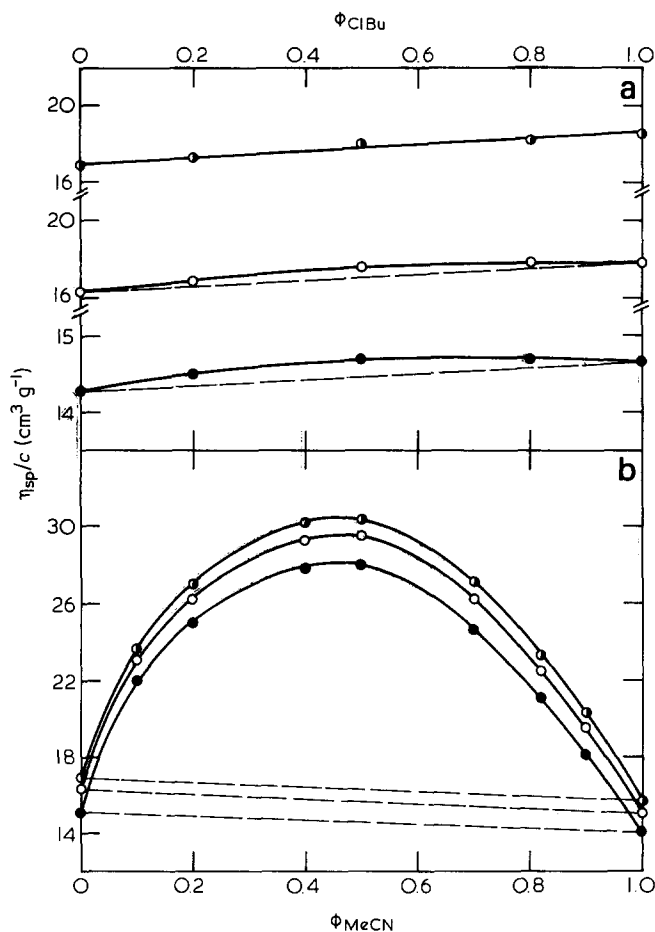

Figure 3 Specific viscosity of PMMA at various polymer concentrations in the mixtures ClBu + PAc (a), and MeCN + PAc (a), as a function of ClBu (a) and MeCN (b) volume fractions, for sample B. (●) $c=0$ $(\eta_{sp}/c=[\eta])$, (O) $c=4\times10^{-3}$ g cm^{-3} and (◑) $c=6\times10^{-3}$ g cm^{-3}

imply that $\Delta\pi>0$ at $c\rightarrow0$ (intrinsic viscosity results), that $\Delta\pi$ vanishes at finite c $(\Delta(\eta_{sp}/c)$ results), and that $\Delta\pi$ should even become negative for the higher c's to explain the T_p measurements. All three conditions are possible simultaneously if $\chi_{12}<0$ and $2\chi_T<\chi_{12}$, namely, if the interactions between both liquids are favourable in their binary mixture $(G^E<0)$, and if in the presence of polymer (ternary interactions) they are of the same sign and larger magnitude.

The constant k_s expressing the concentration dependence of η_{sp}/c in the linear region also contains useful information on the polymer/mixed solvent systems. *Figures 4* and *5* show the variation of k_s with ϕ for the three systems studied here. In the pure liquids, k_s attains large values $(0.9<k_s\leqslant1.8)$. In the cosolvents at intermediate compositions k_s is around 0.4. This value is close to the those typical of coils in good solvents where no association is present and the coil is in expanded form. For example, in benzene at 25°C we have determined $k_s=0.3$ with the same PMMA samples here studied. In the ClBu + PAc mixture k_s also decreases on mixing liquids but not so much as in the cosolvent mixtures and k_s remains rather high $(k_s\simeq0.65)$ at its minimum.

The values usually found for the Huggins constant, k_H in θ solvents are $k_H\simeq0.5$–0.55. Higher values are indicative of polymer association[17]. We shall see below, when we come to discuss unperturbed dimensions and excluded volume, that the value of k_s for θ conditions in the systems here studied is $k_s\simeq0.75$. By definition, the values of k_H are higher than those of k_s. Therefore, some tendency to association of PMMA is detected in these solvents. The tendency is disrupted by cosolvent mixing when k_s drops to $k_s=0.3$–0.4 at intermediate compositions.
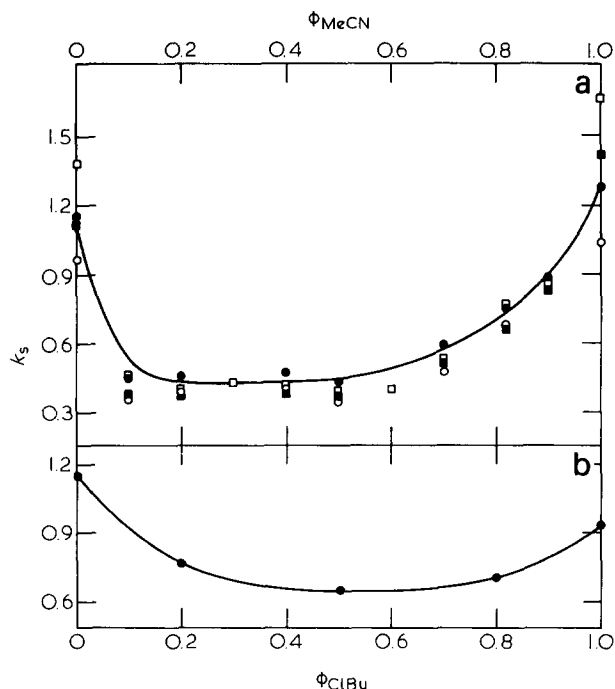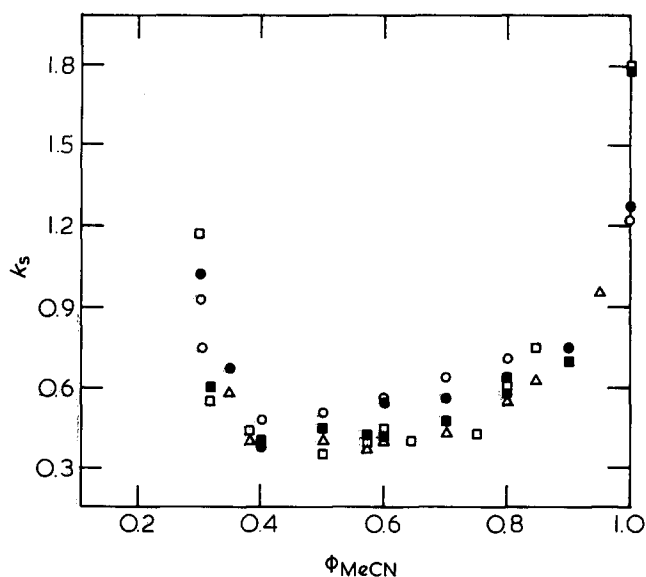

Figure 4 Schulz–Blaschke constant for PMMA in the mixtures of MeCN + PAc (a) and ClBu + PAc (b), as a function of MeCN (a) or ClBu (b) volume fractions, respectively. Samples: (O) A; (●) B; (□) D; (■) E. The curves correspond to sample B

Unperturbed dimensions and excluded volume

Unperturbed dimensions, K_θ, have been obtained from the $[\eta]$–M_w results for samples A–E by plotting them according to the Stockmayer–Fixman method:

$$[\eta]M_w^{-1/2}=K_\theta+C'\Phi B M_w^{1/2} \qquad (4)$$

where $\underline{B}$ is an interaction parameter, Φ is Flory's viscosity constant ($\Phi = 2.6 \times 10^{23}$), and $\underline{C}'$ a numerical factor. The values thus obtained for K_θ in the pure solvents are: $K_\theta = 5.9 \times 10^{-2} \mathrm{cm^3\,g^{-1}}$ in MeCN, and $K_\theta = 6.4 \times 10^{-2} \mathrm{cm^3\,g^{-1}}$ both in PAc and in ClBu. These values are larger than the ones usually reported for conventional atactic PMMA (which are in the range 4.3–5.3 $\times 10^{-2} \mathrm{cm^3\,g^{-1}}$)[18–22]. Our polymer samples have a predominance of heterotactic triads. The unperturbed conformation of this heterotactic-like PMMA is then more open or expanded than that of atactic PMMA. A larger value of unperturbed dimensions for the heterotactic-like polymer than for the atactic one is in accordance with rotational isomeric state theoretical calculations (as we have discussed before[8]).

Our results show a solvent effect in MeCN, where K_θ is lower than in the other two solvents. A similar effect is found with atactic PMMA[19]. It has been attributed to a more coiled conformation of the polymer in MeCN[21]. Acetonitrile is a somewhat ordered liquid[23] and the self ordering of the solvent molecules may influence the coiling of the polymer chain.

The values of K_θ in the mixture studied here depend on solvent composition. The variation of K_θ with ϕ in the cosolvent mixtures is shown in *Figure 6*. The increment, ΔK_θ, for K_θ in the mixture over the weighted mean in the pure liquids is in all cases $\lesssim 20\%$. The increase in K_θ has been supposed to be proportional to the G^E of the liquid mixture[24]. *Figure 7* shows a plot of $K_\theta(\phi)$ *versus* $G^E(\phi)$. We can see that in fact K_θ follows a linear dependence with G^E in each system but that this dependence is different for each mixture. There are thus specific effects superimposed on the G^E dependence. The value of K_θ determined in the mixture ClBu + PAc at $\phi_{ClBu} = 0.5$ is $K_\theta = 6.8 \times 10^{-2} \mathrm{cm^3\,g^{-1}}$, also above the value corresponding to the pure liquids ($K_\theta = 6.4 \times 10^{-2} \mathrm{cm^3\,g^{-1}}$). The ClBu + PAc system is not shown in *Figure 7* since its G^E is not known. However, as explained above it is expected to be small and possibly negative. But ΔK_θ in this mixture is of the same sign as the ones in the cosolvent mixtures where G^E is large and positive.

It has been proposed that the K_θ's determined by extrapolation in mixed solvents may be only apparent values due to the concentration dependence of the long range interaction parameters[25]. Exploratory calculations estimated that this effect could change the apparent value
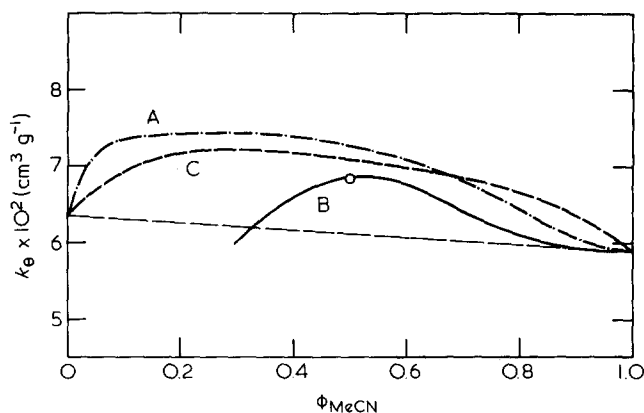

Figure 7 K_θ for PMMA as a function of G^E in the mixtures: MeCN + PAc ($\square$); MeCN + BuOH ($\bullet$); and MeCN + ClBu ($\bigcirc$)[8]

Figure 8 Mark–Houwink exponent, a, of PMMA in the mixtures: (a) curve A, MeCN + PAc; curve B, MeCN + BuOH and curve C, MeCN + ClBu as a function of MeCN volume fraction; and (b) ClBu + PAc as a function of ClBu volume fraction

Figure 6 Unperturbed dimensions, K_θ, for PMMA in the mixtures; curve A, MeCN + PAc; curve B, MeCN + BuOH; and curve C, MeCN + ClBu[8] as a function of MeCN volume fraction. The point corresponds to the equimolar ClBu + PAc mixture
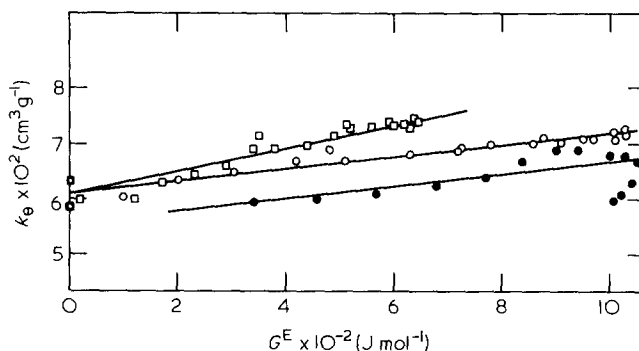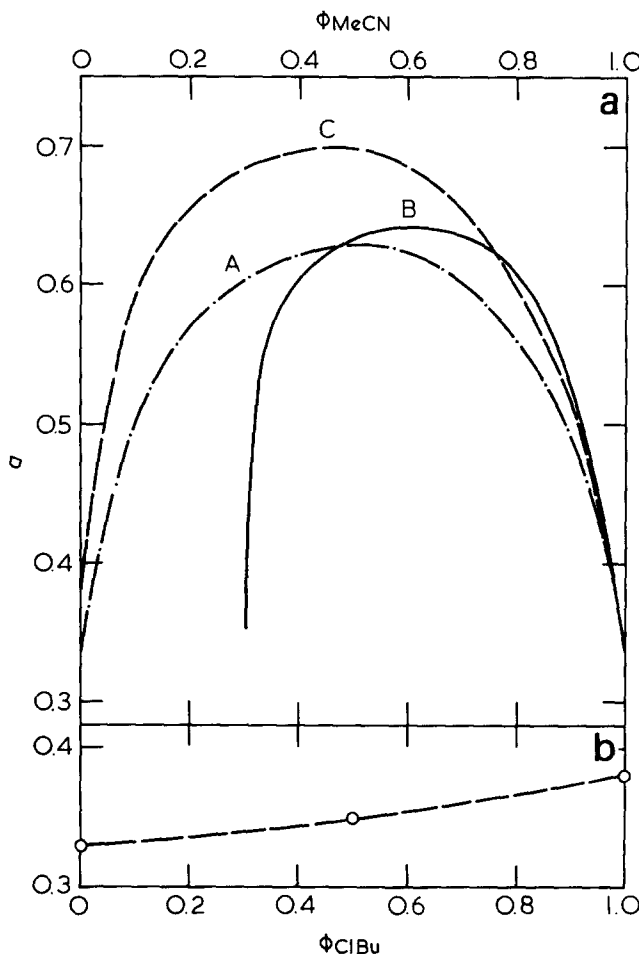
of K_θ by about 20% for a mixture having a typical value of $\chi_T = 1.6$ at $\phi_1 = 0.5$.[25] Our ΔK_θ values are all within this estimate and can, thus, very well be due to such an effect. In fact, the example value $\chi_T = 1.6$ coincides with the one experimentally determined for χ_T in the MeCN + ClBu system at $\phi_1 = 0.4$.[26]

The Mark–Houwink exponent a determined from our $[\eta] - M_w$ results for samples A–E, presents a large variation with cosolvent composition. The results are shown in *Figure 8*. We can see that a is much lower than 0.5 in the pure solvents. A confirmation that the polymer is below θ in these liquids at 25°C. On mixing cosolvents, a

rises above 0.5 and reaches a maximum which is comparable to the value in good solvents. In the cononsolvent mixture ClBu + PAc, however, PMMA remains below θ at any composition and a varies monotonously between the two pure liquid extremes. In each cosolvent pair there are two isothermal theta points at which $a = 0.5$ and $B = 0$ (both conditions are met simultaneously). They are: $\phi_{MeCN} = 0.1$, 0.91 (MeCN + PAc), and 0.31, 0.93 (MeCN + BuOH).

As discussed before[8], in cosolvent systems it is possible to produce an isothermal transition from a contracted conformation $(\alpha_\eta < 1)$ to an expanded one $(\alpha_\eta > 1)$, and back again to the contracted state $(\alpha_\eta < 1)$, by progressively always adding the same liquid, the cosolvent, at constant temperature. Here, α_η is the coil expansion coefficient calculated as:

$$\alpha_\eta^3 = [\eta]/K_\theta M_W^{1/2} \qquad (5)$$

As an example of this transition (in the MeCN + PAc mixture) we get, for sample E:

$$\alpha_\eta^3 (\phi_{MeCN}) = 0.68(0.0),\ 1.0(0.1),\ 1.44(0.5),\ 1.0(0.91),$$
$$0.67(1.0)$$

Theories of the Huggins constant predict that k_H (and hence k_s) should be a decreasing function of α_η^3.[17] For many systems, this k_H–α_η^3 universal relationship has been qualitatively verified[17]. In *Figure 9* we represent the k_s–α_η^3 plot of our results for sample E in the three cosolvents studied here and in the two very good single solvents benzene and chloroform. In this representation we have taken a constant K_θ to calculate α_η^3 ($K_\theta = 6.3 \times 10^{-2}$ cm³ g⁻¹, corresponding to the pure liquids and neglecting ΔK_θ). We can see in *Figure 9* that k_s is approximately a unique function of α_η^3. The chemical groups involved in the cosolvents differ from one system to another. However, the variation of k_s is approximately dependent only on coil expansion and not so much on chemical nature of the solvent. The other molecular weight samples give a similar relationship. In the case of the mixture ClBu + PAc, k_s is also a decreasing function of α_η^3 (if as unperturbed dimensions we take the constant value corresponding to the pure liquids and neglect ΔK_θ).
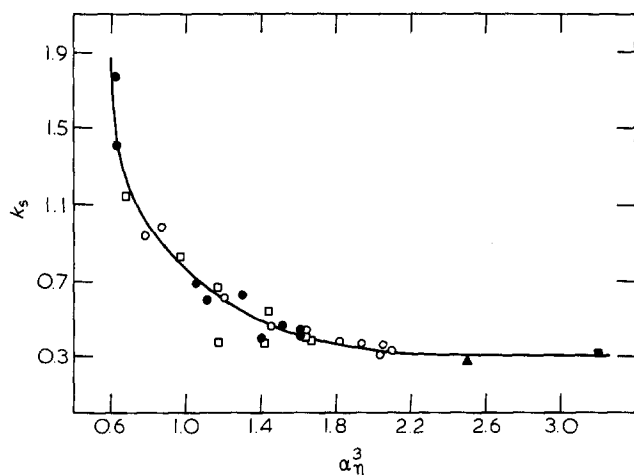

Figure 9 Correlation between the Schulz–Blaschke constant, k_s, and the coefficient of coil expansion, α_η^3 for PMMA (sample E) in the cosolvent mixtures MeCN + PAc (□) MeCN + BuOH (●) and MeCN + ClBu (○)[8] and in the pure good solvents benzene (▲) and chloroform (■)

The value of k_s at the θ state $(\alpha_\eta^3 = 1)$ defined by these results is $k_s \simeq 0.75$. This is higher than the value usually found for nonassociating polymers at θ. This indicates, therefore, that PMMA has an association tendency in the solvents studied here, as we discussed above.

Cosolvency and interactions

Cosolvency should ultimately be interpreted in terms of the molecular characteristics of the system, especially in terms of molecular interactions. In the powerful cosolvents of PMMA described here and in the literature[1-3,8,26], one of the liquid components is always either acetonitrile or an alcohol. These are non-random liquids with a certain degree of order in their structure. The relevance of such liquid order for cosolvency has been discussed already[2,5]. Also, the importance of the tendency of the polymer towards association[2]. The roles of these two factors, polymer association tendency and order in the liquid structure, were considered to interpret solvation of PMMA chains in the case of the MeCN + ClBu cosolvent[26]. We now have additional information on other cosolvent systems. Let us interpret the mechanism of their cosolvency in terms of the different types of molecular interactions present in them.

We start by considering the cosolvent MeCN + BuOH in comparison with the previously discussed MeCN + ClBu system[26]. The mixture MeCN + BuOH differs chemically from MeCN + ClBu in that the Cl is replaced by an OH capable of hydrogen bond formation. This replacement affects the cohesive energy density of the pure liquid, which is much larger in BuOH than in ClBu, thus rendering the MeCN + BuOH mixture a non-symmetric cosolvent of PMMA, where both liquids have larger values of the solubility parameter than the polymer, and it affects also the θ temperature of PMMA, which is higher in BuOH than in ClBu. But it does not destroy the cosolvent character of the system. Both MeCN + ClBu and MeCN + BuOH are powerful cosolvents. The G^E values in these two liquid mixtures are large and very similar (see *Table 2*). Both systems use this large G^E as potential to produce large coil expansions and to disrupt any tendency of the polymer to associate. Some evidence for the breaking of polymer association on liquid mixing has been given for the system PMMA/MeCN + ClBu[27].

The molecules of MeCN and BuOH are highly polar and they could, in principle, interact with those of PMMA to dissolve the polymer readily. MeCN can attach to the polar ester group lateral to the chain. BuOH can interact through its OH group establishing a bridge with the –CO group of PMMA through a hydrogen bond. However, the θ temperatures for the PMMA/MeCN and PMMA/BuOH pairs are both higher than room temperature. MeCN and BuOH are non-random liquids in the pure state (they are ordered liquids, as mentioned above). But the kind of order in these two liquids is very different. BuOH forms an autoassociated three-dimensional network through hydrogen bonds, while MeCN is an anisotropic liquid in which the molecules are orientationally correlated in parallel and perpendicular dispositions. In the polymer/single liquids systems, self interactions between BuOH or MeCN molecules are preferred over crossed interactions with the polymer, the result being that the macromolecule is not properly solvated. Mixing of the two liquids disorders their non-random structure and frees their molecules to individually solvate the polymer chain thus producing increased

solubility (cosolvency) and expansion of the polymer coils by sorption of the mixed solvent. This view that mixing MeCN with BuOH disorders the system is supported by the large positive S^E value estimated for the MeCN + BuOH mixture (see *Table 2*).

Let us discuss now the mechanism of cosolvent action in the case of the MeCN + PAc mixture. In the MeCN + PAc mixture S^E has been estimated to be negative (see *Table 2*), contrary to what happens in the case of MeCN + BuOH. This means that in the MeCN + PAc mixture some kind of order is present. The small and highly dipolar molecules of MeCN are very likely responsible for such an order, although in the mixture the order formed could be different from that in the pure liquid.

Probably the order forming mechanism giving $S^E < 0$ in MeCN + PAc is also present in MeCN + BuOH. However, in this last system such order can be overridden by the disorder generated in the breaking of the auto-associated structure of the alcohol on mixing, and the overall result in MeCN + BuOH is $S^E > 0$. The system MeCN + PAc is a symmetric one for PMMA, the same as MeCN + ClBu, since PAc has lower a solubility parameter than PMMA. Hence, symmetric δ's and negative S^E are the characteristics of MeCN + PAc, while non-symmetric δ's and positive S^E are the ones of MeCN + BuOH.

Based on the analysis of viscosity and mixing properties of MeCN + n-alkyl acetate systems, we have suggested elsewhere that two different and opposing interactions may contribute to the overall value of G^E in the MeCN + PAc mixture[13,28]. One is an attractive or favourable interaction between the nitrile and the ester groups. Another is an unfavourable interaction between the nitrile and the methylene groups (of the pentyl chain).

The influence of this unfavourable interaction between –CN and –CH$_2$-groups has been deduced to contribute also to the G^E of the MeCN + n-alkyl alcohol mixtures (such as MeCN + BuOH)[13]. It should be very important in determining the G^E of the MeCN + ClBu mixture as well. The fact that these unfavourable interactions can be partly compensated by the favourable nitrile–ester interactions in the case of the mixture MeCN + PAc, may help in explaining why G^E is smaller in this mixture than in the MeCN + BuOH mixture or in the MeCN + ClBu mixture. The two types of interactions, nitrile–ester and nitrile–methylene just discussed, should act also between MeCN and the polymer, since PMMA has both methylene and ester groups. Thus the solvent properties of MeCN towards PMMA reflect a complicated balance between the order forming MeCN self interactions and the favourable and unfavourable MeCN–PMMA cross-interactions.

The mechanisms of cosolvent action of MeCN with either PAc, ClBu, or BuOH as second liquid probably have some features in common. When a second liquid having a high proportion of methylene units in its molecule is mixed with MeCN, the unfavourable nitrile-methylene interactions between MeCN and PMMA loose importance relative to the strength of such interactions between the two liquids, and extensive polymer solvation becomes possible favoured by the nitrile–ester group interaction. (In dilute solution, PMMA is always in a small amount compared to any one of the mixed liquids.)

The number of methylene units or length of the n-alkyl chain is very important for reaching cosolvency when the second liquid is an ester (acetate). On the one hand, G^E of the MeCN + acetate mixtures is larger for long alkyl chains such as in PAc, and this favours cosolvency. On the other hand, the θ temperature of PMMA in acetate solvents is below room temperature for the shorter alkyl chains (for example, EtAc is a good solvent of PMMA), so that only when the chain is long enough, as in PAc, θ gets above room temperature and normal cosolvency can be observed.

No mechanism of cosolvency is present in ClBu + PAc. Both liquids are poor solvents, and no strong interaction or structure breaking mechanism seems to operate in them.

The liquids MeCN, ClBu and BuOH form a trio in which any two of them give a powerful cosolvent pair for PMMA. The system ClBu + BuOH, although not studied here, should be powerful cosolvent of PMMA by analogy with the closely related ClBu + sec-BuOH one, which is known as powerful cosolvent[1].

A curious laboratory demonstration is possible with these three liquids. If we prepare three demixed (two phase) solutions of PMMA, one in MeCN, another in ClBu, and the third in BuOH, all at room temperature, and we blindly mix any two of them, the polymer readily solubilizes and the mixture forms a single phase, no matter what the pair of initial solutions we choose.

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