Coil dimensions of poly(methyl acrylate) in the cosolvent medium of carbon tetrachloride and methanol

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The intrinsic viscosities $[\eta]$ of some poly(methyl acrylate) fractions at 35°C have been measured in a mixture of carbon tetrachloride and methanol ($CCl_4 + CH_3OH$) at different liquid compositions. The $[\eta]$-composition plot shows a maximum for each fraction at composition ϕ_{CH_3OH} (volume fraction of methanol) = 0.33. Values of the Huggins constant, determined from the slope of a plot of η_{sp}/C *versus* C, exhibit a minimum at the same composition in the Huggins constant–composition plot for almost all fractions. Huggins constant values indicate association of poly(methyl acrylate) chains in the poorer cosolvent mixtures and the association increases as the solvent becomes poorer. The molecular association decreases with increase in molecular weight. The unperturbed dimension (K_θ), determined from a Burchard, Stockmeyer, Fixman plot and also from other methods, varies with solvent composition and exhibits a maximum at $\phi_{CH_3OH} = 0.33$. The molecular extension parameter α_η decreases with decrease in molecular weight. Its variation with cosolvent composition is rather different: α_η shows a minimum at $\phi_{CH_3OH} = 0.33$. A possible reason for this is discussed.

(Keywords: cosolvency; poly(methyl acrylate); intrinsic viscosity; Huggins constant; unperturbed dimension; molecular extension factor)

INTRODUCTION

In a binary liquid mixture it is the interaction between the liquids that governs the solubility of a polymer in the mixture. According to Scott's[1] 'single liquid approximation' the overall interaction parameter of the polymer in the liquid mixture is:

$$\chi_{\text{overall}} = \phi_1\chi_{13} + \phi_2\chi_{23} - \phi_1\phi_2\chi_{12}$$

where subscripts 1, 2 and 3 refer to liquid 1, liquid 2 and polymer, respectively. A mixture of two non-solvents may behave as a cosolvent to the polymer when χ_{12} is sufficiently positive to make the χ_{overall} value below the critical χ of the polymer[2–5]. In the opposite case, a mixture of two solvents may behave as a co-non-solvent if χ_{12} is sufficiently negative to make χ_{overall} greater than the critical χ of the polymer[2,6]. The χ_{12} is dependent on the excess Gibbs free energy of mixing, G^E[7]:

$$\chi_{12}x_1x_2 = G^E/RT$$

where x terms represent the mole fractions of the components. From the literature[8] it is evident that G^E for the mixture of carbon tetrachloride and methanol ($CCl_4 + CH_3OH$) is sufficiently positive that it behaves as a cosolvent for a polymer. Deb and Palit[9] reported polymer cosolvency for poly(methyl methacrylate) (PMMA) in this liquid mixture. Here we report a polymer, poly(methyl acrylate) (PMA), that shows cosolvency behaviour in this liquid mixture. The coil dimensions of the polymer at various solvent compositions of the mixed solvent are presented.

In spite of the negative excluded volume of a polymer in non-solvents, if the mixture behaves as a cosolvent, expansion of the polymer coil takes place in the liquid mixture. This is manifested in the intrinsic viscosity of the polymer which exhibits a maximum with solvent composition[9–12]. There are two main causes for expansion of the coil: (i) increase of the molecular extension factor (α) and (ii) change of the unperturbed dimension of the polymer due to interactions of the two component liquids[2,13]. We have investigated which factor is playing the major role in the coil expansion of PMA chain in the $CCl_4 + CH_3OH$ mixture, with the aim of understanding the mechanism of cosolvency more clearly.

It has been established that the unperturbed dimension of polymer is dependent on the medium and the temperature. This has also been found to be true in the cosolvent mixture of acetonitrile and chlorobutane for PMMA[10]. PMA is a more flexible polymer than PMMA, so the effect of liquid composition on the unperturbed dimension and molecular extension factor of PMA is expected to be more prominent than for PMMA.

The property of solution viscosity has been studied here. The intrinsic viscosities $[\eta]$ of the polymer have been measured for different molecular weight fractions of the polymer and also in different compositions of the cosolvent mixture. From the $[\eta]$–M relation, the unperturbed dimension (K_θ) and molecular extension factor (α_η) have been measured. The Huggins constant value for each case was also determined in order to study

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the influence of cosolvent system on the aggregation of the polymer.

EXPERIMENTAL

Polymer

PMA was synthesized from methyl acrylate monomer by a solution polymerization technique. The crude monomer was washed repeatedly with 5% NaOH solution to remove hydroquinone inhibitors and finally with distilled water. It was then dried over fused $CaCl_2$ and distilled at reduced pressure. A 20% solution of the monomer in benzene was taken in a 1 l three-necked R.B. flask through which N_2 was continuously bubbled. The system was kept under thermostat with constant stirring at 60°C. Azobis(isobutyronitrile) (0.54% w/v) and dodecyl mercaptan (0.11% w/v) were used as initiator and chain transfer agent, respectively. After polymerization for 2 h, the polymer was precipitated out by pouring the reaction mixture into a large quantity of petroleum ether. The precipitated polymer was fractionated from a 2% solution in benzene at 20°C by a phase separation method using petroleum ether as non-solvent.

Two other sets of polymerizations were carried out in a similar fashion with different concentrations of chain transfer agent: 0.007% (w/v) and 0%, to obtain medium molecular weight (MM) and high molecular weight (HM) samples, respectively. All the samples were fractionated as described above and were dried in vacuum at 60°C for 3 days. The fractions used and their molecular weights (determined from intrinsic viscosity measurement in benzene at 30°C) are given in *Table 1.*

The solvents used in this work – benzene (E. Merck), carbon tetrachloride (BDH) and methanol (E. Merck) – were purified[14] and fractionally distilled before use.

Viscometry

Intrinsic viscosity $[\eta]$ was determined by measuring specific viscosity (η_{sp}) and using the Huggins equation for extrapolation:

$$\eta_{sp}/C = [\eta] + K[\eta]^2 C \qquad (1)$$

where C is the concentration of the polymer solution. $CCl_4 + CH_3OH$ mixtures were prepared by volume. The viscosities of the polymer solutions were measured using a Schulz–Immergut-type viscometer[15]: in the widest arm a sintered disc was fitted to filter the solution/solvent from dust particles. The viscometer was kept under thermostat at 35 ± 0.01°C. The flow times were reproducible to within ±0.1 s. Kinetic energy correction of the viscometer was small (~1.8%) and was neglected. No shear correction was required for the work. Initially about 0.2% (w/v) polymer solutions were taken and specific viscosities at different dilutions were measured by diluting within the viscometer.

Table 1 Molecular weights of PMA fractions

Fractions[a]	$\bar{M}_v$
HMI	842440
MMI	587870
MMII	370810
MMIII	231170
LMI	99860
LMII	81640
LMIII	59540
LMVI	27450

[a] HM, MM and LM indicate high, medium and low molecular weight polymers, respectively, and the Roman numbers represent the fraction numbers of the samples

RESULTS AND DISCUSSION

Figure 1 shows the variation of intrinsic viscosity for various molecular weight fractions of PMA with composition of the cosolvent mixture. It is clear that the intrinsic viscosity reaches a maximum at composition $\phi_{CH_3OH} = 0.33$ for every fraction of PMA. The polymer was insoluble in the pure component liquids at the temperature of interest, so the intrinsic viscosity could not be determined. But it is clear that at $\phi_{CH_3OH} = 0.33$, the intrinsic viscosity was ~1.5 times greater than the lowest value determined in any set. This indicates a powerful cosolvent effect of the mixture for the polymer. The high intrinsic viscosity of all the fractions at this composition is due to the preferential solvation of the polymer at this composition.

Figure 2 shows a plot of Huggins constant against the cosolvent composition. The Huggins constants (K) were calculated from the least square slope of equation (1). Unlike *Figure 1,* there is a minimum at the solvent composition $\phi_{CH_3OH} = 0.33$ for all fractions except the HMI sample. This again indicates that a liquid mixture of composition $\phi_{CH_3OH} = 0.33$ has the best cosolvent property. For HM and MM fractions the Huggins constant is small, but for the low molecular weight (LM) fractions the Huggins constant is much higher than the normal value[16] of 0.3–0.4. This higher value indicates

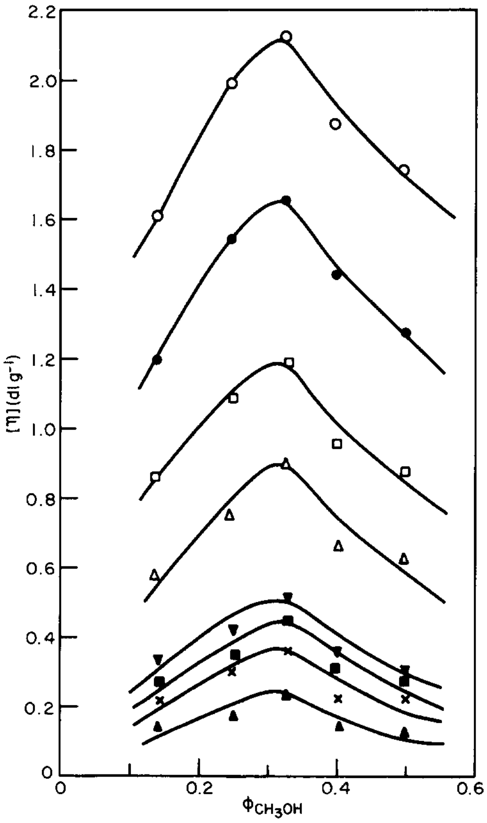

Figure 1 Plot of intrinsic viscosity of PMA fractions at 35°C *versus* volume fraction of methanol: ○, HMI; ●, MMI; □, MMII; △, MMIII; ▼, LMI; ■, LMII; ×, LMIII; ▲, LMVI

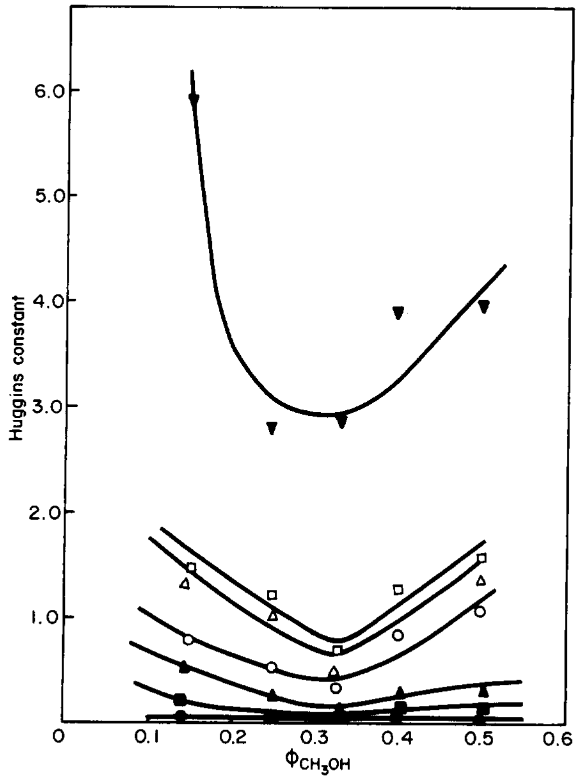

Figure 2 Plot of Huggins constant of PMA fractions at 35°C *versus* volume fraction of methanol: ▼, LMVI; □, LMIII; △, LMII; ○, LMI; ▲, MMIII; ■, MMII; ●, HMI

the presence of polymer association in these systems[10,17]. The association is certainly smallest at the best cosolvent composition: the poorer the cosolvent the greater the aggregation of polymer chains. Deb and Palit[9] did not observe such large values of the Huggins constant for PMMA in the same cosolvent media. However, similar results to ours were found by Prolongo *et al.*[10] for PMMA in acetonitrile + chlorobutane cosolvent system. For the same polymer, the difference in behaviour in different cosolvent systems is probably due to the molecular weight of the samples used by the two groups of workers: Deb and Palit[9] used PMMA fractions with molecular weights ~10^6 whereas for the other group of workers the molecular weight was ~10^5. This is also evident in our study.

Figure 3 shows a plot of Huggins constant values against log(molecular weight) for different solvent compositions (only three solvent compositions are shown in the figure to avoid overlap). The curve for $\phi_{CH_3OH} = 0.33$ has the lowest position. For all curves it is clear that there is a decrease in the Huggins constant value with increase in molecular weight. This indicates that the tendency of intermolecular aggregation for LM samples is higher than for HM samples, and the tendency for aggregation becomes larger as the cosolvent becomes poorer. The HM sample has a larger excluded volume than the LM samples. Therefore, at a particular concentration (expressed in wt%) for both the HM and LM polymers the number density of polymers with lower excluded volume is larger than the number density of polymers with higher excluded volume. So, at a particular cosolvent composition, the LM samples tend to aggregate much more than the HM sample under the same conditions because of the number of available polymer molecules and this is valid for all concentrations of the polymer, thereby increasing the value of the Huggins constant. Deb and Palit[9] also noticed the decrease in Huggins constant value with increase in molecular weight for PMMA in each cosolvent composition of $CCl_4 + CH_3OH$. There are two reasons for the relatively high value of the Huggins constant observed here compared to ref. 9: (i) the molecular weight range studied here is much smaller than in ref. 9 and (ii) the PMA chains are more flexible than PMMA chains, giving lower excluded volume values than in ref. 9 for the same molecular weight sample.

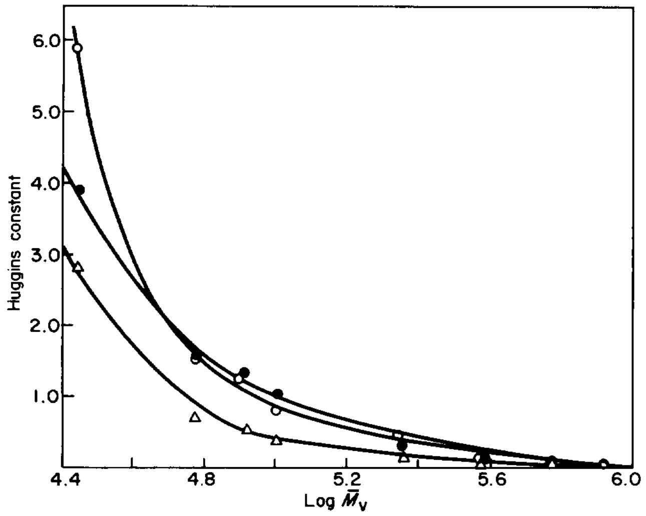

Figure 3 Plot of Huggins constant *versus* log(molecular weight) at different cosolvent compositions: $\phi_{CH_3OH} = 0.14$ (○); 0.5 (●); 0.33 (△)

Unperturbed dimension

The unperturbed dimension of a polymer chain is important in understanding the physical properties of a polymer both in solution and in the solid state. It is the dimension of the polymer chain where the volume exclusion due to long range segmental interaction is nullified by its interaction with a definite solvent (θ solvent)[16]. That is, the unperturbed dimension is the end-to-end dimension of polymer chain under θ conditions and can be determined from the intrinsic viscosity measurement at this condition:

$$[\eta]_\theta = \Phi_0(\bar{r}_0^2/M)^{3/2}M^{1/2} = K_\theta M^{1/2} \qquad (2)$$

where Φ_0 is the Flory constant and $\bar{r}_0^2$ is the mean square unperturbed dimension. Under non-θ conditions the chains have perturbed dimension and then:

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

where α_η is the molecular extension parameter which varies from solvent to solvent and also with molecular weight. Due to the unknown value of α_η, K_θ is determined by the Burchard, Stockmeyer, Fixman (BSF) equation using the dependency of intrinsic viscosity on molecular weight under given conditions[18,19]. This method is now widely used to determine unperturbed dimension[2,10,20–22]. For non-θ conditions some workers also determined $[\eta]_\theta$ indirectly[9,12,23] and calculated the unperturbed dimension of polymer chains from that value using equation (1).

Here we have used the BSF method for determination of the unperturbed dimension in different cosolvent media by plotting $[\eta]/M^{1/2}$ against $M^{1/2}$ from the equation:

$$[\eta]/M^{1/2} = K_\theta + 0.51B\phi_0 M^{1/2} \qquad (4)$$

where B is a polymer–solvent interaction free energy parameter. The plots are shown in *Figure 4*. Cowie[20] and Lewis *et al.*[21] have shown that there may be some deviation from linearity of the BSF plot at higher molecular fractions ($\bar{M}_v^{1/2} > 600$), as they found in poly(α-methyl styrene) in CCl_4, polystyrene in toluene, polystyrene in n-BuCl etc. But such deviation from linearity was not observed here. However, it is clear from *Figure 4* that the intercept value (K_θ) for the composition $\phi_{CH_3OH} = 0.33$ is about twice as large as for the extreme compositions studied here. Such an unusual variation of unperturbed dimension with cosolvent composition is uncommon. So to confirm values of the unperturbed dimension, other methods for its determination were explored[20,24,25]. The results are summarized in *Table 2*. It is clear that for cosolvent composition $\phi_{CH_3OH} = 0.33$ the K_θ values obtained by different methods are almost equal, but for other compositions there is some variation. However, the results obtained by Cowie and the BSF method are nearly equal, but considerable variation is observed when they are compared with the values of Bohdanecky and Tanaka. Disregarding the merits and demerits of various methods for the calculation of the correct value of unperturbed dimension, one can easily conclude that the unperturbed dimension changes by a factor of 2–3 at the best cosolvent composition compared to the poorest cosolvent composition, determined by any method. The unperturbed dimension ($K_\theta \times 10^3$ in dl $g^{-3/2}$ $mol^{1/2}$) of PMA reported in the literature[26] varies from 0.68 to 0.81, as determined by intrinsic viscosity measurements from solvent or solvent mixture under θ conditions. Of course, this variation (~15%) cannot be accounted for by the personal error of different workers and may be due to the solvent and temperature dependency of the parameter. However, in our system this variation is quite significant (100% or more). Such a large variation of unperturbed dimension is rare though dependence of unperturbed dimension on solvent/solvent mixture is not uncommon[2,10,27,28]. The reason for this large variation is not clear. However, a plot of ΔG^E *versus* ϕ_{CH_3OH} of $CH_3OH + CCl_4$ mixture[8] shows a maximum at approximately the same position as the maximum value of unperturbed dimension. Perhaps the strong repellent tendency of the two solvents at this composition causes the polymer to have the largest value of unperturbed chain.

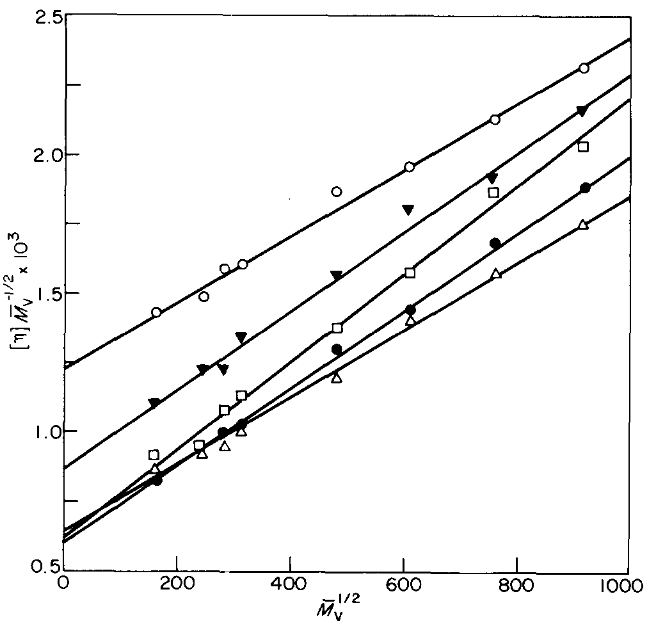

Figure 4 BSF plots for PMA fractions at various cosolvent compositions: $\phi_{CH_3OH} = 0.33$ (○); 0.5 (●); 0.14 (△); 0.4 (□); 0.25 (▼)

Table 2 Unperturbed dimension of PMA in $CCl_4 + CH_3OH$ mixtures at 35°C, determined by different methods

	$K_\theta \times 10^3$ (dl $g^{-3/2}$ $mol^{1/2}$)			
ϕ_{CH_3OH}	BSF[18,19]	Cowie[20]	Bohdanecky[25]	Tanaka[24]
0.14	0.652	0.627	0.536	0.513
0.25	0.871	0.868	0.756	0.709
0.33	1.233	1.289	1.257	1.157
0.40	0.624	0.515	0.412	0.345
0.50	0.596	0.513	0.417	0.367

Molecular extension factor (α_η)

The cosolvents, owing to their solvation power, extend the polymer chains by increasing the molecular extension factor and thus cause an increase in excluded volume of the polymer[10]. We have calculated the molecular extension parameter from the relation, $\alpha_\eta^3 = [\eta]/K_\theta \bar{M}_v^{1/2}$ using K_θ of the BSF plot; this is presented in *Table 3*. The actual end-to-end distance, $\alpha_\eta K_\theta$, is also included in the table. It is clear that at $\phi_{CH_3OH} = 0.33$, $\alpha_\eta K_\theta$ has a higher value than at other compositions for all molecular weights, as expected. However, the α_η value at this composition is lower than at other compositions. The α_η value is dependent on contributions from intermolecular and intramolecular interactions; in the former, the interaction of polymer molecule with solvent molecules plays the major role, whereas in the latter it is the long-range segmental interaction of the polymer molecules. The polymer–solvent interaction can be measured from the slope of the BSF plot but there is some question about its reliability[29]. The composition $\phi_{CH_3OH} = 0.33$ is the best cosolvent composition so polymer–solvent interaction is expected to be a maximum here, and therefore the extension factor should exhibit the highest value. However, in contrast it is clear from the table that for all molecular weight samples the value of α_η is a minimum at this composition. The intramolecular interaction is probably responsible for the low value of α_η at $\phi_{CH_3OH} = 0.33$ because the unperturbed dimension is larger in this composition than in other compositions. This causes long range segmental interaction to decrease greatly giving the lowest value of α_η. The molecular weight dependency of α_η is also clear from the table; α_η increases with increase in molecular weight, for almost the same reason as above. Here, the number of segmental interactions increases as the number of segments in a molecule increases with molecular weight, causing the larger value of the extension parameter α_η.

CONCLUSIONS

It can be concluded from this study that the α_η value of the polymer is greater than unity for all cosolvent

Table 3 Molecular extension factor and coil dimensions of PMA fractions at 35°C in $CCl_4 + CH_3OH$ mixtures

	HMI		MMI		MMII		MMIII		LMI		LMII		LMIII		LMVI	
ϕ_{CH_3OH}	α_η	$\alpha_\eta K_\theta \times 10^3$	α_η	$\alpha_\eta K_\theta \times 10^3$	α_η	$\alpha_\eta K_\theta \times 10^3$	α_η	$K_\theta \times 10^3$	α_η	$\alpha_\eta K_\theta \times 10^3$	α_η	$\alpha_\eta K_\theta \times 10^3$	α_η	$\alpha_\eta K_\theta \times 10^3$	α_η	$\alpha_\eta K_\theta \times 10^3$
0.14	1.39	0.905	1.34	0.873	1.31	0.853	1.23	0.799	1.18	0.769	1.13	0.736	1.12	0.729	1.10	0.717
0.25	1.35	1.176	1.30	1.132	1.27	1.106	1.21	1.058	1.15	1.002	1.12	0.975	1.12	0.975	1.08	0.941
0.33	1.23	1.516	1.21	1.492	1.16	1.434	1.15	1.418	1.09	1.344	1.09	1.344	1.06	1.31	1.05	1.294
0.40	1.48	0.926	1.44	0.899	1.36	0.849	1.30	0.811	1.22	0.762	1.20	0.750	1.15	0.715	1.14	0.709
0.50	1.47	0.877	1.41	0.842	1.34	0.799	1.29	0.773	1.20	0.715	1.19	0.708	1.16	0.694	1.12	0.665

compositions and for all molecular weights studied here. This is certainly due to the better solvent power of the cosolvent system than the components. But the relative dimensions of the polymer chains in the cosolvent compositions studied are not due to α alone. The unperturbed dimension, which changes with solvent mixture composition, plays a major role.

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