

POLYMER COSOLVENT SYSTEM: POLY(VINYL-2-PYRIDINE)/TOLUENE/ETHYL ACETATE

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Abstract—A study of the cosolvent ternary system, poly(vinyl-2-pyridine)/toluene/ethyl acetate, was carried out by viscometry and light scattering. An anomalous behaviour of the intrinsic viscosity in a certain composition region was observed and attributed to a conformational transition of the chain. The transition is interpreted in terms of the interactions between the constituents of the system.

INTRODUCTION

An important case of polymer solutions is that of cosolvent systems. In these systems, the polymer is dissolved within a certain region of the binary solvent mixture whereas it is insoluble in each of the pure solvents [1].

In many such systems, it has been observed that a maximum of both the intrinsic viscosity $[\eta]$ and the second virial coefficient, A_2 , is reached near that composition where the preferential adsorption coefficient, λ' , undergoes inversion. On the other hand, inversion in λ' does not always occur in every cosolvent system [2].

We have recently studied the cosolvent system poly(vinyl-2-pyridine)/nitromethane/carbon tetrachloride [2]. Light scattering measurements indicated that CH_3NO_2 was adsorbed by the polymer through the whole cosolvency region.

We now present a new cosolvent system of poly(vinyl-2-pyridine) (PV2P) in toluene and ethyl acetate. In addition to the cosolvency behaviour, the system also exhibits conformational transition within a specific solvent composition region. Similar behaviour of PV2P has previously been observed in a mixture of two good solvents although in a different specific region [3]. A conformational transition is generally observed either in binary mixtures of polymer and solvent where the only intensive parameter is the temperature [4-10] or in ternary systems, such as the above, where the only intensive parameter is the solvent composition [3, 11-16].

EXPERIMENTAL

PV2P samples were fractions of the polymer prepared by anionic polymerization at low temperature using THF as solvent. We have used five fractions of molecular weights 79,000, 43,000, 35,000, 32,000 and 16,000. The sample of molecular weight 16,000 was supplied by Aldrich. The molecular weight of each fraction was determined by light scattering using a model 42,000 Fica P.G.D. operating at the 546 nm green line.

Intrinsic viscosity was determined by the use of a modified Ubbelohde viscometer under constant pressure and temperature (30°). The measurements were repeated several

times especially at the sensitive transition region and were reproducible to $\pm 1\%$.

The preferential solvation coefficient λ' was calculated from light scattering data according to the method proposed by Strazielle and Benoit [17].

$$\lambda' = \left[\left(\frac{M^*}{M} \right)^{1/2} - 1 \right] (dn/dc/dn/d\phi_1), \quad (1)$$

where M^* is the apparent molecular weight as determined by light scattering, M the true molecular weight, dn/dc is the refractive index increment at a certain composition of the binary solvent mixture and $dn/d\phi_1$ is the variation of the refractive index of the solvent mixture (n) with its composition expressed as the volume fraction ϕ_1 of the solvent-1.

RESULTS AND DISCUSSION

1. Intrinsic viscosity

We examine here a case of cosolvency where both liquid constituents (toluene and ethyl acetate) are non-solvents for PV2P. Polymers were dissolved in the mixture only for molecular weights below 100,000 (at 30°).

We have observed a relatively wide cosolvent region $\phi_1 = 0.2-0.9$. Figure 1 shows the intrinsic viscosity as a function of ϕ_1 , the volume fraction of toluene, for three of the studied molecular weights. The polymer exhibits anomalous behaviour in $[\eta]$ around $\phi_1 = 0.7$ which is attributed to a chain conformational transition. A transition is also observed in the unperturbed dimensions K_θ and the long distance interaction parameter B (Figs 2 and 3). The unperturbed dimensions of PV2P were determined by the Stockmayer-Fixman extrapolation [18]. The value of $[\eta]/M^{1/2}$ was plotted vs $M^{1/2}$ for all the fractions of PV2P for different solvent mixture compositions. The parameter B was calculated from the slope of the Stockmayer-Fixman straight lines.

Intrinsic viscosity values of low molecular weight polymers were especially important in revealing the conformational discontinuities in the unperturbed dimensions of the polymer. The value of $[\eta]$ is affected by both K_θ and long distance interactions,

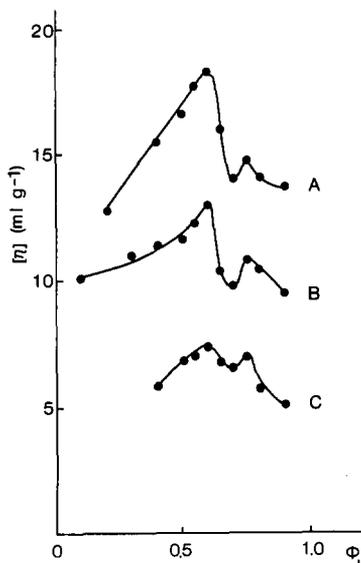


Fig. 1. Intrinsic viscosity of the ternary mixture (PV2P/toluene/ethyl acetate) vs composition in terms of toluene. A, $M = 79,000$; B, $M = 35,300$; C, $M = 16,000$.

(B), although the latter is comparatively negligible for low molecular weights.

2. Light scattering

Recent experimental evidence indicates that cosolvent systems can be characterized according to their preferential adsorption behaviour. Thus, two types of cosolvent systems may be observed. The first type includes those systems in which the coefficient λ' undergoes inversion. On each side of the inversion point, that component is preferentially adsorbed which is deficient as compared to the composition of the system at the inversion point. At maximum $[\eta]$ none of the components of the mixture is preferentially adsorbed; this is expected by the zero value of the λ' coefficient. The second type includes those cosolvent systems in which inversion of the λ' coefficient does not occur. Only one of the two

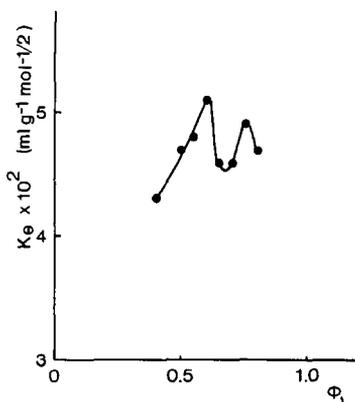


Fig. 2. Coefficient of the unperturbed dimensions vs composition in terms of toluene.

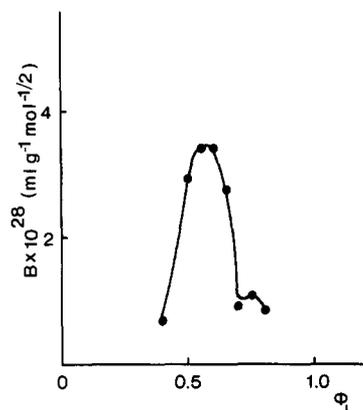


Fig. 3. Long distance interactions parameter vs composition in terms of toluene.

constituents in the mixture is adsorbed over the entire cosolvency region [2].

Figure 4 shows the composition dependence of λ' in the solvent mixture. The characteristic inversion of λ' is around $\phi_1 = 0.67$, where the first maximum of $[\eta]$ is observed. Values of λ' appear in Table 1. Toluene is less preferentially adsorbed as more of it is added to the mixture. Beyond the inversion point, the solvent mixture composition will be richer in ethyl acetate, in the vicinity of the macromolecular coil, rather than to its bulk composition.

The composition where inversion of λ' occurs almost coincides with that of the first $[\eta]$ maximum, i.e. $\phi_1 = 0.6$. Indeed this near coincidence is expected to be due to the very small difference between the solvent molar volumes (1 is 1.1) [19].

In Fig. 5, the second virial coefficient A_2 is plotted vs ϕ_1 . The maximum of A_2 is at $\phi_1 = 0.63$, very near the inversion point of λ' and the first $[\eta]$ maximum.

We have studied here a ternary cosolvent system which also presents a conformational transition. The conformational transition can be attributed to the dynamics of the system as a whole, as no discontinuity is observed in the excess volume of the mixture alone [20], or the viscosity of the solvent mixture [21]. An explanation for the observed discontinuity in $[\eta]$

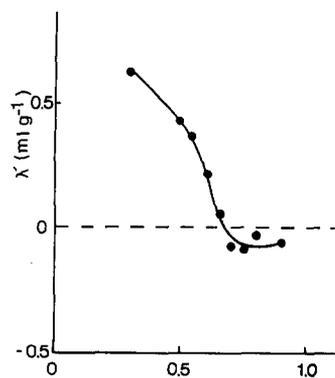


Fig. 4. Coefficient of preferential adsorption vs composition in terms of toluene.

Table 1. Light scattering results for the system (PV2P/toluene/ethyl acetate)

Toluene ϕ_1	dn/dc	M^*	M^*/M	λ'
0.30	0.183	85,600	1.99	0.605
0.50	0.162	76,100	1.77	0.431
0.55	0.156	68,500	1.59	0.327
0.60	0.152	58,100	1.35	0.198
0.65	0.146	47,500	1.10	0.057
0.70	0.140	37,400	0.87	-0.076
0.75	0.135	37,000	0.86	-0.079
0.80	0.130	41,000	0.95	-0.026
0.90	0.120	38,500	0.89	-0.055

$M = 43,000$; $dn/d\phi_1 = 0.1243$.

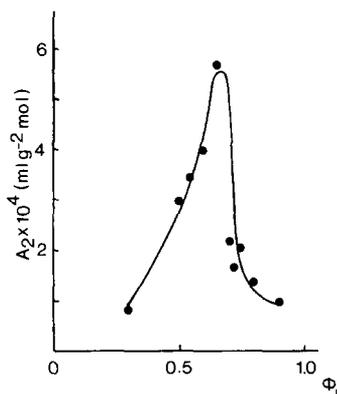


Fig. 5. Second virial coefficient, A_2 , plotted vs composition in terms of toluene.

can be given as follows. At low toluene concentrations ($\phi_1 < 0.8$), as ethyl acetate is added to the mixture, the pyridine ring rotation is hindered by the formation of hydrogen bonding between the N and H atoms of two nearest pyridine rings. Such a picture is expected for PV2P when found in the environment of a relatively low polarity solvent [3]. This pyridine ring interaction is expected to increase the rigidity of the chain and is expressed as an increase of the unperturbed dimensions, K_θ , of the polymer. Further addition of ethyl acetate yields a critical composition where the affinity between the pyridine rings is destroyed and the flexibility of the chain is increased. The transition is observed by a decrease of K_θ and an increase of the parameter B . If even more ethyl acetate is added to the mixture, the intrinsic viscosity goes through a maximum ($\phi_1 = 0.6$), behaving as a

typical cosolvent system. The λ' inversion point and the maximum of A_2 are at $\phi_1 = 0.6$.

Dynamic light scattering measurements can offer additional information on the phenomenon of the chain transition. Such data are expected to relate with viscometric and elastic light scattering measurements and shed more light on the conformation of macromolecular chains in solution.

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