SOLUTION PROPERTIES OF POLYSTYRENE IN MIXTURES OF TOLUENE WITH ETHYL ACETATE

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Abstract—The ternary system polystyrene/toluene/ethyl acetate has been studied by viscometry and light scattering. The intrinsic viscosity of the ternary system has been found to undergo a discontinuity over a narrow solvent mixture composition range. This phenomenon is accounted for by assuming conformational changes of the chain.

INTRODUCTION

Several polymer solutions have been studied to date in which there is discontinuity in the polymer chain dimensions in a solvent mixture. Discontinuities of this type are generally observed either in binary polymer–liquid mixtures where the only intensive parameter is the temperature [1–9], or in ternary systems where the only intensive parameter is the solvent composition [10–17].

The solution behaviour of the polymer poly(vinyl-2-pyridine) (PV2P) in the solvent mixture toluene–ethyl acetate was examined in a recent paper [17]. The system not only exhibited a discontinuity in the polymer dimensions within a certain composition region of the mixture but also showed cosolvency behaviour. In order to extend the study of the discontinuity behaviour of polymer chains, we now present work on the intrinsic viscosity of polystyrene (PS) in the same binary mixture, toluene–ethyl acetate. Light scattering measurements were also employed. A discontinuity in the intrinsic viscosity of the system is observed.

EXPERIMENTAL PROCEDURES

PS samples were fractions of a polymer prepared by anionic polymerization at low temperature using tetrahydrofuran (THF) as solvent. Two fractions of mol. wts 88,000 and 162,000 were studied. Additional samples of mol. wts 200,000 and 260,000 were supplied by "Monotez".

The mol. wt 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 use of a modified Ubbelhode viscometer under constant pressure and temperature (30°C). The measurements were repeated several times especially in the region of a discontinuity and were reproducible to ±1%.

The coefficient of preferential solvation (λ') was estimated from light scattering data by the method proposed by Strazielle and Benoit [18]:

$$\lambda' = \{(M^*/M)^{1/2} - 1\}\{(dn/dc)/(dn/d\phi_1)\} \qquad (1)$$

where M^* is the apparent mol. wt as determined by light scattering, M is 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 with its composition, expressed as the volume fraction (ϕ_1) of solvent-1.

RESULTS AND DISCUSSION

Intrinsic viscosity

The discontinuity in the intrinsic viscosity is observed at toluene concentrations (ϕ_1), between 0.55 and 0.70 [see Fig. 1(a)].

The mixture composition at which the discontinuity occurs does not depend upon the molecular weight of the polymer. The dip in the $[n]$ vs ϕ_1 curve is more prominent the lower the molecular weight of the polymer. Figures 1(b) and (c) show that unperturbed dimensions (K_θ) and the long distance interaction parameter (B) also exhibit a discontinuity within the same region of the mixture composition. The unperturbed dimensions of PS were determined by Stockmayer–Fixman extrapolation [19]. The value of $[n]/M^{1/2}$ was plotted vs $M^{1/2}$ for all fractions of PS for various solvent mixture compositions. The parameter (B) was calculated from the slope of the Stockmeyer–Fixman straight lines. It is noted that the minimum in the unperturbed dimensions parameter (K_θ) appears for that mixture composition for which the parameter (B) has a minimum value. The flexibility of the chain thus shows a dramatic change in the region of the discontinuity.

Light scattering

The preferential solvation parameter λ' as estimated through equation (1) is shown in Fig. 2. The parameter changes sign at $\phi_1 = 0.7$ being positive for $\phi_1 < 0.7$.

The coefficient λ' is defined as

$$\lambda' = [x_1/M]V_1 \qquad (2)$$

where x_1 is the number of molecules of solvent-1 (toluene) in the neighbourhood of the macromolecular chain; V_1 is the molar volume of solvent-1 and M is the molecular weight of the polymer.

From equation (2) and from the fact that toluene is solvent-1, it is concluded that toluene is preferentially
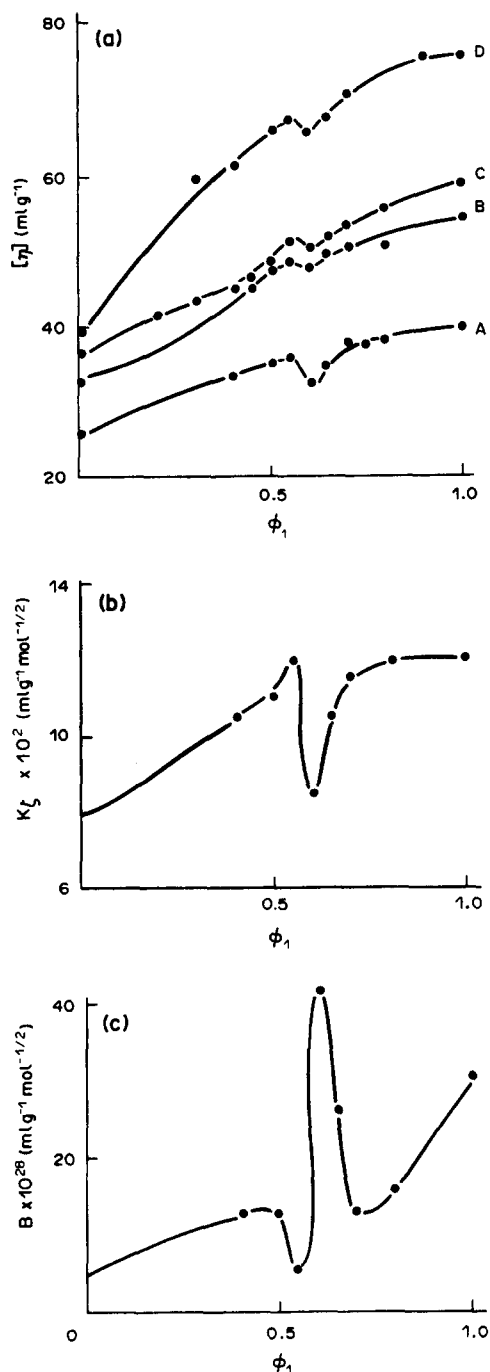
Fig. 1.(a) Intrinsic viscosity of the ternary mixture. PS/toluene/ethylacetate vs composition in terms of volume fraction of toluene. A, M = 88,000; B, M = 162,000; C, M = 200,000, D, M = 260,000. (b) Coefficient of the unperturbed dimensions K_{θ}. (c) Long distance interaction parameter B.
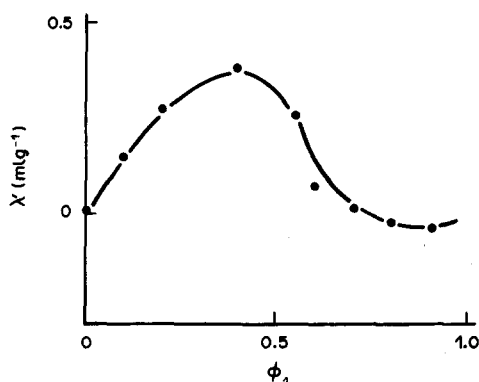

Fig. 2. Coefficient of preferential absorption vs composition in terms of volume fraction of toluene.

The ternary system considered here exhibits a discontinuity in the intrinsic viscosity. There is no discontinuity in the excess volume of the mixture alone [20] or the viscosity of the solvent mixture [21]. It is through this observation that the discontinuity phenomenon should be attributed to the system as a whole and not connected with the solvent mixture alone. It has been observed that the solutions of PS show an anomalous temperature dependence in solution properties at *ca* 50 and 80°C [1, 22–24]. Similar behaviour is observed in our system brought about solely by change in mixture composition.

The polymer PV2P has been studied previously [17] in toluene/ethylacetate and has been found to undergo a discontinuity around the composition in toluene $\phi_1 = 0.7$. The effect of formation of hydrogen bonding between the N and H atoms of the two nearest pyridine rings has been considered as the possible cause for the observed discontinuity. The ternary system studied in this work also exhibits a similar discontinuity, less intense than in the previous case and around the same composition mixture range. We understand that the relatively low intensity of the phenomenon may result from the absence of the N atom in the monomer unit. We notice that the flexibility of the chain changes dramatically in the anomalous region. This effect is shown by the abrupt decrease of the parameter (K_{θ}) and the increase of the parameter (B). We believe that this comes as a consequence of the change in the mobility of the phenyl side group. It would be very interesting to study the behaviour of the ternary system in which the N atom is positioned at a more remote site in the pyridine ring. This problem will be considered in future work.

tially absorbed for those concentrations for which λ' is positive. Consequently for those mixture compositions for which λ' is negative, ethyl acetate is preferentially absorbed. Light scattering results indicate that, in the transition region, the less polar solvent is present at a very small proportion in the vicinity of the polymer chain.

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