Polymer Bulletin 19, 515–520 (1988)

Polymer Bulletin

Viscometric behaviour of the PMMA/acetonitrile/L-menthol system

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SUMMARY

In this paper we have studied the viscometric and refractometric behaviour of several fractions of PMMA in the acetonitrile/L-menthol binary solvent as a function of composition of L-menthol. A conformational transition has been found in the composition interval of 16-19% L-menthol.

INTRODUCTION

Frequently the adition of a non-solvent to a polymer solution make poorer the system (1-10). However, in a few cases it is observed an increase of the solvent power of the binary mixture (11-16). This sinergic effect is evidenced by an increase of the intrinsic viscosity of the polymer. In the literature have been described some of these systems (17-25). For poly(methyl methacrylate) for instance the amil acetate/CCl_4 (26), CCl_4/1-propanol (27), CCl_4/1-butanol(28), acetonitrile/n-butyl chloride (29), etc. mixtures.

In this paper we have studied the viscometric and refractometric behaviour of poly(methyl methacrylate) in the acetonitrile(1)/L-menthol(2) cosolvent mixture in the composition range $10 < U_2 < 24\%$ L-menthol using four PMMA fractions.

EXPERIMENTAL

The acetonitrile (Carlo Erba RPE) used was dried rigously and distilled before use through a packed column and a center cut of constant boiling point was collected. Purity was checked by boiling point and refractive index. The n^{25} of the center cuts ranged from 1.34143 to 1.34148.

Six PMMA fractions of nominal polydispersity indices $\overline{M}_W/\overline{M}_N$ 1.20 were used in thid work.

Viscosities of PMMA fractions were measured, at 298 K, in the binary solvent mixture acetonitrile(1)/L-menthol (2) in the composition range $10 < U_2 < 24\%$ L-menthol, with a modified Ubbelohde type capyllary dilution viscometer.

Solutions were prepared by dissolving a measured quantity of sample in acetonitrile in the viscometer. Concentrations of the solutions were so adjusted that the specific viscosities ranged from 0.1 to 0.6. Each fraction was studied at a minimum of six concentrations. The flow times of the solvent ranges between 120 to 160 s., depending on the composition

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on the composition of the binary mixture; thus no kinetic energy correction was requiered. Flow times were reproducible within ±0.03 s. The shear rate corrections for intrinsic viscosities lower than 3.80 $dl.g^{-1}$ were negligible and therefore omitted.

The values of η_{sp}/c and ln η_r/c were plotted against concentration and extrapolated to c = 0. The Huggins constants k_H were then calculated.

Osmotic pressures were measured in toluene at 308 K in a Knauer osmometer. Five concentrations were examined for each sample in order to extrapolate π/c to c = 0.

The value of dn/dc, for light of wavelength 633 nm, of PMMA in the binary mixture at 298 K was measured using a differential Brice-Phoenix refractometer, equipped with a He-Ne laser which emits with a power of 1 mW. A sealed cell with Teflon stoppers was used. Calibration was effected at 298 K with aqueous solutions of KCl of different concentrations (expressed in g. saltz/100 g. of water).

Solvent mixtures of acetonitrile (1)/L-menthol (2) were made up by weight. The refractive index of the binary solvent mixtures was measured with a Abbé refractometer at 298 K and 633 nm., previously calibrated with several organic liquids for which the refractive indices were known (30,31). The maximum error in determining the refractive index was of $\pm 5.10^{-4}$.

RESULTS AND DISCUSSION

Figure 1 shows the plot of the k and a Mark-Houwink-Sakurada parameters versus the binary mixture composition, U_2. As it can be seen in this figure, the a parameter decreases initially, remaining then constant in the composition range 13-19% L-menthol. At higher L-menthol concentrations the a expone-

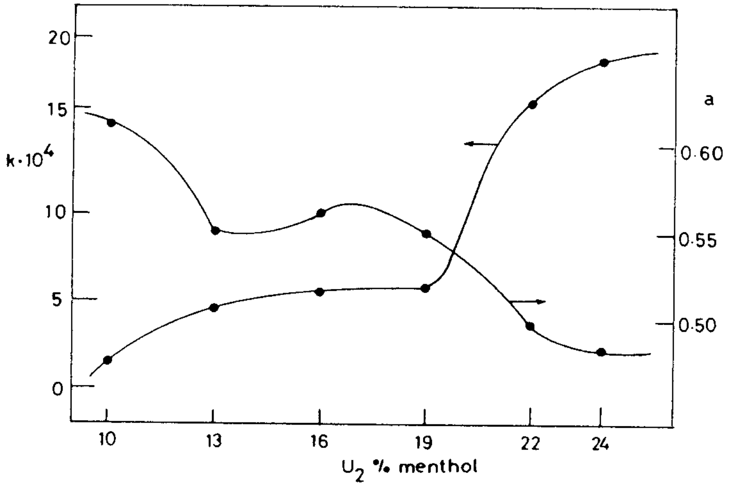

Figure 1. Constants k and a of Mark-Houwink-Sakurada equation versus solvent composition U_2 for the system PMMA/acetonitrile(1)/L-menthol(2).

nt decreases again continuosly. As in our case, the excess Gibbs free energy, G^E, is very small (32); this means the polymer can interact with any of the two components of the binary mixture. However, the obtained experimental results indicate that the PMMA is initially solved by the acetonitrile. The stabilization of the thermodynamic conditions of the system between 13 to 19% L-menthol can be due to the fact that the L-menthol hinders the access of acetonitrile molecules to macromolecule coil, the polymer adopting a more rigid structure.

The sharp variation of a parameter for $U_2 > 19\%$ L-menthol can be due to a conformational transition phenomena in PMMA. dn/dc Measurements confirm this result, as it can be seen in Figure 2. Likewise, the k parameter shows a similar behaviour. We believe that the conformational transition is induced by a selective sorption of acetonitrile molecules on the lateral groups of the PMMA chains, probably due to hydrogen bond formation with the carboxilic groups of the PMMA. As the PMMA is an appreciable polar polymer, the >C=O groups must be the principal responsible for the short distance interactions, and therefore, for the unperturbed dimensions of the chain(33).

At $U_2 \equiv 22\%$ L-menthol the system is under "ideal" condition (theta condition a = 0.5). Away off this binary composition the system is below theta condition and then PMMA-PMMA contacts are more favoured.

Figure 3 illustrates the variation of the K_θ parameter, characterizing the unperturbed dimensions of PMMA, and B, the polymer-solvent mixture interaction parameter, respectively. Both quantities were obtained using the Stockmayer-Fixman equation (34). The obtained values for the K_θ parameter show that PMMA becomes more rigid as in the binary solvent mix-

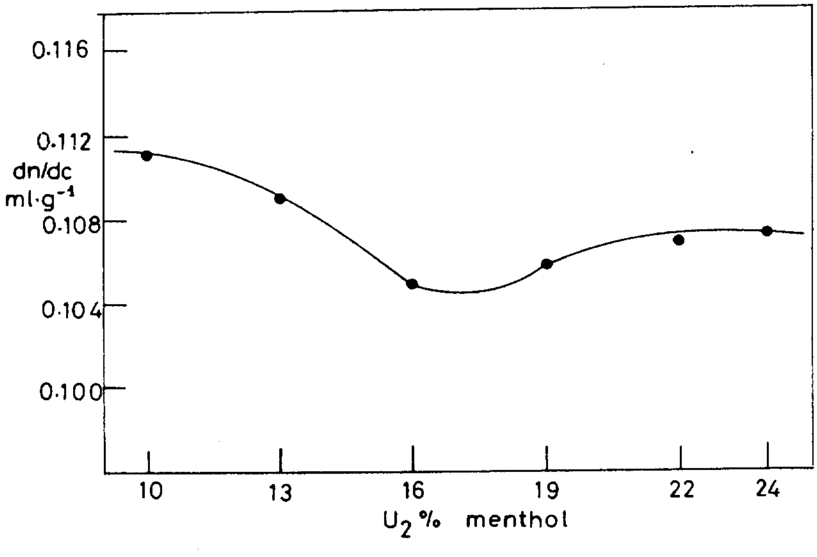

Figure 2. Variation of dn/dc versus solvent composition U_2 for the system PMMA/acetonitrile(1)/L-menthol(2).

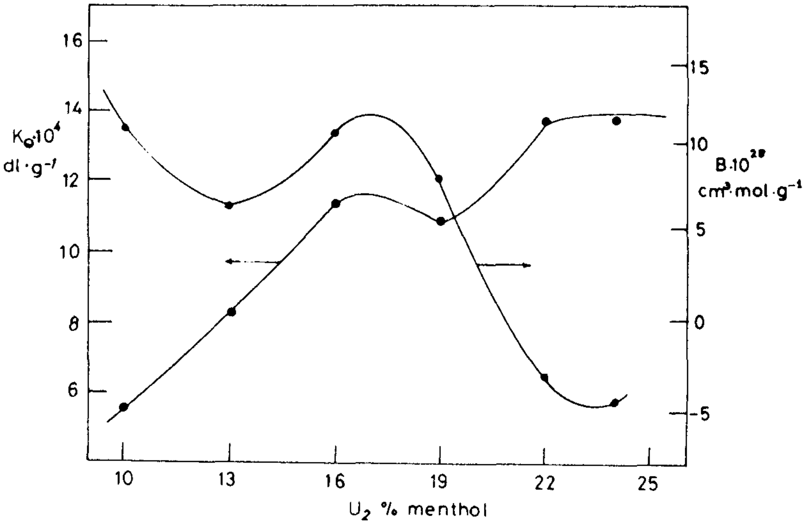

Figure 3. Plot of K_θ parameter versus the solvent composition, U_2, for the system PMMA/acetonitrile(1)/L-menthol(2).

ture increases the L-menthol content. As it can be seen, an anomaly is observed for this parameter in the composition range 16-22% L-menthol, which confirms the existence of the conformational transition. It is interesting to point out that the transition found occurs at lower temperatures than those found in pure solvents (17, 21, 23, 24).

Imai (35) has derived the following equation for the Huggins constant k_H in terms of a numerical constant C_1 and the excluded volume parameter Z:

$$k_H = k_{H_\theta} + C_1 Z \alpha_\eta^{-5} \qquad (1)$$

where α_η is the expansion coefficient defined as α_η^3 $[\eta]/[\eta]_\theta$.

Using the Kurata-Stockmayer-Roig theory (36), the excluded volume parameter Z can be written:

$$Z = 0.330 B A^{-3} M^{1/2} \qquad (2)$$

where A is equal to $(K_\theta/\Phi_0)^{1/3}$. Substituting Eq.(2) into Eq.(1) we obtain:

$$k_H \alpha_\eta^4 = k_{H_\theta} + C_2 B M^{1/2}/K_\theta \alpha_\eta \qquad (3)$$

where $C_2 = 0.330 C_1 \Phi_0$. The plot of $k_H \alpha_\eta^4$ versus $BM^{1/2}N/K_\theta \alpha_\eta$ should be linear with an intercept equal to $k_{H\theta}$ and the slope of C_2. $k_{H\theta}$ is the Huggins constant at the theta temperature, which is completely independent of temperature, solvent and molecular weight. Eq.(3) is very usefull when the polymer suffer a conformational transition or the unperturbed K_θ parameter changes appreciably with temperature or binary mixture composition.

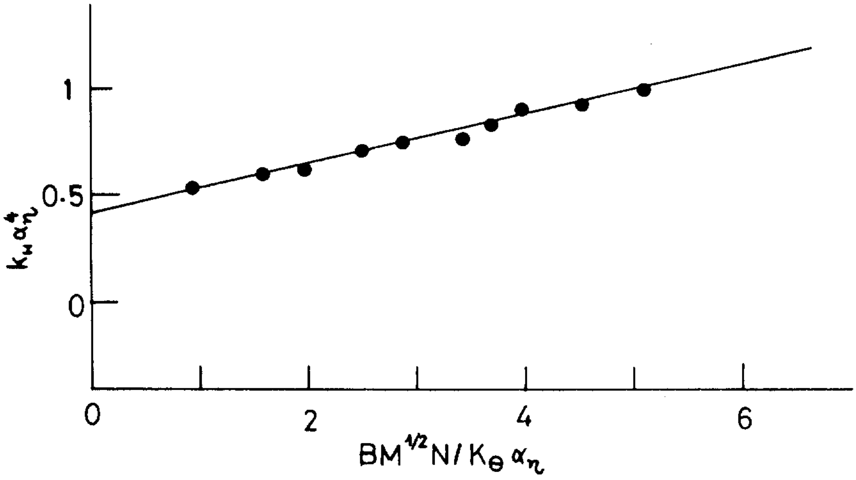

Figure 4. Plot of $k_H\alpha_\eta^4$ versus $BNM^{1/2}/K_\theta\alpha_\eta$ for PMMA in the binary solvent mixture acetonitrile(1)/L-menthol(2) of several compositions.

In Figure 4 we can seen the obtained result according to Eq.(3). Reasonably good linearity is seen to hold if we take into account the experimental difficulties in determining the Huggins constant. The intercept represents $k_{H\theta}$ = 0.43. This value is in good agreement with the theoretical expected value of $k_{H\theta}$ = 0.47 (23). Computer calculation of $k_{H\theta}$ constant is in progress. The slope is equal to $C_2 = 3.63.10^{-28}$ This value is again in good accordance with the theoretical ones ($3.58.10^{-28}$). According to Eq.(3), the slope of the dependence $k_H\alpha_\eta^4$ versus $BM^{1/2}N/K_\theta\alpha_\eta$ ought to be independent of the nature of the solvent and of the polymer.

This result is similar to those found by Huglin et al.(36) for solutions of polystyrene in binary solvents and Bohdanecky (37) for solutions of PVC in several cyclic ketones.

Acknowledgement. We express our thanks to Dirección de Investigación de la UPV for financial support.

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Accepted February 8, 1988 C