Polymer Bulletin 6, 437–445 (1982)

Polymer Bulletin

Selective Adsorption of PMMA in Polar Binary Mixtures
4. Chloroform(1)/Methyl Acetate(2)

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ABSTRACT

In this paper, we study the behaviour of PMMA(3) in the polar binary mixture chloroform(1)/methyl acetate(2). In this system chloroform is preferentially adsorbed by PMMA in the range $0 < u_2 < 88\%$ methyl acetate. A conformational transition has been found for $u_2 = 40\%$ methyl acetate. In order to characterize quantitatively the phenomenon the intra- and intermolecular interactions have been determined using viscometry and light scattering as experimental techniques.

INTRODUCTION

The study of the properties of polymer solutions in binary mixtures presents theoretical and experimental problems of various kinds, some of them similar to those ones found in single solvents and others specific of the ternary systems, such as: preferential adsorption phenomenon, unperturbed dimensions variation, solubility, etc.

In a ternary system three interaction parameters whose values determine the behaviour of the system, can be defined. If both solvents present different affinities for the polymer ($\chi_{13} \neq \chi_{23}$), the chains will be preferentially solvated by one of them, which will be found in a greater proportion in the proximities of the macromolecule with respect to the solution composition (HERT et al.1973; ZIVNY et al.1967). It must be detached that

0170-0839/82/0006/0437/$01.80

the preferentially adsorbed solvent need not be the best solvent from the thermodynamical point of view. On the other hand, if the polymer is solved in a solvent mixture at a fixed composition, the obtained value of the expansion coefficient, α, differs from the values which would be obtained by solving it in each of the pure solvents separately, and it cannot be calculated from them. This particular characteristic of every macromolecular ternary system is due to the preferential solvation of the chain by one of the solvents and because of this, the composition of the binary mixture inside the volume occupied by the chain, is different from the composition in the solution.

The preferential solvation of the macromolecules in binary mixtures, has been studied by physico-chemical and equivalent methods, and from them the different definitions of the preferential solvation, are obtained.

In this paper the behaviour of PMMA in the system Chloroform(1)/Methyl Acetate(2), when both components of the binary mixture are good solvents for the PMMA has been studied by viscometry and light scattering.

EXPERIMENTAL PROCEDURES

All samples were obtained by radical polymerization of methyl methacrylate (Fluka purum) at 323 K in benzene (Cepsa)(KATIME et al. 1974; KATIME et al. 1975) using 1,2-azobisisobutyronitrile (Fluka puriss) as initiator. The number average molecular weight was $7.5 \cdot 10^4$. The obtained sample was fractionated by solubility in the system benzene/methanol in order to obtain low polydispersity fractions ($\overline{M}_w/\overline{M}_n < 1.3$)(KATIME et al.1981).The fractions were redisolved in benzene and freeze-dried at constant weight in a vacuum line.

Light scattering measurements were made with a P.G.D. FICA model 42.000 at 298 K using green light of wavelength 546 nm. Solvents and solutions were clarified by centrifugation for 2 hr. in a preparative Sorvall at 15,000 rpm.

The refractive indices of the solvents and of the binary solvent mixtures were measured with an Abbé refractometer at 298 K.

The viscosities were measured at 298 K using an Ubbelohde suspended level viscometer suitable for dilution in situ. The temperature of the water bath was regulated to ±0.01°C. Values of the limiting viscosity number, $|\eta|$, were determined from the Huggins and Schulz-Blaschke equations by plotting η_{sp}/c and $\ln \eta_r/c$ versus c and extrapolating to zero concentration by the least squares method.

EXPERIMENTAL RESULTS

According to Strazielle and Benoit (1961) the preferential adsorption coefficient in binary mixtures is expressed by the equation

$$\lambda = \{(\frac{M^*}{M})^{1/2} - 1\}\frac{(dn/dc)}{(dn/du)} = \frac{x_1 v_1}{M} \qquad (1)$$

where M is the weight average molecular weight of the polymer determined by light scattering in single solvents and M* is the apparent weight average molecular weight of the polymer determined by light scattering in binary solvent mixtures, dn/du is the variation of the refractive index of the binary solvent mixture with the composition, dn/dc is the concentration dependence of the refractive indices of the polymer solutions, x_1 and v_1 are the number and the partial molar volume of solvent molecules preferentially adsorbed per single polymer chain or coil, respectively.

Values of preferential adsorption coefficient, λ, calculated from Eq.1 for the whole of solvents compositiones are shown in Table 1.

TABLE 1. λ,$\{\eta\}$ and A_2 values of PMMA in the binary mixture chloroform/methyl acetate.

u_2 % methyl ac.	λ $ml.g^{-1}$	$\{\eta\}$ $dl.g^{-1}$	$A_2.10^4$ $cm^3.mol.g^{-2}$
0	0	0.354	10.34
10	0.059	0.372	11.19
20	0.560	0.356	9.03
30	0.759	0.315	14.35
40	0.804	0.263	10.71
50	0.475	0.299	29.42
60	0.739	0.310	34.81
70	0.913	0.299	30.05
80	0.357	0.305	31.08
90	-0.056	0.297	13.32
100	0	0.176	1.35

The second virial coefficient, A_2, is also studied for these systems because it is affected by the preferential adsorption.

This magnitude is evaluated from the general equation

$$\frac{1}{M} + 2A_2c + \ldots. = P(\Theta).K(dn/dc)^2.(c/I)_\Theta \qquad (2)$$

which for a binary system can be written as follow

$$K(dn/dc)^2.(c/I)_{\Theta=0} = \frac{1}{M^*} + 2A_2^*c \qquad (3)$$

where A_2^* is the apparent second virial coefficient which is related to A_2 by the equation

$$A_2 = A_2^* \frac{M_w^*}{M_w} \qquad (4)$$

DISCUSSION

As it can be seen in figure 1, chloroform and methyl acetate are preferentially adsorbed in the composition ranges $0 < u_2 < 88\%$ methyl acetate. The inversion composition u_{2i}, at which the macromolecular coil is equally solvated by both components of the binary mixture, occurs at $u_{2i} = 88\%$ methyl acetate.

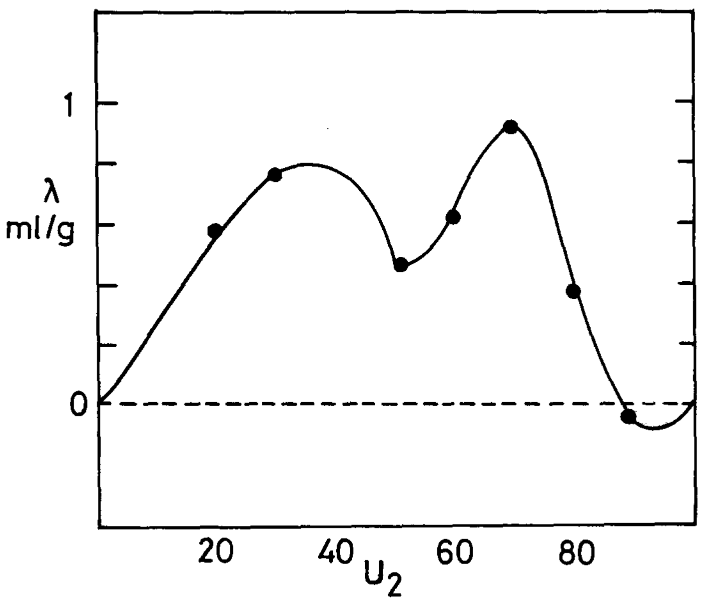

Figure 1. Plot of λ as a function of binary mixture composition, u_2

At this composition the 3-1 (polymer-chloroform) and 3-2 (polymer methyl acetate) contacts are equally favoured and the preferential adsorption coefficient is zero. This inversion in the solvation can be explained only if we considerer the existence of specific interactions between the carboxyl group ($\rangle$C=O) of PMMA and the methyl group of the ester.

On the other hand, the shape of the λ vs U_2 curve, indicates that PMMA suffers a conformational transition from U_2 = 40% methyl acetate. This conformational change, appears to be caused by a strong solvation of the polymer by chloroform. This phenomenon affects the macromolecular dimensions (to the effet that polymers) changes its flexibility(KATIME et al. 1977;KATIME et al 1981). In spite of this conformational change PMMA continues to adsorbs preferentially chloroform until U_2=70% methyl acetate. This behaviour can be confirmed by vis cometry. As can be seen in figure 2, the variation of {η} as a function of U_2, until 40% methyl acetate, is the theorically expected (ZIVNY et al. 1967). However from this composition the limiting viscosity number - strongly increases confirming that chloroform preferentially solvates PMMA which means that PMMA is preferentially solvated by chloroform. DONDOS (1972) using viscosimetric measurements for PMMA samples of molecular weights 115000-36000 (similar to the ones used in this work) observed for the binary mixtures chloroform(1)/acetone(2) a conformational transition at U_2= 50% acetone. In that paper Dondos has observed that the unperturbed dimensions of the polymer, K_θ , decreses and that this phenomenon does not depend on molecular weight. A similar result has been observed in our systen. Besides, the limiting viscosity number,{η}, for the different compositions of the binary mixture is different from the arithmetic mean of the limiting viscosity numbers in the single solvents,being this values superior; however, for the composition at which the conformational

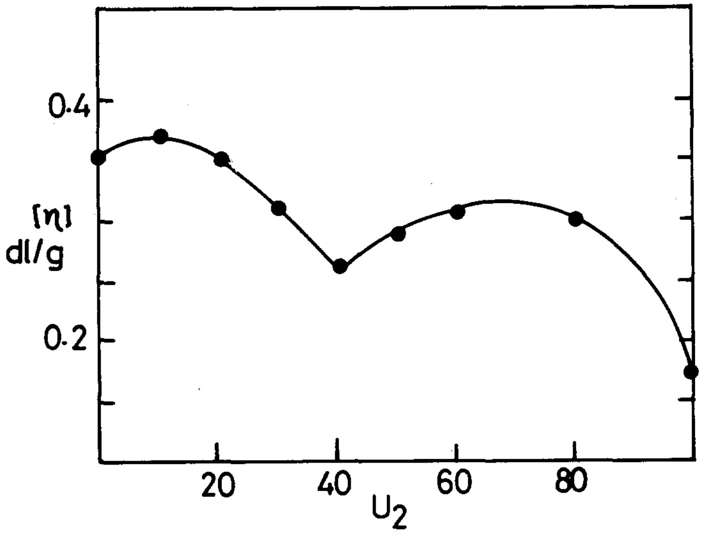

Figure 2. Plot of intrinsic viscosity, {η}, as a function of binary mixture composition, u_2

change is produced, this value is slightly inferior, figure 2.

DONDOS, REMPP and BENOIT (1970) have found that, the limiting viscosity number of a polymer measured in a binary mixture can be bigger or smaller than the arithmetic mean of the limiting viscosity number of each pure component separately $\{\eta\}_1$ and $\{\eta\}_2$ and that this behaviour is rulet by the interction parameter χ_{12} value. From POUCHLY et al. (1968) and STOCKMAYER-FIXMAN (1963) equations:

$$\Delta\{\eta\} = \{\eta\} - U_1 \{\eta\}_1 - U_2 \{\eta\}_2 \qquad (5)$$

$\{\eta\}$ being the limiting viscosity number of the polymer in the binary mixture, U_1 and U_2 the volume fractions of solvents 1 and 2 respectively and $\{\eta\}_1$ and $\{\eta\}_2$ the limiting viscosity numbers in the pure components solvents. According to DONDOS and PATTERSON (1969) the limiting viscosity number and Gibbs free energy are related by equation:

$$\Delta\{\eta\} = \frac{1,02\phi_0 M\bar{v}^2}{N_A} \frac{G^E(U_2)}{VRT} \qquad (6)$$

and being $G^E/RT = x_1(1-x_2)\chi_{12}$

then:

$$\Delta\{\eta\} = \frac{1,02\phi_0 M\bar{v}^2}{N_A} \frac{x_1(1-x_1)\chi_{12}U_2}{V} \qquad (7)$$

where ϕ_0 is the Flory universal constant, M the molecular weight of the polymer, $\bar{v}$ the PMMA specific volume and V the average molecular volume of the binary mixture.

If $\Delta\{\eta\}$ and χ_{12} values this system are studied (table 2) it is observed that when $\Delta\{\eta\}$ gets a positive value χ_{12} gets it as well and if $\Delta\{\eta\}$ is negative, so is χ_{12} (U_2= 40% methyl acetate) .

The value of χ_{12} at U_2=40% can confirms the existence of a conformational transitions due to the fact that when PMMA de decreases, its molecular dimensions $\{\eta\}$ decreases, the molecules of solvent are thrown out of the macromolecular coil, favouring, at this composition

Table 2.-Δ{η} and interaction parameter χ_{12} values in function of composition, U_2

U_2 % methyl ac.	Δ{η} dl g^{-1}	χ_{12}
10	0,036	0,790
20	0,038	0,455
30	0,014	0,136
40	-0,020	-0,162
50	0,034	0,304
60	0,063	0,601
70	0,070	0,782
80	0,093	1,404
90	0,103	1,675

the interactions between both components of the binary mixture at higher compositions an increment in the solvation is observed again.

In figure 3, the variation the second virial coefficient A_2, versus composition is shown.

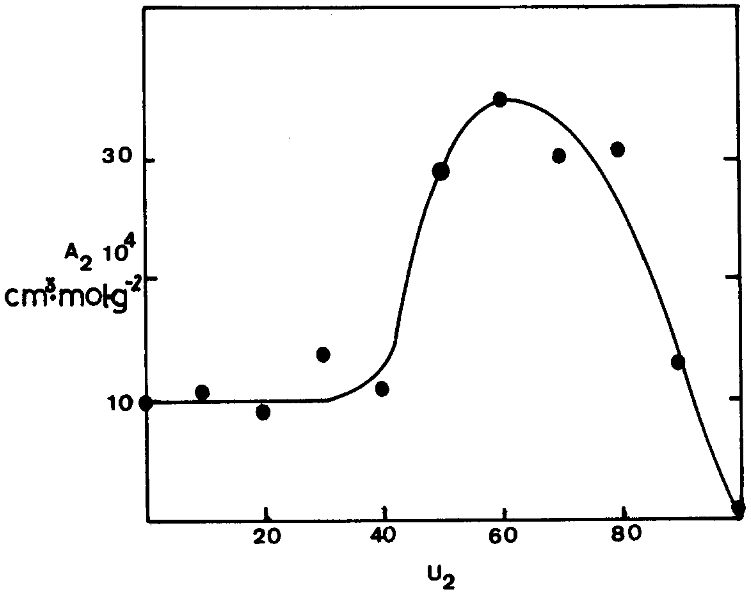

Figure 3. Plot of second virial coefficient, A_2, as a function of binary mixture composition, u_2

As it can be seen A_2 increases regularity until U_2=40%, for this composition a sudden increase of A_2 is observed which indicates that intermolecular interactions are highly favoured, and allow us to explain the conformational transition appearance.

It is to be noted that A_2 and λ, take their maximum values at the same composition U_2 approximately.Therefore chloroform is the maximum responsible for the intermolecular interaction leading us to think that this solvent is responsible for the conformational transition.

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Received December 28, 1981
Accepted January 7, 1982

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