

Preferential solvation of poly(methyl methacrylate) and a bisphenol A diglycidyl ether by size-exclusion chromatography

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Abstract

The preferential adsorption coefficient, λ , of poly(methyl methacrylate), PMMA, in solutions formed by an epoxy resin in tetrahydrofuran (THF), was studied by size-exclusion chromatography (SEC). Only PMMA of lowest molar mass was preferentially solvated by epoxy but at low concentrations of epoxy in the mixture. At higher epoxy content PMMA was preferentially solvated by THF. A simultaneous and competitive solvation between the specific interactions PMMA-epoxy and the self association of epoxy at high concentrations would be the responsible of this inversion point. The more compacted coil of PMMA of higher molecular weights in solution could explain the lack of interaction of these polymers with epoxy. The results also indicated that λ decreased with the molar mass. This variation has been attributed to the influence of the coil segment density on preferential adsorption.

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1. Introduction

Interactions between liquid epoxy resin and dissolved polymers are important in determining the morphology and mechanical properties of the cured two-phase blends. Although the family of carboxy-terminated poly(butadiene-co-acrylonitrile) and derivatives still constitutes the most important group of modifiers used in rubbers-modified epoxies [1], several other types of modifiers have been proposed as well [2]. In the 1980s a novel approach to toughen epoxies [3], consisting of replacing the rubber by an engineering thermoplastics, including polysulfones [4,5] and poly(ether imides) [6] or poly(vinyl acetates) was developed. The advantage of using thermoplastics is that they can provide effective toughening if incorporated correctly into the resin without reducing the thermal and mechanical properties of the matrix. In previous works the curing of a dicyanate ester of bisphenol A with and without catalysts was analyzed [7,8]. In this report we focus our study on poly(methyl methacrylate) (PMMA) as a model additive

because of its solubility in the liquid resin. Although no toughening effects are expected [9], the results will throw valuable light upon resin-polymer interactions.

The preferential adsorption phenomenon is very common in ternary systems containing polymers in diluted solution [10]. The difference in affinity of each solvent with regards to the polymer leads to composition variations of the mixed solvent in the vicinity of the macromolecule. Size-exclusion chromatography (SEC), is one of the most widely used techniques for the evaluation of the preferential solvation parameter, λ , especially in ternary polymer/solvent/solvent [11,12] or even in polymer/polymer/solvent systems [13,14] if the respective sizes in solution of the two polymers are sufficiently different. The height of the so-called vacancy peak, proportional to the amount of injected polymer, provides a rapid and accurate determination of λ [15]. In a previous work [16] we used this method to measure the compatibility between the cyanate ester monomer Arocy B 10 and poly(sulfone), PSF, at different monomer to polymer ratios, in the presence of three organic solvents: tetrahydrofuran (THF), dimethylformamide and dichloromethane. PSF was found to be preferentially solvated by the epoxy in all systems. The variation of λ values with the Arocy B10 concentration was strongly dependent upon the nature of the

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solvent showing the strongest solvation in the presence of THF. In this paper we report the preferential solvation as a tool to measure the compatibility between the epoxy resin diglycidyl ether of bisphenol A and PMMA, in the presence of THF. The quantitative evaluation of the λ parameter has rigorously been made at polymer-diluted conditions. The effect of the epoxy content and the molar mass of the polymer, on the compatibility between epoxy resin and PMMA has been investigated.

2. Experimental

2.1. Materials

The epoxy resin was a commercial bisphenol A diglycidyl ether (BADGE) with the trade name Araldite GY 250 (Fig. 1), gently supplied by Ciba-Geigy. The epoxy content was 5.34 eq./kg, as determined by acid titration [17] (mass per equivalent, WPE = 187.3 g/eq.). This corresponds to $n = 0.122$ in the structural formula of Fig. 1. The selected thermoplastic was a commercial grade of poly(methyl methacrylate), PMMA (Polymer Labs) of different molar masses: 9200 (PMMA-9k), 28,300 (PMMA-28k) and 58,500 (PMMA-58k). They showed polydispersities M_w/M_n of 1.06, 1.04 and 1.03, respectively (where M_w = weight-average molecular mass and M_n = number-average molecular mass). The organic solvent THF was HPLC-grade from Scharlau (Barcelona, Spain).

2.2. Size exclusion chromatography

The liquid chromatograph consisted of a model 590 solvent-delivery system and a U6K universal injector from Waters (Milford, MA, USA). Detection was carried out with a refractive index (RI) detector Model 2410 from Waters (Milford, MA, USA). Data collection and handling were carried out using Millennium³² Chromatography Manager from Waters (Milford, MA, USA). The system was equipped

with two μ Styragel columns (30 cm \times 0.78 cm, i.d.) packed with highly crosslinked styrene–divinylbenzene copolymer of 10³ and 100 Å of nominal pore size from Waters (Milford, MA, USA). The mobile phase flow-rate was adjusted to 1.0 ml/min. The injection volume of samples was 100 μ l.

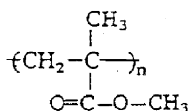
Three sets of experiments were performed according to the three molecular masses of PMMA studied. In all cases, the mobile phases, used as eluents, consisted in diluted solutions of the epoxy in THF, and PMMA was always the solute. The composition of the eluents was the following: 0.1, 0.2, 0.3 and 0.4 g of epoxy/100 ml of THF. The PMMA concentrations of the injected solutions were in the range 0.032–1.200 g/100 ml of mobile phase.

The column was equilibrated overnight before injection of the analyte solution, which was prepared using the corresponding mobile phase as solvent. Eluents were always filtered and degassed through regenerated cellulose 0.45 μ m pore diameter filters from Micro Filtration Systems (Dublin, CA, USA).

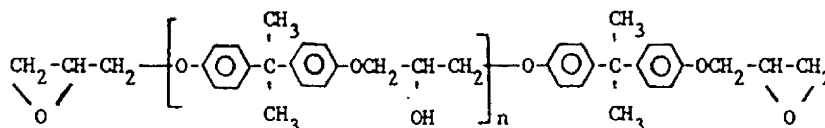
3. Results

3.1. THF/epoxy/PMMA-9k

The goal of the present work is to study the behaviour of ternary systems THF (1)/epoxy (2)/PMMA (3) at diluted concentrations of the polymer through the quantitative evaluation of the preferential adsorption coefficient by SEC. The method to determine λ has been meticulously described in a previous paper [16]. This is possible thanks to the proportionality between the magnitude of the vacancy peak and the amount of injected polymer, as Berek et al. have shown [15], as well as the fact that its elution volume corresponds to that of one of the components of the mixture. A ternary system solvent (1)/polymer (2)/polymer (3), where polymer (2) is much smaller in size than polymer (3), can be considered formed by two phases in equilibrium: the bulk solvent (or binary phase) constituted by the solvent (1), the polymer



poly(methyl methacrylate), PMMA



bisphenol A diglycidyl ether (BADGE)

Fig. 1. Structures of PMMA and BADGE.

(2), and the polymer (3) domain (or ternary phase). In this ternary system, the preferential solvation can be defined as the change in the volume fraction of the component i ($i = 1, 2$) in the ternary phase with respect to the composition of such a component in the binary phase, with the two phases in thermodynamic equilibrium. In such conditions, the preferential solvation coefficient λ express the volume of the solvent (1) or of the resin (2) preferentially adsorbed on the polymer (3) per unity of mass of such polymer (3), at infinite dilution. Then, the λ values at diluted composition of polymer are obtained according to its definition [10]:

$$\lambda = \left(\frac{\Delta v_1}{c_3} \right)_{c_3 \rightarrow 0} = - \left(\frac{\Delta v_2}{c_3} \right)_{c_3 \rightarrow 0} \quad (1)$$

where Δv_i is the difference in the volume fraction of THF (Δv_1) or of epoxy (Δv_2) between the ternary and the binary phase; c_3 is the PMMA concentration. If preferential solvation of PMMA by THF takes place, $\Delta v_1 > 0$ and $\lambda > 0$. In contrast, when PMMA is preferentially adsorbed by epoxy, $\Delta v_2 > 0$ then $\lambda < 0$.

The change in the volume fraction of epoxy per polymer gram ($\Delta v_2/c_3$) with the PMMA-9k concentration, for the eluent compositions 0.1, 0.2, 0.3 and 0.4% (w/v) of epoxy in THF is shown in Fig. 2. As can be seen, the preferential solvation parameter λ obtained from the intercept yielded positive values for all eluent compositions except for the system THF/epoxy (0.2%)/PMMA-9k. That means that PMMA-9k is preferentially solvated by epoxy only in this mobile phase composition.

When size exclusion is the main factor governing the separation mechanism in liquid chromatography, the injection of a polymer solution at c_3 concentration cause a “vacancy peak” [18,19] revealing the existence of preferential interaction of the polymer by one of the remaining components. Δv_2 is determined from the height of such a vacancy peak obtained in the chromatograms of PMMA in THF/epoxy mixtures. Typical elution profiles obtained by injection of

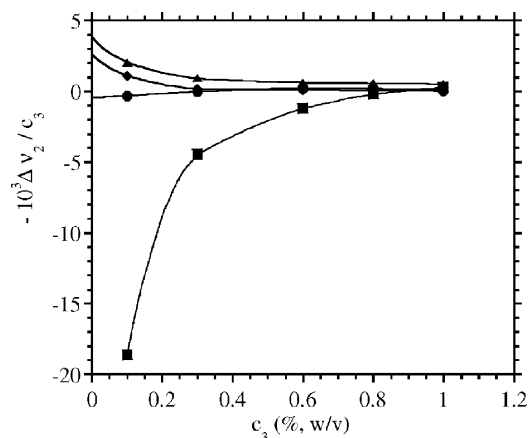


Fig. 2. Change in the volume fraction of the epoxy resin per gram of polymer ($\Delta v_2/c_3$) as a function of the PMMA-9k concentration, c_3 , for different mobile phase compositions: (●) 0.1, (■) 0.2, (◆) 0.3 and (▲) 0.4% (w/v) of epoxy.

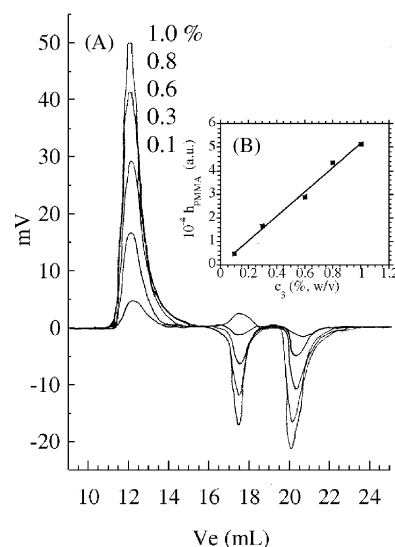


Fig. 3. (A) Chromatograms of PMMA-9k in THF/epoxy (0.20%) at different polymer concentrations (in the figure). Mobile phase: epoxy at 0.20% in THF. (B) Dependence of the height of the PMMA-9k peak on polymer concentration.

various PMMA concentrations in THF/epoxy (0.2%) are shown in Fig. 3A. They show three peaks: the first one (at $V_e = 12.5$ ml), positive, corresponds to the solvated polymer, and its height (h_{PMMA}) linearly increases with increasing polymer concentration (Fig. 3B). From the height of the vacancy peak (h_{probe}), which appears at the elution volume of epoxy in THF, $V_e = 17.5$ ml, Δv_2 is readily calculated through the equation:

$$\Delta v_2 = \frac{\Delta v_2^0}{h_{\text{cal}}} (h_{\text{probe}}) \quad (2)$$

where Δv_2^0 and h_{cal} are the difference in the volume fraction of epoxy and the height of the vacancy peak, respectively. They are obtained from the injection of binary solutions containing known excess and shortages in volume fraction of epoxy at a fixed eluent composition. Fig. 4A illustrates, as an example, the chromatograms of this calibration for THF/epoxy (0.2%)/PMMA. In all cases the epoxy elutes at 17.5 ml and the peak is either positive or negative according to the injected composition, i.e. at c_2 values greater than the baseline (0.2%) the direction of the signal shows an increase, whereas for $c_2 < 0.2\%$ the signal decreases in the relative transmittance. At this stage, one point requires comments. Both THF/epoxy and THF/epoxy/PMMA systems show one vacancy peak at the same elution volume. This is an important detail since the elution volume lets to locate the peak, hence to elucidate the preferentially solvated component. A good linear correlation between the height of this vacancy peak and the concentration of epoxy injected (Fig. 4B) allows to perform the calibration curve for the detector response, Δv_2^0 versus h_{cal} , the slope of which supplies the quotient of Eq. (2). These calibration curves for the four eluent compositions are depicted in Fig. 5. The linearity of

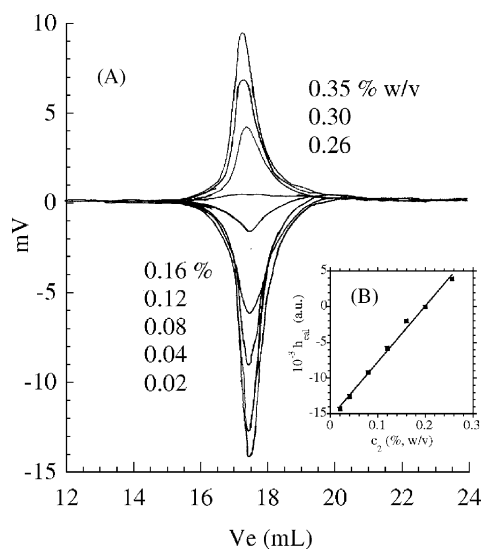


Fig. 4. (A) Positive and negative signal deflections from refractive index detector on injection of different epoxy solutions. Baseline corresponds to a mobile phase composition of 0.20% solution of epoxy in THF. The epoxy concentrations are given in the figure. (B) Dependence of the height of the epoxy peak on its concentration.

the fits provide evidence of the goodness of the experimental measurements in the concentration range assayed.

3.2. THF/epoxy/PMMA-28k

Fig. 6 shows chromatograms recorded for the THF/epoxy/PMMA-28k system at different polymer concentrations in the mobile phase formed by epoxy at 0.2% in THF. Positive peaks due to the polymer appear at 11.5 ml, and their heights are linearly dependent on the polymer concentration injected. The height of the positive vacancy peaks of epoxy ($V_e = 17.5$ ml) together with their calibration curve (filled squares symbols in Fig. 5) have been used to obtain the corresponding Δv_2 value for each polymer concentration and

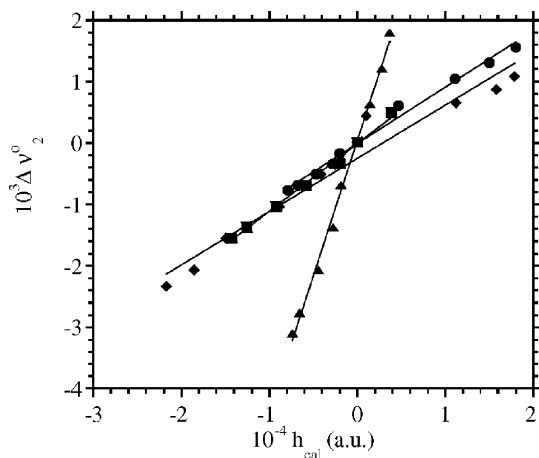


Fig. 5. Calibration graphs for the vacancy peaks obtained from different epoxy solutions. Symbols as in Fig. 1.

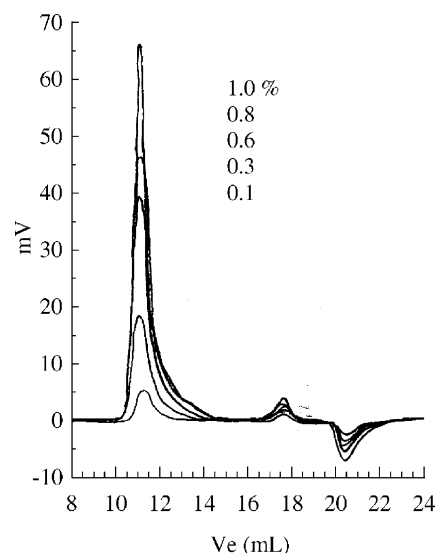


Fig. 6. Chromatograms of PMMA-28k in THF/epoxy (0.20%) at different polymer concentrations (in the figure). Mobile phase: epoxy at 0.20% in THF.

then, $(\Delta v_2/c_3)$ versus c_3 plotted, as shown in Fig. 7A. Again, the extrapolation at $c_3 \rightarrow 0$ gives the λ values. In contrast with PMMA-9k, the λ values obtained for this system are always positive in the epoxy concentration range assayed. That is, PMMA-28k is preferentially solvated by THF.

3.3. THF/epoxy/PMMA-58k

The variation of $(\Delta v_2/c_3)$ with c_3 for the system THF/epoxy/PMMA-58k (Fig. 6B) follow a similar trend to that exhibited by PMMA-28k (Fig. 7A), that is, positive λ values approach 0 at high polymer concentrations and sharply increase as c_3 decreases. In addition these values of the change in the volume fraction of epoxy per polymer gram are higher and the increase more apparent when the binary phase is constituted by epoxy 0.4% ($\Delta v_2/c_3$). Again, PMMA-58k is preferentially solvated by THF.

4. Discussion

Experimental results of preferential sorption by polymers in solvent/epoxy mixtures have shown that the coefficient of preferential adsorption λ depends on the molar mass of the polymer sample as well as on the epoxy concentration of the mixture.

4.1. Dependence of the λ parameter on the polymeric molar mass

The empirical dependence of λ with the molar mass was originally described for systems solvent (1)/solvent (2)/polymer (3) by means of the law [20].

$$\lambda = \lambda_{\infty} + AM^{-1/2} \quad (3)$$

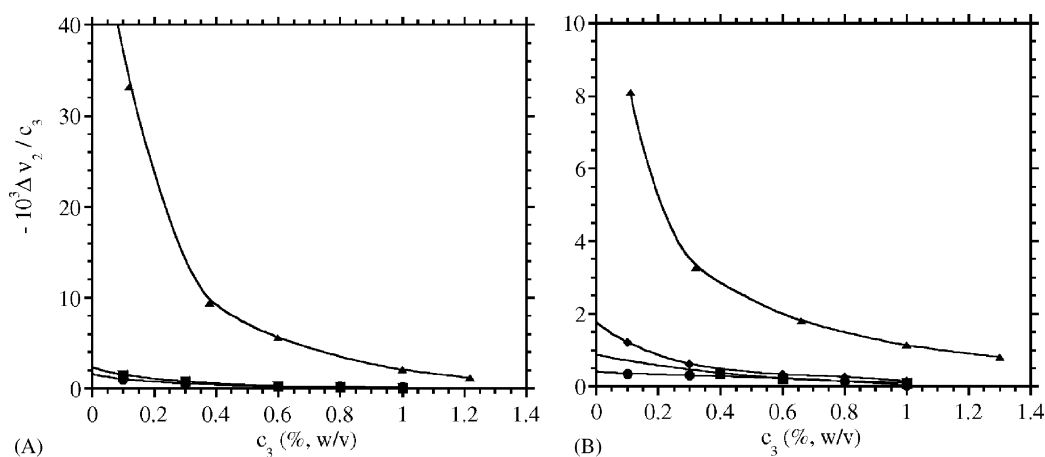


Fig. 7. Change in the volume fraction of the epoxy resin per gram of polymer ($\Delta v_2/c_3$) as a function of the PMMA concentration, c_3 , for different mobile phase compositions (symbols as in Fig. 1). (A) PMMA-28k and (B) PMMA-58k.

where λ_∞ is the value of λ extrapolated to $M \rightarrow \infty$ and A the constant of each solvent composition. Another theoretical expression used to interpret the experimental results of λ is [21]:

$$\lambda = \lambda_\infty + AM^{-1/2} + BM^{-1} \quad (4)$$

with a negative theoretical coefficient B that allows to describe the experimental results. Due to the only three molar masses of the present study, the fitting of our experimental results to these equations is uncertain. From a qualitative point of view, the preferential adsorption behaviour of our systems is analogous to that shown by polymers in mixed solvents like benzene/methanol/poly(styrene), i.e. λ_∞ and B in absolute terms increase with c_2 [21]. The preferential solvation of the polymer increases when the molar mass decreases, in a similar way than different authors [22–24] have evidenced.

The variation of λ with M has been attributed to the influence of the coil segment density on preferential adsorption [20]. The equation deduced by Horta and Katime [25] predicts that the M dependence on λ should be large in solvent + precipitant mixtures and should vanish in solvent + solvent and cosolvent pair systems. In our case, the epoxy would behave as a precipitant of PMMA.

4.2. Dependence of the λ parameter on mixture composition, c_2

Fig. 8 shows the variation of λ as a function of the epoxy concentration in the mixture for the different molar masses of PMMA.

Whereas for PMMA-28k and PMMA-58k the preferential adsorption parameter λ reaches positive values that increase with the epoxy content, PMMA-9k shows an inversion point: λ (initially positive) decreases with c_2 up to a minimum at a threshold concentration of 0.2%, achieving negative values, and then increases getting positive values. Only PMMA-9k

is preferentially solvated by epoxy at lower c_2 whereas at higher epoxy content THF is adsorbed preferentially.

Such a behaviour has also been reported for the preferential adsorption of dilute solutions of poly(alkyl methacrylate)s in 1,4-dioxane–methanol [26]. In these systems, methanol is initially adsorbed by the polymer and there is an inversion in solvation. The inversion is located at 23% (v/v) methanol for PMMA. At higher methanol contents 1,4-dioxane is adsorbed preferentially. This inversion is due to the previsible multiple self-association of methanol. The negative values of λ are explained in terms of specific interactions between the carbonyl groups of PMMA and alcohol. In the system methyl isobutyl ketone/methanol/PMMA [27], methanol is preferentially adsorbed by PMMA with negative values of λ (–0.4 ml/g for methanol concentrations in the range 0–12%, v/v). Such a behaviour is explained by dipole–dipole interactions between carboxylic group of PMMA and methanol. Similar examples of specific interactions by hydrogen bonds between poly(vinyl

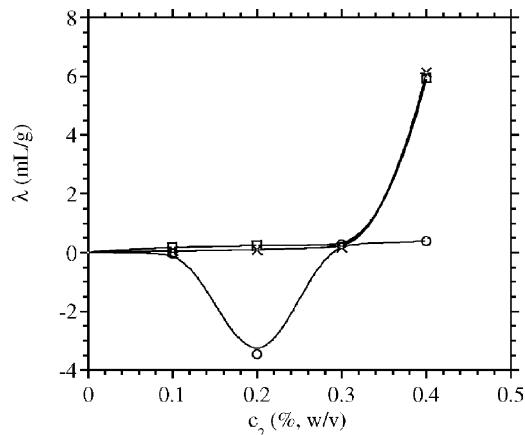


Fig. 8. Dependence of the preferential interaction parameter, λ , on epoxy concentration for (○) PMMA-9k, (□) PMMA-28k, (×) PMMA-58k.

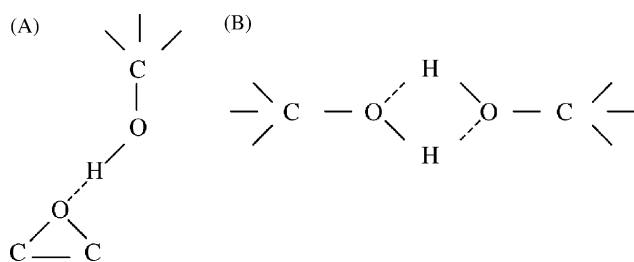


Fig. 9. Schema of the self association of (A) epoxy–hydroxyl groups interactions and by (B) hydroxyl–hydroxyl group interactions.

pyrrolidone) (PVP), and ethanol in the presence of a second inert solvent can also be found in the literature [28].

In order to explain the specific interaction between PMMA or PVP and methanol only at lower concentrations of methanol in the mixture is often mentioned the effect of self-association of the alcohol, admitting its simultaneous and competitive solvation to the polymer to justify that the preferential solvation of methanol by PMMA decreases and vanishes when the proportion of the alcohol in the mixture increases [29].

Preferential interactions between PMMA and alcohols have also been explained by dipole–dipole or hydrogen bond specific interactions between the carboxylic group of PMMA and the hydroxylic group of the alcohol [30]. In our system the specific interaction between epoxy and PMMA could become by hydrogen bonding between the carboxylic group of PMMA and the hydroxyl group of the epoxy (see Fig. 1 for the structures). In addition, at high concentrations of epoxy the self association of the epoxy occurs either by (A) interactions between the epoxy group and the hydroxyl group or by (B) interactions between the hydroxyl groups (see Fig. 9). This kind of interactions would explain the pattern of Fig. 7 for the system THF/epoxy/PMMA-9k. As commented above, PMMA-9k is the lonely polymer preferentially solvated by the epoxy and only at low c_2 . At higher epoxy contents the self-association of epoxy would compete with the specific PMMA–epoxy interactions. Thus, PMMA-9k would be preferentially solvated by THF. On the other hand, the more compacted coil of PMMA of higher molecular masses in solution could explain the lack of interaction of these polymers with epoxy.

Finally, since the molar mass and size of epoxy are small and different enough from the macromolecule, we have compared our results with the preferential solvation behaviour shown by the macromolecule and one of the solvents in ternary polymer/solvent/solvent systems, particularly with chloroform/methanol/PMMA-10k [31]. The comparison yields: (A) in this case the maximal adsorption takes place at concentrations of methanol higher than the contents of epoxy needed in our systems but the epoxy preferential adsorption is 26-fold. (B) In addition, methanol interacts specifically with PMMA of higher molar masses. The strongest adsorption of the system THF/epoxy/PMMA

could be due to the different possibilities of interaction between epoxy and PMMA, as described above. The more mobility of a small molecule like methanol could explain the solvation with PMMA of high molar masses. This study provides preliminary results and valuable light upon resin–polymer interactions. Work focused on miscibility and kinetic behavior of these systems is currently in course.

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