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Nature of PMMA dissolution process by mixtures of acetonitrile/alcohol (poor solvent/nonsolvent) monitored by FTIR-imaging

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Abstract

The dissolution process of poly(methyl methacrylate), PMMA, in mixtures of the binary systems: acetonitrile/alcohol (methanol, ethanol and 1-propanol), individually poor and nonsolvents respectively for the polymer, was studied at 25 °C using FTIR imaging spectroscopy. To investigate this cosolvency phenomenon and the kinetics of the dissolution process, the spatial resolution and sensitivity of FTIR imaging were used. It has been found that the PMMA dissolution rate anomalously increases almost in a parabolic way independently of the solvent system used in this study. These results were interpreted assuming that the dissolution of a polymer by a mixture of solvents is governed by a complex dependence of the solvent molecules size and their thermodynamic characteristics. The kinetics of the PMMA dissolution by AcN/alcohol solvent mixtures were interpreted using conventional Arrhenius behavior in which the activation energy has a simple dependence on the thermodynamic quality and the molecular weight of the solvent mixture.

Keywords: Polymer dissolution; Mixture of solvents; Cosolvency

1. Introduction

Polymer dissolution in a solvent is an important phenomenon in a variety of industrial applications. The semiconductor industry has an interest in controlling the dissolution rate of resist films and the quality of the final patterns obtained. Multiple solvents are often used. Particularly interesting cases of binary solvent mixtures are those for which one or both solvents do not dissolve the polymer under consideration but when they are used together in a homogeneous mixture, they create a powerful polymer dissolving system. This phenomenon has been named cosolvency when the solvents used are individually nonsolvents for the polymer.

Particularly, PMMA has been reported to be dissolved in several nonsolvent pairs, including benzyl alcohol/*sec*-butyl chloride, tetrachloromethane/*tert*-butyl chloride, tetrachloromethane/butyl chloride [1], and CCl_4 with several alcohols (MeOH, EtOH, PrOH, and BuOH) [2]. Fernández-Piérola et al. [3] reported mixtures based mainly on acetonitrile that act as cosolvents of the PMMA. However, the cosolvency phenomenon is not understood [3–7]. González-Benito et al., using FTIR imaging spectroscopy investigated this cosolvency phenomenon in poly(methyl methacrylate) with mixtures of methanol and carbon tetrachloride [7]. The spatial resolution and sensitivity of FTIR imaging to interactions between the components suggested that the dissolution process of the PMMA in a high weight fraction of the CCl_4/CH_3OD solvent mixtures consisted initially of swelling of the PMMA by the CCl_4 allowing the methanol to penetrate into the PMMA and specifically interact by means of hydroxyl–carbonyl hydrogen bonds with the polymer to separate the polymer chains.

Examining polymer dissolution by mixed solvents is made difficult by its analytical requirements. In many cases, the dissolution of polymers in mixed solvents has been characterized by observing the effect of the composition of solvent mixtures on the dissolution rate of the polymer but not the role of each individual component in the mixture during dissolution [8–10]. It is unknown in these experiments whether all of the components are diffusing into the polymer at the same rate, i.e. is one solvent excluded and whether solvent concentration at the polymer–solvent interface is different than in the bulk solution.

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Probably, the easiest way to understand this dissolution behavior is by making use of the simple solubility parameter (δ) theory. This approximations considers an ideal cooperative effect between the nonsolvents and assumes that the mixture of solvents can be treated as an intermediate liquid having individual contributions to the δ value (dispersion forces, δ_D, dipolar interactions, δ_P, and hydrogen bonding, δ_H, contributions) equal to the averages of the δ's of the two liquids [3]. Nevertheless, some of the cosolvent systems, such as water/2-propanol [4,11] and formamide/ethanol [3] do not fit this approximation, and this suggests that there must be another explanation for the cosolvency, at least for these systems. Probably, among other reasons, these discrepancies may be due to a kinetically controlled process more than a thermodynamically controlled one. In general, solvent mobility is primarily related to its molecular size whereas thermodynamic compatibility is associated with the strength of the interactions between structural groups of the polymer and solvent molecules. There are several works related to the study of the dissolution process of polymers; all of them suggest that the solvent penetration and dissolution is controlled kinetically [8,12,13].

One way to study this problem is to select several nonsolvent/nonsolvent systems acting as cosolvents systems of a particular polymer and for which one of the components could be varied within a homologous group of liquids. This group of cosolvent systems should allow better understanding of the effect of the molecular size of one of the components (kinetic aspects) jointly with the effect of the solubility parameter changes (thermodynamical aspects).

This paper reports the dissolution of a low molecular weight polymer by binary solvent mixtures. Entanglement effects do not complicate the dissolution process, and the diffusants, acetonitrile and low molecular weight alcohol (methanol, ethanol and 1-propanol) are poor and nonsolvent for the polymer, respectively. The effectiveness of FT-IR imaging as a tool to characterize this process is examined. Determining the type of diffusion process, segregation of components, and obtaining the dissolution rates are primary aims of the paper.

2. Experimental part

Atactic PMMA with molecular weight ($M_w \sim 12{,}000$ g/mol) and polydispersity ~ 2 was used as received from Aldrich Chemical Co. (Milwaukee, WI). Acetonitrile (AcN) and three alcohols: methyl alcohol-*d* (CH_3OD), ethanol (EtOH) and 1-propanol (POH) were supplied by Aldrich Chemical Co. (Milwaukee, WI), and used as received without further purification. For the sample used and under the conditions of our study, these liquids proved to be poor solvents for PMMA as FTIR experiments reflected, and is in accordance with reported data [14]. Experiments were conducted using the contact method [15]. To prepare a thin layer of polymer sandwiched between two salt plates, a solution of 10% (w/w) of PMMA in chloroform was prepared. After that, a small drop of the solution was placed on a 2 mm thick CaF_2 substrate and then remained at room temperature for 30 min to remove the solvent. Another substrate was then placed on top of the polymer, and the two plates were clamped together and heated in an oven at 200 °C for 2 h. After that, it was allowed to cool in ambient air at room temperature. The clamps were removed to yield a polymer film with 5 μm of thickness partially occupying the space between the two plates. The dissolution experiments were performed by introducing the solvent or the mixture of solvents from the empty end after the interface of the sample was positioned in the spectrometer. The solvent entered the space between the substrates by capillary action and came into contact with the polymer; at that moment it was considered that the dissolution process started. Great care to have good sample contact with the optical windows was taken, and the resulting images (in the polymer zone) showed no solvent behind the dissolution interface. FTIR images were sequentially acquired during the dissolution time in the region of view in which is included the polymer/solvent system interface. Solvent was added as necessary.

To study the effects of the solvent mixture composition on the dissolution rate of PMMA, several compositions for every AcN/alcohol mixture were prepared (Table 1).

Infrared images were collected using a Bio-Rad Stingray imaging spectrometer (Digilab Laboratories, Cambridge, MA). The Stingray is comprised of an FTS6000 step-scan interferometer bench coupled to a microscope accessory, UMA-500. The imaging detector used is a Santa Barbara focal plane array, FPA, consisting of a 64×64 array of mercury cadmium telluride (MCT) elements imaging an average spatial area of $400\times400\ \mu m^2$. A long pass filter to eliminate unwanted wavelengths and prevent Fourier fold-over perturbations was inserted into the beam path. The spectral region recorded was from 1000 to 4000 cm^{-1}. Furthermore, an 8 cm^{-1} nominal spectral resolution and an undersampling ratio (UDR) of four were used for the study. A mirror stepping rate of 5 Hz was used, yielding a total scanning time of about 300 s. The number of camera frames (frame rate = 316 Hz) averaged during each spectrometer step was 24. Image processing and data extraction were carried out using the hyperspectral imaging software package environment for visualizing images (ENVI) (Research Systems Inc.). Lower noise absorbance profiles were extracted from each image by averaging spectra stored in an image region of five pixels perpendicular to the dissolution direction [16].

Table 1
Solvent mixtures prepared

Solvent mixture	AcN/MeOD	AcN/EtOH	AcN/POH
Composition in alcohol (%w, w)	0–15, 20, 25, 30, 40, 50, 60, 80, 100	0–10, 15, 20, 25, 30, 40–80, 100	0, 5, 10, 15, 20, 25, 30, 40–80, 100

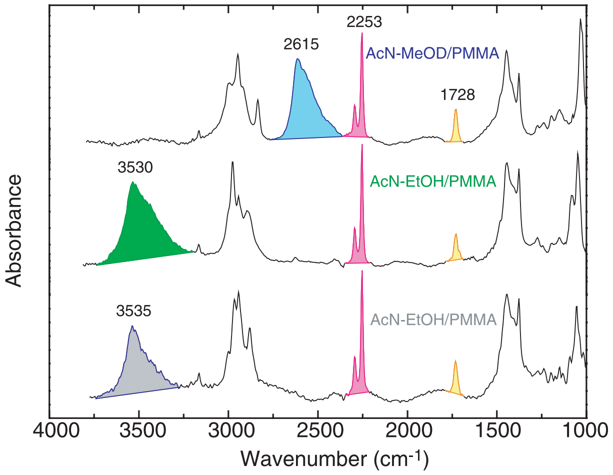

Fig. 1. FTIR spectra for the mixtures of three components, a polymer (PMMA) and two solvents (AcN and alcohol): (i) AcN + MeOD/PMMA; (ii) AcN + EtOH/PMMA and (iii) AcN + POH/PMMA.

3. Results and discussion

To analyze each component of the system (polymer/solvent) separately using FTIR imaging, it is possible to use their characteristic IR spectra. In general, a characteristic band of each component is selected and their absorbance values can be obtained for any region of the image. Fig. 1 shows the FTIR spectra for the mixtures of three components, a polymer (PMMA) and two solvents (AcN and alcohol): (i) AcN + MeOD/PMMA; (ii) AcN + EtOH/PMMA and (iii) AcN + POH/PMMA. As can be seen (Fig. 1), the AcN band centered at 2253 cm^{-1} assigned to the –C≡N stretching mode, the CH_3OD band centered at 2490 cm^{-1} and assigned to the O–D stretching mode, the EtOH band centered at 3530 cm^{-1} assigned to the O–H stretching mode and the POH band centered at 3535 cm^{-1} assigned also to the O–H stretching mode do not overlap with any of the PMMA bands, while the PMMA band centered at 1728 cm^{-1} and assigned to –C=O stretching mode does not overlap with any of the bands of the solvents under consideration. Therefore, these five bands are good choices for monitoring selectively every component of each polymer/cosolvent system in the region of study. Chemically specific images for PMMA, AcN and alcohol within the systems were obtained by plotting the absorbance of the selected IR peaks in each pixel of the FPA. Each absorbance value is associated with a color in order to see the images as a gradient of colors indicating the distribution of the components in the image.

In Fig. 2, an example of the variation of this image for each component as a function of the PMMA dissolution process when the solvent mixture composition is 30% (w/w) in EtOH is shown. In this way, it is possible to have not only spatial data but also chemical information associated with it.

In Fig. 2, the chemical response of PMMA reflects the polymer interface movement as a function of the polymer–solvent contact time. The same observations were made for the rest of the solvent mixtures and compositions studied except for the pure alcohol solvents (for which, practically, there is not dissolution of the polymer). This result is in accordance with the nonpure cosolvent behavior observed in the AcN–methanol/PMMA and AcN–POH/PMMA systems [17].

Absorbance profiles for the polymer and each of the solvents in the solvent solution can be extracted perpendicular to the film edge. As an example, Fig. 3 shows the normalized absorbance profiles for PMMA, AcN and MeOD as a function

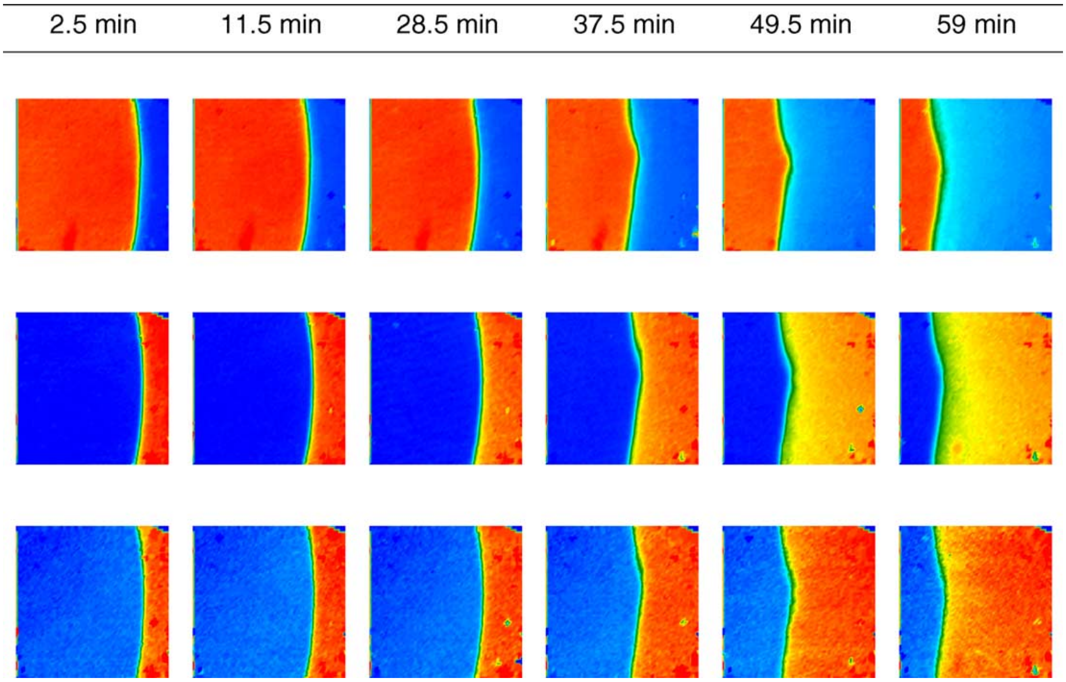

Fig. 2. Images of PMMA (top), AcN (middle) and EtOH (bottom) evolution during one dissolution study in the AcN/EtOH solvent mixture with a composition of 30% (w/w) in EtOH.

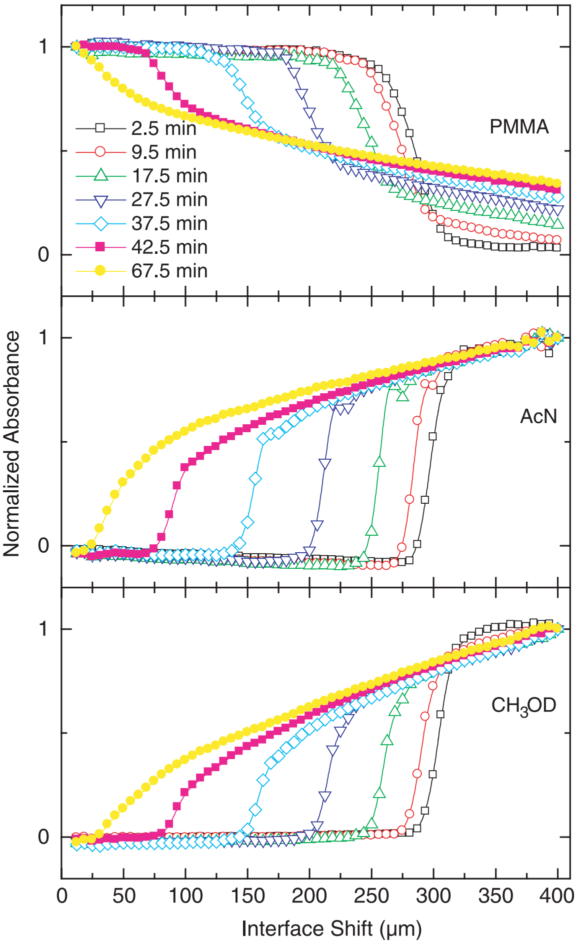

Fig. 3. Normalized absorbance profiles for PMMA (top), AcN (middle) and CH_3OD (bottom) as a function of the dissolution time when the AcN/CH_3OD solvent mixture is 20% in CH_3OD.

of the dissolution time when the AcN/MeOD solvent mixture is 20% in MeOD. Therefore, Fig. 3 is an example of the concentration profiles for the PMMA, AcN and the MeOD extracted from a sequence of images similar to those of Fig. 2. The rest of the systems studied (other solvent mixtures and compositions) showed similar results. All the concentration profiles show similar behavior, a maximum absorbance in the region of the component bulk, a sharp absorbance decrease at the solvent/polymer interface, and finally no absorbance for the solvent in the bulk polymer region and a weak absorbance, which depends on the system, for the polymer in the bulk solvent region. The last observation shows that after dissolution the polymer can diffuse through the solvent but without being removed completely as no stirring occurred.

The rate of dissolution can be determined by plotting the position of the polymer–solvent interface as a function of time. The local slope of the fitted curve is the velocity of the interface at that time (Figs. 4–6). The dissolution rate is then, simply, a product of this solvent ingress velocity multiplied by the perpendicular area exposed to the solvent. The dissolution rates were calculated from the absorbance profiles, first, as the polymer interface moved with time and, second, as the solvents

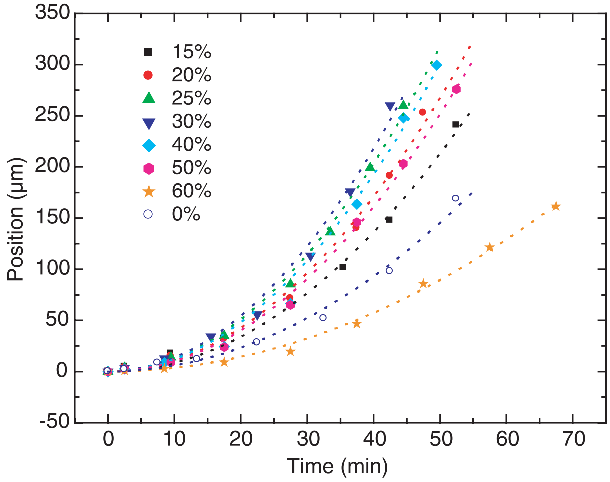

Fig. 4. PMMA/AcN–CH_3OD interface position as a function of dissolution time for different compositions (CH_3OD wt%) of the AcN–CH_3OD mixture.

front moves with time; in both cases the rates were the same within an error of 0.4 μm/min. To improve the accuracy in taking the values of the interface position, differentiation of the absorbance profiles was done, and the maxima or minima were used. Therefore, the polymer/solvent interface was plotted as a function of time to determine the dissolution rate. Figs. 4–6 show these plots for the three systems respectively and for all the compositions studied. The position of the interface was translated into microns considering that each pixel in the images corresponds to 6.25 μm.

It is noteworthy that the velocity of the dissolving front is not a linear function of time or of the root square of time as it was commonly found for other systems [7,18–20]. Examining the velocity of the diffusion front for every case (Figs. 4–6), the rate clearly increases with time. Besides, Figs. 4–6 show that the dissolution is clearly dependent on the composition of the mixture of solvents. A possible explanation for the nonconstant dissolution rate along the dissolution process may be the existence of compositional changes in the solvent throughout the dissolution process at the interface PMMA/solvent. For instance, there is the possibility that the diffusion of one of

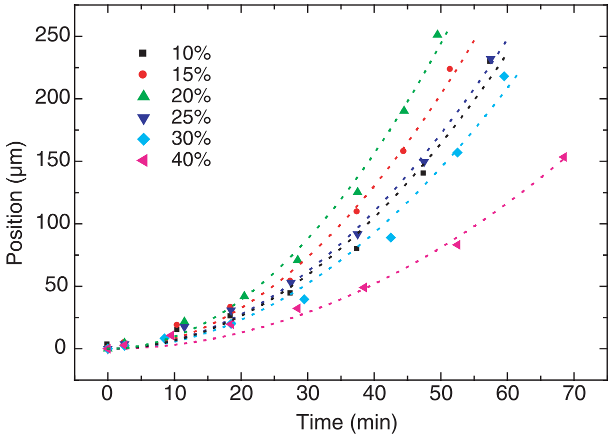

Fig. 5. PMMA/AcN–EtOH interface position as a function of dissolution time for different compositions (EtOH wt%) of the AcN–EtOH mixture.

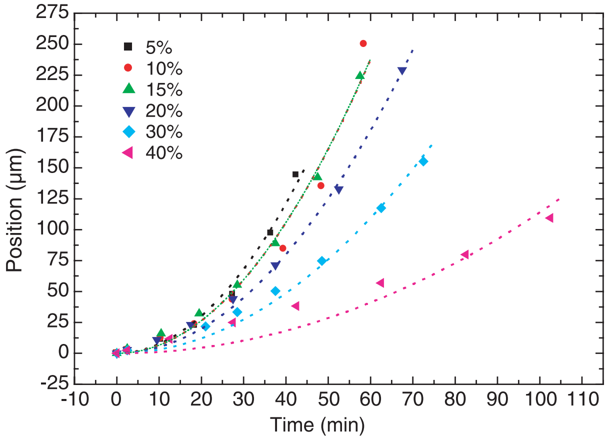

Fig. 6. PMMA/AcN–POH interface position as a function of dissolution time for different compositions (POH wt%) of the AcN–POH mixture.

components of the mixture of solvents through the dissolved polymer layer was faster than the other. This would create a mixture at the interface with a higher concentration of that component than the solution that was being added. To determine whether this was the case, Figs. 7–9 show for the three systems studied the absorbances of the characteristic bands of the solvents in the mixtures as a function of the PMMA dissolution time (at a specific location of the region under inspection). The position of the points collected were chosen from the first image in each experiment (at the beginning of the dissolution experiment) and they are the first ones for which there is an absence of PMMA, that is, when its concentration profile reaches a minimum value.

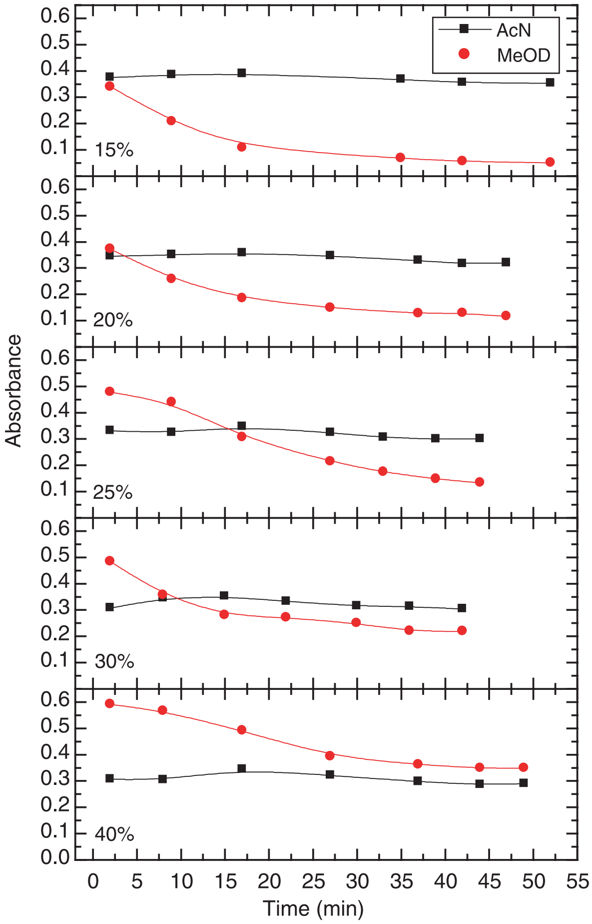

Fig. 7. Absorbances of the AcN and MeOD characteristic bands in the cosolvent mixture at a constant location of the region under inspection as a function of the PMMA dissolution time. From top to the bottom the initial composition of the cosolvent mixtures are: 15, 20, 25, 30, 40 (wt% of MeOD).

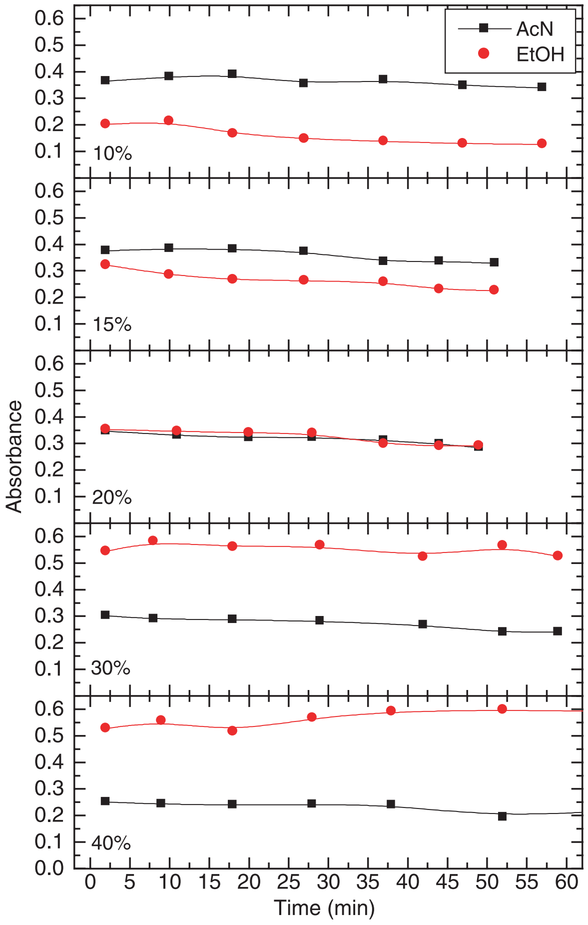

Fig. 8. Absorbances of the AcN and EtOH characteristic bands in the cosolvent mixture at a constant location of the region under inspection as a function of the PMMA dissolution time. From top to the bottom the initial composition of the cosolvent mixtures are: 10, 15, 20, 30, 40 (wt% of EtOH).

It can be seen in the cases of using AcN/MeOD and AcN/POH mixtures (Figs. 7 and 9) that, in fact, there are changes in the composition along the dissolution process (although not shown, the effect is more pronounced the nearer the polymer edge). However, in the systems under study, the trend for the composition change is not to reach the initial composition for which the dissolution rate is faster at each specific time (30% of MeOD, Fig. 4, in one case and 5% of POH, Fig. 6, in the other). Furthermore, when AcN/EtOH is used as the mixture of solvents, no changes in composition are observed (Fig. 8) although there is an increase in the dissolution rates as the dissolution progresses (Fig. 5). Therefore, although these changes in composition may affect the dissolution process, they do not seem to be the main cause of the increase in the dissolution rate along the dissolution process. It can be observed in Fig. 4 that when pure AcN is used

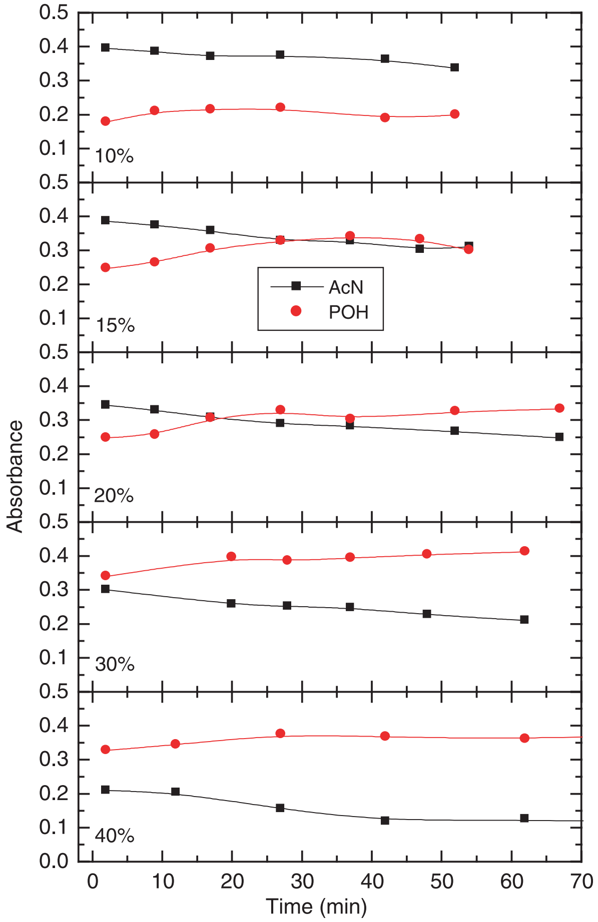

Fig. 9. Absorbances of the AcN and POH characteristic bands in the cosolvent mixture at a constant location of the region under inspection as a function of the PMMA dissolution time. From top to the bottom the initial composition of the cosolvent mixtures are: 10, 15, 20, 30, 40 (wt% of POH).

as the solvent, a similar behavior is obtained; therefore the particular action of this solvent seems to be the cause of this uncommon increase on the dissolution rate.

In general, the amount of solvent absorbed by a polymer as a function of time, M_t, can be used to characterize the diffusion process, i.e. for

$$M_t = kt^n \tag{1}$$

the exponent n characterizes the diffusional behavior. An exponent of 0.5 implies Fickian (case I) diffusion while an exponent close to 1 implies non-Fickian (case II) diffusion. An exponent between 0.5 and 1.0 signifies anomalous diffusion. Case II and anomalous diffusion are usually observed for polymers whose glass transition temperatures are higher than the experimental temperatures. In general, case II behavior is observed for solvents with high activities. Case II diffusion is characterized by a rapid increase in solvent concentration in the polymer region with a sharp penetration front, which advances at a constant rate. There is also an induction time for the non-Fickian concentration profile that precedes the solvent penetration front. Therefore, in the systems under consideration, is this induction time which seems to cause the continuous increase of the dissolution rate observed in Figs. 4–6.

Particularly, for this group of solvent mixtures, the dissolution process in terms of the variation of the front position seems to have a quadratic dependence with time. In fact, all the curves of Fig. 4–6 can be fitted to Eq. (1) (dotted lines in Figs. 4–6) giving the value of 2 to the parameter n.

On the other hand, for the systems under study, AcN is a somewhat better solvent for the PMMA than the alcohols. In fact the AcN, under the conditions of study, can dissolve the PMMA while the alcohols cannot. Furthermore, it is observed that the greater the size of the alcohol the higher increase in its concentration near the interface. Therefore, all of these results suggest that the dissolution of a polymer by a mixture of solvents is governed by a complex dependence of the size of the solvent molecules and their thermodynamic characteristics.

Considering, that for this group of solvent mixtures, the dissolution action seems to be similar (all of them can be described by the Eq. (1) with $n=2$), it is reasonable to analyze qualitatively the data for each composition in terms of the relative dissolution rates since the ratio of rates (empirical mathematical functions) should be a constant. Normalizing therefore all the fitting functions with respect to that obtained when pure AcN is used as the solvent, relative dissolution rates can be obtained for each composition in the three mixtures of solvents used in this work.

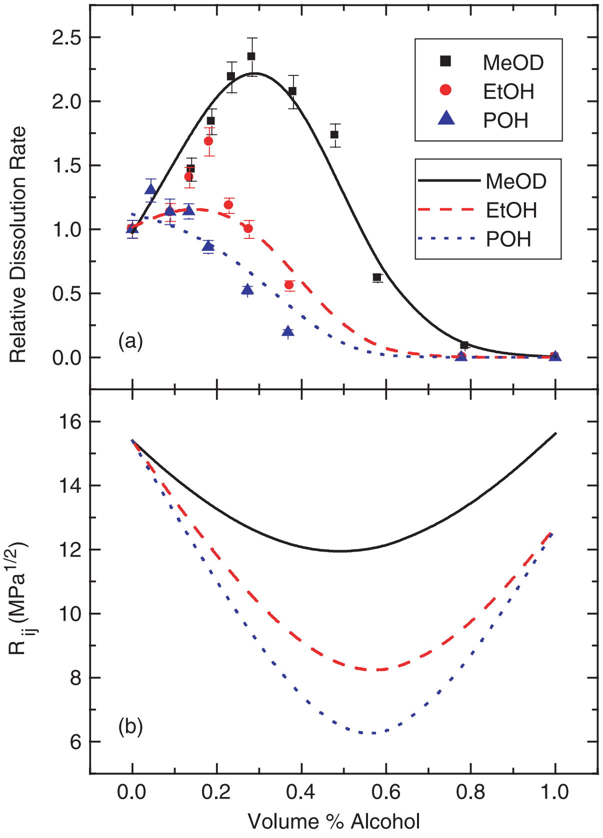

Fig. 10. (a) Relative dissolution rates as a function of the composition of the cosolvent mixtures (lines denote the fits with an empirical model function). (b) Calculated values of R_{ij} as a function of volume percentage of alcohols in the solvent mixtures.

Fig. 10(a) represents the values of the relative dissolution rates as a function of the composition of the mixtures of solvents. It can be observed that for all the solvent mixtures studied the profiles are similar. First, the dissolution rate increases when the amount of alcohol increases, then there is a certain composition for which a maximum is reached and finally, the dissolution rate decreases reaching the value of zero when pure alcohol is used. However, some differences can be observed depending on the alcohol used: (i) for most of compositions the data indicates that the smaller the molecular weight of the alcohol, the faster the PMMA dissolution by the AcN/Alcohol mixture and (ii) the amount of alcohol at which the maximum dissolution rate is reached is higher the smaller the molecular weight of the alcohol.

Qualitatively, this type of cosolvency effect may be explained in thermodynamic terms as was done for other systems [21]. The quality of a solvent toward the dissolution of a polymer should be the higher the smaller the differences between the solubility parameters, δ. In the case of mixed solvents, it is usually assumed that the mixture can be treated as an intermediate liquid having a δ value, which is the average between those from each component. In addition to this, if one considers δ decomposed into contributions from dispersion forces, δ_D, dipolar interactions, δ_P, and hydrogen bonding or other specific forces, δ_H, it could be assumed that these contributions also can be averaged in the case of solvent mixtures. In this way, a region of solubility has been characterized by the distance between solvent and solute coordinates [14]

$$R_{ij} = [4(\delta_{1D}-\delta_{2D})^2 + (\delta_{1P}-\delta_{2P})^2 + (\delta_{1H}-\delta_{2H})^2]^{1/2} \tag{2}$$

where subscript 1 indicates the solvent and subscript 2 the solute (the polymer). Therefore, the greater the R_{ij} is the lower the solubility of the polymer is expected to be. In Fig. 10(b) the calculated value of R_{ij} was plotted as a function of volume percentage of alcohols in the solvent mixtures, averaging each contribution to the solvent mixture solubility parameter. Independently of the alcohol in the mixture of solvents, as the alcohol proportion increases, there is a decrease in R_{ij} and therefore a solubility increase of the polymer. R_{ij} reaches a minimum (maximum expected solubility), and finally there is an increase in R_{ij}. Thus, in a general sense, there seems to be a correspondence in behavior between the dissolution velocity and solubility power. However, there is not a good correspondence between the experimental data (Fig. 10(a)) and the R_{ij} calculated data (Fig. 10(b)). Three mismatches can be found between Fig. 10(a) and (b): (i) the maxima for dissolution rates do not correspond with the maximum ability of the polymer to be dissolved (minimum R_{ij} value); (ii) for the group of solvent mixture studied in this work, R_{ij} predicts a better miscibility the higher the molecular weight of the alcohol was and (iii) R_{ij} predicts that the amount of alcohol at which the best miscibility is attained does not seem to follow any particular trend with respect to the molecular weight of the alcohol.

Therefore, these results suggest that actually the thermodynamic quality of the solvent mixture is an important aspect to take into account to predict the dissolution rate since it seems to affect it greatly. However, as the results of Fig. 10 suggest, to predict the dissolution rates, one should take into account the molecular size of the solvents used, for instance, in terms of their molecular weights.

Let us assume for the kinetics of the PMMA dissolution by AcN/alcohol solvent mixtures, a conventional Arrhenius behavior.

$$\mathrm{DR} = A \exp(-E_a/RT) \tag{3}$$

where DR is the dissolution rate, A is the preexponential factor, R the gas constant, T the absolute temperature and E_a the energy required for the dissolution to proceed (activation energy). Therefore, the relative dissolution rate, RR, could be described with the equation

$$\mathrm{RR} = B \exp[-E_a(\text{solvent is a mixture})/RT] \tag{4}$$

where B is a constant since:

$$B = \frac{A(\text{Solvent mixture})}{A(\text{AcN})} \exp[E_a(\text{AcN})/RT] \tag{5}$$

In order, to explain the behavior observed in Fig. 10(a) it is proposed that E_a has a simple dependence with the thermodynamic quality of the solvent mixture and with the molecular weight of the solvent used in the solvent mixture.

$$E_a = KR_{ij} + K'M_w \tag{6}$$

where M_w is the averaged molar weight of the solvent mixture (again the solvent mixture is assumed to behave as a single solvent with averaged properties) and K and K' are constants defining the dependence of R_{ij} and M_w, respectively.

In Fig. 10(a), the fitting curves for the relative rate data are presented. It is interesting to notice that the profile and even the values for the fitting function defined by the Eq. (4) are acceptably close to the experimental data, at least at compositions higher that 30% in volume for the alcohol. However, one should be very careful when more than one fitting parameter is taken into consideration. Assuming therefore Eq. (4), as a good choice, after looking for the best fit of the data in Fig. 10(a), the fitting parameters (K and K') are similar for the three systems under consideration $K=0.85\pm 0.01$ and $K'=0.7\pm 0.1$ while the value of the constant B can oscillate within two orders of magnitude of difference, which is acceptable if one considers the errors associated to the K and K'.

On the other hand, in the model proposed only the enthalpic factor (in terms of the solubility parameters) has been considered to account for the thermodynamical quality of the solvent mixture. However, it is well known that dissolution of an amorphous polymer in a solvent is governed by the free energy of mixing

$$\Delta G_m = \Delta H_m - T\Delta S_m \tag{7}$$

where ΔG_m is the Gibbs free energy change on mixing, ΔH_m is the enthalpy change on mixing, T is the absolute temperature, and ΔS_m is the entropy change on mixing. A negative value of the free energy change on mixing means that the mixing process will occur spontaneously and the more negative the more favored the process. In general, the dissolution of a high molecular weight polymer is always associated with a very small positive entropy change and therefore, the enthalpy term is the crucial factor in determining the sign of the Gibbs free energy change. However, two aspects were not considered in the model proposed: the polymer chosen can not be considered as a high molecular weight one and besides, the molecular weights of the samples are not monodisperse. Therefore, a small correction in the contribution KR_{ij} (Eq. (6)), which considers the entropy change on mixing might improved the fits of Fig. 10(a).

It seems therefore that the dissolution process of PMMA by cosolvent mixtures of AcN/alcohol can be described by a classical Arrhenius kinetics model for which the activation energy depends on the thermodynamic quality of the solvent mixture and the averaged size of the molecules that form the cosolvent system.

4. Conclusions

The dissolution process of poly(methyl methacrylate) in mixtures of the binary systems: acetonitrile/alcohol (methanol, ethanol and 1-propanol), individually poor and nonsolvents respectively for the polymer, was studied at 25 °C using FTIR imaging spectroscopy.

It has been found that the PMMA dissolution rate anomalously increases almost in a parabolic way independently of solvent system used in this study. Although, there are compositional changes in the solvent mixture throughout the dissolution process at the PMMA/solvent interface, it seems that mainly there is a case II behavior showing an induction time which seems to cause the continuous increase of the dissolution rate observed. On the other hand, the results obtained were interpreted assuming that the dissolution of a polymer by a mixture of solvents is governed by a complex dependence of the solvent molecules size and their thermodynamic characteristics. It was proposed for the kinetics of the PMMA dissolution by AcN/alcohol solvent mixtures, a conventional Arrhenius behavior in which the activation energy has a simple dependence with the thermodynamic quality of the solvent mixture and with the molecular weight of the solvents used in the solvent mixture.

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