

Poly(vinyl alcohol) as a Stabilizer in the Suspension Polymerization of Styrene: The Effect of the Molecular Weight

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ABSTRACT: The interfacial tension of the water–(PVA)/styrene system was measured as a function of the poly(vinyl alcohol) (PVA) concentration and temperature. Average size and particle-size distribution were obtained for a suspension of styrene in water using PVA as a stabilizer. We discuss the interfacial tension through the Zykowski equation to establish the behavior of the adsorption isotherms in unstirred systems and discuss the apparently contradictory results of the stirred experiment. We propose a simple configuration model that is congruent with both results. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 71–77, 1998

Key words: poly(vinyl alcohol); interfacial tension; suspension polymerization; styrene; stabilizer

INTRODUCTION

Many commercially important polymers and copolymers are manufactured by the suspension polymerization process. This process is a very old one. The stabilizers usually used in the process may be of two groups: water-insoluble inorganic powders, like tricalcium phosphate, or hydrosoluble polymers, like hydroxy ethyl cellulose or poly(vinyl alcohol) (PVA). This work focused on the study of the latter.

PVA is a copolymer of vinyl alcohol and vinyl acetate and is used as stabilizer in different industrial fields, as in textiles, adhesives, and coatings. It is also used in the suspension polymerization of styrene. It has been established that the stabilizing properties are dependent on the concentra-

tion, the degree of hydrolysis, and the molecular weight. The stabilizing properties are also dependent on the stage of the styrene polymerization when the PVA is added.^{1,2} Mendizabal et al.^{3,4} found that low molecular weight PVA produced more stable suspensions than did high molecular weight PVA when the test of the stability was to determine how long a water–styrene suspension lasted after the steering was interrupted. But when the polymerization process was carried out on with high molecular weight PVA, it gave single, well-defined particles, while low molecular weight PVA gave clusters. This behavior is not completely understood. To study this phenomenon, we measured the interfacial tension in the system of water–PVA/styrene as a function of the molecular weight, concentration of PVA, and temperature. We also report the Sauter diameter and the particle-size distribution as a function of the molecular weight of the PVA in a styrene/water suspension. With these data, we discuss the shape

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Table I Polymer Samples

Alcohol	Molecular Weight	Hydrolysis Degree
PVA-1	13,000–23,000	87–89%
PVA-2	31,000–50,000	87–89%
PVA-3	127,000	88%
PVA-4	85,000–146,000	87–89%

of the adsorption isotherms and propose a schematic model to explain the behavior of the stabilization properties of PVA.

EXPERIMENTAL

The determination of interfacial tension was done through the method of a pendant drop. The drop was generated in an isothermal cell ($\pm 0.1^\circ\text{C}$), recording the image using a video camera. The interfacial tension was determined from the digitized image with the method proposed by Andreas et al.⁵ The method was tested by the measurement of the interfacial tension in the air–water and benzene–water systems and by comparing these results with the literature.⁶ The styrene used was of industrial grade and water was tridistilled. Four different samples of PVA (Aldrich) were used. Table I gives a list of molecular weight and degree of hydrolysis of the PVAs used, as specified by the supplier. Interfacial tension was measured on the interface styrene/water without PVA and for concentrations between 0.1 and 10 g/L, in a temperature range between 25 and 70°C.

The suspension experiments were made in a reactor with the dimensions and characteristics as shown in Figure 1; two different stirring velocities were used. The temperature was held constant through a recirculation bath (70°C). The particle-size distribution of some samples of the suspensions was measured with a procedure similar to that of Kono et al.¹ The samples were taken with a pipette in the zone showed in Figure 1 and dropped in a saturated solution of PVA–water to guarantee the stability and prevent coalescence. The samples were recorded on a videotape with the help of a microscope. Some parts of the videotape were digitized to obtain the particle-size distribution; More than 300 drops were analyzed for each distribution. The average diameter that we calculated is the Sauter diameter⁷ (d_{32}) defined by the following equation:

$$d_{32} = \frac{\sum_i^n d_i^3}{\sum_i^n d_i^2} \quad (1)$$

The d_{32} was calculated for the water–styrene suspensions with and without PVA. The PVA concentrations were of 1 g/L with PVA-1 and PVA-2. The stirring velocities were 300 and 500 rpm.

RESULTS

Figures 2–5 show the interfacial tension as a function of the concentration of PVA for different molecular weights and for different temperatures. In all cases, the first point is without PVA. The drop of the interfacial tension is bigger as the mo-

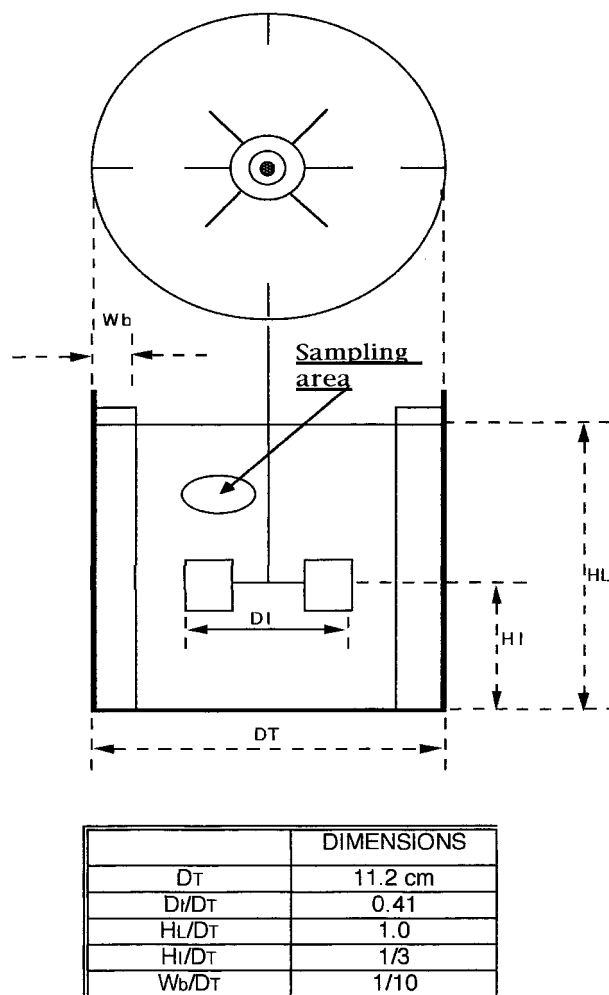


Figure 1 Schematic diagram of the stirred-tank reactor and impeller.

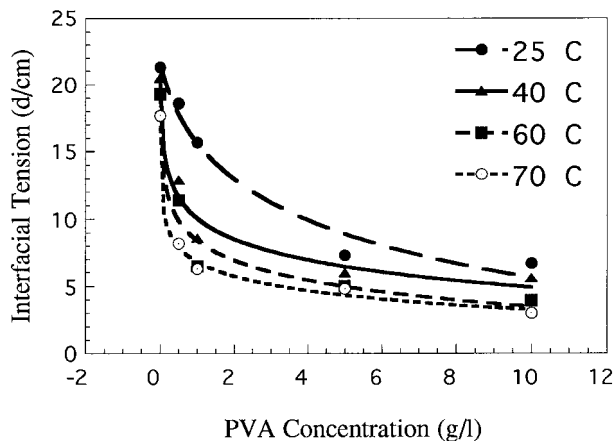


Figure 2 Interfacial tensions between styrene and aqueous solution as a function of the PVA concentration at different temperatures for the PVA-1.

lecular weight is lower. The temperature effect has always the same trend, since the interfacial tension always decreases as the temperature increases, but this effect is smaller for the larger molecular weight and especially at higher concentrations.

Figure 6 shows the evolution of the average diameter as the molecular weight increases for the two stirring velocities. The difference of the Sauter diameters for the two velocities without PVA is considerable, and as the molecular weight increases, the difference almost disappears, showing that at high molecular weight the stirring velocity does not affect the average diameter and, consequently, the large influence of the PVA in it. Figure 7 shows the evolution of the particle-size distribution: without PVA and with PVA of 18,000

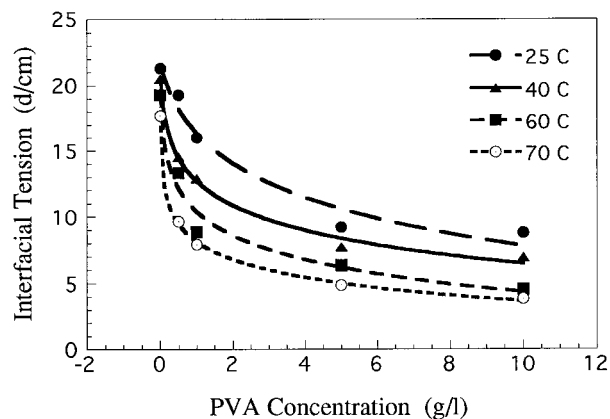


Figure 3 Interfacial tensions between styrene and aqueous solution as a function of the PVA concentration at different temperatures for the PVA-2.

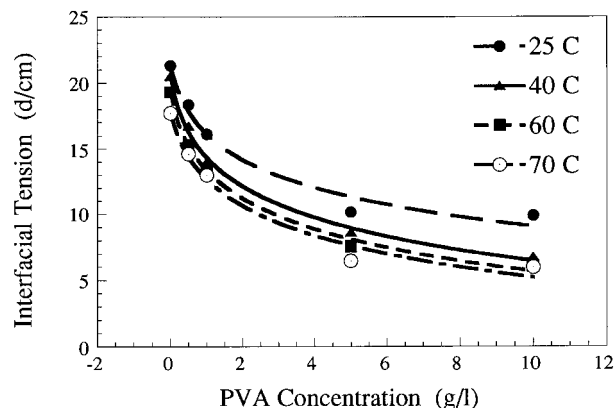


Figure 4 Interfacial tensions between styrene and aqueous solution as a function of the PVA concentration at different temperatures for the PVA-3.

(PVA-1) and 40,000 (PVA-2) molecular weight with 300 rpm as the stirring velocity. The distribution shows that the average diameter decreases when the molecular weight increases according to Figure 6. This is done by breaking the larger particles and stabilizing the small ones as the PVA is added. The effect on the distribution is that it became narrower as molecular weight increases. In the case when the stirring velocity is 500 rpm (Fig. 8), without PVA, the distribution is narrower than for when it is 300 rpm, and the effect of the PVA is the same, giving as a result the narrowest particle-size distribution.

DISCUSSION

The data in Figures 2–4 show the way PVA affects the interfacial tension, but it is not clear

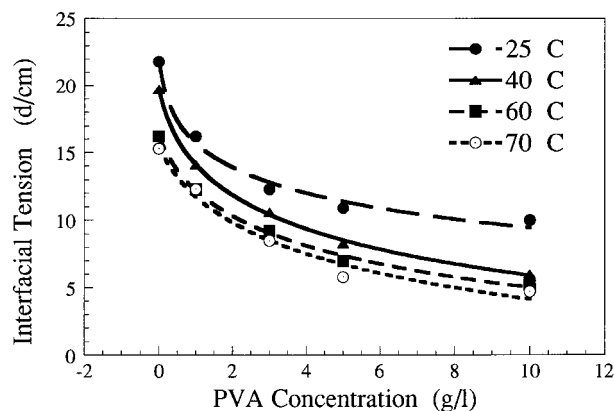


Figure 5 Interfacial tensions between styrene and aqueous solution as a function of the PVA concentration at different temperatures for the PVA-4.

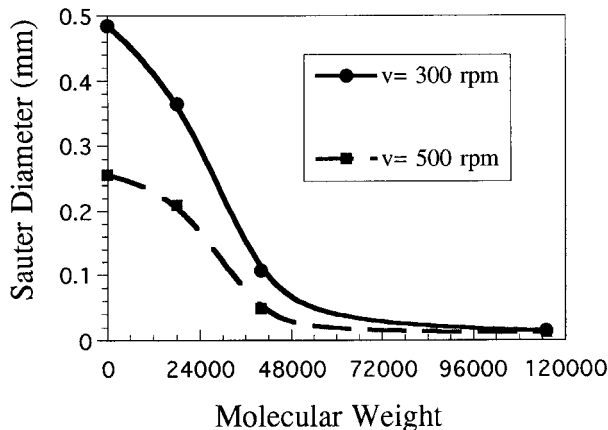


Figure 6 Sauter diameter as a function of the molecular weight of the PVA for two different stirring velocities.

what will be the effect of PVA on the behavior of the suspension. Mendizabal et al.³ carried out experiments to determine the behavior of the suspensions of styrene in water using PVA as a stabilizer. They found that if stirring is stopped once the suspension is developed the time the suspension remains stable (i.e., before the suspension becomes a system with two continuous phases) depends on the molecular weight of the PVA. In the case of PVA with 88% of hydrolysis, they found that the molecular weights higher than 40,000 gave a suspension that lasted less than 48 h. For

lower molecular weights, the suspension lasted greater than 48 h.

To interpret the interfacial tension curves, we needed a model that gives the relationship between the interfacial tension difference (Π) and the PVA concentration. Π is given by

$$\Pi = \gamma - \gamma_0 \quad (2)$$

where γ is the interfacial tension measured at a given concentration and γ_0 is the interfacial tension without PVA. The model proposed was the Szyszkowski equation⁶ given by

$$\Pi = \Gamma_s RT \ln(1 + \beta C) \quad (3)$$

where Γ_s is the amount of polymer per unit surface when the surface is saturated; R , the Boltzmann constant; T , the temperature; C , the concentration of PVA; and β , the temperature-dependent adsorption intensity, given by the equation

$$\beta = A \exp\left(\frac{-E_a}{RT}\right) \quad (4)$$

where A is a constant and E_a is the activation energy.

With the state eq. (3), we can suggest the Gibbs equation to obtain the adsorption density and

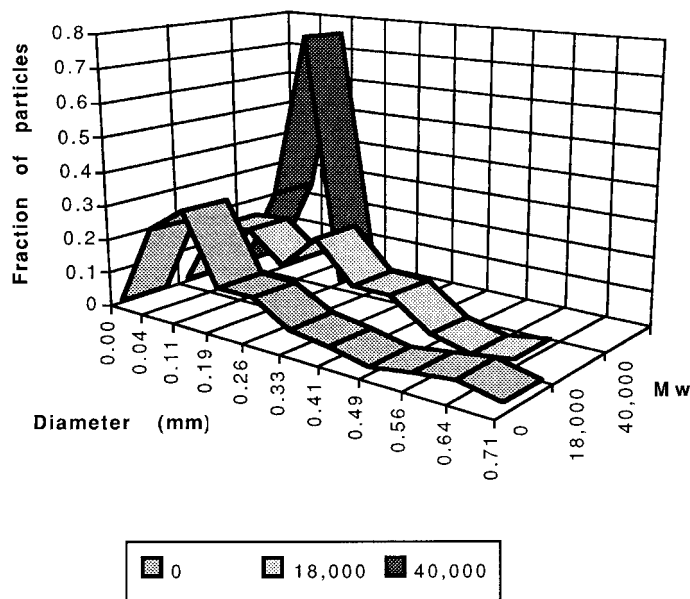


Figure 7 Particle-size distributions for the suspensions, at a stirring velocity of 300 rpm, (○) without PVA for two different molecular weights (PVA-1 and PVA-2).

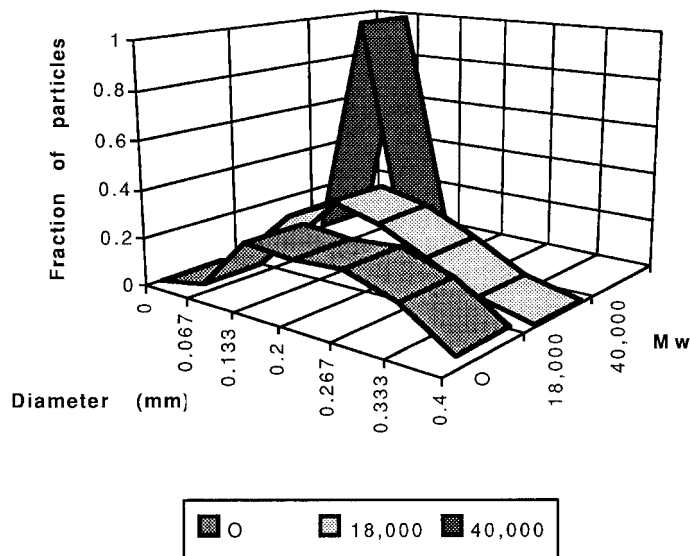


Figure 8 Particle-size distributions for the suspensions, at a stirring velocity of 500 rpm, (O) without PVA for two different molecular weights (PVA-1 and PVA-2).

with this obtain the adsorption isotherms. The Gibbs equation can be represented by

$$\Gamma_2 = \frac{C}{RT} \frac{d\Pi}{dC} \quad (5)$$

where Γ_2 is the amount of polymer per unit surface at a given concentration. The substitution of eqs. (2) and (3) on (5) gives

$$\theta = \frac{\Gamma_2}{\Gamma_s} = C \frac{d \ln(1 + \beta C)}{dC} \quad (6)$$

Doing the derivative and simplifying gives

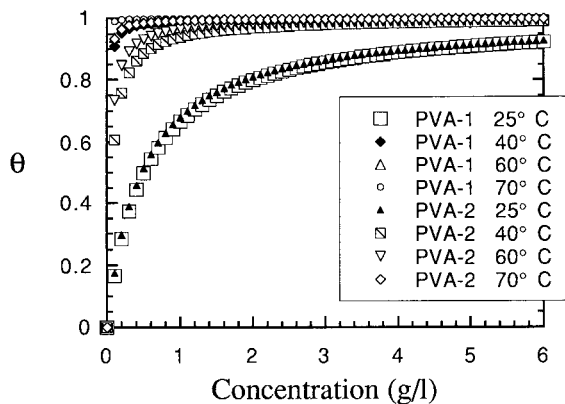
$$\theta = \frac{\beta C}{1 + \beta C} \quad (7)$$

which is the well-known Langmuir equation. It is also well known that polymeric systems normally do not follow Langmuir behavior unless we are dealing with very dilute solutions.⁸ Normally, polymers give isotherms with a higher initial slope. When the polymer is polydisperse, the initial slope of the isotherm also is less and it looks more like Langmuir's. It also has been suggested that polydisperse samples of PVA follow Langmuir's behavior on the air-water interface.⁹ Since the samples that we used were rather polydisperse and the Szyszkowski equation did reasonably fit the experimental data, we decided to de-

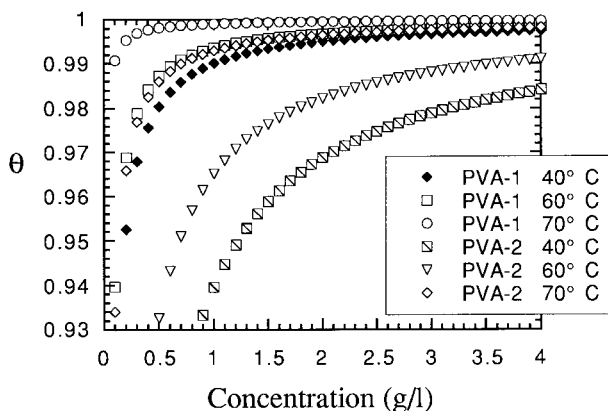
termine the behavior that the isotherms predicted.

Figures 9 and 10 show the isotherms for the different molecular weights and temperatures, calculated by the Langmuir approximation using the β from the fitting of eq. (3) to the experimental data in Figures 2-4. Figure 9 shows the adsorption isotherms of the two low molecular weight samples PVA-1 and PVA-2. In these cases, the coverage increases with the temperature and the lower molecular weight covers more than does the higher. If we look at Figure 10, it shows that for the higher molecular weights the variation is different, since for PVA-3, the coverage first increases with the temperature, and for the last two temperatures, it decreases. For the largest molecular weight, it always decreases with temperature. The coverage in both cases is less than the coverage of molecular weights shown in Figure 9. All these suggest a threshold behavior around a 40,000 molecular weight. To see this in a better way, we calculated β from eq. (3) by fitting the experimental data. The logarithmic plot of β against the inverse of the temperature can show if it behaves according to eq. (4). Figure 11 shows that the results reasonably fit a line; the first two curves have positive activation energy and the last two have a negative activation energy (almost zero for PVA-3). These reinforce the threshold behavior that we pointed out before.

If we look at the experimental data of Mendizabal et al., we can see that they obtained the same



(a)



(b)

Figure 9 (a) Adsorption isotherms for PVA-1 and PVA-2 at four different temperatures; (b) Also shown is a close view of the way the isotherms behave when they approach the asymptotic value for the three larger temperatures.

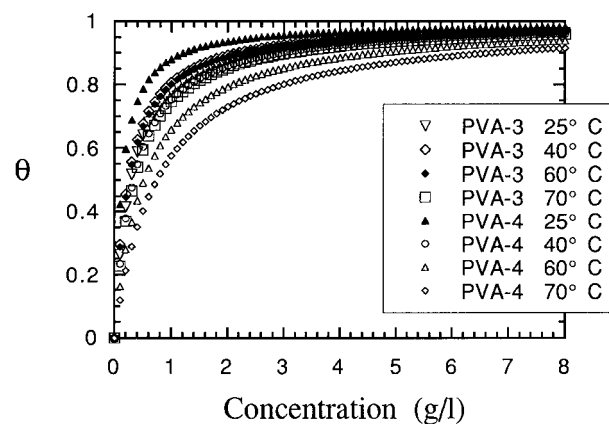
behavior in the case of no stirring. Their suspensions were more stable when the molecular weight was less than 40,000 and showed coalescence if it was larger. It is also important to point out that if the hydrolysis ratio increases the stability will decrease.

With stirring, the results change, because the data of Mendizabal et al. showed that the particle is clean without aggregation when the molecular weight is the highest and it has little clusters when the molecular weight is the smallest; again, the threshold is around 40,000. From the particle-size distribution curves in Figures 7 and 8, we can also see a big difference in the distribution; this can be interpreted as that the stabilizing effect of the PVA is better with higher molecular weight. It

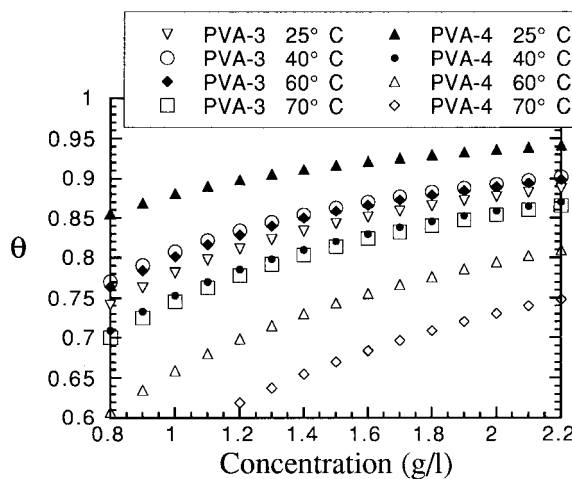
gives a smaller average particle size and becomes almost independent of the stirring velocity.

The use of simple models to interpret the interfacial tension data may be questioned, but their results are supported by the data of Mendizabal et al. These data are also consistent with the ones that we get once we stir the suspension, although these two behaviors are in apparent contradiction. We can propose that the amphiphilic character of the PVA would be influenced by the stirring and it would be mostly altered for the higher molecular weights, since in this case, there could be a fair number of conformations that will change the absolute number of hydroxyls exposed on the polymer surface.

Study of the partial molal volume of the poly-



(a)



(b)

Figure 10 (a) Adsorption isotherms for PVA-3 and PVA-4 at four different temperatures. (b) Also shown is a close view of the way the isotherms behave when they are getting close to the asymptotic value.

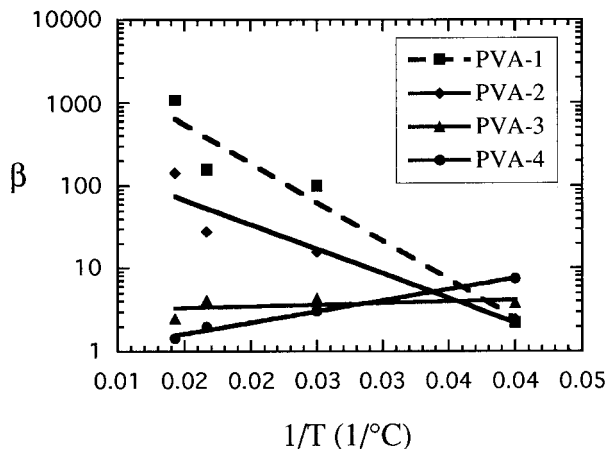


Figure 11 Arrhenius plots for the adsorption intensity for the four molecular weights.

(vinyl alcohol–vinyl acetate) copolymer in water solutions has shown that the macromolecule undergoes a temperature-dependent conformational change which is sensitive to changes in concentrations¹⁰ and also that the temperature-dependent hydrophobic effects upon the molal volumes are initiated by the vinyl acetate/vinyl alcohol (VAC/VAL) dyads.¹¹ Polymer adsorption in a water-1-butanol interface has been established to depend on the polymer VAC sequences and on the overall VAC content.¹² This information allow us to expect that the adsorption behavior of the P(VAC–VAL) copolymer is highly related to the lyophilic–lyophobic balance in the molecule, and this balance may be altered with the temperature since the change in molal volume may imply a different VAC content at the periphery of the copolymer coils. Therefore, in higher molecular weights, the conformational change will modify the intramolecular VAC distribution, and as temperature increases, the amount of VAC content in the periphery of the copolymer will decrease, since the hydrophobic character of the VAC will move them

to the interior of the copolymer, giving less surface coverage. In the case of lower molecular weights, there is no clear periphery or interior of the copolymer, so the temperature will only help to expose the VAC content.

When the solution is stirred and especially to the rates used in suspension polymerization, the shear rate modifies the conformation and the thermodynamic balance is no longer valid so the conformation is always larger and the temperature just helps to increase the amount of VAC exposed, giving always a higher surface coverage and, as a consequence, a smaller particle size and higher stability.

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