

# Grafting and adsorption of poly(vinyl) alcohol in vinyl acetate emulsion polymerization

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## Abstract

Poly(vinyl alcohol) is often used in vinyl acetate emulsion polymerization as a protective colloid, but its role is complex and controversial since it partakes in grafting reactions with the monomer, influencing process mechanisms, and affecting the colloidal properties of the latex. Furthermore, in industrial operations, the wide scatter of macromolecular properties of the commercial types of poly(vinyl alcohol) causes process irreproducibilities. In this work different types of polyvinyl alcohol were used to perform a series of polymerizations, and their kinetics were compared. A selective solubilization procedure was applied to separate the three fractions of poly(vinyl alcohol) in the final latex: free in the water phase, physically adsorbed onto the polymer particles and chemically grafted. These results were compared with those obtained from pure adsorption measurements of polyvinyl alcohol onto ‘emulsifier-free’ polyvinyl acetate dispersions. The rheological behavior of the different latexes was also compared, and the results were used to formulate an hypothesis on the interaction mechanisms acting in these systems.

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## 1. Introduction

Poly(vinyl alcohol) (PVA) is widely adopted as a protective colloid in vinyl acetate (VA) emulsion polymerization, particularly for the production of latexes for wood and paper adhesives, or to be spray dried to obtain redispersible powders. PVA is capable of providing a series of desirable properties to the final product, such as better shear resistance, and superior stability. In emulsion polymerization a partially hydrolyzed PVA—at an 88% hydrolysis degree—is commonly used in order to exploit its hydrophobic–hydrophilic characteristics. Usually PVA is viewed as a steric stabilizer, where hydrophobic groups attach onto the polymer particles, while hydrophilic moieties stretch out in the water phase to provide stability to the dispersion. However, PVA also partakes in reaction

kinetics, involved as it is in grafting reactions with vinyl acetate (VAc), influencing both particle nucleation and stabilization in ways that have not been completely understood yet. At the same time PVA is a major source of process irreproducibility, since its macromolecular properties can vary widely. As a matter of fact, reviewing literature kinetic studies on this system one can discover very different conclusions [1,2], and this is probably due to the fact that different types of PVA have been used in the experiments by various researchers’ groups. It has been recognized that in principle the degree of blockiness, that is the distribution of PVA and PVAc blocks in the chain, is a fundamental parameter, since it determines the stabilization properties of the protective colloid. The effect on polymerization kinetics and mechanisms of PVA blockiness has been studied in some detail [3]. In this respect, in order to understand polymerization mechanisms, it is very important to be able to separate the different fractions of PVA in the latex. These fractions are: (1) PVA free in the water phase; (2) PVA physically adsorbed onto the polymer particles; (3)

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PVA chemically grafted. A selective solubilization procedure has been suggested in the literature to attain this separation [4,5]. On the other side, the partition of PVA should have a strong effect on stabilization mechanisms in the final latex, what might affect many end-use properties. Rheological measurements can be a powerful tool to investigate this aspect, since the flow behavior is not only a fundamental property by itself, but it also carries the fingerprints of the microstructure of the dispersion and the forces acting between the particles [6].

## 2. Experimental

### 2.1. Materials

In order to reproduce industrial operations, VA currently used in the plant, produced by BP, was employed in the experiments described in this paper, without any further purification. Potassium persulfate (Sigma-Aldrich), PVA (Mowiol 25/88, Poval 217, Poval 217E, Poval 217EE by Kuraray) were used as received. Deionized water was used in all polymerizations. Hydroquinone (Sigma-Aldrich) was used as an inhibitor to stop the polymerization in samples withdrawn from the reactor. Acetonitrile (Sigma-Aldrich) was employed in the selective solubilization procedure, and used as received.

### 2.2. Polymerization procedure

Emulsion polymerizations were performed in a batch mode using a 7-neck cylindric glass reactor with an external jacket, 3.5 l by volume, equipped with a mechanic anchor stirrer, a reflux condenser, a thermocouple, a nitrogen inlet tube to blanket the reactants. Water from a thermostat was circulated in the jacket. The reactor was fully automated, and controlled by a PC, using an in-house developed software, allowing data acquisition during the polymerization. Polymerization recipe reported in Table 1 was adopted, while PVA type was varied. Samples were withdrawn during polymerizations, and inhibited with hydroquinone, to measure conversion by gravimetry and particle size by light scattering. In order to perform PVA adsorption measurements, ‘emulsifier-free’ latexes were produced, at low solid content, using the recipe shown in Table 2, that gives a latex, with an average diameter of 170 nm and particle sizes are in the 150–180 nm range.

Table 1  
Polymerization recipe for PVA-stabilized latexes

Water	1800 g
PVA	100 g
VAc	240 g
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.5 g
Stirring rate	150 g
Temperature	60 °C

Table 2  
Polymerization recipe for ‘emulsifier-free’ latexes

Water	1960 g
VAc	50 g
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.25 g
Stirring rate	150 g
Temperature	60 °C

### 2.3. PVA characterization

A qualitative method to estimate the degree of blockiness of the various PVAs used in the experiments was used. PVA water solutions in the presence of iodine form a brown complex that absorbs in the visible spectrum. The intensity of the color of this complex is related to structural properties of PVA, namely its blockiness. A blockier PVA shows higher specific absorptions [7]. In particular absorbance at 490 nm was measured for the different PVAs. By dividing adsorbance with PVA concentration in the solution, the so called ‘iodine index’ is obtained. Table 3 summarizes the iodine indexes for the four PVAs, from which this qualitative classification of PVAs in terms of blockiness follows: Poval 27EE > Poval 217E > Poval 217 > Mowiol 25/88.

### 2.4. Latex particle size

Particle size distribution in samples withdrawn from the reactor during polymerization, in the final latex, and samples produced in PVA adsorption isotherm measurements, was measured via light scattering, using a Coulter LS230 instrument. Light scattering requires an appropriate dilution of the sample, 1:1000 in distilled water.

### 2.5. Rheological measurements

The rheological behavior of the latexes was investigated by using a stress-controlled AR 2000 rotational rheometer, manufactured by TA Instruments. All measurements were obtained using a standard concentric cylinder tool, that has a conical end, a stator with an internal radius of 15 mm, a rotor with an external radius of 14 mm, and a gap of 5.92 mm. Flow curves were obtained by varying the shear rate,  $\dot{\gamma}$ , between 0.02 and 1000 s<sup>-1</sup>, and by performing measurements in steady-state conditions. Frequency sweep was obtained by varying frequency between 0.1 and 10 Hz, at a constant stress of 1 Pa, that falls in the linear zone for these systems.

Table 3  
Iodine indexes for the PVAs used in the experiments

PVA type	Iodine index
Mowiol	0.28
Poval 217	0.3
Poval 217E	0.41
Poval 217EE	0.54

## 2.6. Measurement of free PVA in the serum

The amount of PVA free in the serum (not adsorbed nor grafted) can be simply determined by centrifuging the latex for 1 h at 26,200 rpm and 25 °C, in order to separate particles from the serum, and determining the solid content in the latter by gravimetry.

## 2.7. PVA selective solubilization

The method is very similar to that proposed by Magallanes Gonzàles [2], with slight modifications that, however, can have a significant impact on the precision of the measurements. It consists in two steps. In the first step PVAc homopolymer is extracted with a solvent. Acetonitrile (AcN) was chosen for its ability to dissolve pVAc selectively and because it forms an azeotrope with water at a relatively low concentration (16.3%). This operation realizes a water-to-solvent exchange in the latex. Separation of the insoluble material (PVA) is then accomplished by ultracentrifugation. In the second step, linear PVA is separated from grafted PVA, by exploiting the fact that the latter is insoluble in hot water. In order to optimize the separation procedure, every operation is performed in the same container, a vial for ultracentrifugation, since any material transfer decreases the accuracy of the method since the quantities involved are very small.

Distillation of the azeotrope is performed using a heating plate and a Claisen, connecting tightly to it a 20 cm<sup>3</sup> vial for ultracentrifugation, that contains a small magnetic stirrer, in order to help the dissolution of 1 g of latex in AcN. The AcN/water mixture is heated up to 78 °C, using a water bath, and the azeotropic mixture was distilled until the temperature of the vapors reached AcN boiling point (82 °C). After distillation the vial was inserted in an ultrasound bath (Branson 3200), containing water, for about 12 h, a time sufficient to solubilize all the pVAc present in the latex. The separation of the solids insoluble in AcN is obtained by ultracentrifuging the AcN/pVAc/PVA mixture for 1 h at 25 °C (in an Allegra 64R centrifuge manufactured by Beckman). The fraction insoluble in AcN settles at the bottom of the vial, and the supernatant is removed with a pipette. Centrifugation is then repeated two more times, after redispersing sedimented material in fresh AcN. Solutions removed after each centrifugation are united together. The total quantity of pVAc solubilized is determined gravimetrically, by drying the solution in an oven. The degree of separation was verified by IR, comparing the spectra of separated materials with those of pure pVAc.

The second step, that is the separation of the fraction soluble in hot water is similar to the separation of the fraction soluble in AcN. The material sedimented in the first step is dried, mixed with distilled water, and then heated in an ultrasound bath for 24 h at 60 °C. This allows to separate linear PVA from grafted PVA. The supernatant is removed,

the centrifuged fraction is redispersed in distilled water, heated again in an ultrasound bath, and then ultracentrifuged again. The quantity of solubilized PVA is determined gravimetrically. The settled material is dried and weighted.

At the end of this procedure, the amounts of linear PVA and PVAc and grafted PVA, with crosslinked PVAc, were determined by mass balance. Linear PVA is given by the water-soluble fraction. Linear pVAc is given by the AcN soluble fraction. The amount of grafted PVA in the water-insoluble material is estimated by calculating the difference between the total PVA used in the recipe and the linear PVA in the water-soluble fractions. The fraction of linear PVA physically adsorbed on the polymer particles is estimated by the difference between the total linear PVA and the amount of free PVA as measured after latex centrifugation.

## 2.8. Adsorption isotherms

In order to evaluate adsorption isotherms of PVA onto PVAc particles, the ‘emulsifier-free’ latex has been used to obtain samples that were mixed with water solutions of PVA at different concentrations. These mixtures were kept under stirring for 24 h at 25 °C. This step was also repeated at 60 °C, in order to obtain curves at two different temperatures. A portion of this sample was analyzed via light scattering in order to estimate particle size variations due to PVA adsorption. Another portion of these samples were ultracentrifuged for 1 h at 26,200 rpm and 25 °C, and the free PVA fraction, that did not adsorb, was determined via gravimetry on the serum, and the adsorbed fraction by difference with the total amount. Adsorption isotherms are expressed in terms of grams of PVA adsorbed divided by total particle surface vs. serum PVA concentration.

# 3. Results and discussion

## 3.1. Polymerization kinetics and PVA partition

A series of polymerizations were performed, using the recipe reported in Table 1, with the four different PVA types. A comparison of polymerization kinetics is shown in Fig. 1, in terms of conversion vs. time: no great difference in polymerization kinetics can be noticed. Also latex particle diameter seems relatively constant in the different reactions, around 150 nm, and with a relatively narrow distribution. It is however important to remind that particle diameter as measured here includes as well the width of the PVA adsorbed on the particle surface.

On the other side there are clear differences in the behavior of the various PVA types in terms of partition between the three fractions (Fig. 2). Grafted fraction stays relatively constant, and therefore the structure of PVA does not seem to have a great effect on the chemistry of the process. The fraction physically adsorbed, however, increases quite markedly with PVA blockiness. These

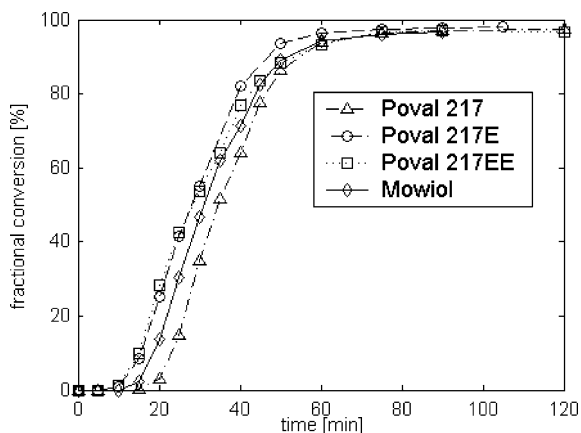


Fig. 1. Conversion vs. time curves for the four polymerizations performed, same recipe different PVA commercial type.

results were confirmed in PVA adsorption measurements. Fig. 3 shows adsorption isotherms at 25 °C as quantity of adsorbed PVA per unit of particle surface vs. PVA serum concentration, together with lines showing Langmuir-like dependence. There is a clear dependence of the adsorbed amount from PVA blockiness that can be explained in terms of the better stabilizing properties of the highly blocky PVA types, and greater affinity towards the particle surface. Adsorption measurements at 60 °C, coincident with reaction temperature, were also performed, but no major difference was noticed. The figure also contains the adsorbed amount as measured in the polymerization reactions that are relatively well comparable, if somehow lower, which is understandable since in this case the available particle surface is inferior, since it is partially occupied by grafted chains. The results seem to contradict previous evidence supporting as a solution phenomenon, where increasing with increasing PVA blockiness was argued to be due to the different conformation in aqueous solution of different PVA types [3]. Grafting as an interfacial event could explain low grafting efficiencies, since PVA concentrations used in the recipes investigated in this work fall into saturation conditions. Furthermore, the amount of free PVA in the water phase seems to be mainly controlled by the total interfacial area available in the dispersion. However,

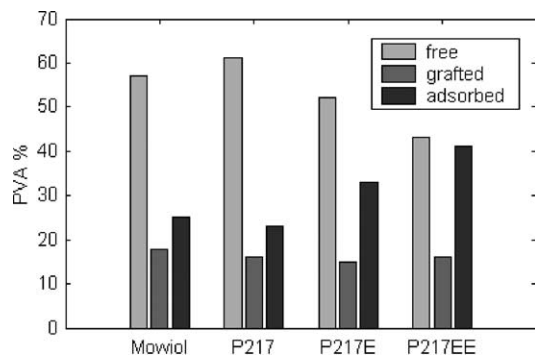


Fig. 2. PVA partition for the four latexes produced, same recipe different PVA commercial type.

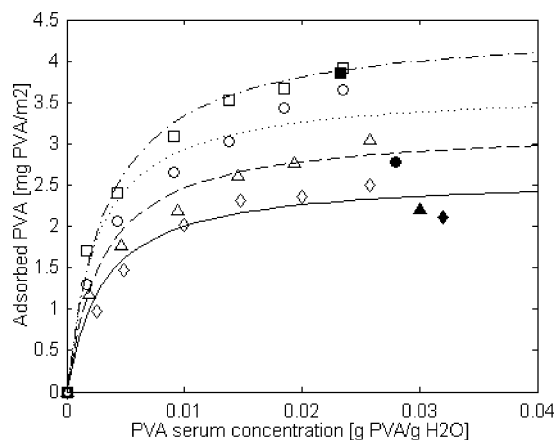


Fig. 3. PVA adsorption isotherms at 25 °C for the four PVAs on PVAc 'emulsifier-free' dispersion (same symbols as in Fig. 1; closed symbols refer to adsorption as measured in polymerization reactions).

selective solubilization experiments at lower PVA concentrations will be needed to better clarify this point. We also measured particle size in the same samples used to estimate adsorption isotherms, in order to evaluate the value of  $\delta$ , that is the width of the adsorbed layer, calculated as  $\delta = (D_p - D_{p0})/2$ , where  $D_p$  is the diameter of the particles with adsorbed PVA, while  $D_{p0}$  is the diameter of 'bare' emulsifier-free particles. Results are shown in Fig. 4, in terms of  $D_p$  vs. PVA serum concentration.  $D_{p0}$  is evidently the value of  $D_p$  at zero PVA serum concentration. One can notice that  $\delta$  increases significantly with PVA serum concentration, approximately paralleling the adsorption curve, without displaying intermediate maxima, registered elsewhere and attributed to bridging at partial coverage [8].  $\delta$  at saturation is significantly higher (more than double) than  $R_g$  in solution (around 15 nm), meaning that adsorbed PVA progressively elongates into the water phase, and it weakly depends on PVA blockiness, since it goes from a minimum value of about 30 nm for Mowiol 26/88 up to a maximum value of about 40 nm for Poval 217EE.

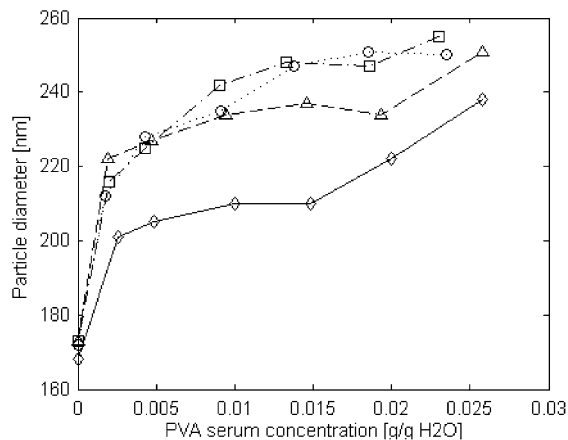


Fig. 4. Particle size vs. serum concentration, measured on samples used for adsorption measurements (same symbols as in Fig. 1).

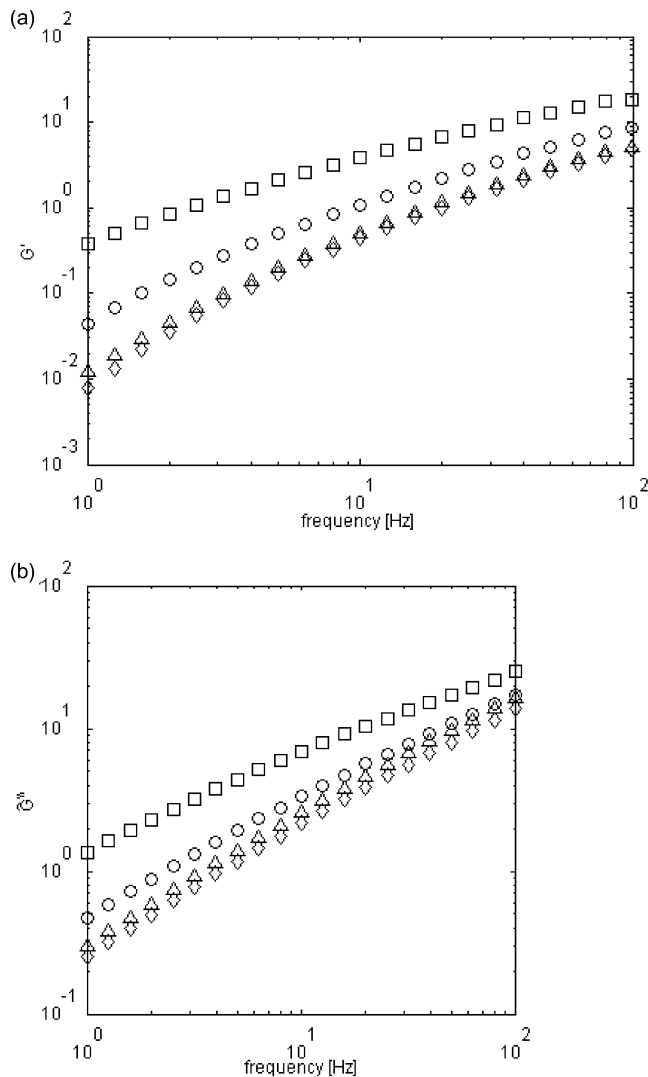


Fig. 5. (a) Elastic modulus  $G'$  as a function of oscillation frequency for the four latexes produced, same recipe different PVA commercial type (same symbols as in Fig. 1). (b) Loss modulus  $G''$  as a function of oscillation frequency for the four latexes produced, same recipe different PVA commercial type (same symbols as in Fig. 1).

### 3.2. Rheological behavior

The effect of PVA type is particularly significant on the rheological behavior of the latex. Elastic and loss modulus  $G'$  and  $G''$  have also been measured, as a function of oscillation frequency, (Fig. 5). Investigated latexes are markedly viscous but  $G'$  increases clearly with PVA blockiness.

Fig. 6 shows the flow curves of the four latexes, as  $\eta_r$  vs.  $\dot{\gamma}$ .  $\eta_r$  is the relative viscosity, given by the ratio  $\eta/\eta_s$ , where  $\eta$  is the viscosity of the latex, and  $\eta_s$  is the viscosity of the continuous phase, that can be estimated as  $\eta_s = A \exp(b\varphi_s)$ .  $A$  and  $b$  are two experimental parameters, estimated by viscosity measurements on PVA solutions at different concentrations.

Zero-shear viscosity is a pronounced function of PVA

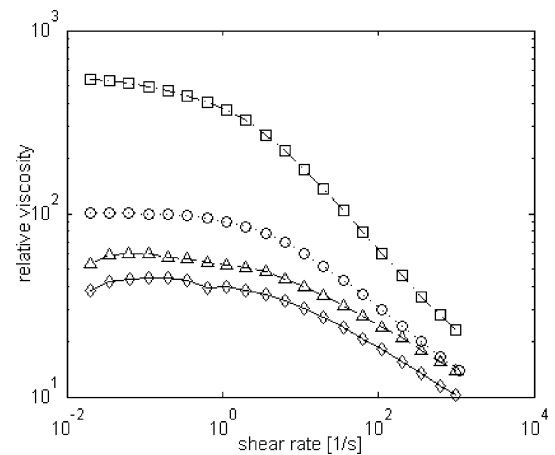


Fig. 6. Flow curves, in terms of  $\eta_r$  vs.  $\dot{\gamma}$  for the four latexes produced, same recipe, different PVA commercial type (same symbols as in Fig. 1).

blockiness. The influence of PVA type on rheological behavior at low shear can be explained in terms of association of pVAc blocks from PVA chains in the water phase, generating reversible particle flocks through bridging mechanisms [6]. The tendency to associate is likely stronger for blockier PVAs. In every latex anyway PVA concentration in the water phase is above the limit corresponding to saturation in the corresponding adsorption curve (Fig. 3), a situation in which hydrophobic PVAc blocks in PVA chains, finding no free adsorption sites on the polymer particle, tend to extend and associate in the water phase, creating bridges among different particles, similar in this respect, to associative polymers [9]. These flocs are not permanent and are destroyed by shear, in fact flow curves are markedly pseudoplastic. Using a rotational rheometer it is not possible to perform measurements at very high shear, but values of  $\eta_{r\infty}$  can be extrapolated using Cross [10] equation:

$$\frac{\eta_r - \eta_{r\infty}}{\eta_{r0} - \eta_{r\infty}} = \frac{1}{[1 + (k\dot{\gamma})^m]} \quad (1)$$

where  $\eta_{r0}$  and  $\eta_{r\infty}$  represent, respectively, the low shear and the high shear relative viscosity,  $k$  is a constant parameter with the dimension of time and  $m$  is dimensionless constant. Estimated  $\eta_{r\infty}$  values go from a maximum value of 9.3 (for Poval 217EE) to a minimum value of 5.8 (for Mowiol) that correspond approximately to a hard-sphere behavior. In fact hard sphere relative viscosity  $\eta_r$  can be calculated with a hard-sphere equation such as Krieger-Dougherty's [11]:

$$\eta_r = \left(1 - \frac{\tilde{\phi}}{\phi_m}\right)^{-[\eta]\phi_m} \quad (2)$$

$[\eta]$  is the intrinsic viscosity of the dispersion, and  $\tilde{\phi}$  is the effective particle volume fraction, accounting for the adsorbed layer width:

$$\tilde{\phi} = \phi_0 \left(1 + \frac{\delta}{a}\right)^3 \quad (3)$$



$\phi_0$  being the polymer particle volume fraction and  $a$  the particle radius. Eq. (2) can be used to estimate  $\eta_r$  for hard-sphere systems at all shear rates, allowing  $[\eta]$  and  $\phi_m$  to vary with shear rate [12]. Assuming  $[\eta]=2.7$  and  $\phi_m=0.73$ , one finds values of  $\eta_{r\infty}$  between 5.8 and 9.3 by varying  $\delta$  between 25 and 30 nm, slightly lower than those previously measured.

#### 4. Conclusions

The results obtained allow to derive some conclusions that help understanding the role of PVA in pVAc emulsion polymerization, particularly focusing on the effect of blockiness on polymerization and latex properties. Conclusions, for polymerization conditions investigated in this work, can be summarized as follows:

- (1) PVA blockiness does not influence greatly polymerization kinetics;
- (2) Grafted fraction is relatively lower than physically adsorbed fraction;
- (3) Grafted fraction is almost constant with different PVA types, but the physically adsorbed fraction increases with PVA blockiness, and this conclusion was confirmed from pure adsorption measurements. This result seems to contradict some of the evidence in favor of grafting as solution event, but it should be further confirmed by performing experiments at lower PVA concentrations.
- (4) The adsorbed layer thickness  $\delta$  increases with PVA serum concentration, approximately paralleling adsorption isotherm.  $\delta$  at saturation is significantly higher (more than double) than  $R_g$  in solution (around 15 nm), meaning that adsorbed PVA progressively elongates into the water phase, and it weakly depends on PVA blockiness.
- (5) Low shear viscosity and elastic modulus increase greatly with PVA blockiness, while high shear viscosity is almost the same for all latexes and it can be described according to a hard-sphere behavior: association of pVAc blocks from PVA chains in the water phase, generate reversible particle flocks through bridging mechanisms, destroyed by shear. Flocs are probably bigger with latexes stabilized by blockier PVAs.

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