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Kinetics of styrene minisuspension polymerization using a mixture PVA–SDS as stabilizer

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Abstract

The kinetics of minisuspension polymerization of styrene at 70 °C using 2-2′-azobisisobutyronitrile (AIBN) as initiator, polyvinyl alcohol (PVA) and mixture PVA–sodium dodecyl sulfate (SDS) as stabilizers, were studied. The monomer was pre-dispersed by using a high-speed homogenizer apparatus that allowed use mild agitation conditions during the polymerization. It was observed that addition of SDS to a polymerization initially stabilized with PVA highly enhances the colloidal stability of the system. Interfacial tension, viscosity and stability ratio measurements suggest that the PVA and SDS molecules form associations that lead to an electroesteric stabilization mechanism.

Keywords: Minisuspension polymerization; Kinetics; Polystyrene

1. Introduction

A typical suspension polymerization system is characterized by the use of initiators and monomers that are relatively insoluble in water (continuous phase) and by the fact that monomer droplets are dispersed by the combination of strong agitation and the use of small amounts of suspending agents (stabilizers) [1]. Water-soluble polymers are frequently used as stabilizers [2]; among these, partially hidrolized polyvinyl alcohol (PVA) is one of the most employed [3].

The suspension polymerization process can be divided into three stages [4,5]. In the first stage, when the viscosity of the dispersed phase remains low, the bulk monomer phase is dispersed in small droplets due to the shear stress imposed by the stirring conditions. Simultaneously, through the reverse process of coalescence, the drops tend to revert to the original monomer mass. This is, the droplet size distribution results from a breakup-coalescence dynamic equilibrium. The adsorption of polymeric stabilizers at the monomer droplet-water interface have an influence in this equilibrium in two ways: it decreases the interfacial tension to promote the dispersion of droplets and, in the other hand, produces a thin layer that hinder the coalescence.

During the second stage, the viscosity within the droplets rises with increasing conversion causing that coalescence tends to overcome breakup. If the stabilizer is present and efficient enough, the coalescence is delayed, and the particles size increases slowly. Toward the end of this stage, the coalescence is stopped due to the elastic nature of particle collisions. After this point, which is called particles identity point (PIP), the particles size remains constant giving place to the third stage.

The degree of agitation and the design of the stirrer/reactor system have influence on the dispersion of monomer droplets as well and on the overall process. Agitation has conflicting effects. An increase of the agitation improves the mixing and the heat transfer and promotes breakup of droplets, but also increases coalescence because the frequency of collisions between particles (or droplets) and the energy of each collision is higher [6]. This conflicting effect is evident in the typical U-shaped curve obtained when particle size is plotted versus agitating speed, as reported in Refs. [7,8]. They found that initially the particle size decreases with increasing stirring speed from 200 to 500 rpm, but then the particle size increases as the agitating speed is raised from 500 to 800 rpm.

The present work focus on the kinetics of an alternative polymerization method avoiding the negative aspect of agitation and leading to particle sizes intermediate between

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conventional emulsion and suspension polymerizations. This objective was achieved in the following way: (i) by performing a pre-homogenization of the reaction components: water, monomer (styrene), initiator (2,2′-azobisisobutyronitrile, AIBN) and non-ionic stabilizer (PVA) at very high stirring speed and, (ii) by adding an anionic co-stabilizer (sodium dodecyl sulfate, SDS) toward the end of the first stage of the polymerization. Steps (i) and (ii) have concomitant effects to reduce coalescence. Due to the pre-homogenization step, high stirring speed is not necessary anymore during the polymerization so that this can be performed under mild agitation. By adding SDS, the colloidal stability of the system is highly increased in agreement with the behavior of a ferrofluid emulsion stabilized with the PVA–SDS mixture reported by Philip et al. [9].

A similar method called microsuspension polymerization for obtaining average particle sizes intermediate between those obtained by suspension (10^1–10^3 μm) [1,4] and emulsion polymerizations (10^{-2}–10^{-1} μm) [10] has been reported [11–15]. This process leads to particles in the average-size range of the order of 10^0–10^2 μm, whereas in the minisuspension polymerization method studied in the present work, particles with average size of 10^{-1}–10^0 μm were detected. Another similar method (in the sense of particle size) is miniemulsion polymerization where, in contrast with minisuspension polymerization, usually a water-soluble initiator is used and a low-molecular weight water-insoluble compound (e.g. a linear long chain alcohol or alkane) is needed [16], although in some cases oil-soluble initiators are used [17,18].

As far as the authors know there are not works reported in the literature in which the mixture PVA–SDS is used as stabilizer in polymerizations in dispersed media.

2. Experimental

2.1. Materials

Distilled styrene monomer (Aldrich) and deionized water were used for all the reactions and the remaining materials were used as received. PVA (Aldrich, 87–89% hydrolyzed, average M_w 85,000–146,000) and sodium dodecyl sulfate (SDS, Fluka, $\geq 99.0\%$,) were used as stabilizers. 2,2′-Azobisisobutyronitrile (AIBN, Aldrich, $\geq 98.0\%$) and hydroquinone (HQ, Aldrich) were used as initiator and inhibitor (short-stopper), respectively. Nitrogen ultrahigh purity grade (Infra-México, $>99.999\%$) was used to remove oxygen from the reaction mixture. Distilled-deionised water was used in all the polymerizations. Toluene reactive grade (Aldrich, 99.8%) was used in the interfacial tension measurements.

2.2. Equipment and instruments

Batch suspension polymerizations were carried out in a cylindrical round-bottom glass reactor with jacket and without baffles. The volume and diameter of the reactor were 1 l and 10 cm, respectively, (Fig. 1). The reaction temperature was controlled by means of a circulator temperature bath. Two 3-bladed propellers mounted one on the other one were used (Fig. 2). A high-speed homogenizer apparatus (biomixer) was used to emulsify the monomer.

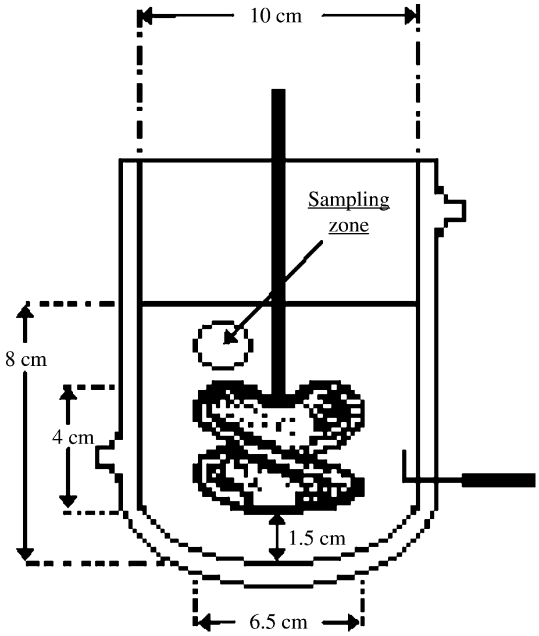

Fig. 1. Schematic diagram of the stirred-tank reactor and impeller.

The samples were freeze-dried in a Labconco 6 freeze dry system. MWDs were obtained by size exclusion chromatography using a Hewlett–Packard Instrument (HPLC series 1100)

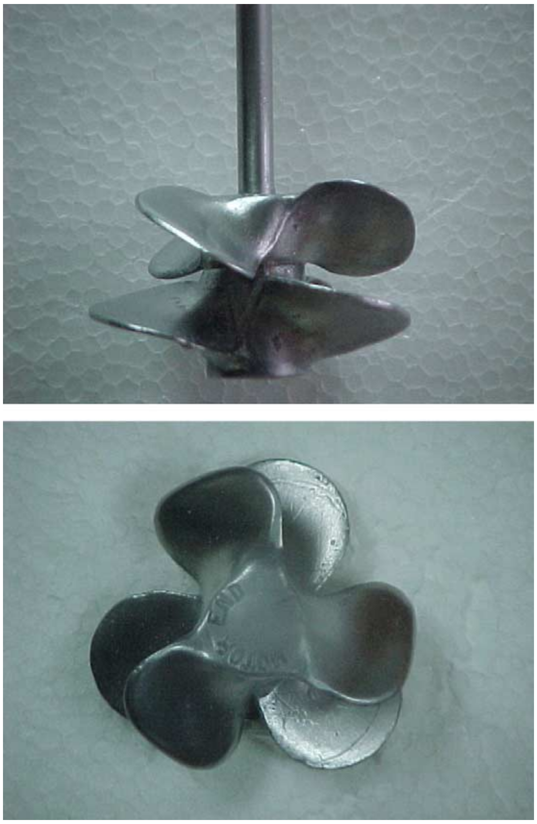

Fig. 2. Impellers setup used in the polymerizations.

with refractive index detector. A series of three Hewlett–Packard PLGel columns were used: 10^3, 10^5 and 10^6 Å. MWDs were normalized with respect to conversion.

Particle size was measured at 25 °C and an angle of 90° in a Malvern 4700 dynamic light scattering (DLS) apparatus. A Paar Physics UDS 200 rheometer with double gap geometry was used for the viscosity measurements at 25 °C. Interfacial tension measurements were obtained with a Sigma-703 digital tensiometer (KSV), by means of the Du Nouy ring method at 70 °C. The film morphology was studied at ambient conditions with an atomic force microscope (AFM) Nanoscope III Dimension™ 3100 from Digital Instruments. The tapping mode was used at scanning rates of 0.5 Hz.

2.3. Polymerization and methods

The initiator dissolved in the monomer was added to a glass vessel containing the aqueous solution of PVA. The monomer was emulsified at a stirring speed of 10,000 rpm with the Biomixer during 9 min. After this, the emulsion was transferred to the reactor whose heating fluid was already circulating in the jacket at 70 °C. The stirring speed was set at 200 rpm and then nitrogen was passed through the reactor. This moment is considered as the start of the reaction.

Two polymerizations were performed, one using only PVA as surfactant, and the other one in which besides the PVA initially present, there was an addition of a concentrated aqueous solution of SDS at 22 min after starting the reaction. This addition time is an arbitrary point during the stage I. The idea was to add the SDS solution before the second stage where the performance of the stabilizer(s) is (are) showed up. The recipe is shown in Table 1.

Samples were withdrawn periodically with a pipette from the zone showed in Fig. 1, short-stopped with a 2% aqueous hydroquinone solution and placed in an ice-bath. Most of the sample was freeze-dried and the rest was used for particle sizing by DLS. The weight of polymer was calculated by subtracting the known weights of surfactant and hydroquinone from the total weight of the freeze-dried sample.

For the GPC runs, the freeze-dried samples were extensively washed with deionized water to eliminate surfactant and freeze-dried again. The flow rate was 0.6 ml/min. The calibration curve was created from 10 monodisperse polystyrene standards with molecular weights in the range of 1.62×10^2–1.14×10^7.

The following equation was used to calculate the number of particles (N) from experimental data of conversion and particle size distribution

$$N=\frac{6M_0x}{\pi d_p D_v^3} \tag{1}$$

where

$$D_v=\left(\sum_i n_i D_i^3\right)^{1/3} \tag{2}$$

where n_i is the number fraction of particles with unswollen diameter D_i, x is the fractional conversion of monomer and d_p is the polymer density. M_0 is the initial monomer concentration (g/cm^3 water).

Table 1
Recipe used in the polymerizations

Ingredient	Amount (g)	Concentration
Styrene	22.5	53.0 g/l water
Water	427.5	
AIBN	0.675	30 g/l monomer
PVA	2.56	6.0 g/l water
SDS	0 or 1.28	0 or 3.0 g/l water

3. Results and discussion

Fig. 3(A) and (B) shows the evolution of monomer conversion (%X) and the rate of polymerization ($R_p = d(\%X)/dt$) for the runs effected with PVA only (reference run; black circles) and with addition of SDS (open circles). The moment at which (22 min) the SDS solution was added to the reactor is indicated with an arrow. It can be observed that, once the SDS solution has been added, %X and R_p becomes higher with

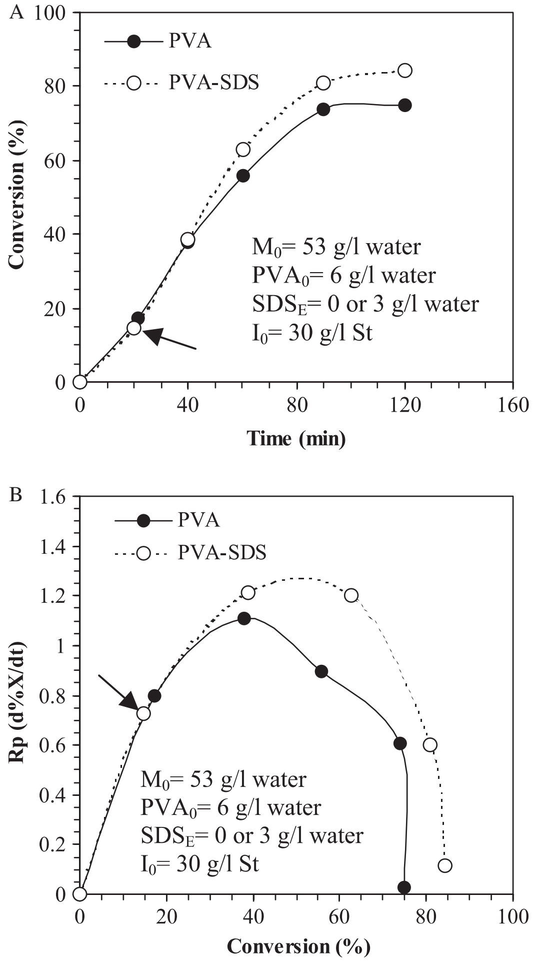

Fig. 3. Evolutions of (A) monomer conversion and (B) rates of polymerization for the minisuspension polymerizations of styrene (St) at 70 °C and 200 rpm using PVA and a PVA–SDS mixture. Arrows indicate the moment in which SDS was added.

progress of the reaction in the run with PVA–SDS compared to the reference one. It can also be observed that the curves overlap before the addition of SDS, which indicates that the reproducibility of the polymerization method is reasonable. The reason for this difference is discussed next.

It is well know [4] that in suspension polymerization the R_p does not depend on the type and concentration of stabilizer, but on the initiator concentration. However, it is also well known that a significant amount of polymer particles are formed by emulsion polymerization during styrene suspension polymerization using PVA as stabilizer and AIBN as initiator [12,14]. Creation of small particles formed from small monomer droplets produced during the homogenization process at high stirring speeds cannot be discarded. These small particles (of the order of 10^1 nm) can be formed from the small fraction of initiator dissolved in the aqueous phase [19–21]. As can be observed in Fig. 4, the evolution of the average particle size in the reference run agrees with the three stages of typical suspension polymerization described above, which limits are represented by the vertical dotted lines. That is, the particle size is constant at low conversions, increases at intermediate conversions and becomes constant at high conversion, during the first, second and third stages, respectively. In contrast, in the run where SDS is added toward the end of the first stage, the average size slightly decreases so that the typical second stage is not observed. Particle size becomes constant during the third stage of the polymerization and the PIP is defined at the beginning of this stage also in agreement the typical behavior.

Therefore, it is evident that SDS strongly enhances the colloidal stability of the particles formed by both the suspension end the emulsion mechanism. Because more emulsion particles 'survive' in the PVA–SDS run, the R_p is higher in this case. An additional cause of the R_p increment may be the occurrence of micellar nucleation; however, this possibility seems to be unlikely as will be discussed later.

In order to obtain more evidences about the enhanced stabilizing properties of the PVA–SDS mixture, a coagulation kinetic study was done.

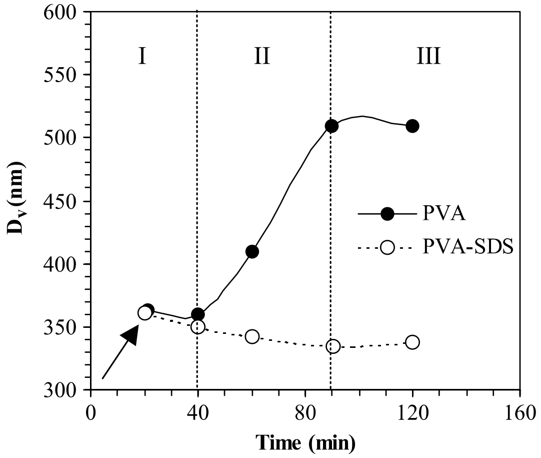

Fig. 4. Evolutions of average diameter for the polymerizations of Fig. 3. Arrow indicates the moment in which SDS was added. The vertical dotted lines represent the limits of the three stages of typical suspension polymerization.

This study consisted in monitor the size evolution of polystyrene particles (in the absence of polymerization) synthesized by using PVA as stabilizer. Four aliquots (1 g each one) from this latex were taken. One of these was not modified (reference) and to the others certain amount of SDS, PVA and mixture PVA–SDS predissolved in 1 g of destilled-deionized (DDI) water, were added. The added amount of a given stabilizer was such that weight ratio (PVA in aliquot)/(added stabilizer) were equal to 2.0, which is the same weight ratio used in the PVA–SDS run. The reference and the modified aliquots were diluted with DDI up to complete 66.5 g of DDI water and heated at 70 °C by means of a water bath.

N was calculated from the polymer content and the particles size distributions (PSDs) measured by dynamic light scattering (DLS) by using Eqs. (1) and (2).

The coagulation rate for identical particles in dilute dispersions is given by [22]

$$\frac{dN}{dt} = -\frac{k_r}{W}N^2 \tag{3}$$

where k_r is the rate constant for rapid coagulation and W is the stability ratio which accounts for the barrier against coagulation. The greater the value of W is, the greater the colloidal stability of the particles in question. k_r is given by

$$k_r = \frac{4k_B T}{3\eta} \tag{4}$$

where k_B, T and η are the Boltzmann constant, absolute temperature and viscosity of the fluid, respectively.

Eq. (3) can be solved easily to obtain

$$\frac{1}{N} - \frac{1}{N_0} = \left(\frac{k_r}{W}\right)t \tag{5}$$

where N_0 is number of particles at time $t=0$. By plotting the left hand side term versus time the value of W can be estimated from the slope. The results for the systems described above are shown in Fig. 5 and the correspondent values of W are reported in Table 2.

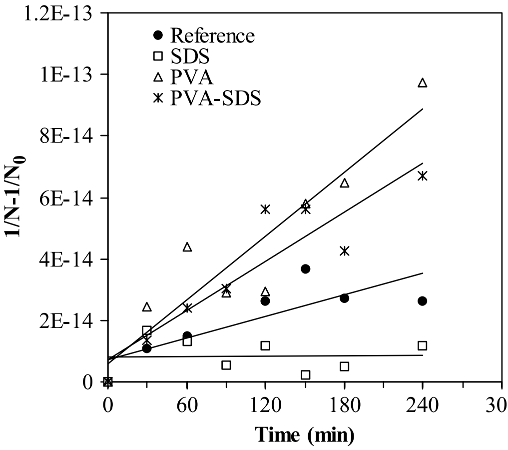

Fig. 5. Experimental data of the evolution of the number of particles according to Eq. (5) and the corresponding fits by linear regression.

Table 2
Stability ratios correspondent to the data shown in Fig. 5 and according to Eq. (5)

	W
Reference	6.32×10^{04}
SDS	6.32×10^{06}
PVA	1.83×10^{04}
PVA–SDS	2.37×10^{04}

As can be observed, in the case where SDS is added to the latex previously stabilized with PVA, W is two orders of magnitude greater than in the other systems. It is also interesting to note that W is smaller in the cases where PVA and mixture PVA–SDS are added, than in the reference. It is not clear at this stage the origin of this unstability induced by the extra-addition of stabilizers. As speculation, this behavior could be caused because certain degree of bridging flocculation is occurring [23]. The important point in this coagulation kinetic study is that, indeed, addition of SDS greatly enhances the colloidal stability of the system relative to the other cases.

The effect of the stabilizing properties of PVA and the PVA–SDS mixture on the final PSDs is shown in Fig. 6. It can be observed that the PSD is wider in the PVA run compare with the PVA–SDS run. In the first case, particle sizes up to the order of microns are observed whereas in the other one particle sizes are in the order of hundred of nanometers.

In typical emulsion systems, 'young' particles are smaller than ∼100 nm; however, these are not observed in the DTPs shown in Fig. 6, as would be expected according to the above discussion. This is not a surprise considering that light scattering weights the larger particles more heavily than the smaller ones, which are not being detected. In contrast, AFM is a technique able to detect such a small particles as can be observed in the image shown in Fig. 7 that corresponds to the final sample of the PVA–SDS run.

A better insight about what is happening in polymer particles can be obtained from the evolution of the molecular weight distributions (MWDs) for the PVA and PVA–SDS runs, Fig. 8(A) and (B), respectively. As can be observed in both figures there are two populations, a main peak and a shoulder,

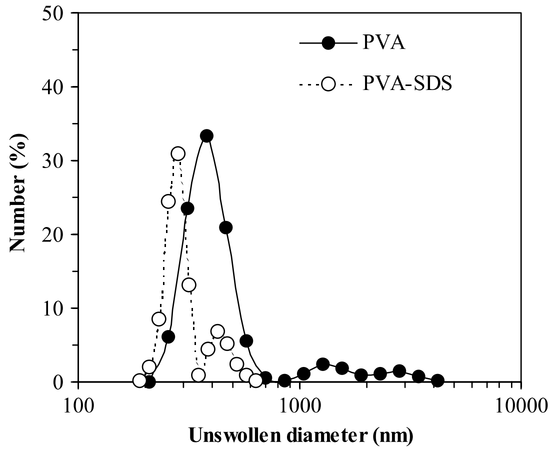

Fig. 6. Comparison of final particle size distributions obtained by dynamic light scattering for the polymerizations of Fig. 3.

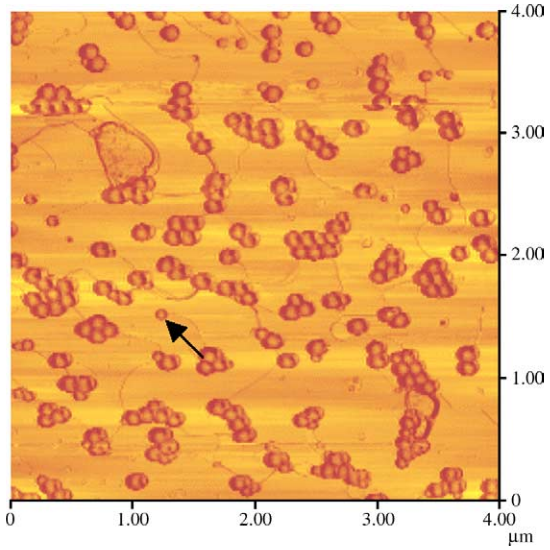

Fig. 7. Phase image obtained by AFM of a diluted sample taken at the end of the PVA–SDS run. The arrow indicates an example of a polymer particle smaller than 100 nm.

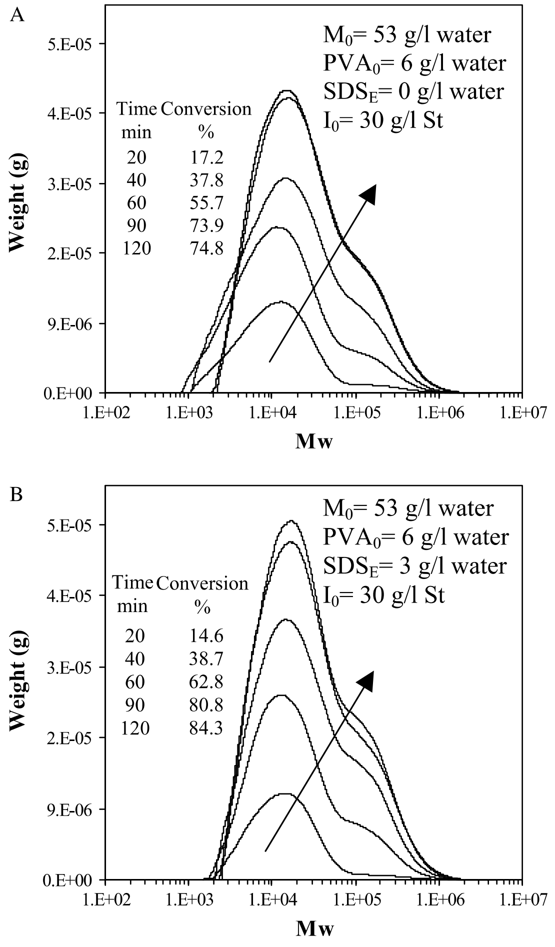

Fig. 8. Evolution of the molecular weight distributions using (A) PVA and, (B) a PVA–SDS mixture (weight ratio 2:1) as stabilizers; SDS was added at 15% of monomer conversion. MWDs were normalized with respect to conversion. The arrow indicates the sense in which monomer conversion increases.

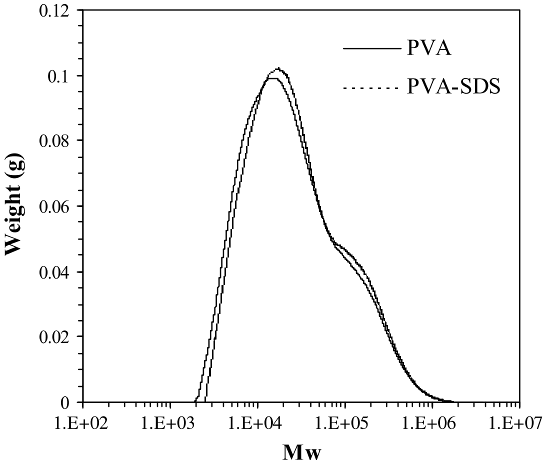

Fig. 9. Comparison of final molecular weight distributions obtained by dynamic light scattering for the polymerizations of Fig. 3. MWDs were normalized with respect to conversion.

which correspond to typical molecular weights observed in suspension (10^3–10^4) [11,14,24] and emulsion polymerization (10^4–10^6) [25–27], respectively. It can also be observed in both figures that at low conversions (15–17%), the shoulder is almost imperceptible meaning that most of the polymer has been formed by the suspension process. However, when the conversion increases the shoulder becomes more and more evident in both MWDs; therefore, emulsion polymer was formed even in the absence of SDS which was added at 22 min of reaction (15% conversion). This is, emulsion polymer particles were formed in both runs, which were initially stabilized by PVA. The similarity of the final molecular weights obtained in both runs is more evident if we look at the final MWDs shown in Fig. 9. As can be observed these MWDs are practically the same. This implies that the SDS addition did not lead to the formation of polymer particles by micellar nucleation but only stabilize the particles formed by the homogeneous and monomer minidroplet nucleation mechanism. Otherwise, it would be expected that a more significant amount of emulsion polymer be formed as it has been observed in the styrene emulsion polymerization above the critical micellar concentration of SDS and using AIBN as initiator [19,20].

The origin of the stabilizing properties of the PVA–SDS mixture is considered now. Philip et al. [9], provide experimental evidences about the enhanced stability of colloids (an oil-in-water emulsion of a ferrofluid) stabilized with this mixture. They proposed that the adsorption at the interface depends on the competition between the formation a complex in the bulk and adsorption at the interface. This interaction between PVA, SDS, and colloid can lead to three distinct scenarios, depending on the sequence of adsorption of polymer and surfactant onto the colloidal interface. In the first case the emulsion was initially stabilized with SDS and after that PVA was added; in the second case premixed PVA–SDS was added to the emulsion and in the third case the emulsion was initially stabilized with PVA and after that SDS was added.

They concluded that in the first two cases, where the colloidal interface is adsorbed with or without SDS molecules, polymer–surfactant complexation occurs in the bulk phase but without being adsorbed at the interface. In the third case polymer–surfactant interaction leads to dramatic changes in repulsive forces due to conformational changes of polymers at the interface, enhancing the stability of the colloid considerably.

The colloidal behavior observed in the present study agrees with the third scenario described by Philip et al. This was not only confirmed by the higher stability of polystyrene particles when the PVA–SDS mixture was used, but also by viscosity measurements of aqueous solutions. The effect of SDS, PVA and PVA–SDS mixture concentrations on the viscosity is shown in Fig. 10, curves A, B and C, respectively. In the case of the PVA–SDS (C) curve, this was plotted as a function of the PVA concentration in the mixture; that is, curve 'C' represents how the viscosity is affected when SDS is added to the PVA solutions with the concentrations indicated in the 'B' curve. As can be observed the SDS by itself (curve A) does not have a significant effect on the viscosity as it was expected given its low molecular weight. On the other hand, this effect is very marked in the cases of PVA and the PVA–SDS mixture. At relatively low concentrations (< ~8 g/l water) practically there is not difference between these curves (B and C); however, when the PVA concentration was increased the viscosity of the mixture (keeping the PVA/SDS weight ratio = 2:1; curve C) became higher than the viscosity of PVA solution (curve B).

More viscosity measurements are shown in Fig. 11, where this parameter is plotted as a function of the SDS/PVA weight ratio for several PVA concentrations. It can be observed the presence of a maximum at high PVA concentrations, which is considered a demonstration of the interaction between amphiphilic polymer chains and anionic surfactants, although the detailed mechanism behind these phenomena is not well understood ([28] and references cited there in).

This confirms there are associations between both surfactants that leads to conformational changes of the PVA

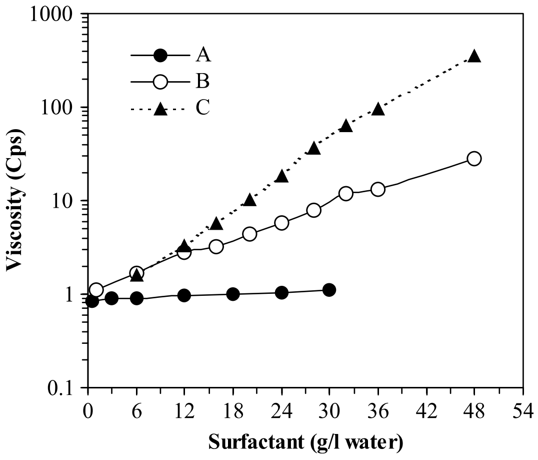

Fig. 10. Effect of stabilizer concentration on the zero-shear viscosity at 25 °C of aqueous solutions of (A) SDS, (B) PVA and (C) PVA–SDS mixture (weight ratio 2:1) reported in terms of the PVA concentration in the mixture.

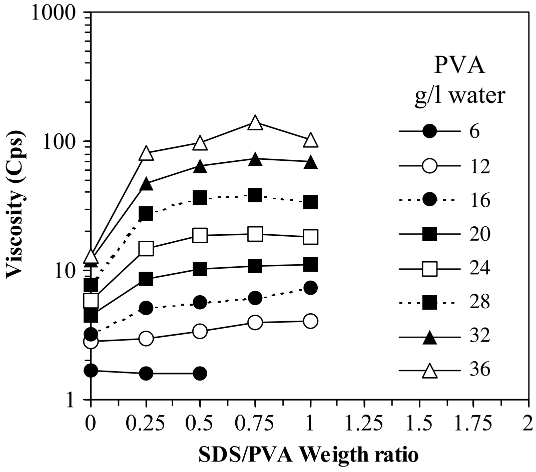

Fig. 11. Effect of SDS/PVA weigth ratio on the zero-shear viscosity of aqueous solutions of PVA at 25 °C.

molecules. As it was pointed out by Philip et al., the SDS molecules associated to the PVA molecules provide charges that repel each other; this electrostatic repulsion collectively lead to chain stretching. This implies that when the SDS is added to PVA pre-adsorbed on polystyrene particles, this conformational change gives place to a kind of electro-steric repulsive forces between the polymer particles, which explain the higher stabilizing properties of the PVA–SDS mixture in the minisuspension polymerization studied in this work.

Notwithstanding the PVA concentration used in the present work was 6 g/l water, that is, in the range in which curves B and C overlap (Fig. 10) and the viscosity profile is flat (bottom curve, Fig. 11), the colloidal stability of particles observed in the minisuspension polymerization performed in this work confirm that indeed such association exist. Therefore, viscosity measurements are not sensitive enough to these low concentrations. In contrast, interfacial tension measurements are sensitive under these conditions, as can be observed in Fig. 12. In this figure, the effect of stabilizer concentration on the interfacial tension (γ) between toluene (a very similar molecule to styrene) and aqueous solutions of SDS (curve A), PVA (curve B) and PVA–SDS mixtures (curves C-1 and C-2) is shown. In the later case, one curve (C-1) corresponds to the system in which the toluene was carefully added to premixed PVA–SDS aqueous solution. In the other case (curve C-2), SDS was added to the system in which PVA was pre-adsorbed at the toluene-aqueous solution interface. This is, curves C-1 and C-2 corresponds to scenarios II and III of Philip et al., mentioned above, respectively.

As can be observed in Fig. 12, γ for the PVA–SDS mixture (curve C-1) is greater than that of the SDS and PVA aqueous solutions (curves A and B). This indicates that PVA–SDS mixture does not adsorbs at the interface as efficiently as their components do alone. It seems to be that the hydrophobic parts of the PVA–SDS complex are not as available as in the parent solutions, such that adsorption at the interface is more difficult. It has been pointed out [3] that, in the absence of stirring, PVA of high molecular weight tends to have a conformation in which the hydrophobic parts of the molecule are surrounded by the hydrophilic parts. The fact that C-1 curve is above the A and B

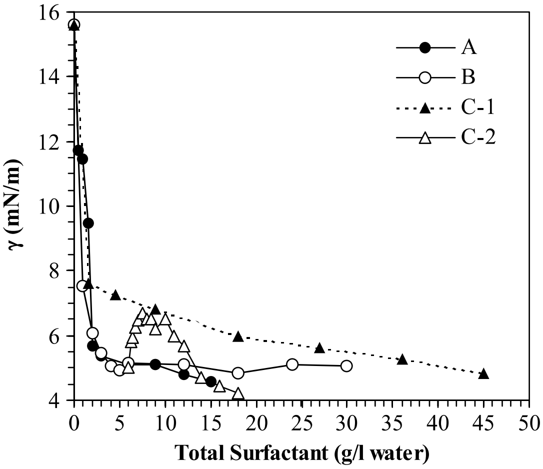

Fig. 12. Effect of total stabilizer concentration on the interfacial tension of toluene and aqueous solutions of (A) SDS, (B) PVA and, (C) PVA–SDS mixtures at 70 °C. Curve C-1 corresponds to case in which PVA and SDS are mixed before the interface is formed. In curve C-2, SDS is added after the interface toluene-aqueous solution of PVA was formed. The data are the average of at least five measurements.

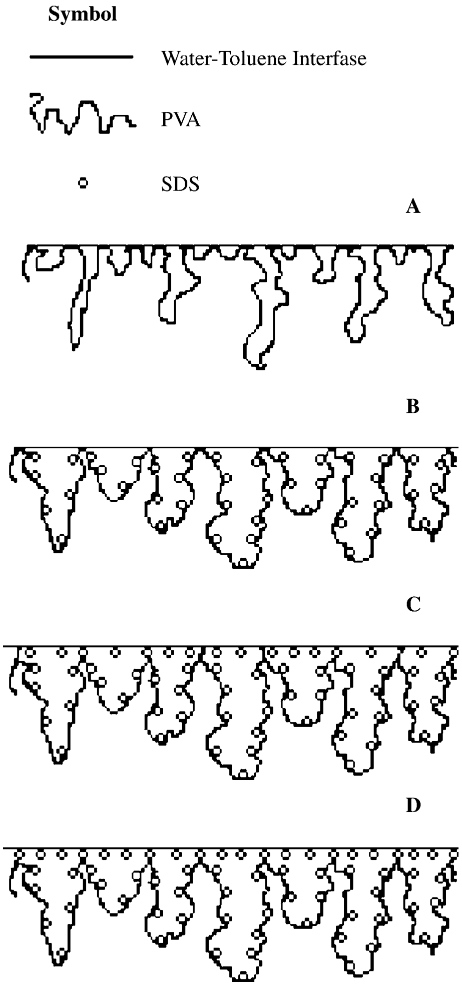

Fig. 13. Schematic description of the PVA adsorption on the toluene-aqueous phase interface in the presence of SDS where the concentration of the latter increases from top (A) to bottom (D). See text for a detailed explanation.

curves suggests that this kind of core (hydrophobic)–shell (hydrophilic) conformation is more pronounced because the SDS molecules associated to the PVA backbone provides net charges that enhance the hydrophilic character of the periphery.

In the case of curve C-2 (scenario III), a maximum was observed. This rise of γ could be explained in terms of the associations between PVA and SDS as follows (Fig. 13). Because in the measured that more SDS is added, γ increases which suggest that SDS makes associations with the PVA chains rather than adsorb on the interface (B), otherwise the value of γ would not change because SDS and PVA leads to similar γ for the system and conditions studied. As more SDS is added, more segments of the PVA molecules become more hydrophilic and strength causing that those segments desorb back to the aqueous phase increasing in this way the value of γ. When the amount of SDS is such that it has saturated most of the possible association points with the PVA chains, SDS tends to adsorb now on the interface (C, D) and then γ diminishes up to point where this parameter is predominantly determined by the SDS adsorption and coincides with the curve for pure SDS (curve A).

4. Conclusions

The kinetics of minisuspension polymerizations of styrene using PVA and a PVA–SDS mixture were experimentally studied. In the PVA run the evolution of particle size followed the three stages typical of suspension polymerization whereas in the PVA–SDS run the second stage was not observed (particle size slightly decreases). The reason for this difference is the higher stabilizing properties of the PVA–SDS mixture, which was confirmed with coagulation kinetics studies. This behavior seem to come from associations between the PVA and SDS molecules that leads to a electroesteric stabilization mechanism, as it is inferred from the viscosity and interfacial tension measurements of the aqueous solutions. The evolution of the molecular weight distribution suggest that formation of emulsion polymer particles is significant compared to the minisuspension particles but not predominant. The addition of SDS did not seem to lead to the formation of this kind of particles; the SDS only stabilizes the particles previously formed under the conditions studied.

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