Soft Matter: Synthesis, Processing and Products

Shear Stability of Inverse Latexes During Their Polymerization Process

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The shear-stability of inverse latexes (IL) during their polymerization process is studied. The IL is made of water droplets containing a copolymer of acrylamide and dimethyl-aminoethyl-methylenechloride emulsified in a paraffin oil. It is found for the first time that the shear stability of the ILs is a nonmonotonic function of the monomer conversion. At low conversions the shear stability increases as the conversion increases, but at a certain conversion value it reaches a local maximum and then decreases with conversion. Moreover, at the final stage of the conversion, the shear stability can increase again. A proper interpretation of this behavior is proposed and related to the combined effects of the polymer properties, fractal aggregation, and coalescence. © 2015 American Institute of Chemical Engineers *AIChE J*, 61: 1380–1384, 2015
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Introduction

Polyelectrolytes are of great importance in various areas, such as water treatment, mineral processing, and paper making.[1] A typical preparation method of polyelectrolytes preparation is via inverse emulsion or inverse miniemulsion polymerization.[2] In this way, as the produced polymer is solubilized in the water-in-oil droplets, such dispersions are here referred to as inverse latexes (ILs).[3] Owing to the presence of mechanical agitation and high particle volume fractions, the shear-stability of the ILs is very crucial both during and after the polymerization.[3,4] Insufficient shear stability would cause particle aggregation during the polymerization, leading to the formation of fractal clusters, eventually resulting in full percolation (gelation) within the reactor vessel.[5]

Previous studies highlighted the key parameters affecting shear stability of latexes and ILs after polymerization.[3,6,7] It was found that in the case of ILs where the particles are very soft, due to the plasticization of the water, besides the aggregation (affected by shear rate, colloidal interactions, and temperature),[6,7] also interparticle coalescence plays an important role.[3] This is because coalescence after aggregation can lead to the formation of compact clusters (perfect spheres in the limit), which decrease their occupied volume fraction, thus avoiding (or delaying) gelation. It follows that any quantities (e.g., polymer content within the IL particles, the polymer molecular weight, etc.) that vary the coalescence rate can affect the shear stability of the ILs.[3] While a relative clarity exists concerning the shear-stability of such ILs after polymerization, little is known regarding their shear stability during their formation, that is, during the polymerization process in inverse emulsion.

This work aims to shed light on the key phenomena regulating the shear-stability of ILs during polymerization. To do so, we take samples at different monomer conversion stages along the inverse batch miniemulsion polymerization of several IL systems (based on acrylamide and 2-dimethylamino-ethyl acrylate, methyl chloride quaternary salt), and their shear stability is studied by means of a rheometer. It will be seen that the shear stability of the ILs during the polymerization process varies substantially and nonmonotonically with the monomer conversion, reflecting the influence of the amphiphilic nature of the polyelectrolytes, the particle viscosity and the particle volume fraction.

Methods

The IL samples, supplied by an industrial partner, were prepared by miniemulsion polymerization at $T = 40°\text{C}$. The particles, composed of a mixture of water and two monomers, acrylamide and 2-dimethylamino-ethyl acrylate, methyl chloride quaternary salt, are emulsified in a paraffin oil consisting of a mixture of hydrocarbons and stabilized by the nonionic emulsifier, sorbitan mono oleic acid ester. The recipes and characteristics of the various ILs used in this work are summarized in Table 1.

During the polymerization, samples were taken at different times and immediately quenched by exposure to air (i.e., by spraying the reactive mixture into a glass bottle). The acrylamide conversion, x, was then measured as follows: the samples were sprayed into a glass vial containing isopropanol; the polymer precipitates while the residual acrylamide dissolves in isopropanol and is measured via high-pressure liquid chromatography (HPLC). After 2 weeks

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Table 1. Characteristics of the ILs Used in this Work

IL Number	Polymer in Particle w_p (wt %)	Comonomer (mol %)	ϕ (%)	E (wt %)	D (nm)
S01	55	15	61	2.7	594 ± 132
S02	50	15	61	2.7	571 ± 145
S03	55	15	55	2.7	615 ± 150
S04	52.5	15	61	2.7	588 ± 177
S05	52.5	15	58	2.7	563 ± 134
S06	52.5	15	55	2.7	528 ± 243

the quenched samples were measured again: no change in the conversion profiles was observed proving the successful quenching of the reaction (data not shown). The shear-stability of the IL samples at different conversions was then assessed by means of an ARES rheometer (Rheometric Scientific) equipped with a rotating cup and a gridded stator, which has been fully described and characterized in our previous work.[3] The rheometer was equipped with a water bath for the temperature control (set either at $T = 40°\mathrm{C}$ or 50°C). After preheating at the desired temperature, 1.5 mL of each sample were dropwise added into the rheometer cup, a bottom gap of 0.15 mm was selected, and the steady shear experiment was started at 5600 s^{-1}.

Dynamic Light Scattering was used to characterize the size of the polymer particles. It was used only to analyze samples with full monomer conversion, by diluting the samples in a 2.5% emulsifier rich paraffin oil solution, to prevent particle destabilization, as discussed elsewhere.[3]

Results and Discussion

Role of particle volume fraction versus polymer content in particles

Let us first consider the three IL systems, S01, S02, and S03 in Table 1, which have been prepared using the same amount of surfactant and the same molar ratio of cationic comonomer/noncharged monomer. They differ only in the particle volume fraction (ϕ) and the polymer content in the particles (w_p), as described in Table 1. The typical time-evolutions of the shear viscosity, η_E, at the steady shear, $\dot{\gamma}=5600\ \mathrm{s}^{-1}$, in the case of S03 at different acrylamide conversions, x, are shown in Figure 1a. Except for some intermediate situations, the evolutions can be divided into two distinct types: those exhibiting an abrupt increase in η_E after a certain shearing time, and those exhibiting a monotonic decrease in η_E until reaching a plateau. As already shown in previous works,[3,6,7] the former corresponds to the occurrence of the shear-induced gelation due to the fractal growth of the clusters, while the latter indicates that the IL system is stable at the given shear rate. When gelation occurs, the gelation time (t_gel) is identified as the intersection of two straight lines: one extrapolated from the initial viscosity profile and the other from the final viscosity increase.[3] It should be noted that as our systems are extremely concentrated, with the occupied volume fractions of about 60%, the concept of the fractal growth of clusters might become inappropriate; nevertheless it remains, to our knowledge, the most suitable way to describe the competition between shear-induced aggregation and coalescence.

Similar data (not reported) were obtained also for the IL systems S01 and S02. The corresponding t_gel values are shown in Figure 1b as a function of the acrylamide conversion, x. As a general observation, the t_gel vs. x curve in Figure 1b for system S03 is located above the S02 one, which in turn is above the one of S01. When comparing S01 with S02 in Table 1, it is seen that the only difference is a 10% higher polymer content in the particles (w_p). This leads to the t_gel vs. x curve of S01 in Figure 1b being below that of S02, that is, the shear stability is significantly lower for S01 than for S02 during polymerization. This can be explained by recalling that for such soft particles under shear, there is competition between coalescence and aggregation.[3] Note that the glass transition temperature of acrylamide and its copolymers drops by more than 130°C on addition of few 10% (w/w) of water, allowing thus coalescence to occur in our conditions ($w_\mathrm{p} \approx 50\%$).[8] The larger w_p value for S01 signifies that the particles are more rigid, thus with a lower coalescence rate, leading to formation of less compact clusters; it follows that less time is needed for percolation (i.e., gelation) to occur. Thus, w_p is an important parameter in controlling the shear stability of ILs. Let us now compare S01 with S03 in Table 1. Their difference is only a 10% lower particle volume fraction (ϕ) for S03, and this leads to a t_gel vs. x curve for S03 in Figure 1b which is even above the S02 one. This means that ϕ plays a more important role in the shear stability of ILs than w_p does. The strong effect of ϕ on the shear stability has also been evidenced in Figure 1c, where the t_gel values as a function of x are reported for the systems, S04, S05, and S06 in Table 1, which differ only for the ϕ values. Again, the position of the t_gel vs. x curve moves upwards as ϕ decreases. The substantial impact of ϕ on the shear stability arises mostly because the aggregation is a second-order process with respect to the particle concentration, thus very sensitive to the changes in ϕ.

Nonmonotonic shear-stability along the monomer conversion

It is particularly worth noting the shape of the t_gel vs. x curves in Figures 1b, c. For S01 and S04, t_gel does not change significantly in $x \in [0, 40\%]$ and then decreases monotonically with x. For S02, S03, S05, and S06, instead, t_gel increases initially and when $x > 40\%$ it decreases with x. For S03, S05, and S06, however, the t_gel value starts to increase again at the final stage of the conversion. In fact, as shown in Figure 1a, for S03 at x=97% and 100%, no gelation was detected in the given investigation time. Similar behavior occurs also for S06 when $x > 80\%$.

It is easy to explain the common behavior for all the systems in the region, $x > 40\%$, where t_gel decreases with x, that is, the stability of the ILs decreases as the monomer conversion increases. This, based on the above discussion, can be ascribed to the increase in the particle hardness along the polymerization, which reduces the coalescence rate, leading to formation of less compact clusters, thus reducing the time for gelation to occur.

It is somewhat surprising to observe that the t_gel value increases with x at the initial stage of the polymerization for S02 and S03 in Figure 1b, and for S05 and S06 in Figure 1c. It is to be noticed that the same behavior is exhibited in the shearing experiments performed for S02 and S03 at the same shear rate, $\dot{\gamma}= 5600\ \mathrm{s}^{-1}$, but at a higher temperature, $T= 50°\mathrm{C}$. The corresponding t_gel vs. x curves are shown in Figure 1d. It is seen that the shape of the t_gel vs. x curves at $T= 50°\mathrm{C}$ is very similar to that at $T= 40°\mathrm{C}$, except that for

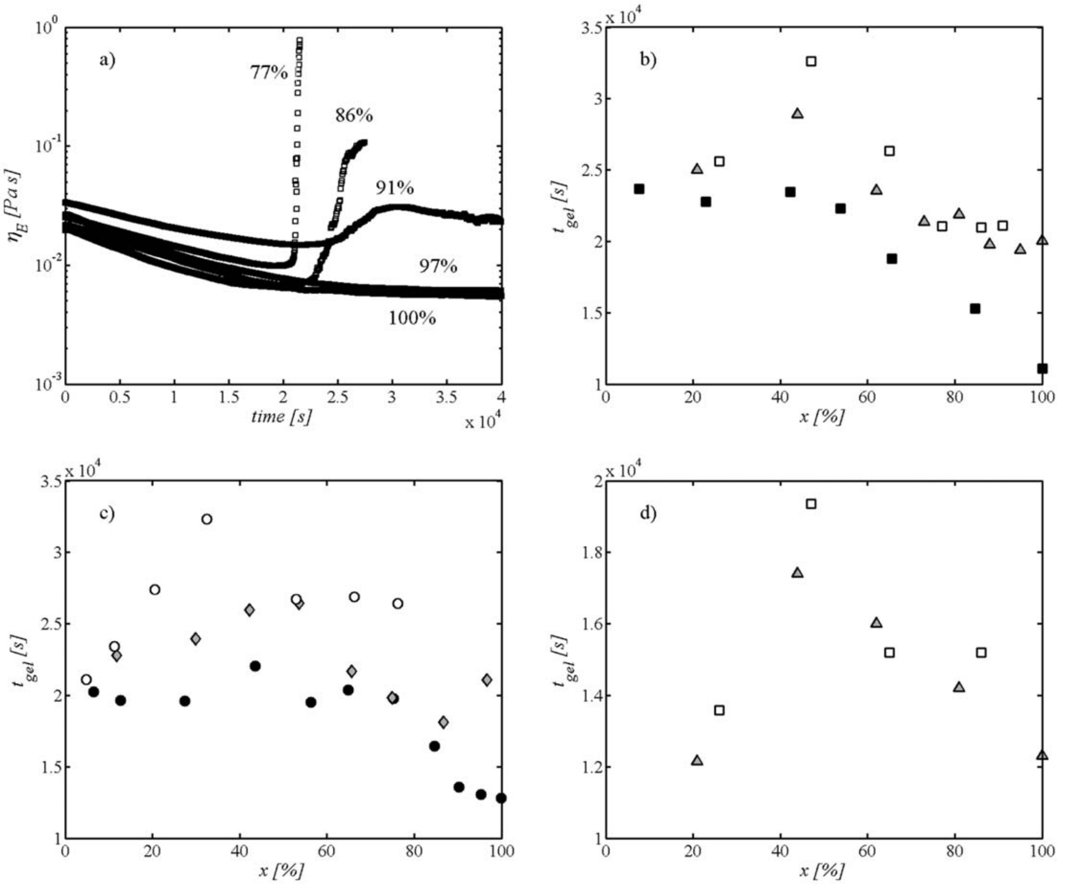

Figure 1. **a) Time evolutions of the shear viscosity (η_E) of IL S03 at different acrylamide conversions (*x*) at *T*=40°C. b) The gelation time, t_{gel}, of the ILs under shear at *T*=40°C as a function of *x* for S01 (filled squares), S02 (triangles), and S03 (open squares). c) The same as b) but for S04 (filled circles), S05 (diamonds), and S06 (open circles). d) The same as b) but for S02 (triangles) and S03 (open squares) at *T*=50°C.**

a given x value the t_{gel} value is significantly smaller for $T = 50°C$ than for $T = 40°C$. The lower shear stability at $T = 50°C$ results from the reduction in the adsorption of the surfactant on the particle surface, thus in the repulsive interaction potential, as already observed previously for these systems.[3]

The above initial increase in the shear stability could be related to the amphiphilic nature of the produced polyelectrolyte chains within the particles.[9] Notably, the presence of the charged comonomer leads to the presence of fixed charges along the polymer chain. While the carbon backbone of the chain defines the hydrophobic nature of the polymer, the charges confer the chain a strong hydrophilicity. Before the polymerization starts, the water/monomer droplets are stabilized by the steric surfactant from the oil phase (Figure 2a). As soon as the first chains are formed, they might start migrating toward the oil/water interface to decrease further the interfacial tension of the emulsified phase. In doing so, the hydrophilic, charged portion of the chains remains in the water phase, and the hydrophobic one is located at the interface (Figure 2b), as if a "second surfactant" adsorbs on the particle surface from the aqueous phase. Such a "second surfactant" may improve the particle stability due to several factors. First, the adsorbed hydrophobic portion of the chain increases the steric stability of the particles. Second, the presence of charges close to the hydrophilic heads of surfactant *E* increases their anchoring stability, thus reducing their mobility. As the surfactant molecules have to be relocated before allowing the particles to come close enough for their aggregation, the improved anchoring force can certainly hinder such relocation, thus reducing the aggregation tendency (increasing the gelation time). To support the above explanation, we have prepared an IL that contains additionally a polyelectrolyte, polyisobutyl amino-functionalized (PIBA) stabilizer. When it was sheared at 5600 s^{-1} at both 40°C and 50°C, no gelation occurred, as shown in Figure 3, clearly proving the surface activity of the polyelectrolyte chains.

When the shear stability increases to reach a local maximum around x=40% (Figure 1b, c), it starts to decrease. This may indicate that the particle surface is saturated by the initially adsorbed surfactant and the "second surfactant," and such improvement in the shear stability stops. Now, the competition between aggregation and coalescence becomes the dominant phenomenon, as previously discussed. The above explanation not only elucidates the initial increase in the shear stability observed for S02, S03, S05, and S06, but also clarifies and supports our previous results,[3] where it was found that increasing the charged/uncharged monomer ratio improves significantly the shear stability of the particles. This observation can in fact be well explained by the role of such a "second surfactant."

It should be mentioned that for the systems, S01 and S04 at the initial stage of the polymerization, the t_{gel} value keeps almost constant until $x \approx 40\%$. This is most likely because

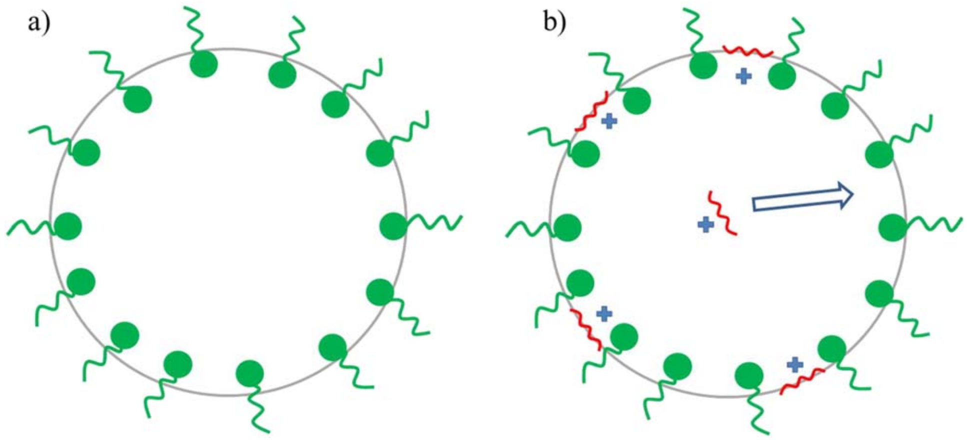

Figure 2. a) A sketch representing a water/monomer droplet stabilized by steric surfactants before polymerization starts. b) A sketch for a water/monomer/polymer particle, stabilized by steric surfactants and by amphiphilic polyelectrolytes formed at the initial stage of the polymerization.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of their high particle concentration and polymer content in particles, such that the aggregation becomes immediately the dominant phenomenon right from the beginning of the polymerization. However, the "second surfactant" role of the formed polymer discussed above still exists; otherwise the t_{gel} value would decrease monotonically starting from the beginning of the polymerization and not only after conversion has reached about 40%.

There is one phenomenon that remains still unexplained, that is, for S03, S05, and S06 the shear stability starts to increase at the final stage of the conversion. From Table 1, their particle volume fraction, ϕ, is among the lowest, which might be responsible for this phenomenon, but the mechanism remains unclear, although it is known that ϕ is a critical parameter for aggregation, leading to deviations from the classical theory when high-concentrated systems are studied.[10,11]

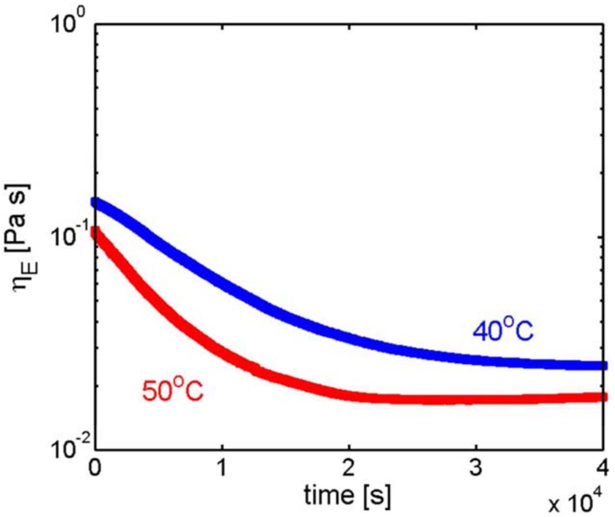

Figure 3. Time evolutions of the shear viscosity (η_E) of the PIBA-stabilized IL.

The surface activity of the PIBA prevents aggregation under the tested conditions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Conclusions

The shear-stability of ILs has been investigated at different monomer conversions during their corresponding polymerization process using a rheometer. The ILs are dispersions of soft, sterically-stabilized particles (made of acrylamide-based polyelectrolyte in water phase) in paraffin oil.

Three stages of the particle shear stability are identified during the polymerization: (1) an initial increase ($x \approx 0-40\%$), (2) followed by a decrease ($x \approx 40-80\%$), and (3) then a final increase at the last stage of the polymerization ($x \approx 80-100\%$). Stage (1) has been explained by the amphiphilic nature of the polyelectrolyte chains, which migrate toward the particle surface, at the beginning of the polymerization, increasing both the steric stability and the surfactant anchoring strength. Stage (2) has been ascribed to a decrease in the particle coalescence rate (caused by the increased particle hardness with the ongoing polymerization), leading to the formation of more open clusters and thus speeding up the gelation. As for Stage (3), instead, only a dependency on the particle volume fraction was assessed. It is concluded that the key parameters affecting the shear stability of ILs during polymerization are the particle volume fraction, the polymer content in particles and the amphiphilic nature of the formed polyelectrolyte chains.

Acknowledgment

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