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On the mechanism of particle formation above the CMC in emulsion polymerization

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Abstract The mechanism of particle nucleation has great influence on the kinetics and the particle size distribution of polymer latexes produced in emulsion polymerization. These are key aspects for the application of these products and for the development of emerging processes, such as living/controlled free-radical polymerizations. One very popular theory publish in the 80s establishes that the newborn (primary) particles undergo limited coagulation even when the concentration of surfactant is above its critical micellar concentration. In this communication, the experiment that was the base for the formulation of such theory is reexamined and discussed to determine whether it can be considered as "typical condition", such that the general character of their conclusions can be justified. In this context, the positive skewness of the PSD observed in that time and taken as an evidence of the coagulative nucleation is discussed as well.

Introduction

Emulsion polymerization is an important process for producing sub-micrometer polymer particles dispersed in water (known as latex) for a variety of applications, such as paints, coatings, sealants, additives for concrete, etc. Latexes have also found applications in the biomedical field, such as immunoassays, test for AIDS, drug delivery systems, etc. With the advent of the living-free-radical polymerization technique, there have been efforts to implement this technique in emulsion

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polymerization [1] as well as to produce nanocomposite materials [2, 3]. In all these applications, control of particle size distributions (PSD) is key aspects, because they have important influence on the product performance. It is well known that these characteristics of the latex are greatly influenced by the mechanism(s) of formation (nucleation), growth, and the colloidal stability of the particles.

Due to the complexity of the phenomenon itself and to the experimental difficulties associated with its study, particle formation still remains a controversial and poorly understood issue [4] When the polymerizations are effected below the critical micellar concentration (CMC) of the surfactant, obviously, there are not micelles, and hence, particles are formed by homogenous nucleation [5–7]. In this mechanism, the radicals generated in the aqueous phase propagate with the small amount of monomer dissolved in the aqueous phase until the oligomers formed reach a critical degree of polymerization (jcr); at this size, they become insoluble and precipitate. Depending on the availability of surfactant, these new-born particles (also known as primary) can undergo what is called limited coagulation. Coagulation of particles implies reduction of the particles surface which in turn leads to an increase of the surface charge density, because the charges that form the parent particles are distributed in a smaller area. Coagulation occurs or it is limited up to the point, where the surface charge density is enough to impart colloidal stability to the particles, so that this phenomenon is named in the literature as "limited coagulation" [8].

In the limiting case where the polymerization is surfactant-free, limited coagulation is very extensive, so that relatively small concentration of mature particles (N) and relatively large particle sizes (of several hundreds of nanometers) are obtained. As the surfactant concentration approaches to the CMC value, more and more mature particles of lower size are generated, because limited coagulation is reduced due the higher surface charge density caused by the higher adsorption of surfactant molecules.

When the polymerizations are effected above the CMC, the oligomeric species formed in the aqueous phase can also get into monomer-swollen surfactant micelles and propagates giving place to a new polymer latex particle. This mechanism is known as micellar nucleation [9, 10], which competes with the homogenous nucleation mechanism [11]. When the surfactant concentration is close and above the CMC, homogeneous nucleation can become more important as the water solubility of monomer increases, as in the case of methyl methacrylate (MMA) and vinyl acetate (VAc) emulsion polymerizations; however, well above the CMC, the experimental evidence [12–15] and theoretical results [16] show that micellar nucleation dominates under these conditions even for MMA and VAc. This is a notion that seems to be generally accepted [17]. What it is still open to discussion is the question of the colloidal stability of the primary particles. The debate about this point was discussed by the authors in a review [18]; for more details, the reader is referred to this reference. For the purpose of the present paper, let us focus to the article published by Lichti et al. in 1983 [19] that was the origin of such debate.

In that article, Lichti et al. proposed that the primary particles (precursor particles, as the former Sydney Group called it) are formed exclusively by the homogenous mechanism and that they are colloidally unstable, so they undergo

limited coagulation until they become mature (stable) particles. This two-step mechanism known as the homogeneous coagulative-nucleation mechanism was formulated on the base of their inferences made by analyzing the positive skewness of an early-time volume particle size distribution (v-PSD). They argue that just after nucleation has ceased, most particles have small volumes; hence, most particles must have been formed late in the nucleation step which is characteristic of coagulation kinetics, where formation of mature latex is through coagulative growth, which is auto-accelerating. If primary particles were formed by the micellar mechanism, the PSD would be negatively skewed, because most particles must have been formed at early times, because the nucleation rate should decrease in time, as micelles disappear. It is worth mentioning that their correspondent diameter particle size distribution (d-PSD) was not positively skewed. In a later paper of the Sydney Group [20], they recognized that micellar nucleation also occurred in competition with the homogenous nucleation and that the primary particles formed in both cases are colloidally unstable. This combined mechanism has been called "coagulative nucleation". In [18], a scheme illustrating this mechanism is shown.

In this work, the experimental conditions employed by Lichti et al. are studied and discussed to determine whether it can be considered as "typical condition", such that the general character of their conclusions and the validity given implicitly by a number of publications, who adopted as correct their hypothesis, can be justified. In this context, the positive skewness of the PSD observed by Lichti et al. and taken as an evidence of the coagulative nucleation is discussed as well.

Experimental section

Materials

Styrene (St), sodium dodecyl sulfate (SDS), and potassium persulfate (KPS), all from Aldrich, were used as monomer, emulsifier, and initiator, respectively. To remove inhibitor, St was distilled under vacuum prior to the polymerization at most one day before the experiment and kept in refrigeration until it was used. SDS and KPS were employed as received. Distilled and demineralized water was used in all cases. Except for the polymerizations performed in the dilatometer, nitrogen (Infra-México, ultrahigh purity grade >99.999%) was used to deoxygenate the reaction. All the reagents were the same than those used by Lichti et al. [19].

Polymerizations

In all the polymerizations, the initial surfactant, initiator, and monomer concentrations were 7.77, 4.16 and 76.10 g/L of water, in that order, and the temperature of the reaction mixture was controlled at 50 °C by means of a circulating bath. The polymerizations were repeated at least twice. A set of experiments (run "10k-d") was carried out in a dilatometer without agitation device, similar to the one employed by Lichti et al. [19]. In this case, St was pre-emulsified by means of a high shear device (Ultraturrax T25®) at 10,000 rpm. The total mass of the reaction

mixture was 114 g. The concentrations, temperature, rpḿs, and mass of reaction were the same than those used by Lichti et al. [19].

Another set of experiments was carried out in a 1 L stirred tank reactor (STR) which is a cylindrical, round-bottom, glass vessel with jacket, sampling valve, and four baffle plates located at 90°. The reaction mixture (600 g) was emulsified at 300 rpm using a typical four pitch-blade impeller; this stirring speed was maintained during the whole polymerization. This set of experiments was named run "300-STR". KPS solution was pre-heated to the temperature reaction and added to the monomer/surfactant mixture to start the reaction. Nitrogen was passed through the reaction mixture during all the experiment. Samples were withdrawn periodically from the reactor for gravimetric analysis and particle size measurement. All the samples were short-stopped with a 2% hydroquinone aqueous solution. The weight of polymer was determined by subtracting the known weights of the SDS, KPS, and hydroquinone from the total weight of the dried sample. Samples for particle sizing were immediately diluted in an SDS aqueous solution and analyzed by dynamic light scattering (DLS) using a Nano S-90 (Malvern) apparatus.

Results and discussion

In Fig. 1, the evolution of monomer conversion for the polymerization performed in a dilatometer and emulsified at 10,000 rpm (run 10k-d; continuous lines) and for the Lichti et al.'s experiment is compared with the one obtained at 300 rpm in a stirred tank reactor (run 300-STR). Error bars in Fig. 1 correspond to three repeated runs. It is worth mentioning here that Lichti et al. do not provide report error bars or experimental data showing the repeatability of their experiment. As it can be observed, the behavior of the set of experiments 10k-d looks more or less as faster as that obtained by Lichti et al. in a dilatometer and emulsified at 10,000 rpm as well. The upper part of the run 10k-d seems to be approaching an asymptotic value. It can also be observed that the run 300-STR is significantly slower than these latter. It is important to mention that in the run performed in the dilatometer, phase separation occurred at intermediate conversions. This is why the correspondent data

Fig. 1 Evolution of (fractional) monomer conversion (X) for the styrene emulsion polymerization performed at 50 °C and the indicated initial monomer (M_0), surfactant (S_0), and initiator concentrations (I_0). Runs performed in a dilatometer: 10k-d and Lichti et al. [19]. Run performed in a stirred reactor: 300-STR

g/L water
M_0=76.10
S_0=7.76
I_0=4.16
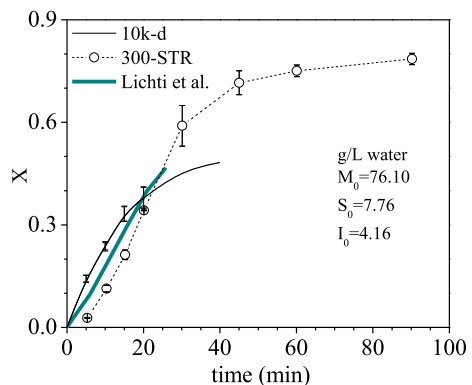
shown in Fig. 1 reach an asymptotic value around 0.45 of monomer conversion. In contrast, Lichti et al.₅s curve seems to be increasing. They do not report data for conversions higher than ∼0.45; however, it is very likely that their conversion versus time curve eventually becomes asymptotic as well. In preliminary dilatometry experiments performed in our lab, phase separation occurred at early times of the reaction if the pre-emulsification is done with a conventional stirrer at 300 rpm instead of using the Ultraturrax homogenizer at 10,000 rpm. On the base of these findings, it is inferred why Lichti et al. pre-emulsified the reaction mixture in this way. Furthermore, phase separation is also expected to occur considering the absence of agitation and the well-known poor capability of SDS as an emulsifying agent for styrene; see, for example, [21]. These results contrast with the much higher final conversion obtained in the STR. It is clear that the rates of polymerization (Rp) of the runs performed in the dilatometer were slower than the runs done in the STR. The reason for this was very well explained by Nomura et al. in a paper [21] published 11 years before the one of Lichti et al. Nomura et al. pointed out convincing evidences and arguments that there is an optimal range for the stirring speed in a given reactor configuration. Below this optimal range, monomer droplets are relatively large (even phase separation can occur), so that their total interfacial area is not enough for maintaining a flux of monomer sufficient to keep the monomer concentration in particles at its saturation value; this is, the polymerization takes place under monomer-starved conditions. On the other hand, above the optimal range, the total interfacial area of monomer droplets increased, because their size diminishes. In this case, there are not monomer mass transport limitations, but the number of micelles available for nucleation decreases, because they disassemble and the surfactant molecules migrates to cover the droplets surface. If the total area of monomer droplets is significant compared to that of micelles, then nucleation in both monomer-swollen micelles and monomer (mini) droplets can occur as it happens in mini-emulsion polymerization. This competition of nucleation mechanisms was not taken into account by Lichti et al.

It is well accepted [22] that the shorter the nucleation step, the narrower the PSD; therefore, it is expected that narrower PSDs can be obtained as the stirring speed increases, because in this way, the number of micelles diminishes as explained above. However, the d-PSDs shown in Fig. 2 are not consistent with this idea. As it can be observed, the positive skewness is more marked as the stirring speed is higher; if the d-PSDs are converted to v-PSDs, the positive skewness is enhanced (results not shown). These results suggest that nucleation in mini-droplets could be taking place and that limited coagulation of primary particles is not the only mechanism that could explain such positive skewness. Besides, the possibility of nucleation of mini-droplets (30–100 nm in diameter) formed spontaneously in the conventional emulsion polymerization systems [23, 24] may be having influence on the PSD shape.

The d-PSD reported by Lichti et al. is shown in Fig. 2 as well. It is evident that their d-PSD is narrower than those obtained in this work by dilatometry. The reason for this difference is not at all clear. It can be ascribed, at least to certain extent, to the different particle sizing techniques used. Lichti et al. employed transmission
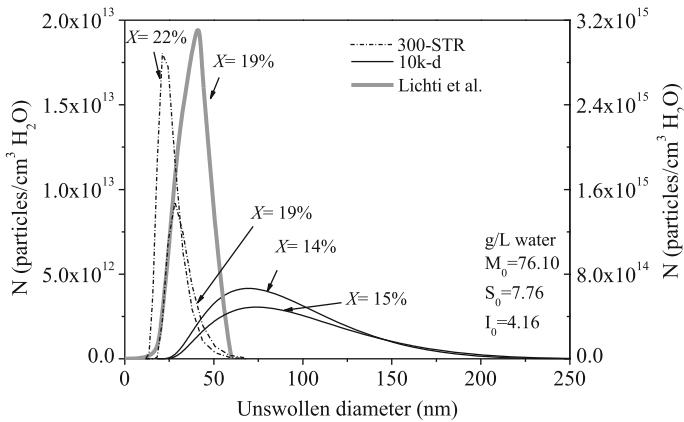
Fig. 2 Comparison of PSDs at the indicated conversions (*X*) for the runs performed in a dilatometer (10k-d, *left axe*), in a stirred reactor at 300 rpm (300-STR, *right axe*) and for the PSD reported by Lichti et al. [19] (*left axe*) performed in a dilatometer as well

electron microscopy (TEM), while here, we employed DLS, a technique that is well known to weight the larger particles more heavily.

As it was explained above, Lichti et al. claim that positive skewness of the PSD can only be explained by an increasing nucleation rate which is not consistent with the micellar mechanism, because micelles concentration diminishes with time. According with them, this mechanism would lead to negatively skewed distributions being the tail toward small particles sizes originated by those primary particles formed toward the end of interval I. In a later paper [20], the Sydney Group which recognizes particles can also grow in an accelerated way, because the equilibrium monomer concentration within the particles increases with increasing radius, as predicted by the well-known Morton equation. Furthermore, they did not take into account that the dependence of the free-radical capture (ρ) and desorption rate (κ) coefficients from polymer particles can also explain the asymmetric broadening of the PSD. The authors have proposed that given that ρ increases and κ decreases with particle size, the largest particles go ahead in their growth leading to positive-skewed or even bimodal [25–27] or trimodal [16] PSDs. Desorption makes that preferentially, the smallest particles become inactive; preferential free-radical capture in the largest ones diminishes the probability of a small inactive particle capturing another radical to keep growing. This difference on the growing rate of inactive and active particles reinforces the conclusion pointed out by Coen et al. [28] in the sense that the positive skewness does not provide an evidence that primary particles undergo limited coagulation above the CMC.

There are contradictory arguments and experimental evidences published in the literature regarding the colloidal stability of the primary particles above the CMC. A mathematical model [28] based on coagulative nucleation predicts a minimum in the rate of polymerization (Rp) evolution curve at early times of the reaction, as it is deduced from the shape of the theoretical conversion versus time curve. For the

same monomer (styrene), one of the authors [25] proposed a mathematical model that is able to predict detailed RPs obtained by calorimetry, the PSD, and N assuming that primary particles are colloidally stable. The calorimetric data [29] and the model predictions do not exhibit the aforementioned minimum at low conversions. On the other hand, Araujo et al. [30] argued that oscillatory responses of the emulsion copolymerization of vinyl acetate and Veova10 in a continuous tubular reactor can be obtained by their mathematical model only when coagulative nucleation is considered. In contrast, according to Tauer [31], his experimental results of the development of particle charge density do not support the idea that small particles have a lower surface charge density and hence are unstable to coagulate. In previous reports by our group [26, 27], the PSD evolution in the styrene emulsion polymerization above the CMC by means of asymmetrical flow field-flow fractionation (AFFFF) was monitored. This technique is capable of detecting particles <20 nm dispersed in water and that for experimental issues [16, 26], they are not possible to be detected by DLS or TEM. They obtained bimodal PSDs in which the small-particle peak was ascribed to primary particles and found that under conditions that favors limited coagulation (high N values and/or high ionic strength); the referred minimum in the Rp evolution at low conversions is observed, although the bimodality of PSD is still present. These experimental findings suggest that limited coagulation of particles might take place during the nucleation step but, if it occurs, is not as extensive as the coagulative-nucleation theory states.

Conclusions

The emulsion polymerization performed in a dilatometer in a very similar way as Lichti et al. did, is not, from the kinetic point of view, comparable to the run effected in the stirred reactor. It is very likely that because of the usage of a high shear device to emulsifier the mixture, monomer mini-droplets can be formed and that these can act as nucleation loci in competition with monomer-swollen micelles, contributing in this way to the positive skewness of the PSD. Therefore, the results highly suggest that the reaction conditions studied by Lichti et al. cannot be considered as typical of the conventional emulsion polymerizations effected in stirred reactors. Moreover, the positive skewness of the PSDs does not represent a validation of the coagulative-nucleation theory, because there are other phenomena that can lead to this shape of the PSD. However, notwithstanding these weaknesses of such theory, it seems that limited coagulation of primary particles might occur depending on the monomer and specific reaction conditions.

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