

## Semicontinuous Heterophase Copolymerization of Vinyl Acetate and Butyl Acrylate

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**ABSTRACT:** Vinyl acetate (VAc) and butyl acrylate (BuA) were copolymerized in heterophase by a semicontinuous process (unseeded) and compared with the seeded semicontinuous microemulsion polymerization of the same monomers. A mixture of sodium dodecyl sulfate (SDS) and poly(ethylene oxide) dodecyl ether (Brij-35<sup>®</sup>) were used as surfactants. The effects of monomer addition rate ( $R_a$ ) and surfactants concentrations (4 or 1 wt % with respect to the initial mixture of reaction) on polymer and latex properties were studied. High copolymer content latexes (24–36 wt %) with average particle diameters ( $D_p$ ) from 38 to 55 nm and relatively narrow particle size distributions, high polymerization rates, weight ratios of polymer to surfactant (P/S) from 13.3 to 32.8 were obtained. The number-average molecular weights ( $M_n$ ) were between 96,000 and 188,000 g/mol. Homogeneous copolymer compositions were obtained throughout the reaction for both, seeded and unseeded processes, which is not possible by the usual batch microemulsion process. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** copolymerization; vinyl acetate; butyl acrylate; semicontinuous heterophase

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### INTRODUCTION

In some applications, polymer nanoparticles perform better than larger particles because their smaller size allows them to reach sites that cannot be achieved otherwise, and because their greater surface/volume ratio gives them higher efficiency in those applications in which specific surface area is determining.<sup>1</sup>

Heterogeneous polymerization can be subdivided into precipitation, suspension, microsuspension, miniemulsion, emulsion, microemulsion, and dispersion polymerization. In the cases of polymerization in suspension, microsuspension, miniemulsion and microemulsion, the monomer must be only slightly water soluble as it has to form a separate phase of droplets whose size is controlled by a proper choice of the dispersing technique and the stabilizing system. Many applications of resulting latex particles require not only a specific chemical composition but also a certain particle size and/or a particle size distribution (PSD). Thus, they are important parameters determining both the preparation and the application of latex particles.<sup>2</sup>

In this work, by semicontinuous heterophase polymerization (SHP, also called unseeded polymerization), we refer to a polymerization starting with a surfactant solution with concentration higher than the critical micelle concentration (CMC) and without monomer, so that, only empty micelles are present at the beginning of reaction. In this process, to start the polymerization, monomer is added continuously at a constant rate ( $R_a$ ). For example, Ledezma et al.<sup>1</sup> reported the SHP of methyl methacrylate (MMA) using a mixture of sodium dodecyl sulfate (SDS) and Aerosol-OT (AOT) as surfactants and potassium persulfate (KPS) as initiator varying the  $R_a$  between 0.068 and 0.9 g/min, finding that latexes with high polymer content,  $D_p < 40$  nm and narrow PSD can be obtained by this process. SHP can be used to obtain polymeric nanoparticles with tuned morphology; Esquivel et al.<sup>3</sup> used this method to obtain mesoporous crosslinked polystyrene nanoparticles of approximately 30 nm with narrow PSD.

The best method for obtaining polymeric nanoparticles with  $D_p < 50$  nm has been the microemulsion polymerization, however,

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**Table I.** Recipes Used in the Microemulsion Copolymerizations of VAc and BuA

Run Component (g)	A		B		C		D	
	Initial	SC	Initial	SC	Initial	SC	Initial	SC
H <sub>2</sub> O	94.0		94.0		94.0		94.0	
SDS	3.03		3.03		0.75		3.03	
Brij <sup>®</sup> -35	1.01		1.01		0.25		1.01	
KPS	0.06		0.06		0.06		0.06	
VAc		50.62		51.80		30.60	2.60	51.60
BuA		8.93		9.15		5.40	0.46	9.10
Total VAc + BuA		59.55		60.95		36.00	3.06	60.60
Ra, (g/min)		0.30		0.50		0.30		0.30

SC = semicontinuous stage.

because of the low polymer content and the high surfactant concentrations that are required to form the initial microemulsion very low polymer/surfactant (P/S) ratios are obtained, which makes the process non-suited for practical applications (foaming during formulation and water sensitivity of latex films). To overcome these difficulties, some strategies have been developed: polymerizations in Winsor I-like systems (o/w microemulsion in equilibrium with an upper oil layer), the use of surfactants with high monomer solubilization capacity (which increases the microemulsion region), and the polymerization in semicontinuous regimes.<sup>4–6</sup> SHP is a simpler method than seeded semicontinuous polymerization for obtaining polymeric nanolatexes with high polymer content and higher P/S ratios. Recently, we reported the seeded microemulsion copolymerization of vinyl acetate (VAc) with butyl acrylate (BuA) under monomer starved conditions at different monomer addition rates, obtaining relatively high polymer content (ca. 40 wt %) with particle diameters below 50 nm and with homogeneous copolymer compositions through the reaction<sup>4</sup>. We found that it is possible to control the particle sizes, copolymer composition, and molecular weight by modifying the monomer mixture addition rate. However, it is well known that the emulsion and microemulsion copolymerization of VAc–BuA comonomers is complicated due to their significant differences in reactivity ratios ( $r_{\text{VAc}} = 0.05$  and  $r_{\text{BuA}} = 3.1^7$ ) which makes BuA react preferably, and in water solubilities (25 g/L for VAc and 1.5 g/L for BuA<sup>7</sup>) which causes that most of the BuA resides within the particles and a large amount of the VAc in the aqueous phase. The homogeneity of the copolymer composition within the particle is expected to be a strong function of the monomer composition in the feed and the method of monomer addition<sup>8</sup>. Also, the colloidal characteristics of the resulting latexes will depend on the polymerization conditions.

Polymer latexes of VAc are widely used in industrial and architectural applications (adhesives, coatings and paints) because of the physical characteristics of the films, low cost and availability. VAc can be copolymerized with other vinyl monomers to yield latex particles having a variety of molecular weights and particle—morphological properties depending on the structure of the comonomer and the copolymer composition. In particular VAc/BuA copolymers with a BuA composition of 15–25 wt % is

one of the most important industrial latexes which is widely used in the architectural coatings markets.

The purpose of the work reported here was to examine the effects of monomer addition rate and surfactant concentration on the kinetics, particle size, copolymer molecular weight, and composition in the semicontinuous heterophase copolymerization of VAc and BuA and compare with the results of the seeded semicontinuous process.

## EXPERIMENTAL

### Materials

VAc, BuA, KPS, hydroquinone and Brij-35<sup>®</sup> were purchased from Aldrich (Toluca, Mexico) ( $\geq 99\%$ ); SDS was from Fluka (Steinheim, Germany) ( $\geq 99\%$ ). VAc was washed with a 2N NaOH aqueous solution and dried with CaCl<sub>2</sub> and MgSO<sub>4</sub> for 12 h and subsequently vacuum distilled at 40°C. BuA was dried with CaCl<sub>2</sub> and vacuum distilled at 40°C. All the other reactants were used as received. Deionized, tridistilled grade water (obtained from a system of two ionic—interchange columns, Cole—Parmer Instruments Co., Vernon Hills, IL) and argon of ultrahigh purity from Infra<sup>®</sup> (Saltillo, Mexico) were used. Tetramethylsilane (TMS) from Aldrich was used as internal reference in <sup>1</sup>H NMR analyses.

### Copolymerizations

The recipes and reaction conditions are given in Table I. The polymerizations were carried out in a 250 mL glass—jacketed reactor equipped with magnetic stirring. The surfactant mixture, initiator, and water were charged to the reactor, cooled to 0°C and vacuum degassed, and then the system was saturated with argon. The reactor was heated to 60°C and then, the oxygen-free monomers mixture was added continuously to the reactor using a gas-tight syringe (Hamilton GASTIGHT<sup>®</sup>, Bonaduz, GR, Switzerland) adapted to a calibrated addition pump (Kd-Scientific<sup>®</sup>, Holliston, MA). After the semicontinuous addition period, the reactions were allowed to continue for 30 min. Run D was made by a seeded semicontinuous process (starting in batch mode and changing to semicontinuous process after 4.5 min of polymerization) to compare with the semicontinuous heterophase processes. Conversion was followed gravimetrically: samples (0.5–1.0 g) were withdrawn from the reacting system at

**Table II.** Final Characteristics of the Copolymers and Latexes

Run	$M_n \times 10^{-5}$	PDI <sup>a</sup>	P/S	PC, % <sup>b</sup>	Dp, nm <sup>c</sup>	PdS <sup>d</sup>
A	1.36	3.3	13.3	34.6	42.2	1.40
B	1.88	2.7	14.2	35.9	55.1	1.41
C	1.33	4.0	32.8	24.8	38.9	1.43
D	0.96	3.2	14.2	35.6	47.2	1.40

<sup>a</sup>PDI: Polydispersity index ( $M_w/M_n$ ), <sup>b</sup>PC: Copolymer content, <sup>c</sup>z-Average particle diameter, <sup>d</sup>PdS: Polydispersity index in size by QLS ( $D_{pw}/D_{pn}$ ).

given times and placed in vials (of known weight) immersed in an ice bath containing 0.5 g of an aqueous hydroquinone solution (0.4 wt %). The experiments were carried out by triplicate and the average values were reported. The total sampling amount was below 5% of total mixture. Then, the samples were weighed and freeze-dried (Labconco Freeze Dry System/R45). The weight of polymer was determined by subtracting the known weights of surfactants and hydroquinone from the total weight of the freeze-dried samples.

### Characterization

Particle size was measured by quasielastic-light-scattering (QLS) with a Zetasizer Nano S90 apparatus (Malvern) equipped with an argon laser. Measurements were performed at 25°C at an angle of 90°. Freeze-dried copolymer samples were placed in filter paper, washed with hot water (to remove the surfactants), and vacuum dried for 24 h at 40°C. Copolymer compositions were determined by <sup>1</sup>H NMR in an FTNMR Gemini 200 Varian apparatus (200 MHz), using 10 mg/mL sample solutions in *d*-chloroform. Average molecular weight and molecular weight distributions (MWD) of copolymers were determined in a Hewlett-Packard series 1100 gel permeation chromatograph equipped with a refractive index detector and using HPLC-grade tetrahydrofuran (Aldrich) as mobile phase. Because polystyrene standards were used, for correction of the GPC results, the weighted averages of the parameters in the Mark-Houwink equation,  $\alpha$  and  $K$ , were calculated using the cumulative copolymer composition (obtained previously by <sup>1</sup>H NMR spectrometry) following the procedure reported by Jovanovic and Dubé.<sup>9</sup>

## RESULTS AND DISCUSSION

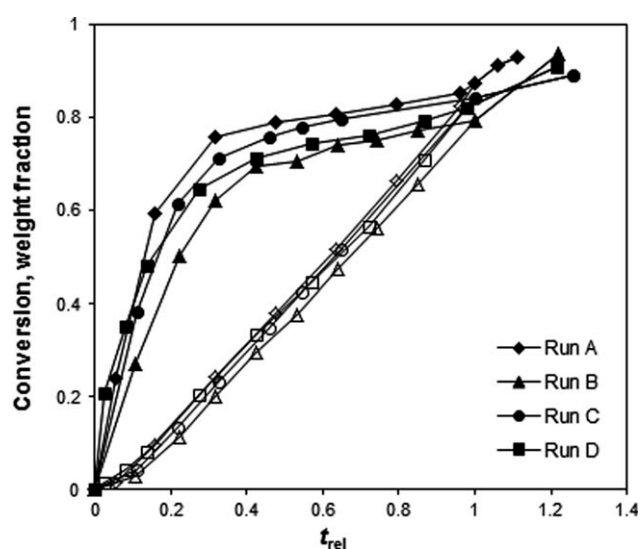
One of the most important factors influencing emulsion and microemulsion polymerization processes is the surfactant used to stabilize the system. In this work, the CMC of the mixture of SDS: Brij-35 (3: 1 wt/wt) was determined measuring the changes in density of solutions with different concentrations of the surfactants mixture in water at 25°C. The resulting value of CMC was 1.82 g/L. Then, all reactions were carried out at surfactant concentrations above the CMC, including the reaction with 1% of surfactants concentration.

The originally clear and translucent mixture charged to the reactor turned bluish and opaque upon polymerization indicating the start of the reaction. As more monomer reacts, the reaction mixture turns more opaque as a consequence of the growing polymer particles and increased monomer conversion. The final characteristics of the latexes and copolymers obtained by the

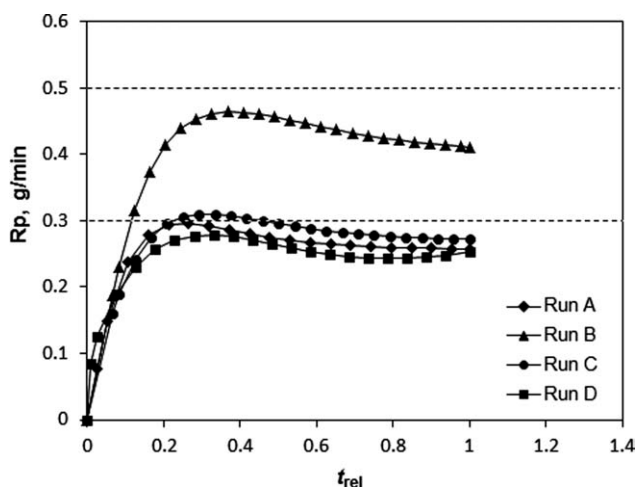
semicontinuous heterophase copolymerization of VAc and BuA are shown in Table II where it can be seen that latexes with high polymer contents (ca. 35 wt %) and P/S ratios around 14 were obtained for reactions with surfactant concentration of 4 wt % (Runs A, B, and D), while a smaller amount of polymer content was obtained when 1 wt % of surfactant was used (Run C), because monomers addition was stopped, before adding the same amount that in the other reactions, since the viscosity of the reaction mixture was so high that stirring became difficult. However, the P/S for run C was much higher (near 33).

Figure 1 shows the instantaneous ( $x$ ) and global ( $X$ ) fractional conversions as a function of relative time ( $t_{rel}$ ) for the different runs as detailed in Table I. Relative time (normalized time) was defined as the ratio of sampling time to the total addition time. Because monomers addition rate was different in run B; time was normalized to compare the polymerizations at the same amount of added monomer. Global conversion is given by the amount of copolymer formed at time  $t$  divided by the total amount of monomers added. Figure 1 reveals that in all cases instantaneous conversion increases rapidly and reaches high values at around a normalized time of 0.4 and for the same surfactant concentrations and similar monomers content (Runs A and B), the instantaneous conversion, at the same relative time, increases as  $R_a$  is decreased. Also, it is observed that the instantaneous conversion decreases when using the same  $R_a$  but lower surfactant concentration (Runs A and C). When the monomers addition was stopped, the reaction was allowed to continue for 30 minutes and in all cases a final global conversion ( $X$ ) of ca. 90% was obtained.

In a semicontinuous process,  $R_p$  can be controlled by the monomers feed rate,  $R_a$ , if this is low enough a point is reached where  $R_p$  is controlled by  $R_a$ .<sup>10</sup> Figure 2 shows the overall polymerization rate ( $R_p$ ) as a function of relative time.  $R_p$  was obtained by taking the derivative of the equation for the global conversion with respect to time multiplied by the total amount



**Figure 1.** Instantaneous (filled symbols) and global (empty symbols) conversions as a function of the relative time ( $t_{rel}$ ), at different polymerization conditions.



**Figure 2.** Overall polymerization rate ( $R_p$ ) vs. relative time for the different runs.

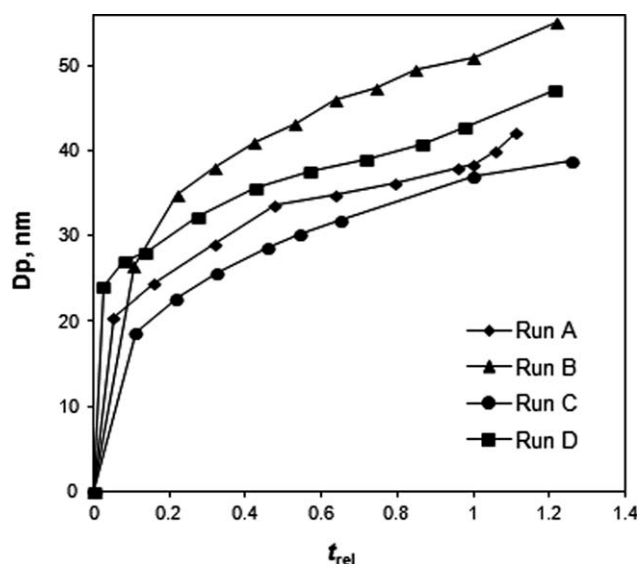
of monomers added ( $M_{tot}$ ). Therefore,  $R_p$  can be expressed by  $R_p = (M_{tot})dX/dt = [M_0 + (t - t_{pp}) R_a]dx/dt + xR_a$  where  $t_{pp}$  corresponds to the time of the batch polymerization period;  $R_a$ ,  $M_0$  and  $x$  represent the monomers addition rate, initial amount of monomers charged to the reactor and instantaneous conversion, respectively. In the case of SHP conditions,  $M_0$  and  $t_{pp}$  are equal to zero. In SHP, the monomer fed first saturates the water and then diffuses to the micelles, which causes that at the onset of the polymerization, reaction rate is slower than that of the seeded semicontinuous process. However, at later  $t_{rel}$  when comparing the polymerizations under SHP conditions (Runs A and C) with the seeded semicontinuous process (Run D) slightly higher  $R_p$  was obtained with SHP. Figure 2 also shows that for the slowest feed rate (0.3 g/min),  $R_p$  is very close to  $R_a$  which indicates that the reaction was carried out at highly monomer starved conditions.<sup>11</sup> When the feed rate was increased to 0.5 g/min, the  $R_p/R_a$  ratio only reaches a value of around 0.8.

It is clear that the rate of the addition of monomers has an important effect on the reaction rate in SHP. Besides, the mode of monomer addition affects the mechanism of particle formation, as well as their growth. For example, a process in which the monomer is added in the pre-emulsified form ( $ME_{fed}$ ) under monomer starved conditions, the surfactant associated to the monomer fed can reside in the water or can diffuse to the growing particles to stabilize them. However, if the same process is carried out in flooded conditions, a small part of the surfactant can be adsorbed at the monomer droplets. When surfactant accumulates in the water phase, secondary nucleation can occur (new particles formation) by homogeneous or micellar nucleation. This secondary nucleation contributes to the broadening of the PSD, which can be exploited to increase the polymer content. The solid (polymer) content of latexes is directly related with the latex viscosity. Thus, since small particles can be accommodated in the empty spaces between bigger particles, the high viscosity found in monodispersed latexes, can be reduced by forming latex with a relatively broad PSDs.<sup>12</sup>

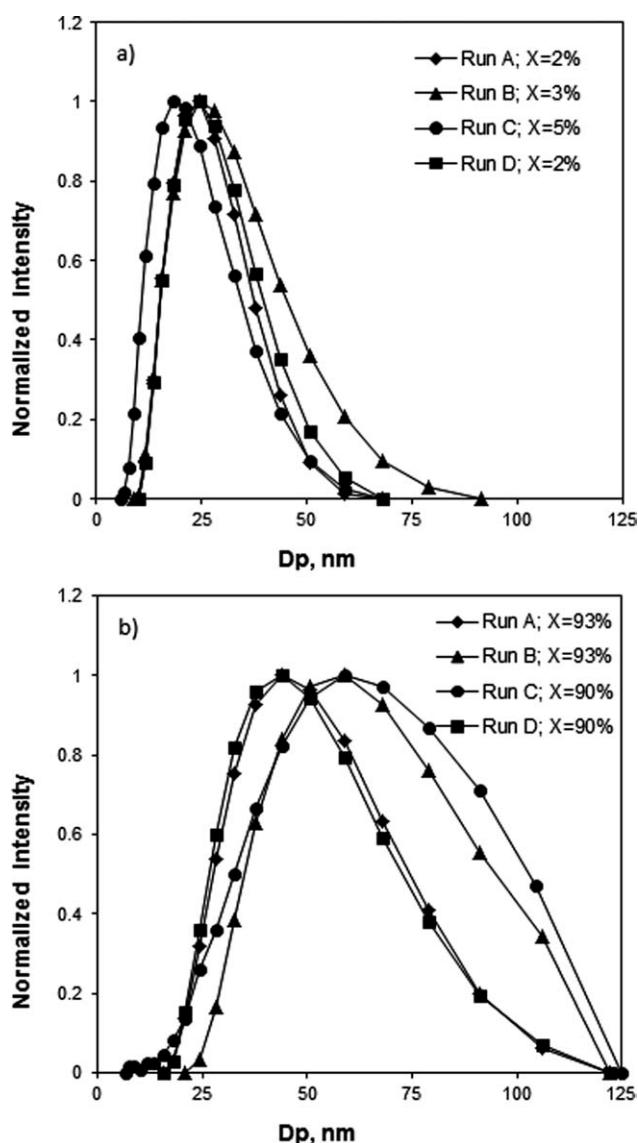
The evolution of the  $z$ -average particle diameter as a function of relative time at the different conditions is shown in Figure 3.

For the SHP runs,  $D_p$  increases from  $\sim 20$  nm at the beginning of reaction up to between 38.9 and 42.2 nm at the end of polymerization for the runs where  $R_a = 0.3$  g/min was used. When  $R_a$  was increased to 0.5 g/min (run B), a final  $D_p$  of 55.1 nm was obtained (Table II). These results show that although particles grew through the reaction, final particle size was still in the nanometric range. A quick analysis of the minimum particle diameter from which a monomeric radical reacts with another monomer molecule rather than escaping from the particle can be estimated with the following equation<sup>13</sup>:  $r^2 = 2Dt$ , where  $r$  stands for the mean displacement,  $D$  represents the diffusion coefficient, and  $t$  represents the time of displacement. At 60°C with a concentration of monomer in the polymer particles of 3.25 mol/L (estimated using thermodynamic equilibrium equations combined with mass balances<sup>14</sup>) and a value of  $k_p = 3700$  L/mol·s, a growing chain adds monomer at the rate of 12,000 molecules/s. Therefore, the new radical formed by chain transfer to polymer might react with a monomer molecule to start a chain after 1/12,000 s, but in this interval it might instead diffuse out of the particle. Using an approximated value<sup>13</sup> of  $D = 5 \times 10^{-8}$  cm<sup>2</sup>/s and  $t = 1/12,000$  s, a value for the mean displacement of  $2.88 \times 10^{-6}$  cm (or  $D_p = 58$  nm) is obtained as the limit of particle size at which a monomeric radical can escape rather than reacting there; however, this is only an approximate calculation. For Run B (Figure 3), average particle diameters between 50 and 55 nm were observed from the middle until the end of polymerization. For this reason, compared with Run A, the probability that a formed radical by chain transfer to monomer in run B initiates a new chain inside the particle rather than to escape is higher, which explains in part the higher particles sizes observed in Run B than those in Run A.

In Figure 4, the PSD at low conversions [Figure 4(a)] and at the end of polymerization [Figure 4(b)] are shown. At low conversions, for all reaction conditions, it can be observed narrow



**Figure 3.** Particle diameter ( $z$ -average) as a function of relative time for systems polymerized at different conditions.



**Figure 4.** Particle size distribution (PSD) obtained by QLS (a) at low conversions and (b) at the end of polymerization.

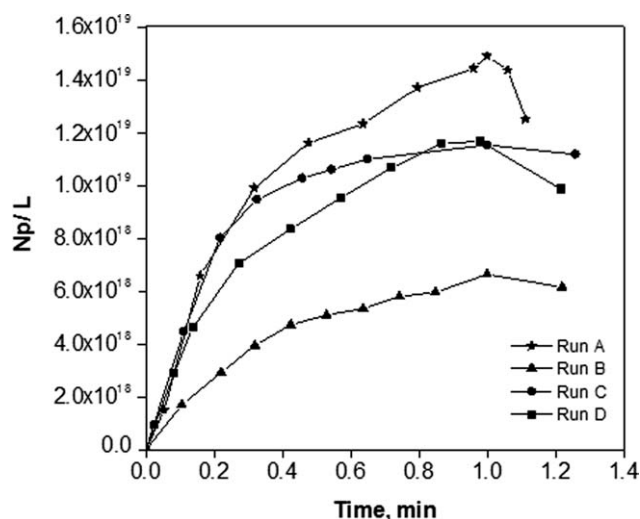
PSDs and, as reactions progress, the PSDs broaden ( $1.40 \leq \text{PdS} \leq 1.43$ , Table II) and are shifted to larger particle sizes. PdS represents the polydispersity index in sizes obtained by QLS and is related to the width of the PSD. For the lowest surfactant concentration used (Run C), the PdS of final latex was slightly larger. The broader PSD for run C is explained by the lower amount of surfactant used which favors particle growth until a point (around 24.8% of copolymer content) where due to the low amount of surfactant the system became unstable and coagulated (Table II).

The total number density of particles  $N_p$  was calculated assuming that all the particles were spherical and using eq. (1). Where  $M(t)$  is the weight (g) of monomer added at the time  $t$ ,  $D_p(t)$  is the experimental average diameter (cm) of the particles obtained by QLS,  $V$  is the reaction volume in L and  $\rho_p$  is the copolymer density ( $\text{g}/\text{cm}^3$ ).<sup>15</sup>

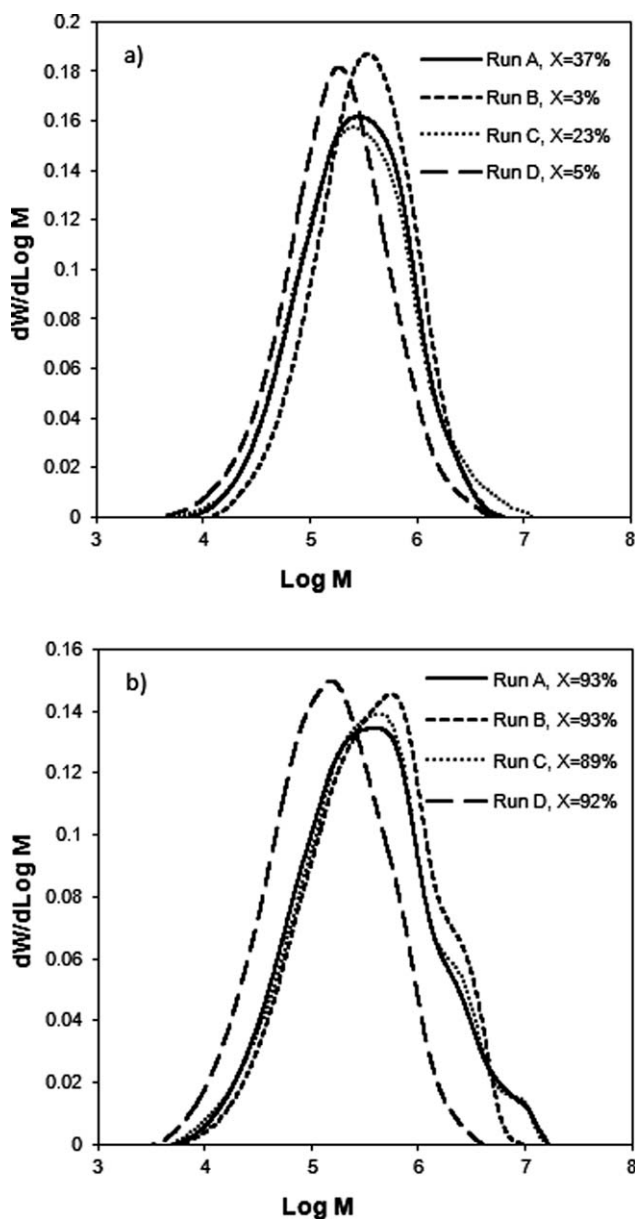
$$N_p = \frac{6M(t)x}{\pi D_p^3(t)\rho_p V} \quad (1)$$

Figure 5 shows the total number density of particles,  $N_p$ , as a function of relative time for the different runs. This figure depicts that  $N_p$  increases continuously as monomer is added, and when monomer addition is stopped,  $N_p$  decreases slightly due to some particle coagulation. Although some of the fed monomer was incorporated in existing particles causing their growth (Figure 3), new particles were formed through the reaction. The lower number of particles was obtained when using the highest  $R_a$  which is in agreement with other reports of SHP.<sup>1,11</sup>

It is known that PSDs have strong correlation with end-product quality indexes<sup>16</sup>. The highly multivariate nature of the polymerization processes, coupled with the complex and interactive characteristics of the underlying mechanisms, as well as the processes constraints, restrict the class of truly reachable PSDs.<sup>17</sup> In microemulsion polymerization (which is similar to the process used in this work), only one report was found addressing this issue.<sup>18</sup> In a batch process, the size of the particles can be controlled by both the surfactant and initiator concentrations ( $[I]$ ). A semicontinuous process lends itself to control the average size and the PSD of the particles at given  $[S]$  and  $[I]$ . For a SHP it is generally observed that  $N_p$  changes throughout the reaction (Figure 5). For seeded polymerizations, Britton et al.,<sup>19</sup> recommend to add between 5 and 10% of total monomer at the onset of the reaction ( $M_0$ ) and to allow its complete polymerization ( $\approx 100\%$  conversion) before starting the semicontinuous addition of the rest of the monomer ( $M_{\text{add}}$ ), as in Run D. This prepolymerization or pre-period of time, can be considered as a seeding stage. The main objective behind this procedure is to separate the particle nucleation step from the particle growth step to increase colloidal stability. Al-Bagoury and Yaacoub<sup>20</sup> found in the copolymerization of BuA with a saccharide monomer that increasing the ratio of  $M_0/M_{\text{add}}$  the size polydispersity index decreases when the polymerization pre-period of time is



**Figure 5.** Particle density number,  $N_p$ , as a function of relative time.



**Figure 6.** Molecular weight distributions (MWD) of the copolymers (a) at low conversions and (b) at the end of polymerization.

long enough to allow complete conversion of the initial monomer charged to the reactor. In the seeded polymerization reported here, the polymerization pre-period of time was not sufficiently long to avoid secondary nucleation during the reaction as can be seen in Figure 5 (run D) and the PSD at the end of the polymerization was similar to that of the SHP carried out at similar conditions (Run A).

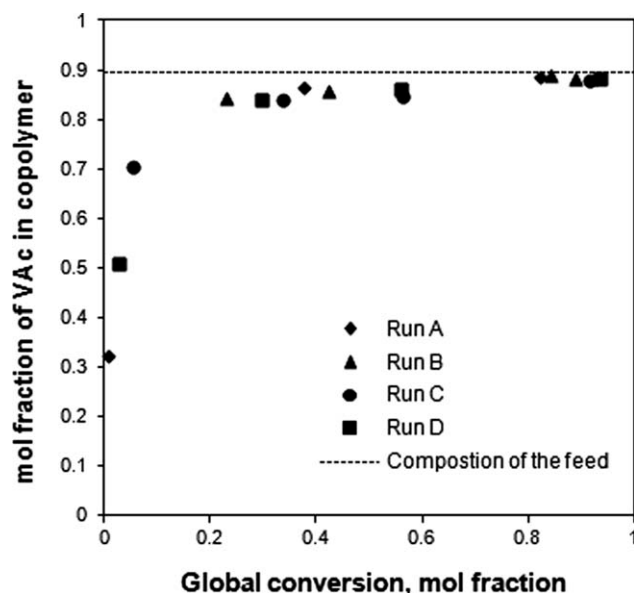
Table II shows that in SHP higher average number molecular weights are obtained than in the seeded process, independently of  $R_a$  and surfactant concentration. Table II also shows that for the SHP when  $R_a$  increases the molecular weights are displaced toward higher values (compare runs A and C with B). As discussed in our previous work for seeded semicontinuous polymerization,<sup>4</sup> under monomer starved conditions when the

monomer feed rate decreases the monomer concentration inside the particles also decreases and  $R_p$  slows down, which gives enough time for the entering of an oligomeric radical to terminate chain growth before chain transfer to monomer can take place and explains the low molecular weights obtained here and that by decreasing feed rate larger molecular weights are obtained. It has been reported that in SHP the dominant chain growth termination is by the entrance of a radical to a growing particle to terminate chain growth by mutual annihilation<sup>4</sup>.

Figure 6 shows the MWD of the copolymers at low conversions (a) and at the end of polymerization (b). At low conversions there are not significant differences among the MWDs of the different runs since all of them are mono-modal. However, at the end of reaction the MWD of polymers corresponding to SHP are broader than that obtained by seeded polymerization and show two or three populations (shoulders) at high molecular weights. These shoulders can be explained by chain transfer to polymer.

At the end of the polymerization, MWD of Runs A and C are very similar with three molecular weights populations. The MWD of Run B presents two populations, while MWD of Run D remains mono-modal through the polymerization. The PDI of the final copolymers varied between 2.7 and 3.3 for runs where 4 wt % of surfactant was used (Table II).

Because of the great difference in water solubility and in reactivity ratios between BuA and VAc it is not possible to obtain copolymers of homogeneous composition by batch microemulsion or emulsion copolymerization<sup>21</sup>. Figure 7 shows that for seeded conditions and SHP, instantaneous copolymer composition close to the feed composition was obtained early and through the reaction. Whereas the copolymer obtained by batch polymerization<sup>22</sup> showed a high drift in composition and at global conversions  $>0.2$ , practically only PVAc homopolymer was formed.



**Figure 7.** Cumulative copolymer composition as a function of global conversion for semicontinuous and batch microemulsion copolymerizations.

## CONCLUSIONS

SHP is a simpler method than seeded semicontinuous microemulsion polymerization for obtaining nanoparticles of copolymers with narrow PSD. By this method, latex with relatively high copolymer content (24–36 wt %) can be produced using much lower surfactant concentration than in batch microemulsion polymerization. Number-average molecular weights ( $M_n$ ) of polymer being formed throughout reaction depend in monomer addition rate. Homogeneous copolymer compositions were observed throughout the reaction for both, seeded conditions and SHP, which cannot be obtained by the usual batch process.

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## REFERENCES

- Ledezma, R.; Treviño, M.E.; Elizalde, L.E.; Pérez-Carrillo, L.A.; Mendizábal, E.; Puig, J.E.; López, R.G. *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 1463.
- Tauer, K. In *Colloids and Colloid Assemblies: Synthesis, Modification, Organization and Utilization of Colloid Particles*; Caruso, F., Ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, **2004**; Chapter 1, p 1.
- Esquivel, O.; Treviño, M. E.; Saade, H.; Puig, J.E.; Mendizábal, E.; López, R. G. *Polym. Bull.* **2011**, *67*, 217.
- Ovando-Medina, V. M.; Peralta, R. D.; Mendizábal, E. *Coll. Polym. Sci.* **2009**, *287*, 561.
- Xu, X.; Fei, B.; Zhang, Z.; Zhang, M. *J. Polym. Sci. Part A: Polym. Chem.* **1996**, *34*, 1657.
- Rabelero, M.; Zacarias, M.; Mendizábal, E.; Puig, J. E.; Dominguez, J. M.; Katime, I. *Polym. Bull.* **1997**, *38*, 695.
- Polymer Handbook*, 2nd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, **1975**.
- El-Aasser, M. S.; Makgawinata, T.; Vanderhoff, J. W.; Pichot, C. *J. Polym. Sci. Polym. Chem. Ed.* **1983**, *21*, 2363.
- Jovanovic, R.; Dubé, M. A. *J. Appl. Polym. Sci.* **2001**, *82*, 2958.
- Sajjadi, S.; Brooks, B. W. *Chem. Eng. Sci.* **2000**, *55*, 4757.
- Sajjadi, S.; Brooks, B. W. *J. Appl. Polym. Sci.* **2000**, *38*, 528.
- Schneider, M.; Claverie, J.; Graillant, C.; McKenna, T. F. *J. Appl. Polym. Sci.* **2002**, *84*, 1878.
- Harriot, P. *J. Polym. Sci. A-1 Polym. Chem.* **1971**, *9*, 1153–1163.
- Morton, M.; Kaizerman, S; Altier, M. W. *J. Colloid. Interface. Sci.* **1954**, *9*, 300–312.
- Martínez-Gutiérrez, H.; Ovando-Medina, V.M.; Peralta, R.D. *Macromol. Symp.* **2009**, *283*, 34.
- Doyle, F. J.; Harrison, C. A.; Crowley, T. *Comput. Chem. Eng.* **2003**, *27*, 1153.
- Wang, Y.; Doyle, F. J. *AIChE J.* **2004**, *50*, 3049.
- Suzuki, K.; Nomura, M. *J. Chem. Eng. Jpn.* **2003**, *36*, 1242.
- Britton, D.; Heatley, F.; Lovell, P.A. *Macromolecules* **2001**, *34*, 817.
- Al-Bagoury, M.; Yaacoub, E. *J. Appl. Polym. Sci.* **2003**, *90*, 2091.
- Kong, X. Z.; Pichot, C.; Guillot, J. *Eur. Polym. J.* **1988**, *24*, 485.
- Ovando-Medina, V. M.; Martínez-Gutiérrez, H.; Mendizábal, E.; Corona, M. A.; Peralta, R. D. *J. Appl. Polym. Sci.* **2009**, *111*, 329.