ELSEVIER

Polymer 42 (2001) 6923–6928

polymer

www.elsevier.nl/locate/polymer

A comparison of the characteristics of poly(vinyl acetate) latex with high solid content made by emulsion and semi-continuous microemulsion polymerization

N. Sosa[a], R.D. Peralta[a], R.G. López[a], L.F. Ramos[a], I. Katime[b], C. Cesteros[b], E. Mendizábal[c], J.E. Puig[c,*]

[a]*Centro de Investigación en Química Aplicada, Av. Ing. Enrique Reyna no. 140, Saltillo, Coah, 25100, Mexico*
[b]*Departamento de Química Física, Universidad del País Vasco, 48080 Bilbao, Spain*
[c]*Departamento de Ingeniería Química, Universidad de Guadalajara, Boul. M. García Barragán no. 1451, Guadalajara, Jal, 44430, Mexico*

Received 7 September 2000; received in revised form 7 February 2001; accepted 7 February 2001

Abstract

A method to produce poly(vinyl acetate) lattices with high-solid content (ca. 30 wt.%) without losing the characteristics of the microemulsion-made particles is presented. The method is based on the multi-stage addition of monomer to a latex produced by the polymerization of 3 wt.% vinyl acetate in three-component microemulsions stabilized with low concentrations (<1 wt.%) of the anionic surfactant, Aerosol OT, to produce lattices with up to 30 wt% solids. The results demonstrated that the poly(vinyl acetate) in the high solid-content latex has much smaller molar masses than the poly(vinyl acetate) in emulsion-made lattices with similar solid content. Also the microemulsion-made lattices contain particles two- to three-fold smaller than those obtained by emulsion polymerization.

Keywords: Microemulsion polymerization; High-solid content latex; Poly(vinyl acetate)

1. Introduction

Even though microemulsion polymerization is a novel process for producing colloidal polymers with unique sizes and shapes [1–4], it usually requires large amounts of surfactant and it yields low polymer-to-surfactant ratios. These drawbacks have hindered the industrial scale-up of microemulsion polymerization. Two approaches to overcome these shortcomings have emerged in the literature: one using surfactants that are able to solubilize large amounts of monomer in the non-polymerized microemulsion [5–9]; the other approach employs methods to increase the amount of polymer produced for a given amount of surfactant [10–15].

Aerosol OT is a well-known surfactant that usually forms inverse (w/o) microemulsions [16]. However, with polar monomers, this surfactant can yield microemulsions with low concentrations (1 wt.%) and monomer/surfactant ratios larger than three [5–8]. The polymerization of these microemulsions allows the formation of stable lattices with high-molar mass polymer particles of nanosize scale. Xu et al. [9] synthesized a special surfactant with a branch in the lipophilic unit of sodium 12-hexynoyloxy-9-octadecenate that was able to produce a microlatex with 16% polystyrene particles by microemulsion polymerization. However, the weight ratio of polystyrene-to-surfactant was close to one.

The synthesis of stable nanolattices with up to 15 wt.% solids by polymerizing styrene or methyl methacrylate in Winsor I-like systems containing only 1 wt.% DTAB (dodecyltrimethylammonium bromide) was reported in the mid 1990s [10,11]. The procedure was to layer pure monomer on top of a microemulsion where the polymerization was induced with a water-soluble redox initiator pair to produce rather monodisperse ($D_w/D_n < 1.13$) polystyrene particles with diameters smaller than 100 nm.

Our group produced high-solid content lattices (>35% polymer) by discontinuous addition of styrene to a reacting microemulsion [12]. However, the weight ratio of polymer to surfactant was rather low (<3). Ming et al. were able to obtain high-solid content lattices of several monomers by semi-continuous addition of monomer to a reacting microemulsion stabilized with low amounts of surfactant [13,14]. The size polydispersity was low ($D_w/D_n < 1.1$) and the

* Corresponding author. Tel.: +52-3-650-3401; fax: +52-3-619-4028.
E-mail address: puig_jorge@hotmail.com (J.E. Puig).

0032-3861/01/$ - see front matter
PII: S0032-3861(01)00157-4

weight ratio of polymer to surfactant was high (>20). More recently, Gan and collaborators devised a hollow-fiber feeding of styrene to a reacting microemulsion to obtain rather uniform polystyrene latex particles of about 40 nm and high molar masses ($1.0–2.2 \times 10^6$ g/mol) [15].

Here we report the synthesis of high solid-content lattices of poly(vinyl acetate) by multi-stage addition of monomer to a reacting microemulsion stabilized with only 1 wt.% AOT. The lattices obtained by this method have smaller particles and quite different average molar masses than the lattices with similar poly(vinyl acetate) content made by emulsion polymerization under similar reaction conditions.

2. Experimental section

Sodium bis(2-ethylhexyl)sulfosuccinate (Aerosol OT or AOT) was 98% pure from Fluka. It was used as received. Vinyl acetate (Aldrich) was distilled at 30°C under reduced pressure and argon atmosphere, stored at 4°C in dark vials and used within 30 h after distillation. Potassium persulfate (KPS) and hydroquinone were 99% pure from Aldrich and they were used as received. Water was doubly distilled and deionized.

A 200-ml glass reactor with magnetic stirring was employed to polymerize microemulsions made along an AOT/H_2O ratio of 1/99 (w/w) and 3 wt.% vinyl acetate. The concentration of KPS was 1 wt.% with respect to monomer. Prior to polymerization, the monomer and the AOT aqueous solution were degassed by cooling, pumping and heating cycles. The reacting system was continuously stirred and purged with argon during the entire reaction. After 1 h of reaction at 60°C, batches of the degassed vinyl acetate were added every hour in order to increase the solid content of the latex. Conversion was determined by gravimetry as follows: samples were withdrawn from the reacting system every hour and put in vials of known weight, immersed in an ice bath, that contained 0.5 g of a 0.4 wt.% hydroquinone aqueous solution. The samples were weighed to determine the amount of latex withdrawn and freeze-dried. The weight of polymer was estimated by subtracting the known weights of AOT and hydroquinone from the total weight of the freeze-dried sample.

Particle size was measured in a Malvern 4700 quasielastic light scattering (QLS) apparatus equipped with an Argon laser ($\lambda = 488$ nm). Measurements were performed at 25°C and at an angle of 90°. Intensity correlation data were analyzed by the method of cumulants to provide the average decay rate, $<\Gamma^2> (= q^2 D)$, where $q[= (4\pi n/\lambda)\sin(\theta/2)]$ is the scattering vector, n the index of refraction and D the diffusion coefficient. The measured diffusion coefficients were represented in terms of apparent diameters (D_z) by means of Stokes law assuming that the solvent has the viscosity of water. Lattices were diluted up to 100 times and filtered through 0.2 μm Millipore filters before QLS measurements to minimize particle–particle interactions and to remove dust particles. Size polydispersity (D_w/D_n) was calculated by the method of cumulants.

To measure average molar masses and molar mass distributions (MMD) by gel permeation chromatography (GPC), the freeze-dried samples were washed with hot water to remove most of the AOT and vacuum-dried. The dried material (polymer and AOT) was dissolved in chloroform. Then AOT-free polymer is precipitated by adding ethyl ether in a volume ratio of 10:1 with respect to chloroform. The precipitated polymer is then filtered, washed and dried, before being dissolved in HPLC-grade tetrahydrofuran (Merck), used as the mobile phase. The chromatographic equipment was composed of a Knauer HPLC64 pump, a Rheodyne injector (loop of 100 μl), two Polymer Laboratories PL-gel MIXED-B columns and a Knauer differential refractometer as a detector. All GPC measurements were calibrated with narrow polystyrene standards (PL) and the molecular weights were calculated with the viscosimetric equation for poly(vinyl acetate) in tetrahydrofuran [17]. This calibration was verified using poly(vinyl acetate) standards (Polymer Laboratories). Measured average molar masses coincide with values given by the supplier within 5%. Deconvolution of the MMD was made with a *peak fit*™ software (version 4.0 AISN Software Inc.).

3. Results

Fig. 1 shows conversion as a function of time for the polymerization at 60°C of vinyl acetate (3 wt.%) in microemulsions stabilized with 0.97 wt.% AOT. Polymerization is fast and conversions over 90% are achieved in less than 40 min. The resulting latex is bluish-transparent and very stable to coagulation.

After 1 h of reaction, vinyl acetate is added every hour as described in the Experimental Section. The temperature of reaction during the multi-stage addition is maintained at 60°C. Conversions of 95–100% are obtained after each

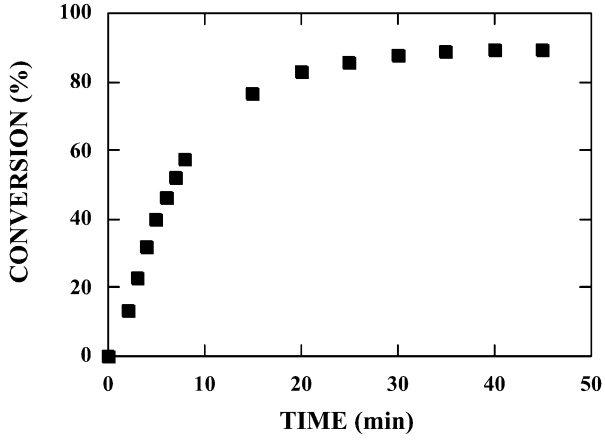

Fig. 1. Conversion as a function of time for the polymerization of a 3 wt.% vinyl acetate in a microemulsion containing a 1/99 weight ratio of AOT/H_2O, initiated at 60°C with KPS. (KPS/vinyl acetate = 0.01 by weight).

addition. Solid content up to 30% is obtained. The latex evolves from bluish-transparent to opaque and white at the end of the addition process as a result of the increase in number density and size of the poly(vinyl acetate) particles. High-solid content lattices were stable to coagulation for over four weeks. Then they became transparent because of hydrolysis to yield poly(vinyl alcohol). However, this drawback can be overcame by polymerizing at a pH of 7 [18].

Fig. 2 shows the evolution of particle size (D_z) upon successive additions of vinyl acetate to the reacting system. Data for four runs are reported to verify reproducibility. Size polydispersity (D_w/D_n) as a function of solid content is depicted in the inset of this figure. Clearly, a monotonic increase in particle size and a near-constant polydispersity are observed which indicates that the existing particles serve as seeds for monomer adsorption and growth and that nucleation of new particles appears to be a less important event.

The evolution of the number-average (M_n) and weight-average (M_w) molar masses is depicted in Fig. 3. Clearly, M_n remains practically unchanged whereas M_w increases steadily with monomer addition, that is, with increasing solid content in the latex. To understand this behavior, it is important to examine the MMD of the polymers obtained at various stages of the addition process.

Fig. 4 shows representative MMD of poly(vinyl acetate) obtained at different conversions during the polymerization of the parent microemulsion, that is, before the multi-stage addition of monomer. At low conversions, the peak is quite symmetric with a very small shoulder at the high-molar mass side of the distribution. As conversion increases, the MMD becomes wider and the high-molar mass shoulder increases. In fact, the high-molar mass shoulder becomes

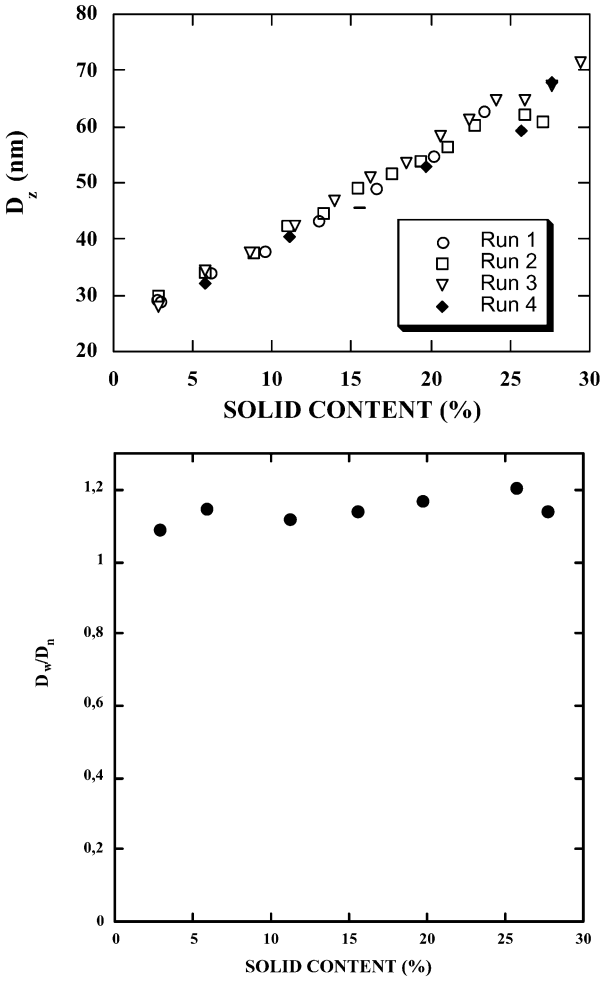

Fig. 2. Top: Particle size as a function of solid content in the latex during the multi-stage addition of monomer. Values for four different runs are reported. Bottom: Size polydispersity (D_w/D_n) at different solid content.

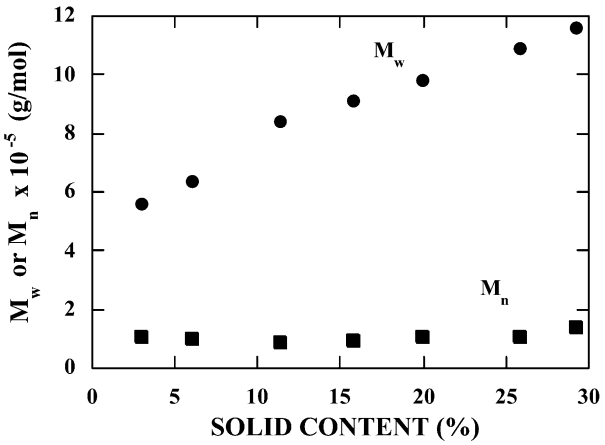

Fig. 3. Number-average (M_n) and weight-average (M_w) molar masses as function of solid content in the latex during the multi-stage addition of monomer.

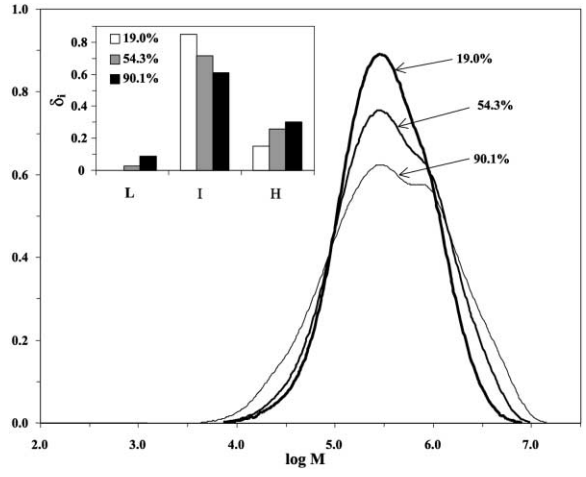

Fig. 4. Molar mass distributions (MMD) for three different conversions for the polymerization at 60°C of vinyl acetate (3 wt.% a/c) in microemulsion containing a 1/99 weight ratio of AOT/H_2O, initiated with KPS. (KPS/vinyl acetate = 0.01 by weight). Inset: Relative areas of the populations obtained by deconvolution of the MMD: low (L), intermediate (I) and high (H) molar mass populations.

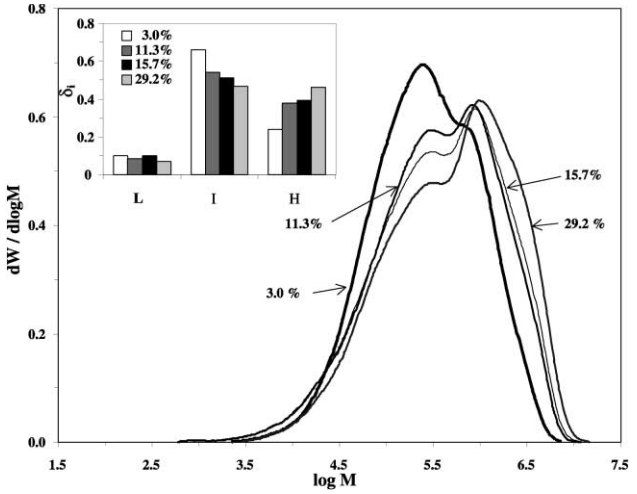

Fig. 5. Molar mass distributions of poly(vinyl acetate) withdrawn from lattices with different solid content produced by the multi-stage addition process at 60°C. Inset: Relative areas of the populations obtained by deconvolution of the MMD: low (L), intermediate (I) and high (H) molar mass populations.

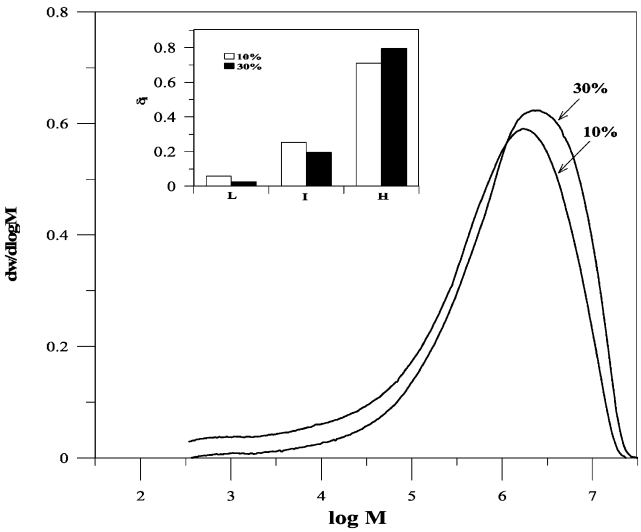

Fig. 6. Molar mass distributions of poly(vinyl acetate) produced by the polymerization of 10 and 30 wt.% monomer in emulsion media ($AOT/H_2O = 1/99$ by weight) initiated at 60°C with KPS (KPS/vinyl acetate = 0.01 by weight). Inset: Relative areas of the populations obtained by deconvolution of the MMD: low (L), intermediate (I) and high (H) molar mass populations.

a well-defined peak at high conversions. By deconvolution, each MMD was best-fitted to two or three Gaussian distributions, from which the number-average molar mass of each population, M_{ni}, and the relative areas under each curve, $\delta_i (\equiv A_i/A_T$, where A_i is the area of the Gaussian curve i and A_T is the area under the whole MMD), were estimated. The distributions are labeled as low ($M_{n1} \approx 34{,}000$–$39{,}000$ g/mol), intermediate ($M_{n2} \approx 160{,}000$–$180{,}000$ g/mol) and high ($M_{n2} \approx 1 \times 10^6$ g/mol). Fig. 4 shows the relative areas under each curve. At low conversions, only two populations are observed where most of the polymer is in the intermediate-molar mass distribution (Fig. 4). As conversion increases, a small population of the low-molar mass polymer evolves whereas the high-molar mass population grows and the intermediate-molar mass population shrinks (Fig. 4).

Fig. 5 depicts representative MMD of the polymers withdrawn from lattices with different solid content. Again, each distribution seems to display two well-defined populations, one at intermediate- and another at high-molar mass. However, deconvolution of these distributions reveals the existence of three populations, whose relative areas are depicted in Fig. 5. It is noteworthy that the high-molar mass population grows at expense of the intermediate-molar mass population.

To stress the novelty of our method in producing high-solid content lattices of poly(vinyl acetate) with different characteristics than those obtained by emulsion polymerization, reactions in emulsions containing 10 and 30 wt.% vinyl acetate were performed, using the same concentration of AOT and similar reaction conditions. The molar masses ($M_w \approx 2.8 \times 10^6$ and 3.4×10^6 g/mol for the 10 and 30 wt.% emulsions, respectively) and particle size ($D_z = 89$ and 169 nm for the 10 and 30 wt.% emulsions, respectively) are much larger than those obtained by microemulsion polymerization (Fig. 4). The MMD of the emulsion-made polymers is skewed toward the high-molar mass side with a shoulder in the intermediate-molar mass region. Deconvolution of the MMD of the emulsion-made polymers also reveals three populations (Fig. 6). Now, the dominant population is the high-molar mass one, as expected from the emulsion polymerization process since chain transfer reactions to polymer are known to be dominant at high conversions [19–22].

4. Discussion and conclusions

Processes to improve the polymer/surfactant weight ratio in microemulsion polymerization have been addressed since the mid 1990s [10–15]. In all these processes more monomer is added to the reacting microemulsion to take advantage of the excess surfactant for particle stabilization which permits the production of lattices with high solid content. Usually in these methods, the characteristics of the polymer particles are maintained (high molar mass and small particle size). Here we use a multi-stage addition method to produce lattices of poly(vinyl acetate) with up to 30% solids. The novelty of this process is that even at solid contents as high as 30%, the poly(vinyl acetate) produced here has a much smaller population of high-molar mass polymer—which is known to form by chain transfer reactions to polymer [19–22], compared to that made by emulsion polymerization. Also the lattices have quite smaller particles than those usually obtained by emulsion

polymerization of this monomer [23]. More important, this is achieved with less than 1 wt.% surfactant.

Previously we reported that the polymerization of vinyl acetate in AOT microemulsions yields an unusually low-molar mass polymer even at high conversions, contrary to what happens in emulsion polymerization [8]. At low conversions, chain termination in emulsion polymerization is mainly due to chain transfer reactions to monomer which produce an $M_n \approx 300{,}000–500{,}000$ g/mol and a low MMD polydispersity; however, at conversions larger than about 30%, chain transfer to polymer and terminal double bond reactions lead to highly branched polymer with high polydispersity ($M_w/M_n \approx 10–15$), particularly at high conversions, where the reacting particles contain a large number density of macromolecules [19–22].

Here, our results for the polymerization of vinyl acetate in AOT microemulsions disclose lower average molar masses (Fig. 3). The MMD becomes wider as conversion increases in the reacting parent microemulsion (Fig. 4) and as the multi-stage addition of monomer proceeds (Fig. 5). Deconvolution of the MMD shows the existence of at least three populations during the polymerization of the parent microemulsion (Fig. 4) and during the multi-stage process (Fig. 5): one of low-molar mass ($M_n \approx 34{,}000–39{,}000$ g/mol), another of intermediate-molar mass ($M_n \approx 160{,}000–180{,}000$ g/mol), and a third one of high-molar mass ($M_n \approx 1 \times 10^6$ g/mol). The low-molar mass population grows with conversion during the polymerization of the parent microemulsion (Fig. 4), but it remains fairly constant during the addition process (Fig. 5). The intermediate-molar mass population, which is the dominant population, diminishes with conversion during the polymerization of the parent microemulsion (Fig. 4) and during the addition process (Fig. 5), whereas the high-molar mass population grows at expense of the intermediate-molar mass one.

At present we cannot provide a feasible explanation for the presence of the low-molar mass population. One hypothesis is that this population arises from the polymerization in the aqueous phase, where the chains could reach high degrees of polymerization (390–450 units) [24]. However, it has been reported recently that the oligomeric radicals in vinyl acetate emulsion polymerization become surface active with a degree of polymerization of about seven, and then they can enter the existing particles with high efficiency [25,26]. Moreover, the probability of an aqueous-phase oligomeric radical growing to a high degree of polymerization is very low in the high number density of particles present in microemulsion. Another possibility is that the low-molar mass population may be an artifact of the deconvolution procedure. However, the deconvolution of the MMD with only two populations did not provide a satisfactory fit. On the other hand, M_n and the low-side of the MMD are very sensitive to base line subtraction and setting, and so, quantitative discussion of this population may not be relevant.

Elsewhere we demonstrated that the intermediate-molar mass population is mainly produced by chain transfer reactions to monomer [8]. The reason seems to be the high escaping probability of monomeric radicals produced by chain transfer due to the smaller particle size in microemulsion polymerization. In fact, we have shown that as particle size increases, chain transfer reactions to polymer start to become important and when particle size is large enough, they dominate at high conversions [8,27–29]. Hence, the high-molar mass population is mainly produced by chain transfer reactions to polymer.

Upon addition of more monomer during the multi-stage addition process, particles grow. This implies that polymer particles formed during the polymerization of the parent microemulsion are acting as seeds to recruit monomer and continue the reaction there. On the other hand, nucleation of new particles appears to be a less important event probably because of the unfavorable partitioning of monomer into the aqueous phase. The fact that size polydispersity is fairly constant during the addition process (Fig. 3) gives support to this hypothesis. Moreover, further evidence can be provided by a crude calculation. Assuming that particle size is uniform and equal to the QLS-measured diameter and that all monomer added is evenly distributed among the particles and reacts there to near 100% conversion, particles will grow roughly to a size equal to the cubic root of the ratio of the final solid content to the original solid content times the initial particle size. This calculation assumes, of course, that the final size is also monodisperse. Then, lattices with 6 and 27% solid content should have particles larger than those of the original latex (29 nm) by a factor of $(2)^{1/3}$ and $(9)^{1/3}$, respectively. This will give particles of 36 and 60 nm for such lattices which are quite close to the experimental values of 34 and 64 ± 4 nm, respectively. However, a transmission electron microscopy study is required to confirm this hypothesis. Parallel to particle growth, it is noteworthy that the population of the high-molar mass polymer increases, which gives support to our hypothesis that the escaping probability of monomeric radicals from the reacting particles diminishes as particle size increases, enhancing the probability of chain transfer reactions to polymer.

As expected, the latex particles produced by emulsion polymerization are bigger than the ones produced by the multi-stage addition process at equal solid content. Moreover, the average molar masses are much larger than the ones produced by microemulsion polymerization. Deconvolution of the MMDs of the emulsion-made polymers also discloses the existence of three populations (Fig. 6). However, here the high-molar mass population is much larger than the other two, as expected for this process since chain transfer reactions to polymer prevail at high conversions in emulsion polymerization [19–22].

In summary, we have presented a method to increase the solid content in lattices of poly(vinyl acetate) with smaller sizes and average molar masses than in those with similar solid content prepared by emulsion polymerization.

Acknowledgements

This work was supported by CONACYT (Grant no. 31262-U) and the Universidad de Guadalajara.

References

[1] Candau F. In: Marks HF, Bikales NM, Overberger CG, Menges G, editors. Encyclopedia of polymer science, Vol. 9. New York: Wiley, 1987. p. 718–24.
[2] Dunn AS. In: Eastwood GC, Ledwith AP, Sigwalt P, editors. Comprehensive polymer science, Vol. 4. Oxford: Pergamon Press, 1988. p. 219–24.
[3] Candau F. In: Eastwood GC, Ledwith AP, Sigwalt P, editors. Comprehensive polymer science, Vol. 4. Oxford: Pergamon Press, 1988. p. 225–8.
[4] Puig JE. In: Salamone JP, editor. Encyclopedia of polymeric materials, Vol. 6. Boca Raton: CRC Press, 1996. p. 4333–41.
[5] Texter J, Oppenheimer L, Minter JR. Polym Bull 1992;27:487–94.
[6] Full AP, Puig JE, Gron LU, Kaler EW, Minter JR, Mourey TH, Texter J. Macromolecules 1992;25:5157–64.
[7] Macías ER, Rodríguez-Guadarrama LA, Cisneros BA, Castañeda A, Mendizábal E, Puig JE. Colloids and Surfaces 1995;103:119–25.
[8] Sosa N, Zaragoza EA, López RG, Peralta RD, Katime I, Becerra F, Mendizábal E, Puig JE. Lagmuir 2000;16:3612–9.
[9] Xu X, Zhang Z, Wu H, Ge X, Zhang M. Polymer 1998;39:5245–8.
[10] Gan LM, Lian N, Chew CH, Li G. Langmuir 1994;10:2197–201.
[11] Loh SE, Gan LM, Chew CH, Ng SCJ. Macromol Sci Pure Appl Chem 1996;A33:371–84.
[12] Rabelero M, Zacarías M, Mendizábal E, Puig JE, Domínguez JM, Katime I. Polym Bull 1997;38:695–700.
[13] Ming W, Jones FN, Fu S. Polym Bull 1998;40:749–56.
[14] Ming W, Jones FN, Fu S. Macromol Chem Phys 1998;199:1075–9.
[15] Xu XJ, Chew CH, Siow KS, Wong MK, Gan LM. Langmuir 1999;15:8067–71.
[16] Eicke HF. In: Eicke HF, editor. Interfacial phenomena in apolar media. New York: M. Dekker, 1987. p. 41 and references therein.
[17] Goedhart G, Opschoor A. J Polym Sci 1970;A2:1227–33.
[18] Sosa N, López RG, Peralta RD, Katime I, Becerra F, Mendizabal E, Puig JE. Macromol Chem Phys 1999;200:2416–20.
[19] Friis N, Nyhagen LJ. Appl Polym Sci 1973;17:2311–27.
[20] Friis N, Goosney D, Wright JD, Hamielec AE. J Appl Polym Sci 1974;18:1247–59.
[21] Friis N, Hamielec AEJ. Appl Polym Sci 1975;19:97–113.
[22] Nomura M, Harada M, Eguchi W, Nagata S. Polym Prep Am Chem Soc Div Polym Chem 1975;16:217–27.
[23] Nomura M, Harada M, Nakagawara K, Eguchi W, Nagata N. J Chem Eng Japan 1971;4:160–6.
[24] Litt M, Patsiga R, Stannett V. J Polym Sci 1970;8:3607–49.
[25] Gilbert RG. Emulsion polymerization: a mechanistic approach. London: Academic Press, 1995.
[26] Poehlein G. Macromol Symp 1995;92:179.
[27] López RG, Treviño ME, Salazar LV, Peralta RD, Becerra F, Puig JE, Mendizábal E. Polym Bull 1997;38:411–7.
[28] Treviño ME, López RG, Peralta RD, Becerra F, Mendizábal E, Puig JE. Polym Bull 1999;42:411–7.
[29] López RG, Treviño ME, Peralta RD, Cesteros C, Katime I, Flores J, Mendizábal E, Puig JE. Macromolecules 2000;33:2848–54.