ELSEVIER

Polymer 43 (2002) 2993–2999

polymer

www.elsevier.com/locate/polymer

Polymerization of vinyl acetate in microemulsions stabilized with dodecyltrimethylammonium bromide and cetyltrimethylammonium bromide

M. Gómez-Cisneros[a], R.G. López[a,*], R.D. Peralta[a], L.C. Cesteros[b], I. Katime[b], E. Mendizábal[c], J.E. Puig[c]

[a]Centro de Investigación en Química Aplicada, Boul. Ing. Enrique Reyna #140, Saltillo, Coah 25100, Mexico
[b]Departamento de Química Física, Grupo de Nuevos Materiales, Universidad del País Vasco Campus Leioa, Bilbao 48080, Spain
[c]Departamento de Ingeniería Química, Universidad de Guadalajara, Boul. M. García Barragán #1451, Guadalajara, Jal 44430, Mexico

Received 27 December 2001; received in revised form 25 January 2002; accepted 28 January 2002

Abstract

The polymerization of vinyl acetate in microemulsions stabilized with dodecyltrimethylammonium bromide (DTAB), cetyltrimethylammonium bromide (CTAB) or mixture of these surfactants is examined. The polymerization rate diminishes as the surfactant mixture becomes richer in DTAB. Also, particles grow with conversion and become increasingly larger as the DTAB content in the mixture increases. Our results indicate that chain transfer reactions to monomer are more important than chain transfer reactions to polymer even at high conversions with CTAB. However, as the content of DTAB increases, bimolecular termination induced by coagulation, terminal double bond polymerization and chain transfer reactions to polymer become increasingly more important. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Microemulsion polymerization; Cationic surfactants; Vinyl acetate polymerization

1. Introduction

Emulsion and microemulsion polymerization are processes that allow the synthesis of colloidal particles of high-molar mass polymer with fast reaction rates [1–3]. This is because the free radical polymerization reactions are carried out in compartmentalized loci. Nevertheless, the reaction mechanisms of these two processes are quite distinct and frequently, the characteristics of the final products are different [2–9].

Among the polymers produced by emulsion polymerization, poly(vinyl acetate) stands out inasmuch as more than 20% of the total production is associated with this polymer [10]. However, because of chain transfer reactions to polymer at high conversions during the emulsion polymerization of vinyl acetate (VA), highly branched polymers are obtained [11–14].

Recently, we reported the polymerization of VA in three-component cationic or anionic o/w microemulsions [15–17]. The most important result is that chain transfer reactions to monomer control chain termination in microemulsion polymerization, even at high conversions, in contrast to emulsion polymerization.

Here, we report the polymerization of VA in microemulsions stabilized with the cationic surfactants dodecyltrimethylammonium bromide (DTAB) and cetyltrimethyl-ammonium bromide (CTAB), alone or mixed in different weight ratios. Our results indicate that chain transfer to monomer is the dominant mechanism for polymerization stabilized with CTAB even at high conversions. Nevertheless, as the content of DTAB increases, other mechanisms take place. We provided an explanation in terms of differences in particle size and of the number density of polymer particles.

2. Experimental section

CTAB (99% + pure from Aldrich) and DTAB (99%+ pure from Tokyo Kasei) were re-crystallized from a 50/50 (v/v) acetone/ethanol mixture. VA, with purity higher than 99% from Aldrich, was dried with $CaCl_2$, distilled at 30 °C

---

* Corresponding author. Tel.: +52-844-438-9847; fax: +52-844-438-9839.

E-mail address: glopez@polimex.ciqa.mx (R.G. López).

PII: S0032-3861(02)00121-0

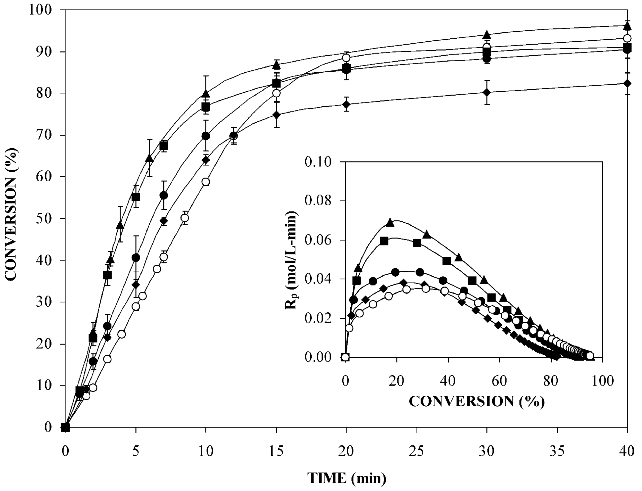

Fig. 1. Conversion as a function of time for the polymerization at 60 °C of VA in microemulsions stabilized with CTAB/DTAB in w/w: 0/100 (○); 25/75 (◆); 50/50 (●); 75/25 (■); 100/0 (▲). Inset: Reaction rate as a function of conversion.

under reduced pressure and argon atmosphere, stored at 4 °C in dark vials and used within 30 h after distillation. 2,2′-Azobis(2-amidinopropane)dihydrochloride (V-50) from Wako Chem., was re-crystallized from methanol. Hydroquinone (99% pure from Aldrich) was used as received. Triple-distilled and de-ionized water was drawn from a Cole-Parmer ionic exchange system.

A 100 ml glass reactor with cooling jacket and magnetic stirring was employed for the reactions at 60 °C in microemulsions containing 4 wt% VA and 5/95 weight ratio of surfactant(s)/water. The surfactants employed were DTAB, CTAB or some of their mixtures in different weight ratio. The concentration of V-50 was maintained constant and equal to 0.3 wt% with respect to monomer. Prior to polymerization, the monomer and the aqueous solutions of surfactant and initiator were degassed by cooling-pumping-and-heating cycles. The reacting system was continuously stirred during the entire reaction and purged with argon each time that a sample was taken. To maintain the reaction temperature constant, thermostated water was re-circulated through the reactor jacket. The reaction temperature was monitored with a thermocouple inserted in the reacting medium. Conversion was determined gravimetrically by withdrawing samples from the reacting system according to a previously defined program 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 in a Labconco Freeze Dry System/Freezone 6. The weight of polymer was estimated by subtracting the known weights of surfactant and hydroquinone from the total weight of the freeze-dried sample.

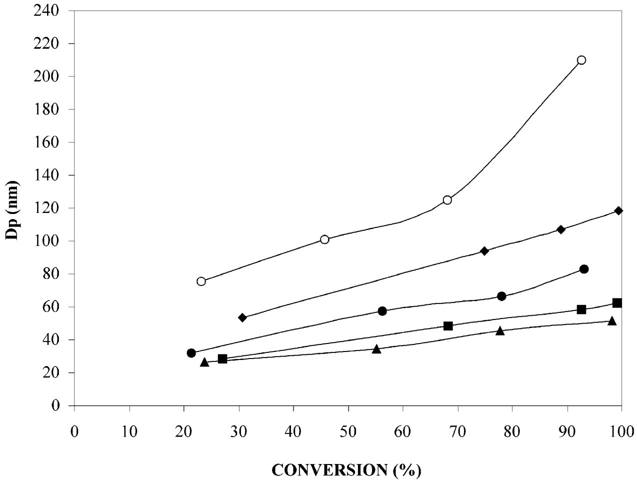

Fig. 2. Particle size, measured by QLS, versus conversion for the polymerization at 60 °C of VA in microemulsions stabilized with CTAB/DTAB in w/w: 0/100 (○); 25/75 (◆); 50/50 (●); 75/25 (■); 100/0 (▲).

Particle size was measured at 25 °C and an angle of 90° in a Malvern 4700 quasielastic light scattering (QLS) apparatus equipped with an Argon laser ($\lambda = 488$ nm). Intensity correlation data were analyzed by the method of cumulants to provide the average decay rate, $\langle \Gamma^2 \rangle (= q^2 D)$, where $q[= (4\pi n/\lambda)\sin(\theta/2)]$ is the scattering vector; n, the index of refraction; D is 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. Latexes 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.

To measure average molar masses and molar mass distributions (MMD) by gel permeation chromatography (GPC), the surfactant was eliminated from the freeze-dried samples by dialysis using porous membranes (Sigma) with exclusion size corresponding to molar masses larger than 12 000 g/mol. The dialyzed solution was then subjected to three freezing-and-thaw cycles to coagulate the polymer. The surfactant-free polymer was recovered by filtration, washed with de-ionized water and dried, before being dissolved in HPLC-grade tetrahydrofuran (Merck), which is used as the mobile phase. The chromatographic equipment was composed of a Knauer HPLC64 pump, a Rheodyne injector loop of 100 μl for poly(vinyl acetate) in tetrahydrofuran [18]. This calibration was verified using poly(vinyl acetate) standards (Polymer Laboratories). Measured average molar masses coincide with values given by the supplier within 5%.

3. Results

Fig. 1 shows conversion versus time for the polymerization at 60 °C of VA in microemulsions stabilized with CTAB, DTAB or their mixtures. Error bars represent the standard deviations calculated from at least four replicated runs. In all cases, reaction rates are fast and conversions

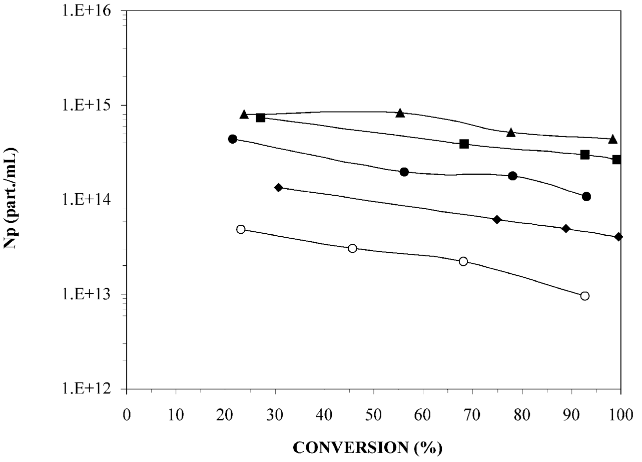

Fig. 3. Number density of particles versus conversion for the polymerization at 60 °C of VA in microemulsions stabilized with CTAB/DTAB in w/w: 0/100 (○); 25/75 (◆); 50/50 (●); 75/25 (■); 100/0 (▲).

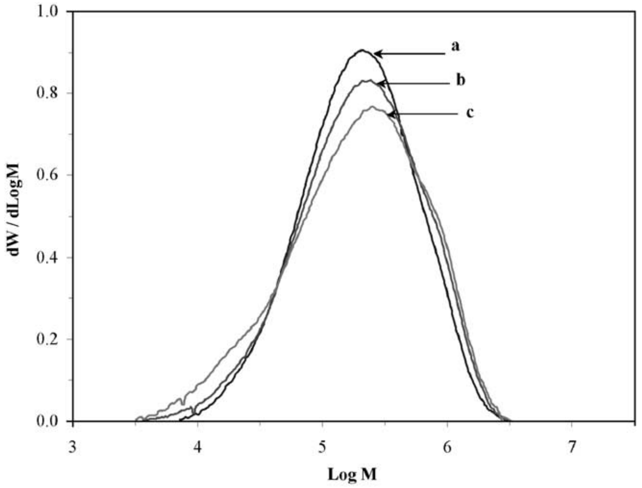

Fig. 4. MMD at different conversions for the polymerization at 60 °C of VA in microemulsions stabilized with 100/0 (w/w) CTAB/DTAB: (a) 28.4, (b) 55, and (c) 96.3%.

higher than 80% are achieved in less than 40 min. The initially transparent microemulsions evolve into bluish-to-opaque latexes as the reaction proceeds. Reaction rates increase as the ratio of CTAB/DTAB goes from 0/100 to 100/0 (inset in Fig. 1). Also, the reaction rates as a function of conversion depict only two intervals, which is typical of microemulsion polymerization [3]. Note that the reaction carried out in the microemulsion stabilized with DTAB speeds up after about 15 min and the final conversion is near to that obtained in the reaction accomplished with CTAB. Nevertheless, the maximum reaction rate follows the order (CTAB/DTAB): $0/100 < 25/75 < 50/50 < 75/25 < 100/0$.

Fig. 2 depicts the evolution of particle size during the polymerization of VA in microemulsions stabilized with CTAB, DTAB or their mixtures. At early stages of reaction, the free radicals generated by V-50 in the aqueous phase would likely react with the dissolved VA molecules to form oligo-radicals as in emulsion polymerization [19]. However, as these species grow, they could either enter microemulsion droplets to continue the reaction there or precipitate to form precursor particles by adsorption of surfactant [20]. These particles grow slightly through the reaction effected in the presence of CTAB or the CTAB-rich mixture. However, as the amount of DTAB in the surfactant mixture increases, particles grow faster and to larger sizes with monomer conversion. This growth is more pronounced at the end of the reaction and it is particularly noticeable for the reaction carried out with DTAB. The largest particle size is obtained with DTAB (Fig. 2).

The number density of particles, N_P, as a function of conversion is shown in Fig. 3. Here, N_P was roughly estimated assuming that the particle size measured by QLS is uniform. Even though this is an uncertain assumption because of the well-known broadening of the size distribution, the relatively great differences between particle sizes may overcome the errors introduced. N_P diminishes with increasing conversion regardless of the surfactant or surfactant mixture used. This decrease is more pronounced as the mixtures become richer in DTAB.

Table 1 depicts weight-average molar masses (M_w) and the polydispersity index (M_w/M_n) at different conversions for reactions carried out in the presence of CTAB, DTAB and their mixtures. M_w increases as the reaction proceeds; also, M_w at the end of the reaction becomes larger as the DTAB content increases in the surfactant mixtures. In fact, M_w of the poly(vinyl acetate) obtained with DTAB is approximately two- to three-times larger than that of the polymer prepared with CTAB. M_w/M_n is also larger for the reactions carried out in the presence of DTAB ($4 \leq M_w/M_n \leq 6$) compared to those achieved with CTAB ($3 \leq M_w/M_n \leq 4$).

To understand better these differences, it is important to

Table 1
Weight-average molar masses (M_w) and polydispersity index (M_w/M_n) at different conversions for the polymerization at 60 °C of VA in CTAB, DTAB or their mixtures in different weight ratios (CTAB/DTAB)

	0/100 (conv. %)			25/75 (conv. %)			50/50 (conv. %)			75/25 (conv. %)		100/0 (conv. %)		
	25.4	59.5	87.5	16.6	44.4	100.0	21.4	56.2	93.1	18.7	93.1	28.4	55.0	96.3
$M_w \times 10^{-5}$	5.5	7.2	8.0	4.9	6.6	7.4	5.0	6.7	6.8	4.4	5.8	3.1	3.4	3.5
M_w/M_n	4.33	4.8	6.3	3.2	6.1	8.8	3.1	5.5	6.6	3.0	5.0	2.8	3.4	4.4

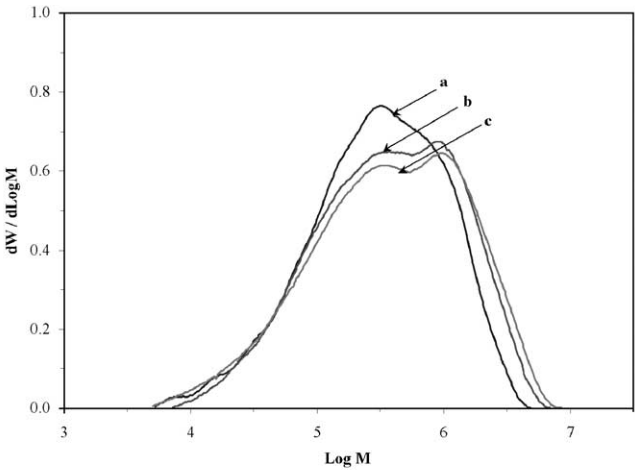

Fig. 5. MMD at different conversions for the polymerization at 60 °C of VA in microemulsions stabilized with 0/100 (w/w) CTAB/DTAB: (a) 25.4, (b) 59.5, and (c) 87.5%.

examine the whole MMD obtained by GPC. Figs. 4 and 5 depict the MMD at three levels of conversions (low, medium and high) for the reactions carried out with CTAB and DTAB, respectively. For the reaction stabilized with CTAB, the MMD is quite symmetric at low conversions. However, as the reaction advances, a shoulder evolves at the high-molar mass side of the distribution and becomes quite noticeable at final conversions. For the reaction accomplished with DTAB, on the other hand, the MMD is not symmetric even at low conversions since a shoulder can be distinguished at the high-molar mass side of the distribution. As conversion increases, this shoulder becomes a well-defined peak and at final conversions the distribution is clearly bimodal with a larger high-molar mass peak.

Fig. 6 displays the MMD for the poly(vinyl acetate) obtained at the end of the reaction with the pure surfactants or their mixtures. As described earlier, the MMD for CTAB displays a shoulder in the high-molar mass side of the distribution whereas the MMD for DTAB is clearly bimodal, with a larger high-molar mass peak. MMD of the polymers produced with the mixtures are also bimodal but the high-molar mass peak is smaller than the low-molar mass peak for mixtures richer in CTAB and becomes increasingly larger as the amount of DTAB in the mixture increases.

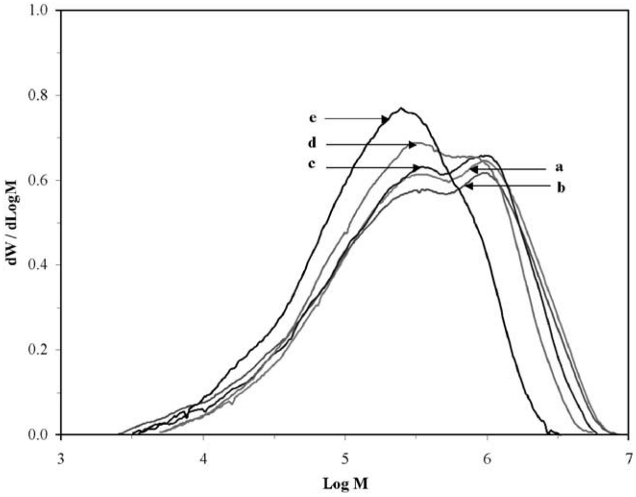

Fig. 6. MMD of poly(vinyl acetate) obtained at the end of the polymerization at 60 °C in microemulsions stabilized with CTAB/DTAB in w/w: (a) 0/100; (b) 25/75; (c) 50/50; (d) 75/25; (e) 100/0.

Fig. 7 shows the weight-fraction distributions of the molar masses of the polymers at final conversion as well as the theoretical distribution calculated by assuming that chain transfer to monomer is the *only* termination mechanism. The theoretical distribution was calculated using a value of 2.2×10^{-4} for $k_{\mathrm{tr,M}}/k_{\mathrm{P}}$, which is the average of the values of $k_{\mathrm{tr,M}}/k_{\mathrm{P}}$ at 60 °C reported in the literature [21]. Fig. 7 discloses that only the polymer obtained with CTAB follows closely the chain transfer-to-monomer distribution. The other distributions deviate considerably and show a large population of polymer with higher molar masses than those expected from chain transfer to monomer. This population increases as the surfactant mixture becomes richer in DTAB. Also note that the population of low-molar mass polymer deviates from the theoretical distribution and that its proportion decreases as the DTAB content in the mixture becomes larger.

4. Discussion

Reaction rates are fast and the maximum reaction rate increases as the mixtures become richer in CTAB (inset in Fig. 1). For microemulsion polymerization, the reaction rate, R_{P}, is given by $k_{\mathrm{P}}[M]_{\mathrm{P}}N_{\mathrm{P}}\tilde{n}/N_{\mathrm{A}}$, where k_{P} is the propagation rate constant, $[M]_{\mathrm{P}}$ the volume fraction of monomer

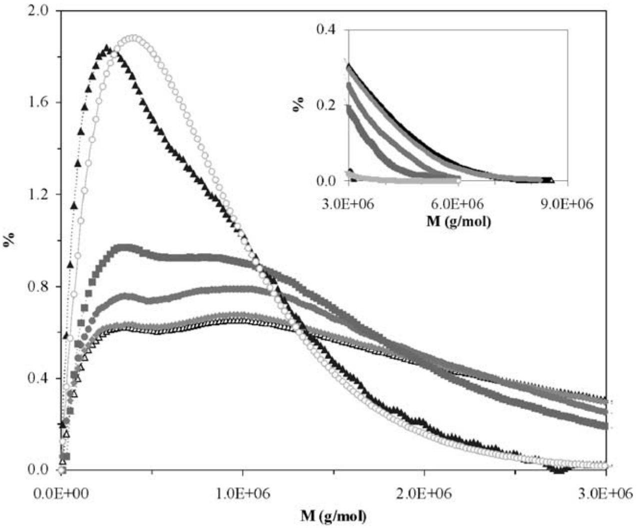

Fig. 7. Molar mass weight-fraction distributions of poly(vinyl acetate) at the end of the VA polymerization at 60 °C in microemulsion stabilized with CTAB/DTAB (w/w): 0/100 (○); 25/75 (◆); 50/50 (●); 75/25 (■); 100/0 (▲). The theoretical distribution calculated by assuming that termination occurs by chain transfer to monomer only is also included (△).

within the particles, $\tilde{n}$ the average number of free radicals per particle and N_A is the Avogadro's number [4–6,22]. Because all reactions reported here were made at the same temperature, k_P must be the same. Moreover, since the initial monomer content is identical in all reactions, the value of $[M]_P$ depends only on conversion (and, of course, temperature). Hence for a given conversion, $[M]_P$ is constant regardless of the surfactant mixture used. Hence, either $\tilde{n}$ or N_P (or both) must cause the dependence of reaction rates with surfactant mixture composition. The probability of radical capture by the particles depends on their size and number density [1]. A simple calculation at conversions around the maximum reaction rate indicates that the average number of radicals per particle rises from 0.06 for CTAB to close 0.14 for DTAB, which should result in a rise in reaction rate with increasing DTAB content, contrary to experimental results. Hence $\tilde{n}$ cannot yield the observed increase in reaction rate. The conclusion is that the number density of particles is the main contributor to the observed trend in reaction rates, in spite of the roughness of our N_P-estimation.

The observed N_P drop with conversion for all the reactions, regardless of the surfactant used, becomes more pronounced as the DTAB content in the surfactant mixtures increases (Fig. 3). This result may contravene the continuous nucleation mechanism proposed for microemulsion polymerization [4–6,22,23]. However, a coagulation process that takes place throughout the reaction could explain the reduction of N_P. In fact, the occurrence of coagulation during the emulsion polymerization of polar monomers has been reported in the literature [14,20]. Hence, we suggest that the rate of coagulation overcomes the rate of continuous nucleation in such a way that a net decrease in the number density of particles is observed. However, the particle size distribution of the latexes as a function of conversion, which can be obtained by transmission electron microscopy, might be necessary to prove this hypothesis.

Inasmuch as the reactions were carried out at the same temperature with the same monomer and initiator concentrations, only the variations in the surfactant structure can explain the differences in particle size and particle size history with conversion. That the particles become larger with increasing DTAB in the mixtures—meaning that N_P becomes decreasingly smaller, suggests that CTAB is more effective in shielding particles toward coagulation at all stages of reaction. It is known that polar monomers such as VA tend to accommodate at the particle surface and act as cosurfactant [7,17,25]. In this fashion, polar monomer molecules can shield head to head interactions of polar surfactants at the interface and decrease the effective head group area. Since DTAB and CTAB (and their mixtures) have the same polar head and counterion, it is unlikely that the interactions are screened differently by the insertion of VA molecules at the interface (unless the number of VA molecules at the interface is different with DTAB and CTAB, which is unlikely). Hence, a most probable explanation is that longer hydrophobic tails of CTAB molecules yield a thicker steric (and more effective) protection layer to the particles than the shorter tails of DTAB molecules. With the mixtures, one should then expect a gradual thickening of the protective layer as the mixture becomes richer in CTAB. Results of Gan et al. [25] support this hypothesis for the microemulsion polymerization of methyl methacrylate using cationic surfactants of different hydrophobic tail.

An unexpected result is the speed up of the polymerization rate carried out in the presence of DTAB at conversions ca. 40% (inset of Fig. 1). This behavior is unusual, since at this conversion $[M]_P$ is below its saturation level as discussed earlier, and so, $[M]_P$ should be about the same in all the polymerizations reported in Fig. 1 at this conversion value. Also, k_P is the same, since the reaction temperature is identical. Hence, one should conclude that the speeding up in the reaction rate for the polymerization stabilized with DTAB, is caused by an increase in $\tilde{n}$ at 40% conversion inasmuch as N_P for the polymerization stabilized with DTAB is the smallest at all conversions (Fig. 3). This increase could be originated by particle growth in such a way that the radicals formed by chain transfer reactions to monomer, add to another molecule instead of diffusing out of the particle. With $k_P = 3700$ l/mol s, the required time for a VA radical to react with a neighboring monomer molecule is 4.5×10^{-5} s [26]. The minimum particle size from which a monomeric radical reacts with another monomer molecule rather than escaping from the particle can be estimated with Einstein's diffusion equation. For two values of the diffusion coefficient, 10^{-6} and 10^{-7} cm^2/s, typical of a small molecule diffusing through a semi-solid and solid medium, which is the case of reacting polymer/monomer particles at high conversions [26], values of 190 and 60 nm, respectively, were obtained as the limits of particle size from which a monomeric radical can escape rather than reacting there. In the polymerization stabilized with DTAB, D_P ranges from 120 to 200 nm for conversions larger than 40% (Fig. 3), which as discussed earlier, might be caused by particle coagulation. Hence, the probability that various radicals can coexist within a particle increases for this particle size range. This is not unusual; in fact, up to 60 radicals per particle have been reported in the emulsion polymerization of VA, depending on reaction conditions [26,27].

As expected from the free radical polymerization of VA in compartmentalized loci, chain termination at low conversion is caused mainly by chain transfer reactions to monomer; however, at high conversions, chain transfer reactions to polymer as well as terminal double bond polymerization are the dominant mechanisms for chain termination [11–14]. This is caused by an increase in the number density of macromolecules within the particles as the reaction proceeds [13]. As a consequence, MMD widens and M_w grows with conversion [11–14]. Here, regardless of the surfactant employed, MMD widens and M_w enlarges with conversion for all the microemulsion polymerizations examined (Table 1 and Figs. 4 and 5). However, this enlargement in M_w and of the MMD are much smaller compared to those achieved in emulsion polymerization [15–17]. Note that the polymer obtained with DTAB contains a larger amount of high-molar mass polymer compared to that obtained with CTAB and that there is a gradual increase in the amount of high-molar mass polymer, as the mixtures become richer in DTAB (Fig. 6).

To understand these differences, we calculate the distribution expected if only chain termination occurred by transfer reactions to monomer and compare with the experimental distributions (Fig. 7). The similitude between the theoretical distribution and the experimental one for CTAB provides evidence that chain transfer to monomer is the main mechanism for chain termination. Since the comparison shown in Fig. 7 is at final conversions, one should conclude that chain transfer to monomer is the most important chain termination mechanism in the polymerization of VA in microemulsions stabilized with CTAB. Of course, other termination mechanisms may be present but they are much less important. For the other reactions carried out in the presence of DTAB, however, chain transfer to monomer is no longer dominant (see Fig. 7) and those mechanisms that give rise to high-molar mass polymer (double bond polymerization reactions, bimolecular termination by particle coagulation and chain transfer to polymer) become much more important.

Elsewhere we proposed that for the polymerization of VA in microemulsions stabilized with AOT, chain transfer to polymer at high conversions is low because of particle size is quite small (<30 nm) and consequently, narrower MMD and lower M_w than those of the poly(vinyl acetate) prepared by emulsion polymerization are obtained [17]. The argument is that the exiting probability of a radical formed by chain transfer to monomer diminishes with increasing particle size. Hence, the probability of a growing radical to react with more monomer molecules increases as the particle grows. This leads to an increase in the number density of macromolecules and, as a consequence, the probability of chain transfer to polymer increases. According to Fig. 2, all the polymerizations reported here show an increase in particle size as the reactions proceed, but the growth ratio of D_P with conversion and the size of final particles are higher as DTAB content augments. In fact, the final particle size in the latex obtained with DTAB is ca. five times than that in the latex prepared with CTAB. This means that the observed enlargement in M_w and the widening of the MMD with the increase in the DTAB content, would be a consequence of the increase in the chain transfer reactions to polymer and terminal double bond polymerization reactions because of the higher particle sizes. However, the increase in coagulation rate (Fig. 2) with DTAB content in the mixtures cannot rule out an increasingly importance of bimolecular termination by collision of active particles. In fact, the negligible amounts of gel detected in all the final polymers as evidenced by the complete dissolution (in most cases) of the polymer in THF and the lack of plugging of the filters before injecting samples in the GPC apparatus, suggest that chain transfer reactions to polymer are less important than in emulsion polymerization. However, no polymer branching measurements were possible for lack of the appropriated techniques, such as viscosimetric or light scattering detector coupled to GPC or NMR spectroscopy.

In the polymerization of polar monomers such as VA, the newly formed particles or ‘precursor particles’, produced by propagation reactions in the aqueous phase, are very unstable, and they become stable by coagulating with other similar particles (homo-coagulation) or with greater particles (hetero-coagulation) [20]. Because these particles are active, their homo-coagulation causes bimolecular terminations leading to low-molar mass polymer. In the case of microemulsion polymerization of VA, because particle nucleation occurs throughout the reaction, a more important contribution of bimolecular termination of precursor particles is expected. However, the contribution of the low-molar mass polymer to the whole distribution is small at all conversions for all the reactions examined here (Figs. 5–7). Hence, this contribution, like in emulsion polymerization of VA, appears to be negligible.

5. Conclusions

In summary, we have shown that an increase in particle size leads to larger molar masses and broader MMD. That the particle size typically produced in the emulsion polymerization of VA is much larger than the ones generated in microemulsion polymerization [9,15–17], gives support to our hypothesis. Furthermore, we have shown conclusively that chain transfer to monomer is the main termination mechanism for the polymerization of VA in microemulsions stabilized with CTAB. However, as the amount of DTAB in the surfactant mixture increases, other mechanisms, such as bimolecular termination by coagulation and double bond polymerization reactions take over. That no gel was observed suggests that chain transfer reactions to polymer, which produced highly branched polymer, are less important.

Acknowledgements

CONACYT (Grant #31262-U), the Universidad de Guadalajara and the Centro de Investigación en Química Aplicada supported this work.

References

[1] Gilbert RG. Emulsion polymerization. A mechanistic approach. New York: Academic Press, 1995.

[2] Puig JE. In: Salamone JP, editor. Encyclopedia of polymeric materials, vol. 6. Boca Raton: CRC Press, 1996. p. 4333–41.

[3] Candau F. In: Kumar P, Mittal KL, editors. Handbook of microemulsion science and technology, New York: Marcel Dekker, 1999. p. 679–712.

[4] Guo JS, Sudol ED, Vanderhoff JW, El-Aasser MS. J Polym Sci Polym Chem Ed 1992;30:691–702.

[5] Guo JS, Sudol ED, Vanderhoff JW, El-Aasser MS. J Polym Sci Polym Chem Ed 1992;30:703–12.

[6] Mendizábal E, Flores J, Puig JE, Katime I, López-Serrano F, Alvarez J. Macromol Chem Phys 2000;201:1259–65.

[7] Full AP, Puig JE, Gron LU, Kaler EW, Minter J, Mourey TH, Texter J. Macromolecules 1992;25:5157–64.

[8] Roy S, Devi S. J Appl Polym Sci 1996;62:1509–16.

[9] Sosa N, Zaragoza EA, López RG, Peralta RD, Katime I, Becerra F, Mendizábal E, Puig JE. Langmuir 2000;16:3612–9.

[10] Industry Study 837. Emulsion polymers. The Freedonia Group Inc, 1996.

[11] Friis N, Nyhagen L. J Appl Polym Sci 1973;17:2311–27.

[12] Friis N, Goosney D, Wright JD, Hamielec AE. J Appl Polym Sci 1974;18:1247–59.

[13] Friis N, Hamielec AE. J Appl Polym Sci 1975;19:97–113.

[14] Nomura M, Harada M, Eguchi W, Nagata S. Polym Prepr Am Chem Soc Div Polym Chem 1975;16:217–22.

[15] López RG, Treviño ME, Salazar LV, Peralta RD, Becerra F, Puig JE, Mendizábal E. Polym Bull 1997;38:411–7.

[16] López RG, Treviño ME, Peralta RD, Cesteros LC, Katime I, Flores J, Mendizábal E, Puig JE. Macromolecules 2000;33:2848–54.

[17] Sosa N, Zaragoza EA, López RG, Peralta RD, Katime I, Becerra F, Mendizábal E, Puig JE. Langmuir 2000;16:3612–9.

[18] Goedhart G, Opschoor A. J Polym Sci A2 1970;8:1227–33.

[19] Litt M, Patsiga R, Stannett V. J Polym Sci A1 1970;8:3607–49.

[20] Yeliseyeva VI. Polymerization of polar monomers. In: Piirma I, editor. Emulsion polymerization. New York: Academic Press, 1982. Chapter 7.

[21] de Bruyn H. PhD Thesis. School of Chemistry, University of Sydney, Australia, 1999.

[22] Mendizábal E, Flores J, Puig JE, López-Serrano F, Alvarez J. Eur Polym J 1998;34:411–20.

[23] Bléger F, Murthy AK, Pla F, Kaler EW. Macromolecules 1994;27:2559–65.

[25] Gan LM, Lee KC, Chew CH, Tok ES, Ng SC. J Polym Sci Polym Chem 1995;33:1161–8.

[26] Harriott PJ. Polym Sci A1 1971;9:1153–63.

[27] Dunn AS, Taylor PA. Makromol Chem 1965;83:207–19.