Available online at www.sciencedirect.com
SCIENCE DIRECT®

Polymer 44 (2003) 5541–5546

polymer

www.elsevier.com/locate/polymer

On the role of an unconventional rigid rodlike cationic surfactant on the styrene emulsion polymerization. Kinetics, particle size and particle size distribution

Erasto Armando Zaragoza-Contreras[a], Dámaso Navarro-Rodríguez[b,*]

[a]Centro de Investigación en Materiales Avanzados, Miguel de Cervantes. 120, Chihuahua, Chihuahua 31109, Mexico
[b]Centro de Investigación en Química Aplicada, Blvd. Enrique Reyna H. 140, Saltillo, Coahuila, 25100 Mexico

Received 8 November 2002; received in revised form 9 June 2003; accepted 23 June 2003

Abstract

An unconventional amphiphile (1-[ω-(4′-methoxy-4-biphenylyloxy)octyl]pyridinium bromide, PC8) was used as surfactant in the emulsion polymerization of styrene. At low surfactant concentration (6, 12 or 36 mmol l^{-1}), curves of polymerization rate versus conversion obeyed the typical behavior characterized by intervals I, II and III. However, at high concentration (48 or 72 mmol l^{-1}) the interval II was not observed. The particle size distribution curves showed two families of polymer particles, indicating the participation of at least two mechanisms of particle formation, one being the simple micellar nucleation and the other probably the coagulative nucleation of precursor particles. The latter was considered to occur during the nucleation interval.

Keywords: Emulsion polymerization; Particle size distribution; Styrene

1. Introduction

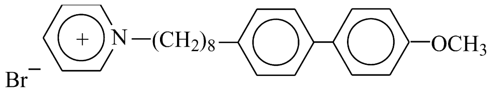
Conventional surfactants are typically characterized by a chemical structure that combines a hydrophilic group with one or two hydrophobic flexible alkyl chains of moderated length. In aqueous phase, small amounts of surfactant are enough to self-assemble into micellar microaggregates. Important modifications on the micellar behavior have been observed by the total or partial substitution of the flexible alkyl chain by a rigid rodlike hydrophobic group [1]. For unconventional surfactants containing rigid hydrophobic groups it has been reported the formation of micellar microaggregates with a specific geometry. One example is that of amphiphiles substituted with an alkylbiphenyl group, which forms in aqueous phase either globular or disklike microaggregates depending on the length of the alkyl spacer [2]. Recently, the synthesis and lyotropic behavior of unconventional amphiphiles has been widely reported [1–10]; however, the use of this new kind of amphiphiles as surfactants in the synthesis of polymers through heterogeneous polymerization techniques (emulsion, miniemulsion or microemulsion) has been scarcely studied [11–14]. One of the few works reported is the emulsion polymerization of styrene using as surfactants a series of 1-[ω-(4′-methoxy-4-biphenylyloxy)alkyl]pyridinium bromides [13,14]. In this case, the typical enhancement in both the polymerization rate (R_p) and molecular weight (M), was observed by increasing the soap concentration. Nevertheless, and contrary to other reports [15,16] on the emulsion polymerization of styrene using series of conventional surfactants, changes in length of the alkyl spacer (from hexyl to dodecyl) seemed to not affect these parameters. In addition, the application of the Clay and Gilbert model [17–19] indicated that the polymer chain stopping process was influenced by the participation of at least two chain transfer mechanisms, which were accentuated at both low surfactant concentration and low conversions [14]. In order to extend the understanding of the effect produced by the use of unconventional amphiphiles in the emulsion polymerization process, in this work special attention was given to the study of the particle size (PS) and the particle size distribution (PSD) of polystyrene

---

* Corresponding author. Fax: +52-844-4389839.
E-mail address: damaso@polimex.ciqa.mx (D. Navarro-Rodríguez).

0032-3861/03/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0032-3861(03)00621-9

latexes obtained by using the 1-[ω-(4′-methoxy-4-biphenylyloxy)octyl]pyridinium bromide (**I**) as surfactant:



I

2. Experimental

2.1. Chemicals

Styrene from Aldrich was distilled under vacuum at 30 °C before polymerization. The initiator, 2,2′-azobis(2-amidinopropane) dihydrochloride (V-50) from Wako, was recrystallized from ethanol and stored for a maximum of 30 days at 0 °C. The 1-[ω-(4′-methoxy-4-biphenylyloxy)octyl]pyridinium bromide (hereafter called PC8 surfactant) was synthesized in our laboratory using the method reported by Navarro-Rodríguez et al. [20].

2.2. Preparation of latexes

Emulsion polymerizations were carried out at 60 °C under mechanical stirring (600 rpm). The concentration of the initiator V-50 (0.2 g) and the water/styrene weight ratio (80/20) were constant for all the experiments. Concentrations of the PC8 surfactant were 6, 12, 36, 48 and 72 mmol l^{-1}. A typical emulsion polymerization experiment was realized as follows: first, the water/PC8 mixture was introduced into a three-neck-round-bottom flask reactor and allowed to stabilize at room temperature for 30 min. Then, the styrene was poured into the flask and the system was bubbled with nitrogen for 30 min. Meanwhile, in a separated recipient a V-50 aqueous solution was prepared and also bubbled with Nitrogen for 20 min. Finally, the initiator solution was injected once the emulsion reached the polymerization temperature (60 °C). Aliquots (latex) were taken at different times along 120 min of polymerization and the polymers were recuperated by the freeze drying method.

2.3. Particle size determination

The average PS was determined by QELS in a Malvern Instrument Series 4700, at 26 ± 0.1 °C and constant scattering angle of 90°; every sample was measured 10 times and the average value was registered as the average particle diameter (D_{QELS}). Measurements were made with solutions obtained by dispersing two drops of latex into 200 ml of triple-distilled water. After intensive mixing, a 2 ml aliquot was poured into the test cell, which was further sealed with a plastic stopper. The average PS was also determined by TEM analysis using a transmission electron microscope from Philips (CM200) operated at 200 kV of accelerating voltage. Samples for TEM analysis were prepared at room temperature by dispersing one drop of latex into 100 ml of an aqueous solution of phosphotungstic acid (0.05 g in 100 ml of water). All latex dispersions were sonicated for 5 min in order to obtain homogeneous dispersions; afterwards, a drop was placed on a holy carbon supported copper grid and blotted up by filter paper in order to form a thin deposition on the carbon support. Images for PS determinations were recorded using a camera solid state charge coupled device (CCD) model 676 TV system (Philips). Data processing was performed with the Pentacle software (4.1a version). For a proper PS determination several images were taken from different fields of each grid. The counting of the polymer particles was performed using the Image-Pro Plus software (4.1 version). All polymer particles were assumed to be perfect spheres; at least 600 particles were counted for every surfactant concentration.

From the TEM analyses different particle diameter moments (number average, D_{n}; weight average, D_{w}; volume average, D_{v}; and z-average, D_{z}) were calculated using the following set of equations [21]:

$$D_{\text{n}} = \sum n_i D_i / \sum n_i \tag{1}$$

$$D_{\text{w}} = n_i D_i^4 / n_i D_i^3 \tag{2}$$

$$D_{\text{v}} = [\sum n_i D_i^3 / \sum n_i]^{1/3} \tag{3}$$

$$D_{\text{z}} = [\sum n_i D_i^8 / \sum n_i D_i^6]^{1/2} \tag{4}$$

$$I = D_{\text{w}} / D_{\text{n}} \tag{5}$$

where n_i is the number of polymer particles with diameter D_i and I is the polydispersity.

The average number of polymer particles per unit of aqueous phase (N_{p}) is obtained from the volume average diameter (D_{v}) according to the following expression

$$N_{\text{p}} = (6mx / \pi \rho_{\text{p}} D_{\text{v}}^3) \tag{6}$$

where m is the weight of monomer per unit volume of water, x is the fractional conversion, ρ_{p} is the density of polystyrene at 60 °C. In this calculation D_{QELS} is not used since it is known that this diameter corresponds to a higher moment of the PS and would produce lower values of N_{p}.

3. Results and discussion

3.1. Polymerization kinetics

Fig. 1 shows the conversion (%) versus time curves for a series of emulsion polymerizations carried out at different concentrations of the PC8 surfactant. In this figure, it is observed that the polymerizations proceed progressively faster as the surfactant concentration ([PC8]) increases. At [PC8] equal or higher than 12 mmol l^{-1} most polymer is formed during the first 90 min, however, at [PC8] of

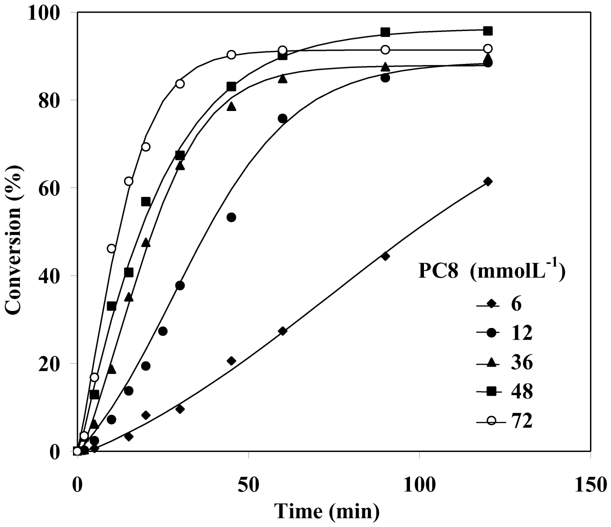


Fig. 1. Conversion versus time curves for styrene emulsion polymerizations stabilized with the PC8 surfactant at different concentrations.

6 mmol l^{-1} the polymerization reaction proceeds rather slowly taking more than 2 h to attain conversions higher than 60%. It should be pointed out that for all experiments the surfactant concentration was well above its critical micelle concentration (1.47 mmol l^{-1}) [13]. Another typical representation of the emulsion polymerization kinetics is depicted in Fig. 2, where the polymerization rate (R_p) versus conversion (%) curves are presented for different surfactant concentrations. At [PC8] of 6, 12 and 36 mmol l^{-1} the curves show the intervals I, II and III, as expected for this kind of polymerization [22]. The interval I (R_p progressively increasing), corresponding to the particles nucleation period, is observed at conversions lower than 10%. Afterwards, the interval II (R_p constant), associated to an almost constant concentration of monomer inside the growing polymer particles (assuming N_p constant), extends to a conversion near 50%. Finally, in the interval III (R_p decreasing) the declination of the curve indicates the consumption of the remaining monomer into the growing particles. On the other hand, at [PC8] of 48 and 72 mmol l^{-1} the interval II is not observed. At these high concentrations the polymerization rate reaches a maximum and then it decreases monotonically. Miller et al. [18] suggested that the absence of the interval II in these curves might indicate that the nucleation period extends to a high conversion in such a way that the system passes directly from interval I to interval III.

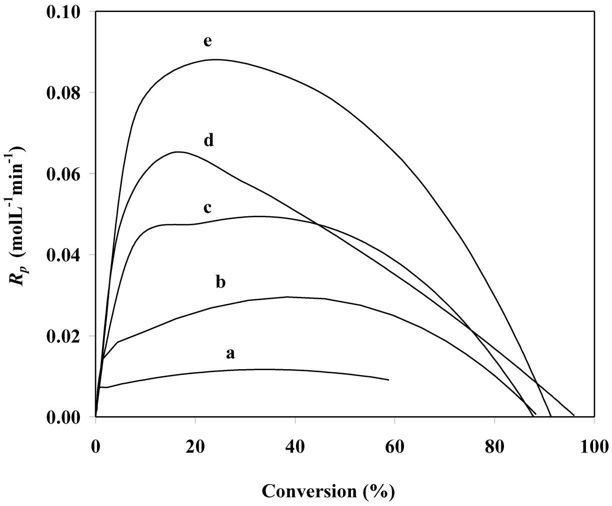


Fig. 2. Polymerization rate versus conversion curves for styrene emulsion polymerizations stabilized with the PC8 surfactant at different concentrations (mmol l^{-1}); (a) 6, (b) 12, (c) 36, (d) 48 and (e) 72.

The polymerization rate determined at the maximum value from the adjusted curves (Fig. 2) are listed in Table 1. The increase in the R_p is directly related to the total micellar surface area, which in turn depends directly on the number of polymerization loci. In other words, the monomer is distributed and polymerized into a higher number of particles as far as the surfactant concentration increases. In a previous work [13] a log R_p versus log [PC8] plot has been reported and the obtained relation between these two variables was $R_p \propto [\mathrm{PC8}]^{0.7}$. The value of the exponent resulted a little bit higher than that predicted (0.6) by the Smith–Ewart theory [23]. Exponents higher than 0.6 have been also reported for other surfactants for similar experiments, for example, an exponent of 1.0 has been reported for the emulsion polymerization of styrene using cetylpyridinium chloride (CPC) as surfactant [24].

3.2. Particle size and particle size distribution

The different average moments of the particle diameter, determined by TEM and QELS, are presented in Table 1. Although, both techniques show the same tendency in the PS as a function of the surfactant concentration (i.e. the average PS decreases as [PC8] increases), it is evident that in most cases the values determined by QELS are slightly higher than the number, weight or volume moments calculated by TEM. Such difference is normally due to the fact that the PS moment obtained by QELS corresponds to a higher diameter moment. It this respect it is commonly reported that D_{QELS} corresponds to the harmonic z-average diameter [25–27], however, this is not the general opinion [28,29]. In this study, D_{QELS} and D_z were quite similar for high surfactant concentration experiments (48 and 72 mmol l^{-1}) and only slightly different for those carried out at low concentrations (6 and 12 mmol l^{-1}). In practice, D_{QELS} and D_z are just average values thus it is more reasonable to make a discussion over the entire PSD curves. In Fig. 3, it can be noticed that PSD curves move towards lower diameter domains (left side) as far as the surfactant concentration increases and that in almost all cases the distributions show two well distinguished fractions of polymer particles; the biggest one located towards the right side of the curves. Moreover the small fraction becomes in appearance the predominant one at the next higher surfactant concentration, but this behavior has been

Table 1
Average particle size moments (D_n, D_w, D_z, D_{QELS}), average number of particles (N_p) and average radicals per particle (i), determined from the polystyrene latexes (final conversion) obtained by emulsion polymerization using the PC8 surfactant at various concentrations

PC8	R_p (mol l^{-1} min^{-1})	D_n (nm)	D_w (nm)	D_v (nm)	D_z (nm)	I	D_{QLS} (nm)	$N_p \times 10^{-15}$ (ml^{-1})	i
6	0.115	144.5	149.7	146.4	167.4	1.04	155.8	0.094	0.82
12	0.290	101.7	107.4	103.9	110.2	1.06	102.1	0.365	0.54
48	0.651	69.1	75.1	71.3	79.5	1.09	77.8	1.130	0.39
72	0.878	54.5	59.8	56.5	63.5	1.09	64.9	2.270	0.26

considered coincident. The fact that these PSD curves are bimodal suggests that the formation of particles occur by two different mechanisms; one being a simple micellar nucleation mechanism. The other mechanism could be associated to a coagulative nucleation process similar to that reported in related works [30]. Such process could arise from the instability of the small size and poor surface charge density (related to surface curvature) precursor particles [31], particularly stabilized with rigid rodlike surfactants [2]. Thus, the coagulation would occur mainly in the nucleation interval (interval I), which is longer for experiments carried out at higher surfactant concentrations (Fig. 2). This hypothesis could be supported by the recent works [14] on the evolution of molecular weight distribution (MWD) curves of polystyrene obtained at different conversions using the PC10 surfactant at various concentrations. Such MWD curves showed two fractions (bimodal) of polymer chains whose proportion changed with conversion. The high molecular weight fraction was predominant only at conversions corresponding to interval I (longer for high surfactant concentrations), otherwise, the low molecular weight fraction dominated the MWD curves. These observations indicated that the high molecular weight chains were formed during interval I by a probably chain stopping mechanism associated to a coagulative nucleation process of small particles [30], which was certainly different from that prevailing at high conversion (transfer to monomer) according to that obtained by applying the Clay and Gilbert Model [19].

Fig. 4 shows an example of micrograph obtained from a latex prepared using 12 mmol l^{-1} of the PC8 surfactant. As it is shown, the polymer particles are spherical in shape but they are non-homogeneous in size; a family of big particles dominates and some small particles (around 50 nm) are dispersed in between. It should be mentioned that in some micrographs non-spherical particles (elongated) were observed but their number was negligible respect to the spherical ones. According to the molecular characteristics of similar surfactants [5–7], it is possible to speculate with some molecular restrictions leading to non-spherical or elongated polymer particles, however, a convincing reasoning requires a deeper investigation on the geometries of particles obtained when using rigid surfactants in polymerization systems.

3.3. Average particle number

The evolution of the average number of polymer particles (N_p) as a function of the surfactant concentration is shown in Table 1. N_p was determined from Eq. (6) and it ranges between 0.094×10^{15} and 2.27×10^{15} ml^{-1} from the lower to the higher PC8 concentration. The plot of log N_p versus log [PC8] is illustrated in Fig. 5; the slope of the curve determines the dependence of N_p on the surfactant concentration. For this correlation Smith and Ewart [23] established a typical value of 0.6; here, the correlation was $N_p \propto [\text{PC8}]^{1.1}$. The exponent substantially deviates from the typical value, but this is understood on the basis of the

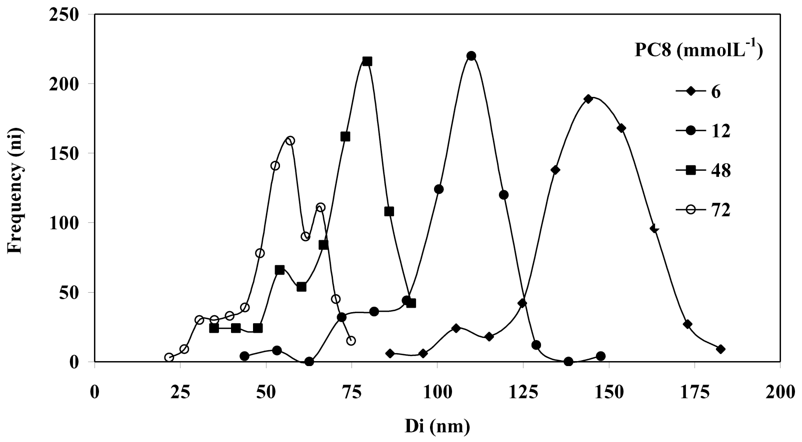


Fig. 3. Particle size distributions (PSD) curves for a series of polystyrene latexes obtained by emulsion polymerization using the PC8 surfactant at different concentrations.

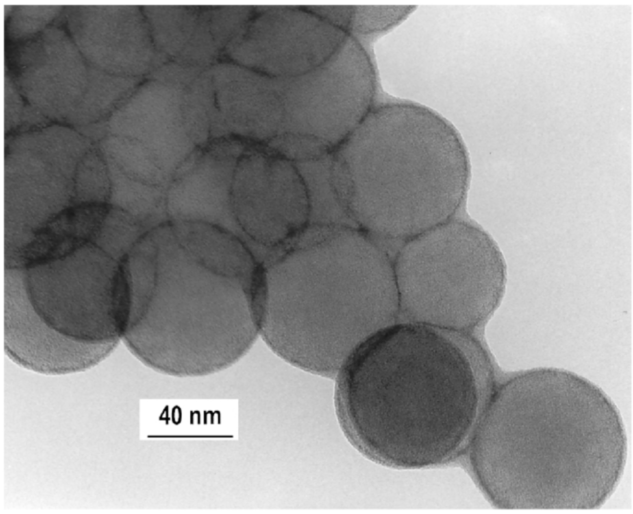


Fig. 4. Transmission electron micrograph of a polystyrene latex obtained with the PC8 surfactant at 12 mmol l^{-1}.

abnormal behavior observed in the PSD curves (Fig. 3), which show the existence of a fraction of small particles (left side fraction of the bimodal PSD curve) that becomes more and more important as far as the PC8 concentration increases. This effect produces higher N_p values than expected and this is clearly reflected in the exponent of the already mentioned $N_p \propto$ [PC8] correlation. It should be mentioned that similar or even higher exponents have been reported for the emulsion polymerization of styrene. One example is the correlation $N_p \propto [PC8]^{2.0}$ reported by Vanderhoff et al. [32] for the emulsion polymerization of this monomer initiated by γ-rays and using sulfonate type soaps as surfactants.

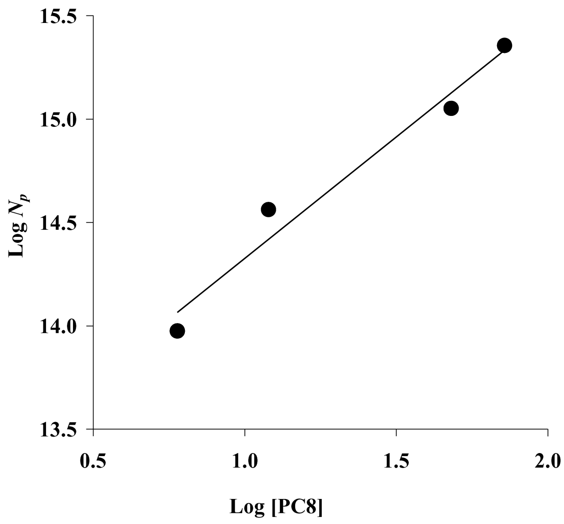


Fig. 5. log N_p versus log [PC8] plot for polystyrene latexes using the PC8 surfactant.

The average number of radicals per latex particle (i) can be determined from R_p (calculated from Eq. (7)) and N_p, according to Eq. (8):

$$R_p = \frac{k_p[M]iN_p}{N_A} \quad (7)$$

$$i = \frac{R_p N_A}{k_p[M]N_p} \quad (8)$$

where k_p is the monomer propagation rate constant, $[M]$ is the molar concentration of the monomer inside the polymer particles and N_A is the Avogadro's number. The values for k_p (258 $dm^3\ mol^{-1}\ s^{-1}$) and $[M]$ (5.8 mol dm^{-3}) where taken from the literature [33,34]. It can be noticed that i decreases from 0.82 to 0.26 from the lower to the higher surfactant concentration. For the lower surfactant concentrations (6, 12 mmol l^{-1}) i resulted to be higher than 0.5, which corresponds to the case 3 of the Smith–Ewart theory. In this case it is postulated that a growing radical, preexisting inside of a polymer particle, is not immediately stopped when a second radical enters into the particle, meaning that at any time some fraction of the polymer particles have more than one propagating radical. This behavior corresponds to the well known pseudobulk behavior (e.g. zero–one–two system) described in the classical emulsion polymerization theory [19]. At high surfactant concentrations (48 and 72 mmol l^{-1}) the i values were lower than 0.5, indicating a zero–one kinetics, in which a spontaneous recombination is produced when a free radical enters into a polymer particle already containing a growing radical. Here, the maximum number of radicals per polymerization locus is one [35]. Miller et al. [18] reported the emulsion polymerization of styrene using sodium lauryl sulfate at concentrations above and below its cmc (8.1 mmol l^{-1} at 25 °C). Below the cmc (5 mmol l^{-1}) these systems showed a pseudobulk behavior with particle diameters (D_v) of around 250 nm and an average number of radicals per particle of 0.8. Above the cmc (10 mmol l^{-1}) the systems were zero–one type, with particle sizes around 105 nm. The R_p versus time curves presented a comparable behavior to that found with the PC8 surfactant. At surfactant concentrations below the cmc it has been reported that the homogeneous-coagulative nucleation is the dominant mechanism for the polymer particle formation producing large particles. However, at surfactant concentrations above the cmc, the monomer swollen micelles are considered the main locus for polymer particle formation generating small latex particles. From our results it is believed that during the nucleation period (interval I) the primary particles were not stable enough as a consequence of the rigidity of the surfactant rodlike structure, which is known to reduce the surface curvature of micellar microaggregates. Therefore, the coagulation between such unstable primary particles occurred in order to form more stable growing particles [31], conferring the systems pseudobulk characteristics. At 48 or 72 mmol l^{-1} it is believed that coagulation of precursor particles is also occurring; however, it is considered that the surfactant concentration is high enough to stabilize faster the primary precursor particles and then showing a predominant zero–one kinetics.

4. Conclusion

The emulsion polymerization of styrene using an unconventional PC8 surfactant has shown particular features. At low PC8 concentration (6, 12 and 36 mmol l^{-1}), the polymerization rate (R_p) versus conversion curves showed the expected intervals I, II and III, however, at high PC8 concentrations (48 and 72 mmol l^{-1}) such curves showed only intervals I and III. This latter result indicates that the nucleation period is extended to a point that the system passes directly from interval I to interval III. The PSD curves showed, for each latex, the existence of two fractions of polymer particles. These bimodal PSD curves suggested the formation of particles by two different mechanisms: one being the simple nucleation and the other a probable coagulative nucleation arising from the small size and instability of precursor particles. It has been proposed that coagulation occurs mainly in the nucleation interval (interval I), which is longer for experiments carried out at higher surfactant concentrations. According to the calculated number of radicals per polymer particle, a pseudobulk behavior and a zero–one kinetics have been considered for the lower and the higher surfactant concentration experiments, respectively.

Acknowledgements

The authors wish to thank the Mexican National Council of Science and Technology (CONACYT) and the Polymer Research Center (CIP) of COMEX for the grant given to E. A. Zaragoza-Contreras during the performance of the present investigation. We also thank Francisco Paraguay-Delgado for his help in obtaining the TEM micrographs and Jorge Herrera-Ordoñez for the useful discussions that encouraged this effort.

References

[1] Lühmann B, Finkelmann H. Coll Polym Sci 1987;265:506.
[2] Kunitake T, Okahata Y. J Am Chem Soc 1980;102:549.
[3] Zhao J, Christian SD, Fung BM. J Phys Chem B 1998;102:7613.
[4] Bernheimer-Groswasser A, Zana R, Talmon Y. J Phys Chem B 2000;104:4005.
[5] Zana R, Lévy H, Danino D, Talmon Y, Kwetkat K. Langmuir 1997;13:402.
[6] Renouf P, Mioskowski C, Lebeau L, Hebrault D, Desmurs JR. Tetrahedron Lett 1998;39:1357.
[7] Gosh P, Sengupta S, Bhraradwaj PK. Langmuir 1998;14:5712.
[8] In M, Aguerre-Chariol O, Zana R. J Chem Phys B 1999;103:7749.
[9] Bissel P, Onda M, Yoshihara K, Koyano H, Ariga K, Kunitake T. Langmuir 1999;15:1791.
[10] Putlitz B, Hentze HP, Landfester K, Antonietti M. Langmuir 2000;16:3214.
[11] Dreja M, Tieke B. Langmuir 1998;14:800.
[12] Dreja M, Pyckhout-Hintzen W, Mays H, Tieke B. Langmuir 1999;15:391.
[13] Zaragoza-Contreras EA, Rodríguez-González RJ, Navarro-Rodríguez D. Macromol Chem Phys 1999;200:828.
[14] Zaragoza-Contreras EA, Maldonado-Textle H, Navarro-Rodríguez D. J Appl Polym Sci 2002;84:1513.
[15] Al-Shahib WAGR, Dunn AS. J Polym Sci: Polym Chem Ed 1978;16:677.
[16] Dunn AS, Al-Shahib WAGR. In: Fitch RM, editor. Polymer colloid II. New York: Plenum Press; 1980.
[17] Gilbert RG. In: Ottewill RH, Rowell RL, editors. Emulsion polymerization: a mechanistic approach. San Diego: Academic Press; 1995. Chapter 3.
[18] Miller CM, Clay PA, Gilbert RG, El-Aasser MS. J Polym Sci: Polym Chem Ed 1997;35:989.
[19] Clay PA, Gilbert RG. Macromolecules 1995;28:552.
[20] Navarro-Rodríguez D, Frère Y, Gramain P, Guillon D, Skoulios A. Liq Cryst 1991;9:321.
[21] Nomura M, Harada M, Eguchi W, Nagata S. In: Piirma I, Gardon JL, editors. Emulsion polymerization. ACS Symposium Series, Washington, DC; 1976. p. 24. Chapter 7.
[22] Harkins WD. J Am Chem Soc 1947;69:1428.
[23] Smith WV, Ewart RH. J Chem Phys 1948;16:592.
[24] Min KW, Ray WH. J Macromol Sci-Revs Macromol Chem 1974;C11(2):177.
[25] Sajjadi S, Brooks BW. J Appl Polym Sci 1981;26:1637.
[26] Co CC, Cotts P, Burauer S, De Vries R, Kaler EW. Macromolecules 2001;34:3245.
[27] Morgan JD, Kaler EW. Macromolecules 1998;31:3197.
[28] Fitch RM, Polymer colloids: a comprehensive introduction, New York: Academic Press; 1997.
[29] Gardon JL. J Polym Sci: Part A-1 1968;6:643.
[30] Morrison RM, Maxwell IA, Gilbert RG, Napper DH. In: Daniels ES, Sudol ED, El-Aasserms, editors. Polymer latexes, preparation, characterization and applications. ACS Symposium Series, Washington, DC, 492.; 1992. Chapter 3.
[31] Feeney PJ, Napper DH, Gilbert RG. Macromolecules 1984;17:2520.
[32] Vanderhoff JW, Bradford EB, Tarkowski HL, Wilkinson BW. J Polym Sci 1961;50:265.
[33] Lichti G, Hawkett BS, Gilbert RG, Napper DH, Sangster DF. J Polym Sci: Polym Chem Ed 1981;19:925.
[34] Hawkett BS, Napper DH, Gilbert RG. J Chem Soc Faraday Trans I 1980;76:1323.
[35] Chen SA, Wu KW. J Polym Sci: Part A 1988;26:1143.