Evolution of Molecular Weight and Molecular Weight Distribution in *Ab Initio* Styrene Emulsion Polymerizations Using Series of Rigid Rodlike Cationic Amphiphiles as Surfactants

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ABSTRACT: The emulsion polymerization of styrene is carried out using a series of unconventional rigid rodlike cationic surfactants (1-[ω-(4′-methoxy-4-biphenylyloxy)alkyl]pyridinium bromides, PCX) of different lengths. The evolution of the molecular weight (M) and molecular weight distribution of the polymers is analyzed to obtain information about the chain stopping mechanism. Our results indicate that the M is strongly dependent on the initial surfactant concentration and is not dependent on the alkyl chain length. The Clay and Gilbert model [ln $P(M)$ versus M plots] yields a concave-up region at low molecular weights and a linear region that extends to high values. The slope of the linear region, which is related to the rate coefficient of the chain transfer to the monomer versus the propagation rate coefficient ratio, decreases as the PCX concentration increases. This behavior indicates that as the PCX concentration increases the chain transfer to monomer becomes the dominant chain stopping mechanism. On the other hand, the ln $P(M)$ versus M plots of polymer samples taken at low and high conversions show differences in slope, particularly at low PCX concentration. It is likely that at low conversion the chain transfer to monomer competes with other chain stopping mechanisms that could be associated with a coagulative nucleation process. The formation of a high molecular weight fraction at low conversion supports this explanation. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 1513–1523, 2002; DOI 10.1002/app.10489

Key words: emulsion polymerization; molecular weight; molecular weight distribution; styrene; rodlike surfactants

INTRODUCTION

One practical valuable method for extracting information about kinetic processes involved in polymer chain formation is the quantitative analysis of the evolution of the molecular weight distribution (MWD) traces obtained in the course of a polymerization reaction.[1,2] In fact, the MWD of a polymer is a register of kinetic events occurring during polymerization, and its overall shape is therefore a useful tool for obtaining information on the termination modes leading to dead polymers. The experimental MWD of a polymer is a curve showing all chain lengths (molecular weights M) in a relative concentration. The MWD obtained by GPC corresponds to a cumulative MWD of all instantaneous discrete distributions

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($\mathrm{MWDs_{inst}}$) produced from the beginning to the end of the polymerization time (t). In other words, the experimental MWD integrates all $\mathrm{MWDs_{inst}}$ produced along the reaction[3]

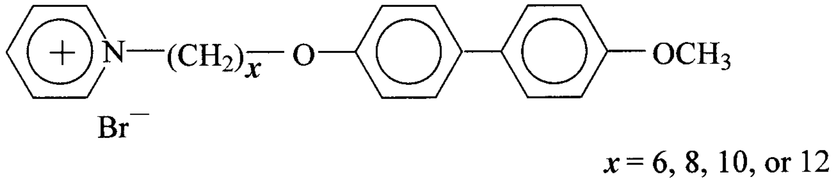
$$\mathrm{MWD}(t) = \int_0^t \mathrm{MWD_{inst}}\, dt \qquad (1)$$

Despite the large number of publications on polymer synthesis, there are few reports that relate theoretical models to experimental MWDs of polymers obtained in compartmentalized systems. In recent years, studies on the M and MWD of polymers obtained by emulsion polymerization were reported.[1–6] In these studies analytical models were applied to linear[1–4] and branched[5,6] polymers. In one of these publications Clay and Gilbert[1] developed a theoretical model for calculating MWDs that considers all possible events involved in a polymerization reaction. They considered that MWD traces of free-radical polymerizations are complex because many events (initiation, propagation, transfer, and termination) occur along the reaction. Moreover, it seems that the MWD is quite dependent on the termination rate coefficients, which in turn are a function of the length of the radicals involved in the chain formation. Emulsion polymerization kinetics is usually divided into two categories: *zero–one*, which is characterized by an instantaneous termination, and *pseudobulk*, in which the termination rate is a determining parameter. These two categories show different MWDs due to differences in their chain stopping events. One of the simplest procedures for calculating the MWD concerns the zero–one compartmentalized system (i.e., when the maximum number of radicals per locus of polymerization is one). Here an instantaneous termination occurs when any radical species enters into a particle already containing a radical. In fact, in a zero–one system, transfer and entry are the only events leading to a dead polymer.

It is well established that in emulsion polymerizations the particles are formed by means of a homogeneous and/or micellar mechanism. At surfactant concentrations higher than the critical micelle concentration (cmc), monomer swollen micelles are the principal locus of particle formation (micellar mechanism); otherwise, the homogeneous–coagulative nucleation mechanism prevails. Miller et al.[3] applied the Clay and Gilbert model[1] and reported the termination modes of *ab initio* styrene emulsion polymerizations using sodium dodecyl sulfate as a surfactant at concentrations higher and lower than the cmc. This model uses ln $P(M)$ versus M plots (the theory about this plot will be discussed later) to deduce the dominant mode of chain termination in any type of free-radical polymerization. Their ln $P(M)$ versus M plots were characterized by two well-defined regions: a concave-up region at low molecular weights and a linear region at high molecular weights, each region being related to a different mode of chain termination. A zero–one kinetics was concluded for small particles produced above the cmc while large particles obtained below the cmc showed pseudobulk behavior. The Clay and Gilbert model[1] can also be applied to emulsifier-free emulsion polymerizations. Thus, Ganachaud et al.[4] studied the emulsifier-free emulsion copolymerization of styrene with two cationic monomers. A dependency of both the particle size and the rate of polymerization on the cationic monomer concentration was found. The ln $P(M)$ versus M curves showed two different chain termination mechanisms: one generates long polymer chains as a result of combination or transfer to a monomer mechanism (or both) and the other generates short polymer chains in which the termination is produced via a transfer to the cationic monomer.

The present study focuses on the analysis of the molecular weight and MWD of styrene polymers obtained by *ab initio* (unseeded) emulsion polymerization. The synthesis of these polymers was carried out using a series of unconventional pyridinium surfactants (PCX) whose general chemical structure is shown in the structure following this paragraph (**I**). These mesogenic molecules were first reported by Navarro-Rodríguez et al.[7] in a study related to thermotropic liquid-crystalline properties. Further studies revealed the typical behavior of colloidal electrolytes, thus suggesting the possibility of using these molecules in the emulsion polymerization process. Preliminary results were recently reported in the *ab initio* emulsion polymerizations of styrene involving these unconventional surfactants.[8] It was found that the polymerization rate (R_p) and number of particles (N_p) were dependent on the surfactant concentration but not on the alkyl chain length. In the present study the evolution of the molecular weight and MWD are discussed in terms of the initial concentration and the alkyl chain length of PCX surfactants. The Clay and

Gilbert model[1] was used to analyze the MWDs of polymers obtained at different conversions. The dominant chain termination modes involved in these polymerizations were determined.



EXPERIMENTAL

Materials

Styrene (Aldrich) was distilled under a vacuum at room temperature and bubbled with argon before use. The initiator 2,2′-azobis(2-amidinopropano) dihydrochloride (Wako) was recrystallized from methanol. Purified water (equivalent to tridistillate grade) was obtained from a series of three ionic exchange columns (activated carbon, $k < 0.3$ μS, Universal Research) provided by Cole Parmer Instruments Co. Four 1-[ω-(4′-methoxy-4-biphenylyloxy)alkyl]pyridinium bromides were used as surfactants. (The alkyl is a hexyl, octyl, decyl, or dodecyl group.) For the sake of brevity these salts were labeled as PCX, the X indicating the number of methylene groups in the alkyl chain. These organic salts were synthesized in our laboratory following the procedure reported by Navarro-Rodríguez et al.[7]

Polymerizations

All emulsion polymerization reactions were carried out at 60°C under mechanical stirring at 600 rpm with a water/styrene ratio of 80/20 and an initiator concentration of 1 wt % with respect to the monomer weight under an atmosphere of nitrogen. The only variable conditions were the surfactant concentration (6, 12, 36, 48, 60, or 72 mmol/L) and the length of the PCX surfactants. It should be pointed out that the surfactant concentration was always above the corresponding cmc value (2.14, 1.47, 0.214, and 0.0097 mmol for PC6, PC8, PC10, and PC12, respectively). Samples of latex were withdrawn at different intervals and conversion was determined by gravimetry. The details of the cmc determination and the polymerization procedure were reported in a previous article.[8]

Molecular Weight and MWD Determination

The molecular weight and MWD were determined by size exclusion chromatography using a Hewlett–Packard instrument (HPLC series 1100) equipped with UV light and refractive index detectors. A series of three PLGel columns covering a wide range of molecular weights were used: 10^3 to 4×10^4, 4×10^4 to 4×10^6, and 4×10^5 to 4×10^7 at porosities of 10^3, 10^5, and 10^6 Å, respectively. A third-order polynomial calibration curve was built up using 10 monodisperse polystyrene standards (molecular weights between 10^3 and 4×10^6). Tetrahydrofuran (HPLC grade, Aldrich) was used as a solvent and elution media; it was previously filtered with 2-μm Millipore filters. The flow rate was 1.0 mL/min for all the experiments. Chromatograms were integrated using the Polymer Laboratories PL GPC software.

MWD in Emulsion Polymerization

As stated in the Harkins[9] and Smith–Ewart[10] theories of emulsion polymerization, the surfactant plays a very important role in the stabilization of the dispersed phase and the kinetics of polymer chain formation. Its concentration is directly related to the number of polymer particles (N_p) to be formed, which in turn determines the R_p and, depending on the initiator concentration, the molecular weight of the polymer. The emulsification properties of surfactants depend on their chemical composition. For ionic surfactants such properties are strongly dependent on the ionic group and to some extent on the size and nature of the nonionic part. Therefore, variations in the initial concentration and chemical composition of the surfactant may have important influences on the kinetics of polymer formation. Al-Shahib and Dunn[11] studied the emulsion polymerization of styrene using a series of sodium alkyl sulfates with an even number of methylene groups on the alkyl chain (C_{10-18}). In order to compare the results, all the experiments were carried out under the same molar surfactant concentration (60 mmol/L). They found small increases in the R_p and N_p values as the alkyl chain length was increased. This behavior is associated with the cmc value, which decreases monotonically from the C_{10} to C_{18} surfactant (i.e., the cmc falls as the alkyl chain length increases and the concentration of the micellar surfactant increases, although the total surfactant concentration is the same). Therefore, the number of particles in the latex and the rate of polymerization both increase.

The MWD of polymers obtained by emulsion polymerization is different from that obtained in homogeneous systems (bulk or solution polymerization), and the weight-average (M_w) and number-average (M_n) molecular weights may be several times higher at similar initiator concentrations. This difference was attributed to compartmentalization: in emulsion polymerization the reaction proceeds into dispersed loci of nanometric dimensions, where the growing radical propagates until transfer to the monomer occurs or until a second radical enters into the growing particle.[12] These two termination mechanisms produce polymers with a high degree of polymerization. For compartmentalized systems the main chain termination mechanism is either transfer or entry, whereas for homogeneous systems it is a combination or disproportionation. The resulting overall shape of the MWD of polymers produced by each system is different.

The MWD can be expressed in two forms: as a number MWD [$P(M)$] and as a weight MWD [$W(M)$]. The $P(M)$ in particular has a mechanistic meaning because it represents the number of chains formed by any mechanism of chain termination.[1] The $W(M)$ values obtained from GPC data are related to $P(M)$ through[1,2,13]

$$P(M) = [W(M)/M] = [W(\log M)/M^2] \tag{2}$$

where $W(\log M)$ is the cumulative MWD.

Gilbert[2] showed that for zero–one systems all chain termination events are first order with respect to the average number of free radicals per particle (i). According to this model the only chain termination events are entry and/or transfer of radicals as found in eq. (3).

$$P(M) = \exp\left\{-\frac{([m]k_{\mathrm{tr},M} + [A]k_{\mathrm{tr},A} + \rho)M}{k_p[m]m_0}\right\} \tag{3}$$

where $[m]$ and $[A]$ are the monomer and transfer agent concentrations in the polymer particle, respectively; $k_{\mathrm{tr},M}$ and $k_{\mathrm{tr},A}$ are the rate coefficients of chain transfer to monomer and to the tranfer agent, respectively; k_p is the propagation rate coefficient; m_0 is the molecular weight of the monomer; and ρ is the coefficient of the total rate of entry per polymer particle.

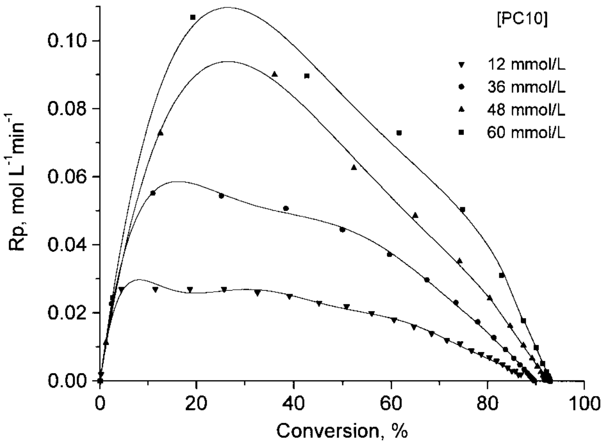


Figure 1 The rate of polymerization (R_p) versus conversion for a series of polystyrene emulsion polymerizations carried out using PC10 as a surfactant at various concentrations.

When chain transfer to monomer termination is the only chain termination mechanism, eq. (3) is simplified as follows:

$$P(M) = \exp - \left(\frac{k_{\mathrm{tr},M}}{k_p m_0}\right) M \tag{4}$$

If the ln $P(M)$ versus M curve is linear, eq. (5) approximates the corresponding value for the chain transfer to monomer termination mechanism.[2]

$$\Lambda = \frac{k_{\mathrm{tr},M}}{k_p} = m(-m_0) \tag{5}$$

where m is the slope of the ln $P(M)$ versus M curve.

Deviations from linearity indicate that chain termination occurs by some other mechanism or by a combination of two or more mechanisms.

RESULTS AND DISCUSSION

Figure 1 shows the R_p versus conversion curves for a series of polymerizations carried out with the PC10 surfactant at various concentrations. It is clear from this figure that there is a great difference in the polymerization kinetic from the lower to the higher surfactant concentration ex-

Table I Final Conversion, Average Molecular Weights (M_w, M_n), and Polydispersity Index (I) of Polystyrenes Synthesized by Emulsion Polymerization Using PCX Surfactants at Various Concentrations

Surfactant	[PCX] (mmol/L)	Conversion (%)	M_w ($\times 10^{-5}$)	M_n ($\times 10^{-5}$)	I
PC6	12	85.1	7.14	1.25	5.13
	36	93.6	10.50	1.67	5.45
PC8	12	88.3	8.30	2.40	3.46
	36	89.7	9.25	2.46	3.76
	48	95.7	13.85	2.38	5.80
	72	91.6	15.00	3.50	4.28
PC10	12	86.9	3.86	1.03	3.75
	36	89.7	8.81	2.24	3.93
	48	92.9	14.60	4.18	3.49
	60	94.7	25.20	5.44	4.63
PC12	12	88.5	8.16	1.83	4.47
	36	95.7	16.70	4.04	4.13

periments. For the lower surfactant concentration (12 and 36 mmol/L) experiments the three typical intervals (I, II, and III) of emulsion polymerization are observed. On the other hand, experiments at 48 and 60 mmol/L do not show the constant rate interval (interval II). In this interval it is supposed that the amount of monomer in the polymer particles remains almost constant as the polymer particles are quickly replenished with monomer from the monomer droplets. The disappearance of the monomer droplets signifies the beginning of interval III in which the rate of polymerization decreases monotonically up to the end of the reaction. It can also be noticed that the particle nucleation interval (interval I) increases as the surfactant concentration increases. The shape of these curves are discussed later along with the MWD results.

The final conversion (C), average molecular weights (M_w and M_n), and polydispersity index (I) of a series of polystyrenes are listed in Table I. As expected, the M_w and M_n values showed important variations when the surfactant concentration was increased. According to these results no clear relation exists between the molecular weight and the surfactant length. It should be pointed out that the comparison is made with samples whose conversion ranges from 85.1 to 95.7%. This difference in conversion is not of crucial importance because the molecular weight and MWD did not show significant differences above 80% conversion in any case. The correlation between the M_w and surfactant concentration ($M_w \propto [\mathrm{PCX}]^z$) for different polymerizations is shown in Figure 2. Note that the experimental data can be roughly adjusted to a straight line; a value of 0.58 for z was obtained by linear regression. This value is close to the lower limit of experimental z values (between 0.6 and 1.0) reported for styrene emulsion polymerizations using cationic surfactants.[14] On the other hand, the polydispersity index of all listed polymers ranges between 3.75 and 5.45. These values are higher than the typical ones for polymers obtained by emulsion polymerization when the only chain termination mechanism is chain transfer to monomer.[2] As discussed later in this article, such high values of the polydispersity index are closely related to the shape of the MWD curves, which for some polymers is clearly bi-

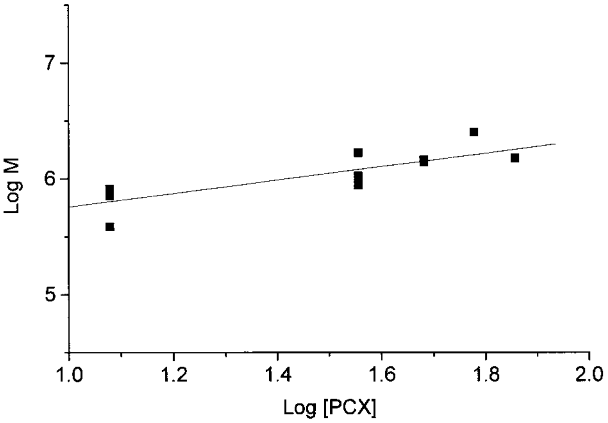


Figure 2 The weight-average molecular weight (M_w) of polystyrenes versus the surfactant concentration (double logarithm plot). For details, see Table I.

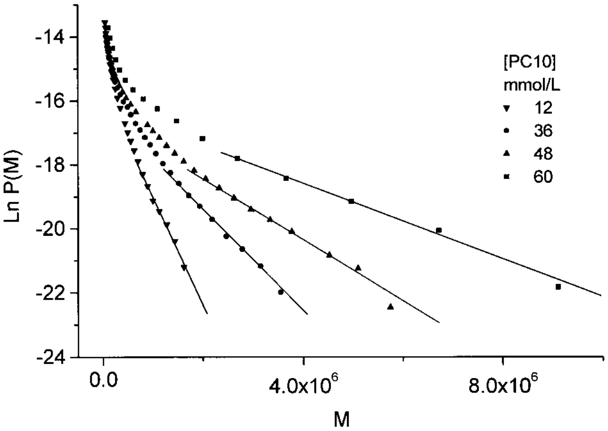


Figure 3 The ln $P(M)$ versus M for polystyrenes obtained by emulsion polymerization using the PC10 surfactant at various concentrations.

modal and for others there is a shoulder either at the high (high conversion samples) or low molecular weight (low conversion samples) regions.

The Clay and Gilbert model[1] must be applied to MWD curves of polymer chains produced at very small conversion intervals ($\mathrm{MWD_{inst}}$ [Δt]). Because these consecutively formed polymer fractions are not separated from each other, the cumulative number MWD [$P(M)$] can be used instead. Figure 3 shows the ln $P(M)$ versus M curves for polystyrenes obtained with PC10 surfactants at several concentrations. All curves exhibit two different regions: a concave-up region at low molecular weights and a linear region that extends to high values. Miller et al.[3] reported ln $P(M)$ versus M curves with a shape similar to those obtained in this study for a system with zero–one characteristics. For the concave-up region a series of possible explanations were proposed.[2–4] Among them are the combination of different chain termination mechanisms (transfer to monomer, transfer to surfactant, or bimolecular termination), a nonhomogeneous monomer concentration within the polymer particles, and differences in radical species generated during polymerization. The linear region is commonly attributed to the chain transfer to the monomer termination mechanism or bimolecular termination or a combination of both.

As mentioned above, the slope of the straight section of the ln $P(M)$ versus M curves decreased as the surfactant concentration increased, and the Λ values (Table II) approached a range of values [$(0.07\text{–}1.37) \times 10^{-4}$ at 60°C] reported in the literature for styrene.[15] This behavior can be explained through the inverse dependence of the N_p in the latex on ρ, as described by Maxwell et al.[16]

$$\rho = \frac{k_p[m_{\mathrm{aq}}][M_{z-1^*}]N_A}{N_p} \tag{6}$$

where $[m_{\mathrm{aq}}]$ is the monomer concentration in the aqueous phase, $[M_{z-1^*}]$ is the macroradical maximum length in the aqueous phase, and N_{A} is Avogadro's number. At high PCX surfactant concentrations the N_p value becomes important; therefore, the probability of termination by a combination of a propagating macroradical and a second radical from the aqueous phase decreases. In addition, the Λ decreases as far as the recombination of radicals is no longer possible and termination due to chain transfer to the monomer becomes the most important mechanism for polymer chain formation. Our results also indicate that a good correlation exists between the molecular weight and Λ; the log M versus log Λ plot (Fig. 4) fits well to a straight line.

The dependence of the molecular weight and MWD on conversion was also studied. Figures 5, 6, and 7 show ln $P(M)$ versus M curves at different conversions for PC10 surfactant concentrations of 12, 36, and 48 mmol/L, respectively. Figure 5 ([PCX] = 12 mmol/L) clearly shows that the slope of the curves changes drastically from the beginning to the end of the reaction. In fact, two regimes can be disclosed from this series of curves. From 0 to 25% conversion the slope of the straight section is similar for all curves and it is different from that of curves obtained at conversions be-

Table II Λ Values Obtained from Straight Part of Ln $P(M)$ Versus M Curves for Polystyrenes Obtained Using PCX Surfactants at Various Concentrations

Surfactant	[PCX] (mmol/L)	Λ ($\times 10^{-4}$)
PC6	12	2.42
	36	1.64
PC8	12	3.53
	36	2.16
PC10	12	3.52
	36	1.68
	48	0.98
	60	0.65
PC12	12	2.10
	36	0.92

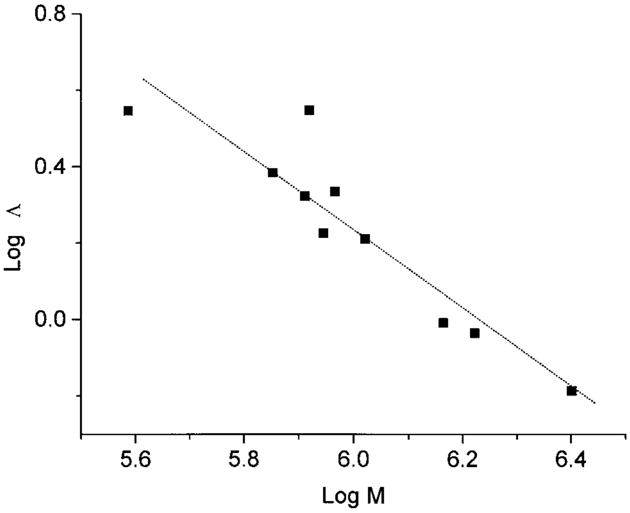


Figure 4 The Λ versus weight-average molecular weight (M_w) of polystyrenes (double logarithm plot).

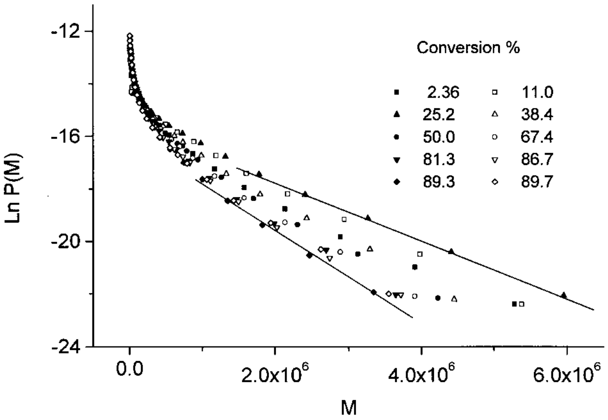


Figure 6 The ln $P(M)$ versus M for polystyrenes obtained at different conversions using the PC10 surfactant at 36 mmol/L.

tween 39 and 86.9%, which seems to attain an upper limit value. At a PCX concentration of 36 mmol/L (Fig. 6) the change in slope from the beginning to the end of the reaction is much less pronounced than in the previous case, and at a PCX concentration of 48 mmol/L (Fig. 7) the slope is practically independent of the conversion. At low surfactant concentration ([PCX] = 12 mmol/L) the behavior at low conversion is certainly due to the combination of various chain termination mechanisms while at high conversions it derives from one dominant mechanism, probably chain transfer to the monomer. The trend observed in these plots is contrary to that reported by Miller et al.[3] and Ganachaud et al.[4] for similar experiments. Deviations from the Clay and Gilbert model[1] at low conversions suggest that some chain termination mechanisms different from chain transfer to the monomer produce mainly high molecular weight chains. These authors reported chain transfer termination mechanisms to some other species (surfactant or functional monomer) that are different from the monomer or a combination of two or more chain termination mechanisms.

The evolution of the MWD for samples synthesized using a surfactant concentration of 12 mmol/L (Fig. 8) is quite drastic and a bit different from that of samples obtained at higher surfactant concentrations (Figs. 9, 10). For a low surfactant concentration (12 mmol/L) and low con-

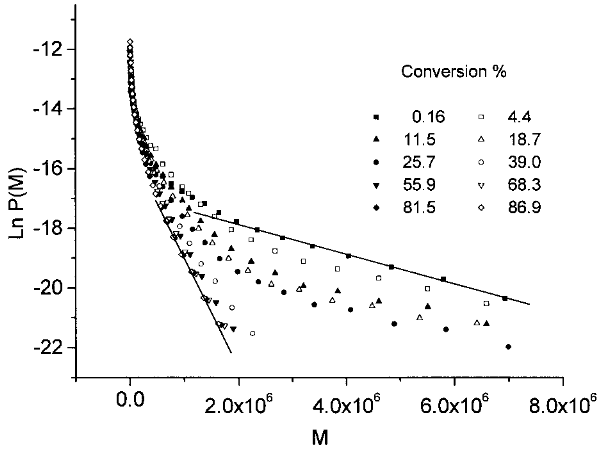


Figure 5 The ln $P(M)$ versus M for polystyrenes obtained at different conversions using the PC10 surfactant at 12 mmol/L.

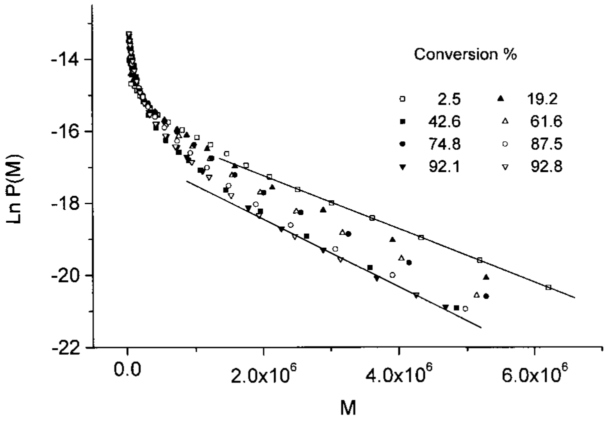


Figure 7 The ln $P(M)$ versus M for polystyrenes obtained at different conversions using the PC10 surfactant at 48 mmol/L.

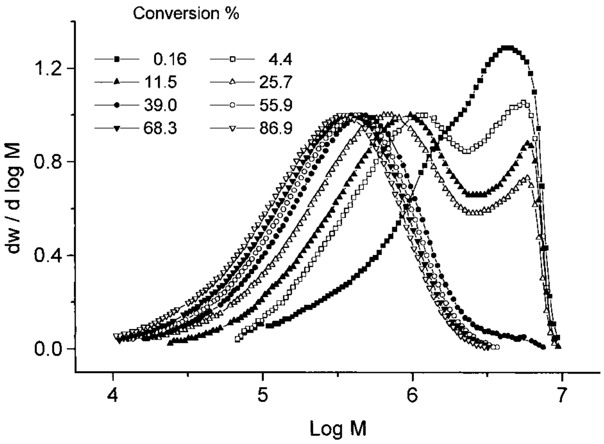


Figure 8 The molecular weight distribution (MWD) curves obtained at different conversions using the PC10 surfactant at 12 mmol/L. The curves are normalized taking into account the maximum of the low molecular weight polymer fraction.

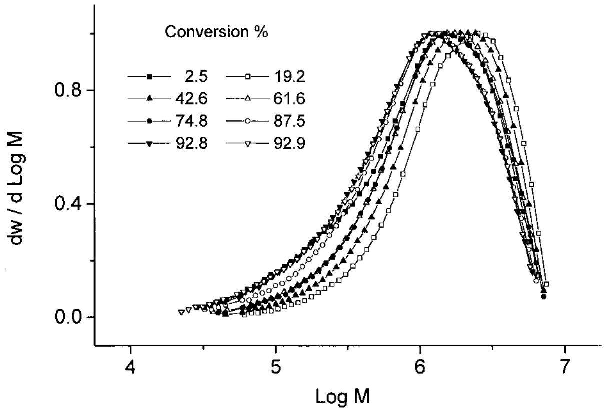


Figure 10 The molecular weight distribution (MWD) curves obtained at different conversions using the PC10 surfactant at 48 mmol/L. The curves are normalized.

versions (0–25%) the MWD curves are clearly of bimodal, indicating that two possible distinct termination processes occur in the same reaction. These two processes produce two different polymer fractions (see bimodal MWD trace in Fig. 8), one in the high molecular weight region and one well separated in the low molecular weight region. The MWD curves of the polymers synthesized using 36 and 48 mmol/L of the PC10 surfactant (Figs. 9, 10) show a shoulder either at the high molecular weight region (high conversion samples) or the low molecular weight region (low conversion samples). This shoulder is quite evident for MWD curves in which the log *M* axis was amplified, as observed in Figure 11 for polystyrenes obtained at different conversions using 36 mmol/L of the PC10 surfactant. The bimodal MWD curves and the MWD curves with a shoulder both explain the high polydispersity indices (Table I) obtained with this kind of surfactant and suggest that at the beginning of the polymerization the high molecular weight chains were formed by a chain termination mechanism different from that prevailing at high conversions (Table III). Certainly the high molecular weight fraction is formed only at the very beginning (nucleation interval) of the polymerization process because it becomes less important as the low molecular weight chains are produced. According to Figure 1, the nucleation interval for the reaction performed with 12 mmol/L of the PC10 surfactant was quite short and it is possible that the high molecular weight chains were formed during this interval. Figure 1 also shows that the nucleation interval for the reaction conducted with 36 mmol/L of the PC10 surfactant was longer than that of the already discussed reaction ([PC10] = 12 mmol/L). In this highly concentrated surfactant polymerization reaction there is also a high molecular weight fraction formed at the beginning of the polymerization (Fig. 11) that becomes less important with conversion. In order to simulate how this high molecular weight fraction (right side shoulder) decreases with conversion, a deconvolution analysis was made using the Peak Fit Program (separation and analysis software) from SPSS Inc. (Fig. 12). Note that in this case (36 mmol/L) the high molecular weight fraction formed at low conversion is still noticeable at high

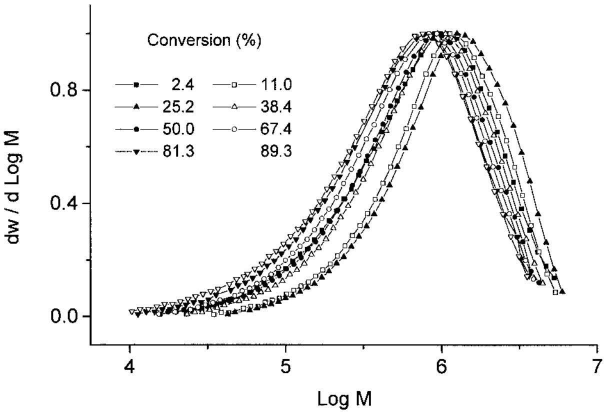


Figure 9 The molecular weight distribution (MWD) curves obtained at different conversions using the PC10 surfactant at 36 mmol/L. The curves are normalized.

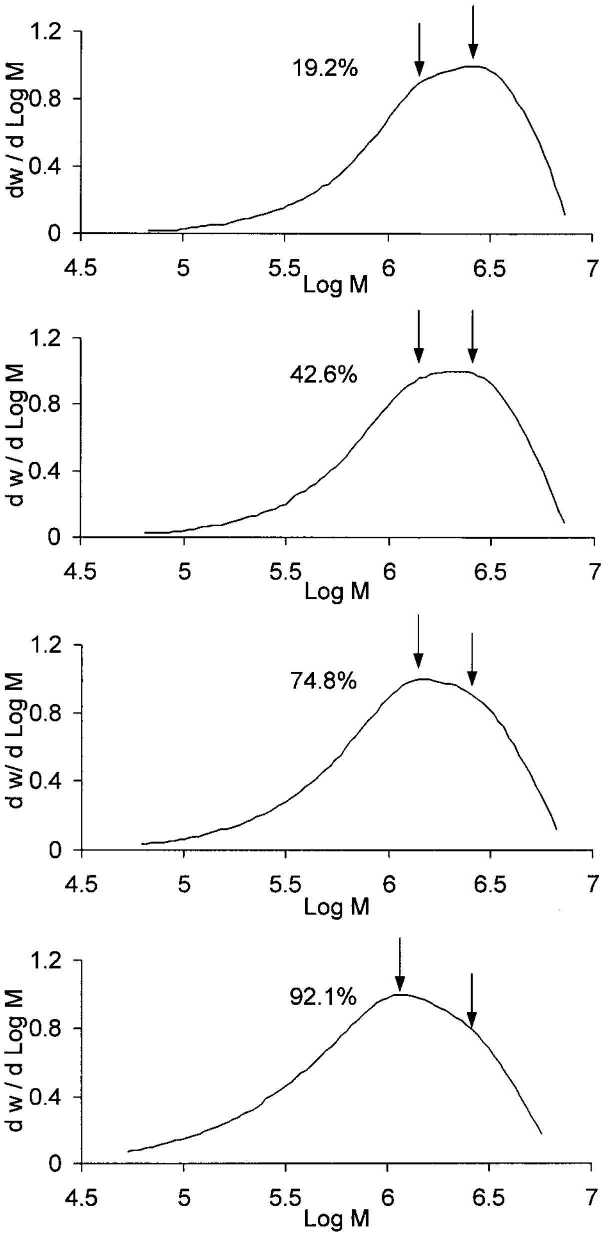


Figure 11 The evolution of the molecular weight distribution (MWD) curves of polystyrene obtained at different conversions (19–92%) using 36 mmol/L of the PC10 surfactant. The curves are normalized.

conversions. The production of the polymer fraction in the low molecular weight region can be easily explained in terms of the Clay and Gilbert model.[1] On the contrary, the explanation of the formation of polymer chains in the high molecular weight region must be different from that proposed in such a model and could be explained in terms of the rigid rodlike structure of PCX surfactants. Under this hypothesis, it is likely that at the very beginning of the reaction (nucleation interval) the polymerization reaction occurs in small precursor particles that are rather unstable because of the rigid rodlike nature of the surfactant. It is assumed here that the small growing precursor particles coagulate with each other to form more stable growing particles, as proposed by Feeney et al.[17] in their coagulative nucleation theory. Coagulation of precursor particles may involve a termination mechanism that is different from that proposed in the Clay and Gilbert model,[1] which could be responsible for the high molecular weight fraction. The colloidal instability of precursor particles arises from their small size and their poor surface charge density. The latter is related to the surface curvature, which is a critical parameter for colloidal stability in small size particles and that could be more critical when rigid rodlike surfactants are used. Thus, the transition from the small unstable growing particles to the large stable growing particles associated with the coagulative nucleation process could explain the bimodal MWD curves and their evolution. Finally, the rigid rodlike nature of PCX surfactants is a parameter to be considered because enhanced polymerization rates were observed when compared with analogous flexible surfactants like *N*-alkylpyridinium bromides.[8] However, further investigation is necessary on the role of this kind of surfactant in both the particle formation process and the kinetics of polymer formation.

CONCLUSION

The molecular weights (M_n and M_w) and MWD of polystyrene synthesized by emulsion polymerization using a series of unconventional cationic surfactants (PCX) showed a clear dependency on the PCX surfactant concentration. The molecular weight increases with the PCX concentration and the MWD show differences whether a low or high PCX concentration is used. On the other hand, the polymerization process seems to not be dependent on the surfactant length. The Clay and Gilbert model[1] was applied to analyze the MWD as a function of the PCX concentration and conversion. From this model the $\ln(P)$ versus M plots permitted the calculation of the Λ values, which showed a high dependency on the surfactant concentration. The results indicated that at high PCX concentration and high conversions the chain transfer to the monomer is the dominant

Table III Weight-Average Molecular Weight (M_w) and Polydispersity Index (I) of Polystyrenes Obtained by Emulsion Polymerization at Different Conversions (C) Using PC10 Surfactant at Three Concentrations

[PC10] = 36 mmol/L			[PC10] = 36 mmol/L			[PC10] = 48 mmol/L		
C (%)	M_w ($\times 10^{-6}$)	I	C (%)	M_w ($\times 10^{-6}$)	I	C (%)	M_w ($\times 10^{-6}$)	I
0.2	2.76	3.52	2.4	1.18	2.96	2.5	1.61	3.69
4.4	2.15	3.25	11.0	1.33	2.31	19.2	2.27	2.17
11.5	1.83	4.48	25.1	1.52	2.25	42.6	2.00	2.35
18.7	1.69	5.05	38.4	1.10	2.60	61.6	1.80	2.70
25.7	1.52	5.70	50.0	1.02	3.00	74.8	1.79	2.56
39.0	0.58	3.49	67.4	0.93	2.94	87.5	1.54	3.10
55.9	0.46	3.32	81.3	0.85	3.28	92.1	1.42	3.35
68.3	0.42	3.30	86.7	0.86	3.47	92.9	1.45	3.44
81.9	0.39	3.50	89.3	0.81	3.90	92.9	1.43	3.41

chain stopping mechanism. The MWD curves (bimodal) demonstrated that a high molecular weight fraction was produced at the very beginning of the reaction (nucleation interval). This unusual behavior was associated with a coagulative nucleation process that may involve a termination mechanism different from that proposed in the Clay and Gilbert model[1] and that could be responsible for the formation of the high molecular weight fraction. In the coagulative nucleation process the instability of precursor particles arises from their small size and their poor surface charge density, which are critical parameters for the stability of small size particles. It is assumed here that such parameters could be more critical when rigid rodlike surfactants are considered.

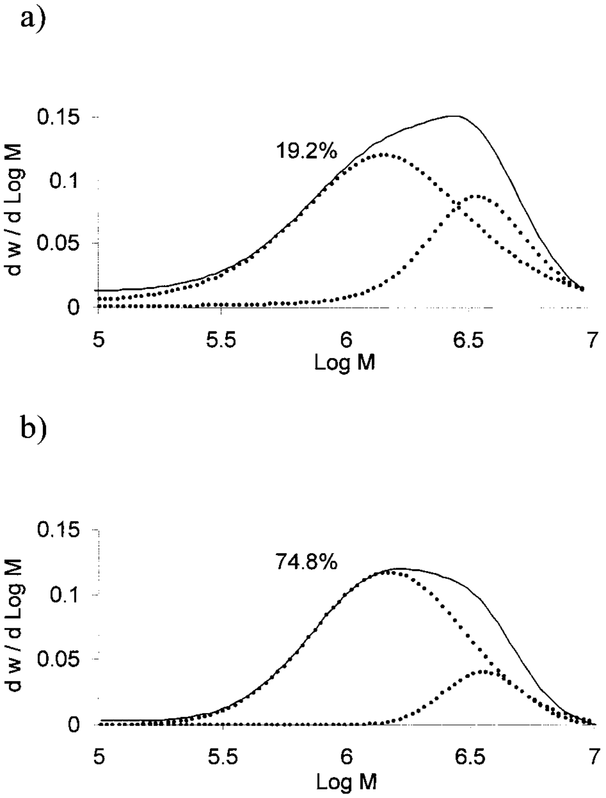


Figure 12 The (—) molecular weight distribution (MWD) and (· · ·) monomodal curves generated from experimental MWD traces using the Peak Fit Program. The polystyrene is obtained at (a) 19.2 and (b) 74.8% of conversion using the PC10 surfactant at 36 mmol/L.

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