Macromolecules **1998,** *31,* 5565−5571

Articles

Diffusive Radical Entry as the Rate-Determining Step in Amphiphilic Block Polyelectrolyte Mediated Emulsion Polymerization

Luc Leemans,[†] Robert Jérôme, and Philippe Teyssié*

Center for Education and Research on Macromolecules, University of Liège, Sart Tilman B6, B-4000 Liège, Belgium

Received July 31, 1997; Revised Manuscript Received June 1, 1998

ABSTRACT: The amphiphilic water soluble block polyelectrolytes PMMA-*b*-SPGMA and PMMA-*b*-QPDMAEMA are efficient surfactants for the radical emulsion polymerization. Negatively charged, neutral, and positively charged entering radicals were used in combination with polyanionically and polycationically tailored PMMA latex particles. It was shown that the rate of polymerization was very high for systems wherein the entering radical species had an electrical charge sign identical with that of the polyelectrolyte corona around the latex particle. PMMA-*b*-SPGMA turned out to be 4 times as efficient as compared to SDS emulsified MMA polymerization at 0.6 wt %. Systems wherein polyelectrolyte block and entering radical were of opposite sign displayed strongly reduced polymerization rates. When the polyelectrolyte barrier became thick enough, as in the case of a $M_n = 26\,000$ PMMA-*b*-QPDMAEMA, no more polymerization was observed. The observed polymerization rate effects are discussed in terms of repulsion of equal charge radicals, leading to enhanced mobility and counterion mobility restriction of the radicals of opposite sign to the polyelectrolyte block. In the latter case, this slowed counterion diffusion of radicals of opposite sign leads to premature aqueous phase termination of free radicals and consequently low flux of entering radicals with low rates of polymerization. The experimental results obtained are consistent with the theoretically predicted case, where the “control by aqueous phase growth” theory for the entry of free radicals in latex particles is invalid.

Thermal decomposition of water soluble initiators in emulsion polymerization generates primary free radicals in the aqueous phase. It is generally accepted that the major locus of polymerization in such systems is inside the surfactant micelle and in the interior of the polymer particle.[1,2] This means that the free radicals have to be transferred from the aqueous phase to the latex particles to ensure an ongoing propagation. The rate of entry of free radicals plays thus a key role in emulsion polymerization.[3] The detailed mechanism whereby free radicals enter latex particles is however far from understood, and several theories have been forwarded. The diffusion theory states the diffusion of radicals to the particle surface as the rate-controlling step.[4−6] The surfactant displacement theory suggests that displacement of surfactant from the particle surface is the rate-controlling step. So the rate of entry should depend on the surface coverage of the latex particle by the surfactant.[7] In the colloidal theory, a colloidal oligomer is supposed to be the actual entering species.[8,9]

In 1991, Gilbert et al. published a new theory on the entry of free radicals in emulsion polymerization.[10] They postulate that the growth of the aqueous phase free radicals to a particular degree of polymerization is the rate determining step for free radical capture by latex particles. They conceive this concept to be different from those generally thought to be rate determining for free radical capture by latex particles, it normally being assumed that free radical capture is controlled by diffusion of the aqueous phase free radicals to the latex particle surface.[7] In their model, this diffusive step is supposed to be so fast as not to be rate-determining.

With the present study, we want to provide for additional qualitative insight in the mechanism of entry of free radicals, in the presence of block polyelectrolytes, in the radical emulsion polymerization. Rates of polymerization have been measured and are discussed in terms of diffusion of the radical species through polyelectrolyte barriers.

These results allow the following conclusions: It appears that the combination of the charge of the entering radical and the charge of the block polyelectrolyte thoroughly impacts the rate of emulsion polymerization. This sustains a model wherein diffusion of free radicals becomes the rate determining step in these emulsion polymerizations.

Experimental Section

Surfactants. The synthesis, characterization and modification of glycidyl methacrylate and *N*,*N*′-dimethylaminoethyl methacrylate block copolymers to the amphiphilic watersoluble anionic and cationic block polyelectrolytes have been described in previous publications.[11−14]

Sodium dodecyl sulfate (SDS) (Janssen Chimica) was 99% purity grade and was used as supplied.

---

* To whom correspondence should be adressed.

[†] Present address: DSM Research, 6160 MD Geleen, The Netherlands.

S0024-9297(97)01162-5 CCC: $15.00

Table 1. Characteristics of Amphiphilic Block Copolymers

block copolymer	M_n	M_w/M_n	composition (wt %) PMMA	PGMA	PDMAEMA
PMMA-*b*-SPGMA	15 000	1.09	15	85	
PMMA-*b*-QPDMAEMA I	12 000	1.15	17		83
PMMA-*b*-QPDMAEMA II	19 000	1.12	15		85
PMMA-*b*-QPDMAEMA III	26 000	1.12	18		82

Monomers. Methyl methacrylate (MMA) and styrene (St) were fractionally distilled under reduced pressure and kept under nitrogen at −10 °C.

Initiators. The initiators for the emulsion polymerization were used as supplied and kept at −10 °C: potassium peroxydisulfate ($K_2S_2O_8$) (Aldrich, 99 +%); 2,2′-azobis(2-amidinopropane) (AAP) (V-50; Wako Pure Chemical Industries), supplied as the hydrochloride; azobisisobutyronitrile (AIBN) (Janssen Chimica).

Chain Transfer Agent. 1-Dodecanethiol (Aldrich, 98%).

Inhibitor. Hydroquinone (Aldrich, 99%).

Free Radical. 1,1-Diphenyl-2-picrylhydrazyl hydrate (DPPH) (Aldrich, 95%).

Water. In-glass distilled water was deoxygenated by purging with high purity nitrogen.

Polymerizations. The emulsion polymerizations were conducted in a thermostated dilatometer at 60 °C, under a high purity nitrogen atmosphere. Batch polymerizations and gravimetric determination of conversion of polymerization as a function of time have equally been used, to ensure the accuracy of the obtained data. Batch polymerizations were immediately quenched with hydroquinone and cooled after a predetermined time of polymerization. Rates of polymerizations were calculated from the slopes of conversion as a function of time in the linear interval at partial conversion (between 20 and 40% conversion).

Results and Discussion

Amphiphilic Block Polyelectrolyte Emulsifiers. To probe the properties of polyanionic and polycationic electrosteric barriers on the mechanism of entry of free radicals in the radical emulsion polymerization, we have devized a series of emulsion polymerization experiments, in which the sign of the electrical charge of the incoming radical was varied against the sign of the electrical charge of the block polyelectrolyte barrier, while the applied experimental conditions were kept constant.

Radical emulsion polymerizations of MMA in water were conducted in the presence of polyanionic and polycationic amphiphilic water soluble block copolymers as emulsifiers. Both of these amphiphilic block copolymers are new and were developed in our laboratory.

For the polyanionic block copolymer, a poly (methyl methacrylate-*block*-sulfonated glycidyl methacrylate block copolymer (PMMA-*b*-SPGMA) was used. Its synthesis and use as emulsifier have been described in previous articles.[11−13] The polycationic block copolymers used were poly (methyl methacrylate-*block*-quaternized *N*,*N*′-dimethylaminoethyl methacrylate) block copolymers. The synthesis and utility of these block copolymers in the stabilization of pigments in multiphase systems have also been reported.[14]

The characteristics of the block copolymers used are given in Table 1.

Radical Initiators. The radical emulsion polymerizations were performed using the following radical initiators: $K_2S_2O_8$, H_2O_2, and two azo initiators, AIBN (2,2′-azobisisobutyronitrile) and AAP (2,2′-azobis(2-amidinopropane).

The primary radical species originating from the thermal dissociation of these initiators yield radicals that are susceptible to induce the radical emulsion polymerization of a large range of partially water soluble vinylic monomers.[5−7]

Table 2. Primary Radicals from Initiators

initiators	primary radicals
$K_2S_2O_8$	$SO_4^{\bullet -}$
H_2O_2	$OH^{\bullet}$
AIBN	$CN(CH_3)_2C^{\bullet}$
AAP (acid medium)	$^{+}(NH_2)_2C(CH_3)_2C^{\bullet}$
AAP (basic medium)	$(NH)(NH_2)C(CH_3)_2C^{\bullet}$

Table 2 represents the initiators and their primary free radicals that were used in this study.

$K_2S_2O_8$ gives negatively charged radicals that are generated in the water phase, while H_2O_2 and AIBN will produce neutral radicals, which will however be generated in different phases, i.e., in the water phase for H_2O_2 and in the monomer oil phase for AIBN. The actual radical species that enter the latex particles are thought to consist of the addition of two or three monomer units to the primary radical particle, e.g. $^{\bullet}RSO_4^{-}$, where R denotes a dimer or trimer of MMA.[15]

From the last two entries in Table 2, it is clear that AAP can yield two radical species of a different nature; i.e., depending upon the pH of the aqueous medium of the emulsion polymerization, it is possible to have at one's disposal positively charged or neutral radicals.

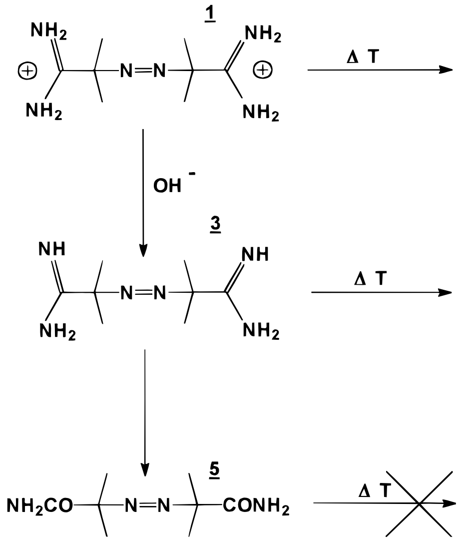
The dissociation of AAP to positively charged radicals in neutral and acidic media has been studied in detail, and AAP has been used as an excellent radical initiator in emulsion polymerizations.[7−8] The thermal dissociation of AAP in basic medium is complicated by the fact that, besides the thermal dissociation leading to neutral radical species, there is equally a competing hydrolysis. This might probably be the reason AAP never has been used under basic polymerization conditions.

Scheme 1 summarizes the fate of AAP depending upon the conditions maintained for its dissociation. AAP in neutral or acidic medium **1** dissociates uniquely to the positively charged radical **2**. In basic medium **1** is neutralized to **3** and yields the correspondingly neutral radical **4**. However, **3** can also hydrolyze to 2,2′-azobis-(2-carbamylpropane), **5** which is stable and will not dissociate upon heating.[9]

In our experiments we have taken care not to expose AAP to basic conditions, except just for the time needed for the emulsion polymerization (less than 15 min). Typical hydrolysis times for transforming **3** to **5** are several hours.[7] Anyhow, the minor extent of hydrolyzed AAP will be the same throughout the series of experiments, given that experimental conditions with respect to the hydrolysis reaction will be identical.

With these initiators the hereafter reported set of emulsion polymerization experiments was conducted. We distinguish six different situations, where R_p has been plotted as a function of the (block polyelectrolyte) emulsifier concentration. The concentrations have been expressed as molar concentrations since it has been shown that the polyionic blocks protrude in the aqueous phase thereby adopting an extended conformation.[12]

Scheme 1. Thermal Dissociation of 2,2′-Azobis(2-amidinopropane)



For the qualitative comparison of behavior of the different combinations of radicals and polyelectrolyte blocks, inferences about the rate of entry of radicals are made on the basis of polymerization rate data. We are well aware of the fact that other physical parameters such as particle number and initiator decomposition rate might be influenced. Particle size data and amount of microcoagulum for the latices obtained in these experiments were comparable. It shall be recalled that the electrosterically stabilized latex contained less microcoagulum and was much more stable than an SDS electrostatically stabilized latex.[12]

(1) Classical SDS Emulsifier vs Block Polyelectrolyte Surfactant. To get some notion of the efficiency of these polymeric emulsifiers, emulsion polymerizations of MMA have been conducted with SDS and PMMA-*b*-SPGMA.

The concentration of the emulsifiers was varied and the rate of polymerization calculated as $-\mathrm{d}[\mathrm{M}]/\mathrm{d}t$ in the linear part of the conversion/time plot. The applied experimental conditions were kept the same, as was already pointed out above.

Polymerizations that were conducted in the presence of up to 3.5×10^{-2} M 1-dodecanethiol did not show any significant difference in R_p compared to polymerizations without chain transfer agent, though the MW's of the polymers were considerably lowered.

Figure 1 shows a large difference in behavior for the two emulsifiers. The slope of R_p is much steeper for the polymerizations with PMMA-*b*-SPGMA. $R_p = 1.7 \times 10^{-4}$ mol L^{-1} s^{-1} is reached with 0.6 wt % of SDS. With the PMMA-*b*-SPGMA polymeric emulsifier at the same 0.6 wt % concentration $R_p = 7.3 \times 10^{-4}$ is obtained. The PMMA-*b*-SPGMA polymeric emulsifier is apparently some 4 times as efficient as SDS in this experiment. Some important theoretical and technological consequences are obvious: absolute polymerization rates that are not possible to reach with a classical emulsifier could be reached with a block polyelectrolyte. This might be of great importance for the polymerization of highly hydrophobic monomers that have very low water solubility. It is known that these monomers are very difficult to polymerize in emulsion and that the resulting latices are not very stable (e.g. emulsion polymerization of octadecyl methacrylate).[16] Another advantage of a much higher R_p could be to render the proces more amenable to continuous operation rather than batch polymerization. A block polyelectrolyte emulsifier could also grant advantages such as avoidance of surfactant migration in the film although it will be much more costly than SDS. A reduced level of surfactant as well as initiator not only would be cost-effective but also would lead to polymers containing less initiator, surfactant, and monomer residues, which have deleterious effects on the final polymeric product.

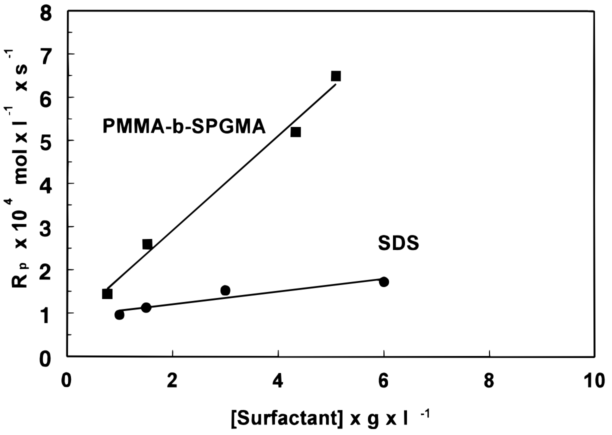
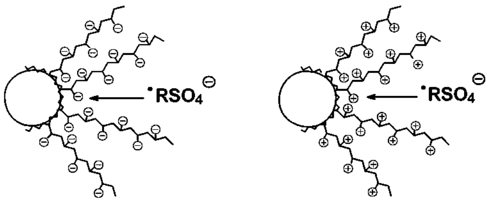


Figure 1. R_p as a function of surfactant concentration for situation 1, classical SDS emulsifier vs block polyelectrolyte surfactant. T = 60 °C; [MMA] = 0.4 M; [$K_2S_2O_8$] = 1.48×10^{-3} M. Key: (■) PMMA-*b*-SPGMA; (●) SDS.



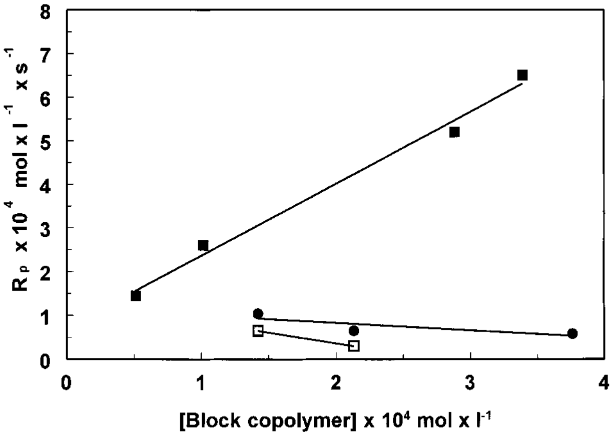


Figure 2. R_p as a function of block polyelectrolyte concentration for situation 2, negatively charged radical–block polyelectrolyte. T = 60 °C; [MMA] = 0.4 M; [$K_2S_2O_8$] = 1.48×10^{-3} M. Key: (■) PMMA-*b*-SPGMA; (●) PMMA-*b*-QPDMAEMA I; (□) PMMA-*b*-QPDMAEMA II.

(2) Negatively Charged Radical–Block Polyelectrolyte. From Figure 2, it is immediately clear that the R_p of the $K_2S_2O_8$ initiated emulsion polymerization of PMMA highly depends on the nature of the polymeric surfactant used.

The R_p with PMMA-*b*-SPGMA shows a steep increase of polymerization with increasing concentration and reaches high values as discussed in situation **1**.

PMMA-*b*-QPDMAEMA I shows a totally different behavior, not only are the absolute values lowered by a factor 15 at a polymer surfactant concentration of 4×10^{-4} mol L^{-1} but also the slope of R_p is negative. Increasing [PMMA-*b*-QPDMAEMA I] leads to reduction in R_p. This observation is not in agreement with the general Smith–Ewart kinetics that predict an increase of R_p with increasing emulsifier concentration. If these effects are due to inhibition of the emulsion polymerization, an induction period should have been observed. However, this is not the case. Moreover, if we proceed the polymerization in the presence of the higher M_n PMMA-*b*-QPDMAEMA II, there is an even lower R_p to be observed.

Finally, in the presence of PMMA-*b*-QPDMAEMA III, no polymer at all was obtained in the emulsion polymerization system, with polymeric surfactant concentrations down to 8×10^{-5} mol L^{-1}, all applied experimental conditions kept constant.

These observations are definitely in favor of an important influence of the electrosteric barrier around the latex particles on the R_p.

The externally (to the polymer particle) initiating radicals have to diffuse through the electrosteric barrier before reaching the latex particle polymerization locus. In the foregoing case, these negatively charged radicals will be subjected to repulsion from a similarly negatively charged polyelectrolyte barrier. The mobility of the negative radicals within the barrier will be high due to this mutual repulsion and the chemical potential, as a consequence of a concentration gradient, should be able to also drive these radicals very efficiently toward the surface of the polymer particle, where entry and subsequent propagation will take place.

The entering radical anions are electrostatically repelled by the fixed charges on the polymer and they may be expected to diffuse in from the external concentration down to very low concentrations.[17]

For negatively charged radicals entering the positively charged polyelectrolyte barrier, the situation is dramatically different as can also be seen from Figure 2. On entering the diffuse polycationic corona, the radicals will be attracted by the positively charged polyelectrolyte and they will compete with the Br^- counteranions of the polycationic QPDMAEMA block; eventually this counterion interaction will lead to territoral or even specific site binding.[18–22] Counterions are hereby supposed to be bound momentarily to the polyelectrolyte chain and hopping from one site to another, thereby having significantly reduced mobility.[23] This makes their diffusion toward the particle surface so slow that it will exceed the average lifetime of the radical. The absolute concentration of initiating radicals being heavily reduced, this will lead to a drastically reduced R_p.

Ultimately, if the diffusion of the free radicals to the latex particle surface becomes too slow, because of increased thickness of the electrosteric layer, there will be massive termination and no more radicals to reach the polymerization locus.

This hypothesis is thus clearly in line with the results observed with the higher M_n, PMMA-*b*-QPDMAEMA II and III.

(3) Neutral Radical–Block Polyelectrolyte. Two systems for emulsion polymerization initiated with neutral radicals are considered.

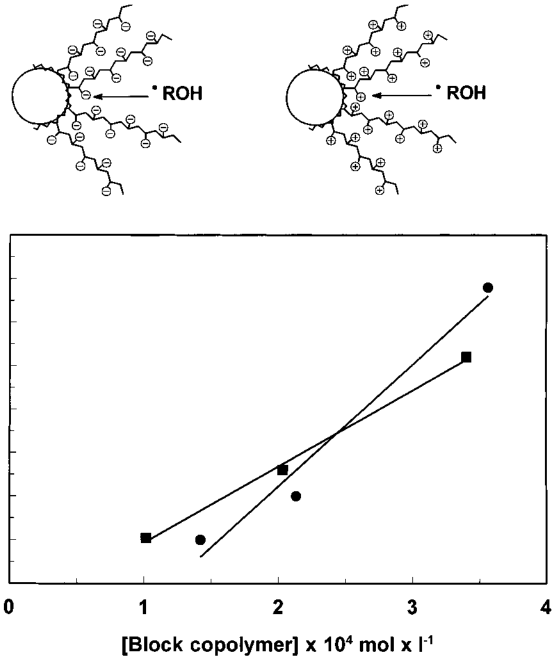


Figure 3. R_p as a function of block polyelectrolyte concentration for situation 3a, neutral radical–block polyelectrolyte. T = 60 °C; [MMA] = 0.4 M; $[H_2O_2] = 2.72 \times 10^{-2}$ M. Key: (■) PMMA-*b*-SPGMA; (●) PMMA-*b*-QPDMAEMA I.

(3a) The first is H_2O_2 that generates hydroxyl radicals in the aqueous phase. These radicals will have to diffuse through the polyelectrolyte barrier, before polymerization can take place.

(3b) AIBN generates cyanopropyl radicals, but these radicals are generated in the oil phase, i.e., in the monomer swollen micelle or polymer particle. Nomura, has published some elegant work to demonstrate that the actual addition of the radical to the monomer takes place in the aqueous phase very near to the surface of the polymer particle.[24,25] This thesis has however been refuted by others.[26] However, the important item in this discussion is that the radical is generated in or close to the oil phase and will not have to diffuse through the polyelectrolyte barrier before being able to start polymerization.

Figure 3 shows the results of the emulsion polymerizations initiated with H_2O_2 in the presence of the two charge opposed polyelectrolyte block surfactants. The absolute R_p values of either polyanionic or polyanionic block surfactant are high and comparable. There is no major difference in R_p, thus undiscriminating the neutral radical between the two oppositely charged barriers.

In addition, it is important to stress that these results deny the polyelectrolyte block inducing any inhibition.

Figure 4 represents AIBN-initiated polymerizations, conducted with either polyanionic or polycationic-*block*-polyelectrolyte surfactant. Again, the R_p values of both systems, although slow, are comparable. This sustains the hypothesis that the "internally" generated, neutral cyanopropyl radical is unaffected by the polyelectrolyte barrier.

(4) Positively Charged Radical–Block Polyelectrolyte. Emulsion polymerizations were conducted in the presence of AAP initiator in buffered acid medium at pH = 4.5. In these conditions, the thermal dissociation leads to positively charged radicals **2** (Scheme 1).

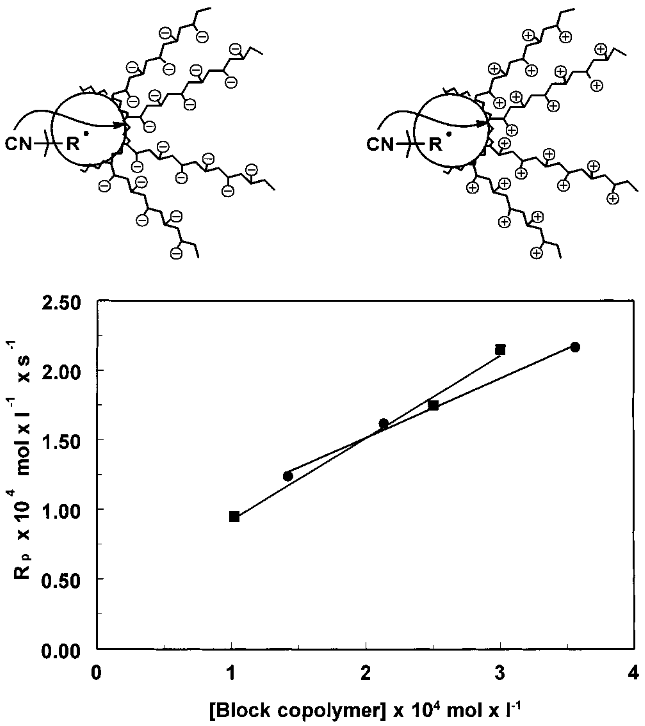


Figure 4. R_p as a function of block polyelectrolyte concentration for situation 3b, neutral radical–block polyelectrolyte. $T = 60$ °C; [MMA] = 0.4 M; [AIBN] = 2.65×10^{-3} M. Key: (■) PMMA-*b*-SPGMA; (●) PMMA-*b*-QPDMAEMA I.

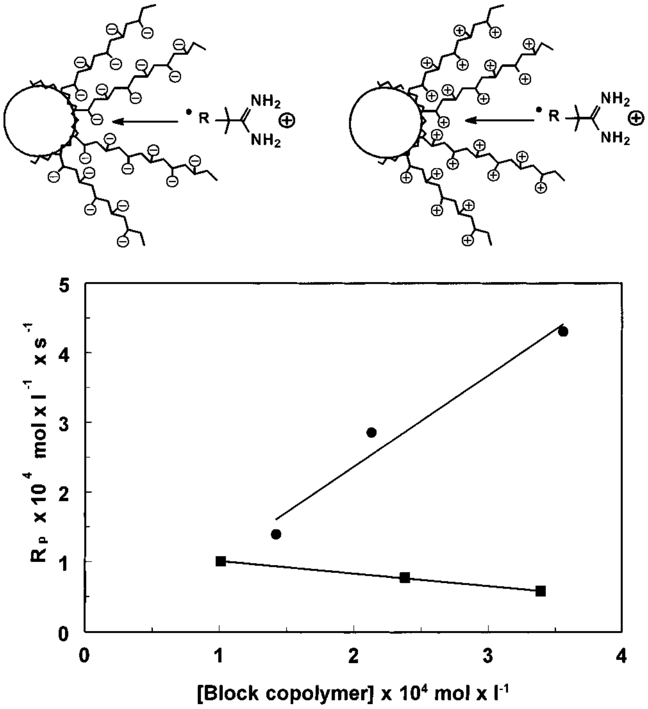


Figure 5. R_p as a function of block polyelectrolyte concentration for situation 4, positively charged radical–block polyelectrolyte. $T = 60$ °C; pH = 4.5; [MMA] = 0.4 M; [AAP] = 1.48×10^{-3} M. Key: (■) PMMA-*b*-SPGMA; (●) PMMA-*b*-QPDMAEMA I.

Figure 5 shows the results of these polymerizations in the presence of either polycationic or polyanionic block polyelectrolyte surfactants.

Again large differences in polymerization behavior are to be seen. The R_p of MMA in the presence of PMMA-*b*-QPDMAEMA I has a steep positive slope and reaches high values as opposed to the R_p values of the polymerizations conducted in the presence of PMMA-*b*-SPGMA that display a negative slope and low absolute values.

A consistent explanation of this anomalous behavior can be given, if we take into account that the positively charged radical will diffuse quickly through the polycationic corona, due to mutual repulsion from the radicals and the oppositely charged QPDMAEMA block. This will lead to fast entry and polymerization rates. In the case of the PMMA-*b*-SPGMA block surfactant, the positively charged radicals are attracted to the polyanionic block and have to compete with the Na^+ counterions in an ion exchange process. This will lead to a slowed diffusion of the initiating incoming radicals with concomitant decrease of radical flux at the polymer particle polymerization locus, thus leading to lower R_p. This is in complete agreement with the results discussed for Figure 2. In the present case, however, the situation with respect to the charge of the incoming radical is reversed, and the highest R_p is consistently found for the situation, where the charge of the radical is opposite to that of the polyectrolyte barrier. In the comparison of Figures 2 and 5 this strong similarity in behavior of oppositely charged polyelectrolyte barriers and radicals is definitely in favor of a phenomenon associated with the diffusion of the radical through the stabilizing barrier.

(5) Neutral Radical–Block Polyelectrolyte. This situation resembles that of situation 3a, in that an "external" neutral radical was used for the emulsion polymerization in the presence of PMMA-*b*-SPGMA and PMMA-*b*-QPDMAEMA, respectively. Exactly the same experimental set up as in situation 4 was used, except for the pH that was brought to a value of 10.5, immediately after which polymerization was started.

In basic medium, AAP will generate neutral radicals **4** upon thermal dissociation and polymerization proceeds fairly fast, though not at rates that are as high as for AAP in acid medium. Dissociation of AAP may become more difficult in basic medium due to lack of assistance of intramolecular charge repulsion, that tends to weaken the azo bond.

Figure 6 shows comparable behavior with respect to R_p for both PMMA-*b*-SPGMA and PMMA-*b*-QPDMAEMA in MMA emulsion polymerization. The fact that the neutral radical **4** could undiscriminatedly diffuse through the polyelectrolyte corona is consistent with the views developed in the situations above.

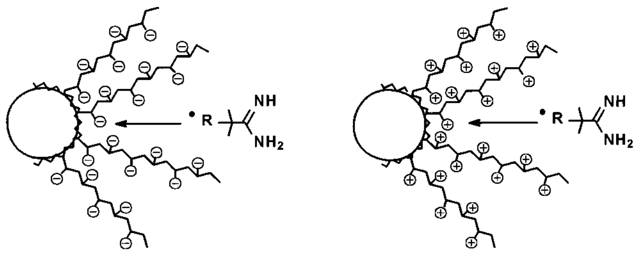
Free radical decay in block polyelectrolyte micelles.

In the foregoing situations (1–5), the rate of polymerization was taken as a sensitive means to try to probe the fate of the radical while diffusing through an elecrosteric barrier on its way to the locus of polymerization in the latex particle.

In the initial stage of emulsion polymerization, it is accepted that the initiating radical enters a monomer swollen micelle. In a block polyelectrolyte micellar system, the same kind of diffusional behavior toward oppositely charged radicals as developed above should equally apply.

In Figure 7, a plot of the absorbance of DPPH dissolved in micellar solutions of SDS, PMMA-*b*-SPGMA, and PMMA-*b*-QPDMAEMA, containing $K_2S_2O_8$, which was thermally dissociated at 50 °C, is presented as a function of time.

It is observed that there is no significant decrease in absorbance for the micellar solution of DPPH/PMMA-



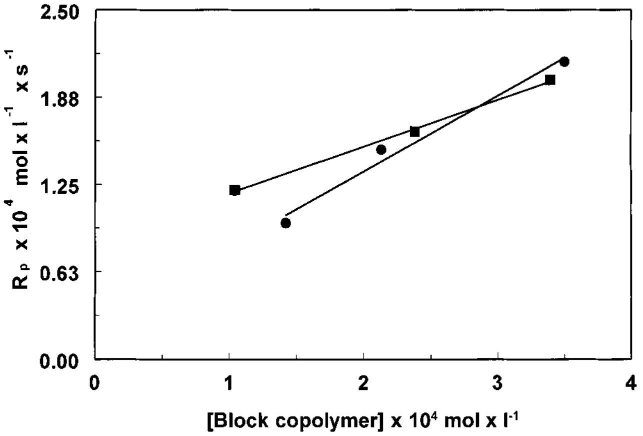


Figure 6. R_p as a function of block polyelectrolyte concentration for situation 5, neutral radical–block polyelectrolyte. $T = 60$ °C; pH = 10.5; [MMA] = 0.4 M; [AAP] = 1.48×10^{-3} M. Key: (■) PMMA-*b*-SPGMA; (●) PMMA-*b*-QPDMAEMA I.

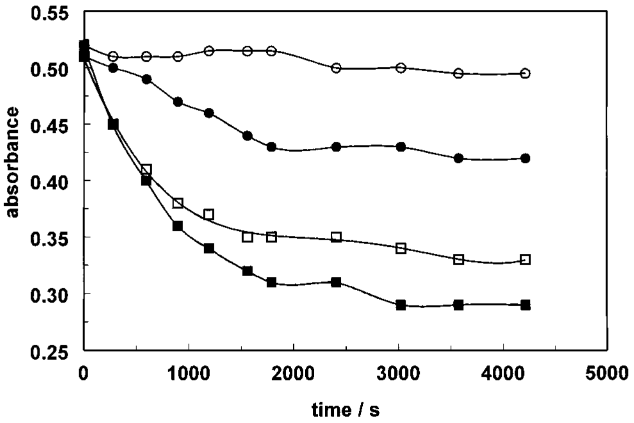


Figure 7. Absorbance of DPPH as a function of time as a measure for free radical decay in block polyelectrolyte micelles. $T = 50$ °C; [DPPH] = 4.3×10^{-5} M; [$K_2S_2O_8$] = 1.48×10^{-3} M. Key: (■) [PMMA-*b*-SPGMA] = 1.4×10^{-4} M; (●) [PMMA-*b*-QPDMAEMA I] = 1.4×10^{-4} M; (○) [PMMA-*b*-QPDMAEMA I] = 1.4×10^{-4} M, reference without $K_2S_2O_8$; (□) [SDS] = 1.0×10^{-2} M.

b-QPDMAEMA I containing no $K_2S_2O_8$, which was used as a reference solution.

In the presence of $K_2S_2O_8$, a decrease in absorbance is to be seen, due to the reaction of the violet DPPH with the persulfate radicals to less colored addition products. A progressively smaller decrease in absorbance is to be seen respectively, with the PMMA-*b*-SPGMA, SDS, and, finally, PMMA-*b*-QPDMAEMA solutions.

These results fully confirm that oppositely charged radicals and polyelectrolyte brushes interact, so as to slow diffusion of radicals, limiting the incoming flux of active radicals that can undergo subsequent reaction, while a corona of the same charge increases their mobility.

One could also argue that a negatively charged corona around a growing polymer particle prevents escape to a similar charged radical thus increasing R_p. A positive-charged corona could allow escape of a negative-charged radical thereby reducing R_p.

Conclusions

The results presented in this study allow the following conclusions to be drawn with respect to the emulsion polymerization of MMA in the presence of PMMA-*b*-SPGMA, anionic, and PMMA-*b*-QPDMAEMA, cationic, block polyelectrolytes.

It is clearly apparent that the combination of the charge of the entering radical and the charge of the block polyelectrolyte thoroughly influence the rate of emulsion polymerization.

Radicals and polyelectrolyte barriers of opposite sign lead to strongly reduced rates of polymerization, presenting anomalous Smith–Ewart kinetics, in that R_p slows down with increasing surfactant concentration and width of the polyelectrolyte block barrier.

For radicals and polyelectrolyte barriers of identical sign, R_p's with steep positive slopes as a function of block polyelectrolyte concentration were found. The rate of polymerization is greatly enhanced for systems using a polyelectrolyte block, as compared to classical low molecular weight surfactant. This has some important technological potential.

These results are consistent with a model wherein the R_p is diffusion controlled by the polyelectrolyte corona around the latex particle.

Radicals entering the polyelectrolyte barrier of opposite sign are thought to be subjected to counterion interaction with loss of mobility, thus becoming more prone to premature aqueous phase termination. Eventually this will lead to strongly reduced R_p, and even to reaction shut off.

This particular and unique situation appears to be totally different from that encountered with low MW surfactants, i.e., the earlier conclusions of Penboss et al.,[9] who observed the entry rate coefficient to be insensitive to the charge carried by the primary free radical. Charge effects have been shown to be unimportant, based on the absence of an ionic strength effect, absence of surface coverage effect, and similarity in behavior between free radicals of different charge.[27]

The experimental results with block polyelectrolyte mediated emulsion polymerization presented by us are consistent with the theoretically predicted case where the "control by aqueous phase growth" theory for the entry of free radicals in latex particles is invalid.[10]

Acknowledgment. The authors are indebted to Mrs. P. Rousseau for skilful technical assistance with the anionic polymerizations and to Mr. M. Achchoubi for performing the preliminary emulsion polymerizations, as well as to Agfa-Gevaert N.V. for generous financial support. They are especially grateful to Prof. B. Gilbert and Dr. P. Louis for refreshing discussions.

References and Notes

(1) Hansen, F. K.; Ugelstad, J. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 3033.
(2) Blackley, D. C. *Emulsion Polymerization*; Applied Science: London, 1975.
(3) Kim, J. U.; Lee, H. H. *Macromolecules* **1994**, *27*, 3337.

(4) Vanderhoff, J. W. In *Vinyl Polymerization*; Ham, G., Ed.; Marcel Dekker: New York, 1969; Vol. 7, Part 2.

(5) Fitch, R. M.; Tasi, C. H. In *Polymer Colloids*; Fitch, R. M., Ed.; Plenum: New York, 1971.

(6) Penboss, I. A.; Napper, D. H.; Gilbert, R. G. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 2247.

(7) Yeliseeva, V. I. In *Emulsion Polymerization*; Piirma, I., Ed.; Academic Press: New York, 1982.

(8) Ottewil, R. H. In *Emulsion Polymerization*; Piirma, I., Ed.; Academic Press: New York, 1982.

(9) Penboss, I. A.; Gilbert, R. G.; Napper, D. H. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 1257.

(10) Maxwell, I. A.; Morrison, B. R.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1991**, *24*, 1629.

(11) Leemans, L.; Fayt, R.; Teyssié, Ph. *J. Polym. Sci. A* **1990**, *28*, 1255.

(12) Leemans, L.; Fayt, R.; Teyssié, Ph.; de Jaeger, N. C. *Macromolecules* **1991**, *24*, 5922.

(13) Leemans, L.; Fayt, R.; Teyssié, Ph.; Uytterhoeven, H.; De Winter, W. *J. Polym. Sci. A* **1990**, *28*, 2187.

(14) Teyssié, Ph. J.; Leemans, L. E.; Verdijck, W. A.; de Jaeger, N. C. US Pat. 5,200,456, 1993.

(15) Maxwell, I. A.; Morrison, B. R.; Napper, D. H.; Gilbert, R. G. *Makromol. Symp.* **1990**, *31*, 1.

(16) Uytterhoeven, H. J. Private communication.

(17) Crank, J.; Park, G. S. Eds. *Diffusion in Polymers*; Academic Press: London and New York, 1968.

(18) Nordmeier, E. *Polymer J.* **1994**, *26*, 539.

(19) Morishima, Y.; Higuchi, Y.; Kamachi, M. *J. Polym. Sci.* **1991**, *29*, 677.

(20) Rios, H. E.; Gamboa, C.; Ternero, G. *J. Polym. Sci., Part B: Polym. Phys.* **1991**, *29*, 805.

(21) Hao, M.; Harvey, S. C. *Macromolecules* **1992**, *25*, 2200.

(22) Itaya, T.; Ochiai, H. *J. Polym. Sci., Part B: Polym. Phys.* **1992**, *30*, 587.

(23) Jakubovic, A. O.; Hills, G. J.; Kitchener, J. A. *Trans. Faraday Soc.* **1959**, *55*, 1570.

(24) Nomura, M.; Fujita, K. *Makromol. Chem. Rapid Commun.* **1989**, *10*, 581.

(25) Nomura, M.; Yamada, A.; Fujita, S.; Sugimoto, A.; Ikoma, J.; Fujita, K. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 987.

(26) Alduncin, J. A.; Forcada, J.; Barandiaran, M. J.; Asua, J. M. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 987.

(27) Adams, M. E.; Trau, M.; Gilbert, R. G.; Napper, D. H.; Sangster, D. F. *Aust. J. Chem.* **1988**, *41*, 179.

MA971162R