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Semicontinuous Emulsion Copolymerization of Styrene and Butyl Acrylate

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Synopsis

Semicontinuous emulsion copolymerization of styrene and butyl acrylate with a constant rate of feed of monomer emulsion was investigated. The integral composition of the copolymer at the end of the feeding was different from the feed composition, and the difference was proportional to the monomer feeding rate. The closer the feed composition was to the composition at the azeotropic point, the lower was the sensitivity of the system to the feeding rate. At low feeding rates, the copolymerization proceeded at conversions of about 90–95%, and the composition of the copolymer was practically equal to that of the monomer feed. The reactivity ratios determined under these conditions were probably influenced by diffusion inside the growing polymer–monomer particles.

INTRODUCTION

Emulsion polymerization of water-insoluble monomers proceeds in the case of a batch process in three stages.[1–3] In the first interval, nucleation of the particles occurs until micellar emulsifier is depleted. In the second interval, growth of the particles takes place, polymerizing monomer being supplied by diffusion from the droplets through the water phase into the polymer–monomer particles. In the third stage, which begins after the disappearing of the monomer droplets, the polymerization is finished by the reaction of the monomer in the swollen polymer–monomer particles.

In the second interval, the polymerization rate is proportional to the number of the particles. The average number of the growing radicals $\bar{n}$ in small particles is supposed to be 0.5, and the polymerization rate in single particles can be expressed in the form of the equation

$$R_p = k \cdot C_M \tag{1}$$

where C_M is the concentration of monomer in the particle. The diffusion rate of the monomer through the water phase into the growing particles is, as a rule, higher than the polymerization rate; thus, the polymerization rate is limited by the maximum swelling of the polymer particles by the monomer.[4]

In conventional emulsion polymerizations, the monomers are frequently fed into the polymerizing system gradually during the process. These so-called semicontinuous polymerizations are carried out with or without the addition of a seed latex, and the monomers are fed either as such or in the form of an emulsion. The manner of the particle growth as well as their final size may differ very much from one case to another. Flocculation of the particles or nucleation of new ones at the end of the feeding period is possible,[5] depending on the emulsifier amount fed into the reaction mixture with the monomers.

If the particle number is constant, the maximum polymerization rate R_p max is proportional to the equilibrium volume fraction of monomer in the particle, v_{eq}:

$$R_p \max = k \cdot v_{eq}. \tag{2}$$

In case of a low feeding rate R_f (less than R_p max), a stationary state appears in the system after some time when $R_p = R_f$ may be supposed. The rate of the approach to the stationary state is indirectly proportional to R_f and directly proportional to the particle number. When the feeding rate exceeds R_p max, the polymerization rate remains constant at R_p max.[6,7] If the mixture of monomers is fed at a constant rate, the concentration of the more reactive monomer decreases. At a suitable feeding rate ($R_f \ll R_p$ max), the stationary state is approached, and at a constant monomer composition a copolymer is produced the composition of which is practically the same as the ratio of monomers in the feed.[8,9]

The behavior of most of monomers during the emulsion copolymerization is, in general, not the same as in the solution systems. They may differ in molar volumes, solubility parameters, polarity, and water solubility, respectively. Only monomers exhibiting equal solvent properties follow strictly the reactivity ratio scheme in emulsion copolymerization.

In this paper, the effect of rate of feed of monomer emulsion on the emulsion copolymerization of styrene and butyl acrylate has been studied.

EXPERIMENTAL

Copolymerizations were carried out in a 2000-cm^3 stainless steel reactor at 70°C in a nitrogen atmosphere as shown in Table I.

Charge A was heated in the reactor to 70°C in a nitrogen–atmosphere; then

TABLE I
Copolymization Charges

		Charge,g	
A. Distilled water		300	
Etoxon AF-5		16	
B. Distilled water		10	
Ammonium persulfate		2.4	
Sodium metabisulfite		1.2	
C. Distilled water		640	
Etoxon AF-5		37.4	
Slovafol 920		32.0	
Ammonium persulfate		5.6	
D. Styrene	160	320	640
Butyl acrylate	640	480	160
E. Distilled water		50	
Sodium metabisulfite		2.8	

charge B was added, and the addition of the emulsion prepared from charges C and D was immediately started. Charge E was fed into the reactor simultaneously with the emulsion, the time of the addition being the same as the feeding time of the monomer emulsion feed.

Styrene (Kaučuk Kralupy); butyl acrylate (BASF); Etoxon AF-5, $C_9H_{19}C_6H_4(OCH_2CH_2)_5OSO_3Na$ (Spolek pro chemickou a hutní výrobu, Boletice); and Slovafol 920, $C_9H_{19}(OCH_2CH_2)_{20}OH$ (CHZWP Nováky) were used. Ammonium persulfate p.a. and sodium metabisulfite p.a. were supplied by Lachema Brno, CSSR. The monomers were freshly distilled.

Free monomers were analyzed during the copolymerization by GLC. Samples taken from the reaction system were precipitated in methanol containing 500 ppm of hydroquinone. Toluene was used as an internal standard. The particle size was determined by electron microscopy.

RESULTS AND DISCUSSION

The polymerization rate in an individual polymer/monomer particle is proportional to the concentration of unreacted monomers. At $R_f < R_p$ max, the polymerization rate may reach R_f. Higher polymerization rates at higher feeding rates are possible due to a higher concentration of free monomers in the particle. In the case $R_f > R_p$ max, excess monomer is present in the binary monomer phase. Thus, the instantaneous monomer/polymer conversion depends on the feeding rate. At $R_f \approx 16 \times 10^{-5}$ mole/kg·sec the butyl acrylate conversion was approx. 30%, whereas at a low value of R_f (approx. 3×10^{-5} mole/kg·sec) instantaneous conversions were very high, up to approx. 90% (Figs. 1–3); t/t_f in all figures means feeding time/total feeding time. At the beginning of monomer addition, styrene (the more reactive monomer) was more quickly consumed; but later, a stationary state with a practically constant conversion ratio c_pSty/c_pBA (Figs. 4–6) was reached. The rate of the approach to the stationary state (constant conversion ratio) is inversely proportional to the feeding rate. The difference in the ratio c_pSty/c_pBA from unity shows the deviation of copolymer composition from monomer feed composition. The effect of the feeding rate and of the feed composition on the integral copolymer composition at the feeding end is shown in Figure 7. It is evident that the nearer the feed composition is to the azeotropic one, the

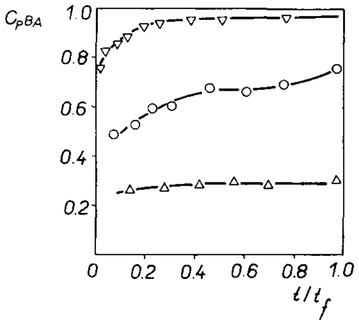

Fig. 1. Conversion of butyl acrylate during feeding of monomer emulsion in relation to feeding rate. Weight ratio BA/styrene = 20/80. R_f (mole/kg·sec): (▽) 2.74×10^{-5}; (○) 9.86×10^{-5}; (△) 18.08×10^{-5}.

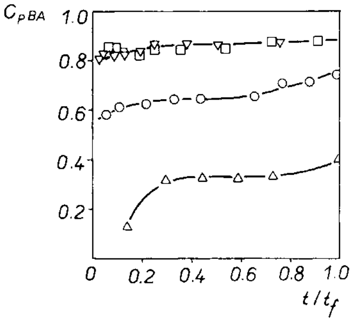

Fig. 2. Conversion of butyl acrylate during feeding of monomer emulsion in relation to feeding rate. Weight ratio BA/styrene = 60/40. R_f (mole/kg·sec): (▽) 2.51 × 10^{-5}; (□) 3.61 × 10^{-5}; (○) 6.60 × 10^{-5}; (△) 17.55 × 10^{-5}.

smaller is the sensitivity of the process on the feeding rate variation, i.e., the smaller is the composition deviation between the monomer mixture fed and the resulting copolymer.

At low feeding rates R_f, the formation of the free monomer equilibrium ratio was comparatively fast. The consumption rate of monomers in the feeding region of 20–80% was very close to the feeding rate of each monomer, as shown in Table II. The conversion values show that the highest copolymerization rates are at a weight ratio BA/Sty = 20/80. This result is in conformity with the results of Mangaraj[10] who found a similar maximum copolymerization rate at a ratio of 20/80. This fact has been explained by the easier addition of the acrylate radicals to the styrene monomer as compared with the addition of the styryl radicals to the acrylate. If only a small amount of acrylate is present, the terminal units are predominantly styrene units, the penultimate being styrene or acrylate. Since both these radicals are well resonance stabilized and the penultimate units may cause steric-hindrance, the termination rate is lower than that in pure styrene and the total polymerization rate is higher. With increase in the acrylic content, more radicals with an acrylic terminal unit will appear, which will facilitate a cross-termination reaction. Since the rate of the cross termination is much greater than the rate of the homotermination, this will lead to a lower rate of polymerization.[10] The higher conversion at a ratio BA/Sty = 20/80 was apparently not caused

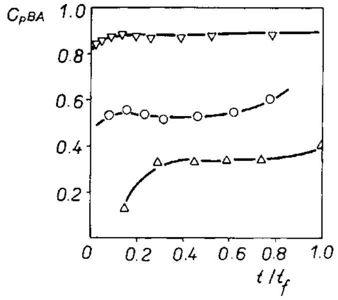

Fig. 3. Conversion of butyl acrylate during feeding of monomer emulsion in relation to feeding rate. Weight ratio BA/styrene = 80/20. R_f (mole/kg·sec): (▽) 2.47 × 10^{-5}; (○) 8.70 × 10^{-5}; (△) 15.52 × 10^{-5}.

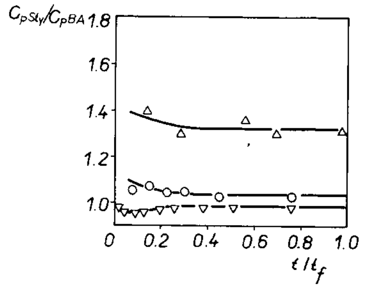

Fig. 4. Styrene/butyl acrylate conversion ratio during feeding of monomer emulsion in relation to feeding rate. Weight ratio BA/styrene = 20/80. R_f (mole/kg-sec): (▽) 2.74 × 10^{-5}; (○) 9.86 × 10^{-5}; (△) 18.08 × 10^{-5}.

by the difference in the particle number, because the smallest particles were found at the ratio BA/Sty = 80/20 (Fig. 8).

The monomer mixture composition in the reaction phase and the differential copolymer composition produced at low feeding rates R_f are summarized in Table III. It is evident that the average values of the differential copolymer composition are very close to the monomer feed composition.

From the values f_{BA} (mole fraction of free BA in the reaction mixture) and F_{BA} (mole fraction of BA in arising copolymer), the reactivity ratios r_1 and r_2 were calculated from three available compositions (see Table IV).

The reproducibility of the above reactivity ratios was fair (see Table IV). On the other hand, the found values differ from those published by other authors (see Table V). It is to be remarked here that only the values[10] $r_1 = 0.24$ and $r_2 = 0.62$ relate to emulsion copolymerization.

The unconverted monomer composition determined at the emulsion process includes all the monomers present; i.e., monomers absorbed in the particles, dissolved in the water phase, and present in the monomer droplets. The copolymerization is influenced by the monomer composition at the actual copolymerization sites, i.e., by the monomer composition in the growing polymer–monomer particles. At low conversions and at low water solubilities of the monomers, the experimentally determined monomer composition practi-

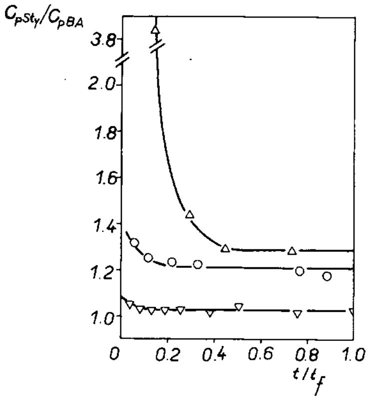

Fig. 5. Styrene/butyl acrylate conversion ratio during feeding of monomer emulsion in relation to feeding rate. Weight ratio BA/styrene = 60/40. R_f (mole/kg-sec): (▽) 2.51 × 10^{-5}; (○) 6.60 × 10^{-5}; (△) 17.55 × 10^{-5}.

TABLE II
Relationship Between Feed Composition, Arising Copolymer, and Conversion of Both Monomers at Low Feeding Rates

Mole ratio BA (feed)	$R_f \times 10^5$, mole/kg·sec			$R_p \times 10^5$, mole/kg·sec			c_p, %		
	BA	Styrene	Total	BA	Styrene	Total	BA	Styrene	Total
0.765	1.89	0.58	2.47	1.67	0.54	2.21	88	92	89
0.549	1.38	1.13	2.51	1.24	1.05	2.29	88	89	88
0.169	0.46	2.28	2.74	0.45	2.20	2.65	96	95	95

cally equals the monomer composition in the binary monomer phase, whereas the composition in the growing particles depends on the composition ratio between the polymeric and water phase.[14] On the contrary, at high conversions (in interval III), the monomers are present practically only within the growing latex particles. In our case, the high instantaneous conversion corresponds to interval III, but a fresh emulsion monomer mixture is continuously fed into the polymerizing system during the process; the fresh emulsifier can be a source of new particle formation.

In the case of low feeding rates, where the monomer content in the latex particles is very low, quick monomer diffusion into the particles takes place and the droplets continuously fed into the system disappear quickly. Thus, the determined content of unconverted monomers in the reaction mixture should practically correspond to their content in the swollen particles.

In case of batch polymerizations, supposing there is one growing radical in every particle, the diffusion rate of monomers from the droplets into the polymer–monomer particles are, in interval II, generally greater than their consumption rate during the polymerization process.[15] On the other hand, at low feeding rates during the semicontinuous emulsion polymerization, the monomer content in the particles does not reach the maximum, i.e., the equilibrium concentration; the polymerization rate in this case is limited by the feeding rate. It is evident from the equilibrium volume swelling ratios, which

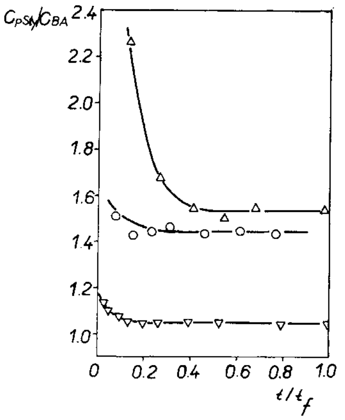

Fig. 6. Styrene/butyl acrylate conversion ratio during feeding of monomer emulsion in relation to feeding rate. Weight ratio BA/styrene = 80/20. R_f (mole/kg·sec): (▽) 2.47×10^{-5}; (○) 8.70×10^{-5}; (△) 15.52×10^{-5}.

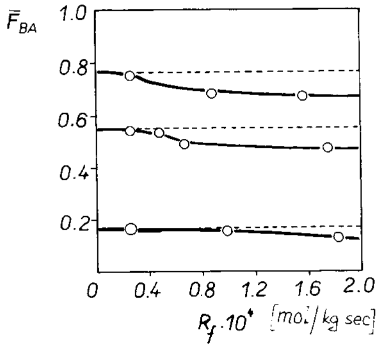

Fig. 7. Integral copolymer composition (mole fraction of butyl acrylate $\bar{F}_{BA}$) at end of feeding of monomer emulsion in relation to feeding rate: (- - -) mole fraction of BA in the monomer feed.

varied in the range of 1.5–1.9 (see Table VI), that the interval III of our system corresponds to conversions greater than 55–65%. Analyzing the monomer mixtures after reaching the swelling equilibrium by GLC, it was found that none of the monomers used was imbibed preferentially.

The ratios of monomers in the reaction mixtures and in the arising copolymers at the conversions corresponding approximately to the range between intervals II and III, i.e., close to the maximum particle swelling, are shown in Figures 9–11, in which also the compositions found at low values of R_f (see Table III) are represented. Supposing that the system is governed by the theoretical copolymerization scheme, the total monomer concentration in the system at higher R_f, i.e., at higher copolymerization rates, should be greater, but their ratio after reaching the stationary state should be the same as at low feeding rates. However, the experimental data indicate that the unreacted monomer ratios at different feeding rates differ. At greater R_f, the f_{BA} is greater, but F_{BA} is lower than at low R_f. This change in the free monomer composition at higher R_f is probably not caused by the presence of a higher content of the binary monomer phase in the system, because the determined composition is more different from the feed composition than in the case of low R_f.

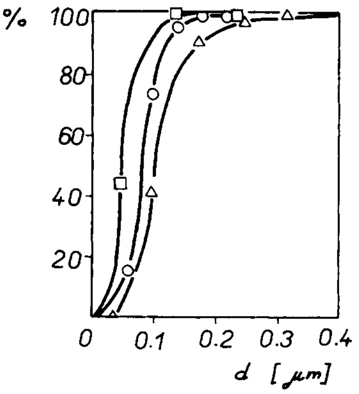

Fig. 8. Cumulative particle size distributions. BA/styrene weight ratios: (□) 80/20; (△) 60/40; (○) 20/80.

TABLE III

Mole Fraction of BA in Reaction Mixture (f_{BA}) and Differential Copolymer Composition (F_{BA})[a]

0.765 mole fraction[b]			0.549 mole fraction			0.169 mole fraction		
t/t_f	f_{BA}	F_{BA}	t/t_f	f_{BA}	F_{BA}	t/t_f	f_{BA}	F_{BA}
0.130	0.850	0.761	0.126	0.591	0.542	0.127	0.136	0.172
0.195	0.832	0.754	0.189	0.596	0.541	0.191	0.136	0.169
0.260	0.838	0.753	0.252	0.602	0.543	0.254	0.135	0.169
0.390	0.842	0.754	0.378	0.595	0.542	0.381	0.137	0.169
0.519	0.846	0.756	0.504	0.614	0.541	0.508	0.139	0.170
0.779	0.836	0.756	0.756	0.593	0.540	0.763	0.134	0.170
Average values	0.841	0.756		0.599	0.542		0.136	0.170

[a] $t/t_f = \dfrac{\text{feeding time}}{\text{total feeding time}}$.

[b] Of BA in monomer feed.

TABLE IV

Reactivity Ratios of BA and Styrene Experimentally Found at Low Feeding Rates R_f

Feed compositions BA/styrene	r_1	r_2
20/80–60/40	0.4775	0.6689
20/80–80/20	0.4707	0.6681
60/40–80/20	0.4690	0.6528
Average values	0.47 ± 0.01	0.66 ± 0.01

TABLE V

Published Reactivity Ratios for Butyl Acrylate (M_1) and Styrene (M_2)

r_1	r_2	Reference
0.24	0.62	10
0.19	0.76	11
0.15	0.76	12
0.19	0.68	12
0.19	0.64	12
0.34	1.03	12
0.21	0.82	13

TABLE VI

Equilibrium Volume Swelling Ratios H_v[a]

Copolymer composition	Monomer mixture used for swelling BA/styrene (weight)				
BA/styrene (weight)	0/100	100/0	80/20	60/40	20/80
80/20	1.5	1.9	1.8	—	—
60/40	1.6	1.5	—	1.6	—
20/80	1.6	1.7	—	—	1.7

[a] Volume of swollen particles/volume of original particles.

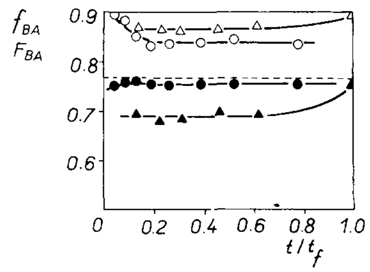

Fig. 9. Instantaneous compositions (mole fractions of BA) of monomer mixture (f_{BA}) and arising copolymer (F_{BA}) during feeding of the monomer emulsion in relation to the feeding rate. Weight ratio BA/styrene = 80/20. Dashed line = mole fraction of BA in the monomer emulsion feed: (△, ○) f_{BA}; (▲, ●) F_{BA}. R_f (mole/kg·sec): (○, ●) 2.47×10^{-5}; (△, ▲) 8.70×10^{-5}.

The ideal stationary state was not reached in any of the feed compositions used. At high R_f within the middle part of the reaction, however, the monomer composition in the system did not change very much. The reactivity ratios r_1 and r_2 were calculated from the unreacted monomer ratio and from the composition of arising copolymer (Table VII) at the point of 50% addition (see Table VIII). These reactivity ratios differ from those found at low feeding rates (see Table IV). We suppose that this difference is caused by the diffusion control of copolymerization proceeding at high conversions. The reactivity ratios determinated at different feeding rates are to be regarded as effective values under the given polymerization conditions. Before a monomer molecule can participate in a polymerization reaction, it has to enter from the monomer droplet into the aqueous phase, diffuse through it to the growing latex particle, cross the water–particle interface, and diffuse into the particle. Monomer transfer from the droplets to the water phase is not impeded, because their surface is convered by only a small amount of emulsifier.[16] Monomer transfer through the water phase is governed by the diffusion flow, which is, in correlation to the droplet and particle sizes, described by the Smoluchowski equation.[17] The monomer flow from monomer droplets to the water phase and from the water phase into polymer particles depends on the droplet and particle sizes, concentration gradients, and diffusion coefficients.

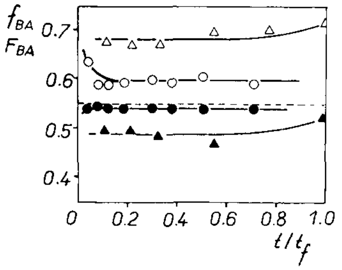

Fig. 10. Instantaneous compositions (mole fractions of BA) of monomer mixture (f_{BA}) and arising copolymer (F_{BA}) during feeding of monomer emulsion in relation to feeding rate. Weight ratio BA/styrene = 60/40. Dashed line = mole fraction of BA in monomer emulsion feed: (△, ○) f_{BA}; (▲, ●) F_{BA}. R_f (mole/kg·sec): (○, ●) 2.51×10^{-5}; (△, ▲) 6.60×10^{-5}.

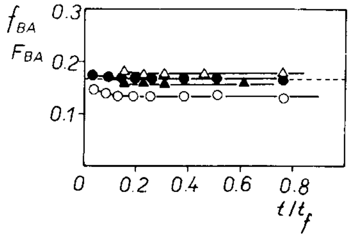

Fig. 11. Instantaneous compositions (mole fractions of BA) of monomer mixture (f_{BA}) and arising copolymer (F_{BA}) during feeding of monomer emulsion in relation to feeding rate. Weight ratio BA/styrene = 20/80. Dashed line = mole fraction of BA in monomer emulsion feed: (△, ○) f_{BA}; (▲, ●) F_{BA}. R_f (mole/kg·sec): (○, ●) 2.74 × 10^{-5}; (△, ▲) 9.86 × 10^{-5}.

For most monomers the value of diffusion coefficient in water was found to be approx. 10^{-5} cm^2/sec, and the polymerization rate does not usually exceed the water phase diffusion rate, unless the propagation rate constant[15] is greater than 10^4 l/mole·sec. The propagation rate constants[10] for butyl acrylate and styrene are in the range of 10^2–10^3 l/mole·sec. The values of diffusion coefficients in highly swollen polymers are about 10^{-5} cm^2/sec, and in less swollen polymers, about 10^{-7} cm^2/sec. In solid polymers at temperatures over T_g, diffusion coefficients are about 10^{-9} cm^2/sec, and at temperatures below T_g or in highly crystalline polymers, about 10^{-11}–10^{-14} cm^2/sec.

In most practical cases, its value is not less than 10^{-7} cm^2/sec,[18,19] and the polymerization is not hindered by diffusion within the particles. This case can be expected also at the semicontinuous copolymerization studied, which was carried out at about 60% conversion, i.e., in the region near the saturation monomer concentrations in the particles. The polymerization conditions at such polymerizations were similar to those of interval II in the batch process, except for the practically constant unreacted monomer ratio. If the polymerization takes place at the saturation monomer concentration in the particle, then the diffusion flow of the monomer into the particle may be restricted. Thus, at high polymerization rates, the influence of the permeability at the phase boundary between the particle surface and water phase could affect the copolymerization.[15,20]

At low feeding rate of the emulsion monomer feed, the polymerization proceeded at high conversions. The value of the monomer concentration inside the particles was then much lower than the saturation one, and the diffusion flow was facilitated by the higher concentration gradient. It may be supposed that, because of the lower polymerization rate limited by the low feed-

TABLE VII
Composition of Monomers and of Arising Copolymer at Higher Feeding Rate R_f and at 50% Feed

Feed monomer ratio BA/styrene (weight)	f_{BA} at 50% feed (monomers)	F_{BA} at 50% feed (copolymer)
80/20	0.865	0.690
60/40	0.680	0.490
20/80	0.180	0.160

TABLE VIII
Reactivity Ratios Calculated in the Range of 60% Conversion

Composition of monomers BA/styrene used (weight)	r_1	r_2
80/20–60/40	0.2630	1.3230
80/20–20/80	0.1903	0.9811
60/40–20/80	0.2453	0.9950
Average values	0.23 ± 0.03	1.10 ± 0.2

ing rate, the monomer diffusion rate into the particles was not impeded by the phase interface permeability. On the other hand, at high conversions, the viscosity inside the polymer–monomer particles increases. This lowers the termination rate of the growing radicals. This is the reason for the possibility of the existence of more than 0.5 radicals in one particle at high conversions. For example, at conversions $\approx$ 95% for the continuous polymerization of styrene, in small latex particles $\bar{n} = 4$ was found, and in great particles ($\bar{d} = 16\ \mu$m), even $\bar{n} = 35{,}000$.[21] Increasing $\bar{n}$ increases also the value of k in eq. (1), this leading to high polymerization rates even at low concentrations of C_M. The polymerization rate is then governed by the monomer diffusion inside the polymer–monomer particle. Thus, the effective reactivity ratios estimated at these conditions should include not only the kinetic but also the physical control of the process.

CONCLUSIONS

The integral composition of the copolymer arising at the semicontinuous copolymerization at the end of the feeding is different from the feed composition, and the difference is proportional to the monomer feeding rate. The closer the feed composition is to the composition at the azeotropic point, the lower is the sensitivity of the system to the feeding rate.

At low feeding rates R_f, the copolymerization proceeded at conversions of about 90–95%, where the composition of the arising copolymer was practically equal to the monomer feed composition. The reactivity ratios determined under these conditions are probably influenced by the disproportion between the polymerization rate inside the highly conversed particles and the monomer transport rate to the polymerization sites. Monomer diffusion factors inside the growing polymer–monomer particle are expected to influence the course of the reaction.

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