Kinetic Investigations of Acrylic–Polyurethane Composite Latex

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ABSTRACT: The effect of various reaction parameters on the rate of polymerization, R_p, and on the particle size and morphology of aqueous acrylic–polyurethane hybrid dispersions, prepared by semibatch emulsion polymerization, was investigated. The particles of polyurethane dispersion were used as seeds during the polymerization of acrylic component: methyl methacrylate (MMA), butyl acrylate (BA), and a mixture of MMA and BA with the ratio of 1:1. These emulsions were found to form structured polymer particles in aqueous media using scanning electron microscopy. The kinetics of the emulsion polymerization was studied on the basis of Wessling's model. The influence of emulsifier and initiator concentrations, including the monomer feed rates, R_m, on the rates of polymerization and on the properties of the resulting dispersions were studied. The number of particles and the particle size were also measured during the polymerization process. The final values were found to be independent of the concentration of the emulsifier, initiator and the monomer feed rate in monomer starved conditions. In the steady-state conditions, during the seeded semibatch hybrid emulsion polymerization, the rate of polymerization and the monomer feed rate followed the Wessling relationship $1/R_p = 1/K + 1/R_m$. The dispersions MMA/PU, BA/PU, and MMA/BA/PU have K values of 0.0441, 0.0419 and 0.0436 mol/min, respectively. The seeded BA/PU hybrid polymerization proceeded according to Smith-Ewart Case I kinetics, while the MMA/PU hybrid emulsions demonstrate Case II of the Smith-Ewart kinetic model. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 2639–2649, 2002

Key words: core-shell polymers; emulsion polymerization; kinetics; polyurethanes

INTRODUCTION

Semibatch emulsion polymerization is a widely used process by which many high value-added polymer emulsions with specific morphology and composition can be produced.

In recent years seeded emulsion polymerization has often been used for preparing structured polymer particles with controlled morphologies (core-shell, inverted core-shell, hemisphere and other structures). The multiphase structure emulsions in each polymer particle provide a broader spectrum of physical properties than emulsions with uniform composition of particles.[1] The properties of the composite particles depend on the type of monomers used in the polymerization process, polymerization conditions, and the sequence of monomer feed. Many studies focus on the kinetics of polymerization and the morphology of the composite particles have been published, but only a few of them are concerned with the structure of acrylic–polyurethane hybrid emulsions which have been widely applied as binders for paints and special coating materials used for various applications.[2–7]

The most representative approach to obtain hybrid emulsions is to polymerize acrylic (AC)

monomers in the presence of a polyurethane (PU) dispersion. Another method is either *in situ*, where the formations of acrylic and polyurethane polymers occur at the same time, or the interpenetrating network formation.[7]

There have been only a few reports concerning the structure and fundamental properties of acrylic–polyurethane hybrid emulsions (AC–PU).[2–8] In the previous article,[8] the AC–PU hybrid emulsions were prepared by semibatch emulsion polymerization of a mixture of acrylic monomers [butyl acrylate (BA), methyl methacrylate (MMA), and acrylic acid (AA)] in the presence of polyurethane dispersion. The weight ratios between AC and PU varied in order to obtain different emulsion properties and morphology of hybrid emulsion particles. The chemical and mechanical properties of hybrid emulsions and physical blends of equivalent chemical compositions were compared. The experimental results indicate better AC–PU compatibility in hybrid emulsions than in blends, resulting in improved chemical and mechanical properties.

The kinetic and mechanistic features of emulsion polymerization are strongly reflected in molecular size and its distribution, chemical composition, particle morphology, and product properties. To contribute to these questions, the kinetic of seeded semibatch emulsion AC–PU hybrid polymerization has been studied.

The rate of emulsion polymerization, R_p, is given in entirely general terms by[9,10]

$$R_p = k_p\left(\frac{\bar{n}}{N_A}\right)[M]_p N_p \tag{1}$$

where k_p is the propagation rate constant, $\bar{n}$ is the average number of radicals per latex particle, N_A is the Avogadro constant, N_p is the total number of latex particles and M_p is the molar concentration of monomer in latex particles.

Two types of semibatch emulsion polymerization have been defined in the literature: monomer-flooded and monomer-starved.[9] When the monomer feed rate, R_m, is large enough to maintain the saturation value of the monomer concentration in the latex particles, M_p, the rate of polymerization is independent of the addition rate (flooded conditions). If R_m is so slow that M_p falls below the saturation concentration, R_p approaches a constant value which depends on the R_m (monomer-starved conditions).

The relations between R_p and R_m for semibatch emulsion polymerization under monomer-starved conditions was first considered analytically by Wessling.[9,11] In his model, both monomer concentration and the number of radicals in the particles are assumed to be constant in the steady-state, and polymerization occurs in monomer-swollen polymer particles.

The objective of this article was to investigate the effects of various reaction parameters on the R_p, and emulsion particle size and morphology during the emulsion polymerization of MMA/PU, BA/PU and MMA/BA/PU in a semibatch reactor. The particles of PU dispersion were used as seeds during the polymerization of acrylic component MMA, BA, and a mixture of MMA/BA. The effect of emulsifier and initiator concentrations on the growth of particles, starting from the same initial number of the seed particles, was also studied. The number of particles and the particle sizes were measured during the polymerization process. Also the influence of the monomer feed rate, R_m, on the rate of polymerization, R_p, and on the properties of the resulting emulsion were investigated.

EXPERIMENTAL

Chemicals

Butyl acrylate (BA; BASF) and methyl methacrylate (MMA; BASF) were used as the acrylic component together with an acrylic acid (AA; BASF). Potassium persulfate (Peroxide Chemie) was used as an initiator. The emulsifier TRITON XN 45 S (ammonium alkylphenoxypolyethoxy sulfate) was supplied by Union Carbide. The chemicals were of commercial purity and were used without further purification. The 34.2% aqueous polyurethane dispersion (PU) was a commercial anionic polyester carbonate Incorez W 830/140 (Industrial Copolymers).

Preparation of AC–PU Hybrid Emulsions

Polymerization was carried out in a 2 L glass reactor fitted with a reflux condenser, a stirrer, a thermometer, a sampling device and addition funnels. Aqueous acrylic–polyurethane hybrid emulsions with the weight ratio AC/PU of 1:1 were prepared by seeded semibatch emulsion polymerization. The particles of PU dispersion with the volume average diameter of 66.0 nm were used as seeds during the polymerization of acrylic component: MMA, BA, and a mixture of MMA and BA in

Table I   Recipe for Preparing MMA/PU and BA/PU Hybrid Emulsions

RUNS	$R_m \times 10^3$ (mol/min)	FEED			
		MMA (g)	BA (g)	EMULSIFIER (g)	INITIATOR (g)
Set 1					
MMA/PU					
1	7.68	137.84		4.38	0.55
2	7.68	137.84		6.56	0.55
3	7.68	137.84		10.94	0.55
4	11.49	137.84		4.38	1.65
5	11.49	137.84		4.38	1.10
6	11.49	137.84		4.38	0.55
7	9.19	137.84		4.38	0.55
8	7.68	137.84		4.38	0.55
9	6.56	137.84		4.38	0.55
10	5.74	137.84		4.38	0.55
Set 2					
BA/PU					
11	7.17		137.84	4.38	0.55
12	7.17		137.84	6.50	0.55
13	7.17		137.84	10.94	0.55
14	7.17		137.84	10.94	1.10
15	7.17		137.84	10.94	1.65
16	8.96		137.84	10.94	0.55
17	5.97		137.84	10.94	0.55
18	5.12		137.84	10.94	0.55
19	4.48		137.84	10.94	0.55

the ratio of 1:1. The seeded semibatch emulsion polymerization of MMA/PU and BA/PU was carried out using the recipes given in Table I. The recipes for the experimental set of MMA/BA/PU co-polymerization are presented in Table II. In each run, only one parameter was varied, while others remained unchanged in order to estimate the effect of the parameter under investigation.

The AC–PU hybrid emulsions were prepared by putting 400 g of aqueous PU dispersion as an initial charge into reactor. Fifty milliliters of distilled water was added and the mixture was heated to 70°C. The preemulsion was made by dissolving emulsifier Triton XN 45 S (63% of solid content) in water, followed by a slow addition of 137.84 g of acrylic monomer (MMA, BA, or a mix-

Table II   Recipe Used for Polymerization of MMA/BA/PU Hybrid Emulsions

RUNS	$R_m \times 10^3$ (mol/min)	FEED			
		MMA (g)	BA (g)	EMULSIFIER (g)	INITIATOR (g)
Set 3					
MMA/BA/PU					
20	10.22	68.92	68.92	10.94	0.55
21	10.22	68.92	68.92	10.94	1.10
22	10.22	68.92	68.92	10.94	1.65
23	8.18	68.92	68.92	10.94	0.55
24	6.82	68.92	68.92	10.94	0.55
25	5.84	68.92	68.92	10.94	0.55
26	5.11	68.92	68.92	10.94	0.55

ture MMA/BA in the weight ratio of 1:1) and 0.15% of AA (based on the total weight of MMA and BA) under constant stirring at 100 rpm. Afterwards the preemulsion and the initiator solution were fed into the reactor in two separate streams at constant flow rates. After complete addition of the preemulsion and initiator solution to the reactor, the polymerization continued in batch for half an hour.

Variables

The polymerization variables in each system (MMA/PU, BA/PU, and MMA/BA/PU) were:

- Initiator concentration: 0.4%, 0.8% and 1.2% based on the acrylic monomer.
- Emulsifier concentration: 2%, 3% and 5%, based on the acrylic monomer.
- Monomer feed rate, R_m: $4.48 \times 10^{-3} - 11.49 \times 10^{-3}$ mol/min.

Conversion Determination

The conversion was determined gravimetrically. During polymerization the samples were taken out of the reactor and the reaction was stopped with hydroquinone. The overall and instantaneous conversions were calculated. The overall conversion was defined as the ratio of the polymer present in the reactor to the total monomer used in the recipe. Instantaneous conversion at a given time t, was calculated as the ratio of the polymer formed in the reactor to the total monomer feed into reactor by the time t.

Particle Size and Particle Size Distribution

The particle size and particle size distributions of acrylic–polyurethane hybrid emulsions were measured with photon correlation spectroscopy on a Malvern Zetasizer 3000. The measuring range of the apparatus was 3 nm to 3000 nm. The samples of the emulsions were diluted and directly placed in a capillary cell. The temperature of the cell was kept at approximately 25°C. Number $(\overline{d_n})$, volume $(\overline{d_v})$ and weight $(\overline{d_w})$ average diameters were calculated as follows:[9]

$$\overline{d_n} = \frac{\sum\limits_i n_i d_i}{\sum\limits_i n_i} \qquad (2)$$

$$\overline{d_w} = \frac{\sum\limits_i n_i d_i^4}{\sum\limits_i n_i d_i^3} \qquad (3)$$

$$\overline{d_v} = \left(\frac{\sum\limits_i n_i d_i^3}{\sum\limits_i n_i} \right)^{1/3} \qquad (4)$$

where n_i is the number of particles of diameter d_i. The polydispersity index, PDI, is defined as[9]

$$\text{PDI} = \frac{\overline{d_w}}{\overline{d_n}} \qquad (5)$$

From the results of particle size and conversion measurements, the number of particles, N_p, was calculated[12]

$$N_p = \frac{(M_s + M_t)x_0}{\frac{4}{3}\pi\rho\left(\frac{\overline{d_v}}{2}\right)^3} \qquad (6)$$

where M_s is the weight of the seed polymer, M_t is the weight of the monomer added to the reactor up to a certain reaction time, x_o is the overall conversion at the certain time, ρ is the polymer density, and $\overline{d_v}$ is the volume average diameter of the emulsion particles.

Observation of Emulsion Particles Using Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) analysis was performed using JEOL T 300 emission scanning electron microscope. The samples were imaged at 20 kV accelerating voltage and analyzed by the conventional secondary electron imaging technique. Highly diluted samples were coated with a thin layer of gold to reduce any charge build-up on the fracture surface.

RESULTS AND DISCUSSION

Initiator and Emulsifier Concentrations

The influences of different emulsifier and initiator concentrations on the rates of polymerization were studied during the experimental work for the systems MMA/PU, BA/PU, and MMA/BA/PU. The amount of emulsifier varied from 2–5%, and

the initiator concentration was within the range from 0.4–1.2%, with regard to the total weight of acrylic monomer. As shown in Figures 1 and 2, neither the emulsifier nor the initiator concentration had a significant effect on the polymerization rate of MMA/PU hybrid emulsions. The same results were observed for the other two polymerization systems. In the initial charge there was no emulsifier. It may be assumed that the emulsifier added to the system during the monomer addition period (in preemulsion) was used to stabilize the seed PU particles and did not affect R_p. This is in agreement with the results of Unzueta and Forcada.[12] They found that the type and amount of emulsifier had no influence on the rate of seeded semibatch co-polymerization of MMA and BA. The results of Chern and Hsu[13] investigations on MMA/BA copolymer emulsions also indicate that the initiator concentration has very little effect on R_p and particle size. The emulsifier concentration controlled R_p and the particle numbers only if it was added in the initial reactor charge. Further, the Smith-Ewart Case II kinetic model predicts that R_p does not increase with the increase of the initiator concentrations if the number of particles is constant.[14]

The S-shaped conversion curves presented in Figure 1 show the minimal formation of secondary particles. The particle growth stage begins after ≈ 50 min of the reaction. This may be attributed to the electrical repulsion forces between PU seeds and oligomeric radicals which cause the
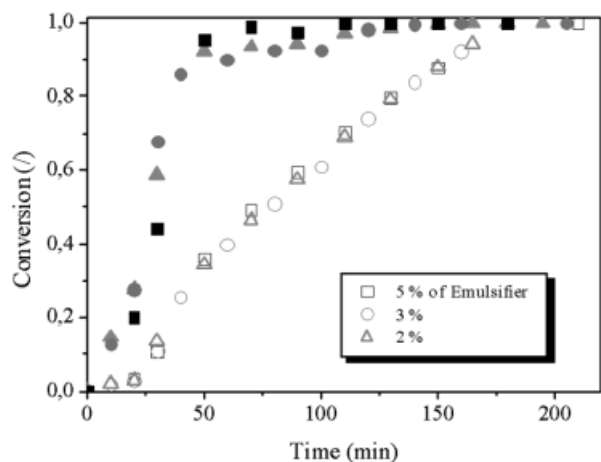

Figure 1 The influence of different emulsifier concentrations on the overall (empty symbols) and instantaneous (filled symbols) conversion during the polymerization of MMA/PU hybrid emulsions (Initiator concentration is 0.4%, $R_m = 7.68 \times 10^{-3}$ mol/min).
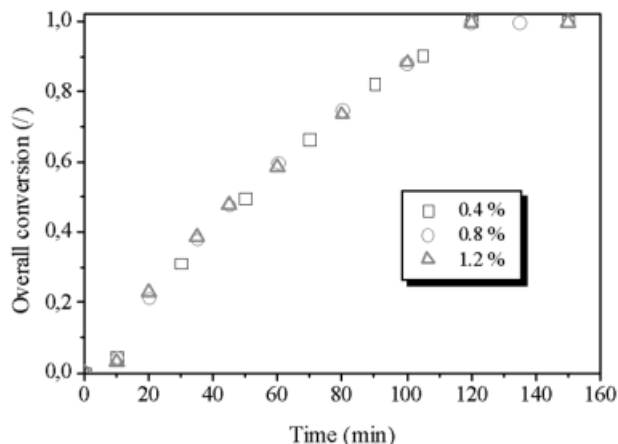

Figure 2 The influence of different initator concentrations on the overall conversion during the polymerization of MMA/PU hybrid emulsions (Emulsifier concentration is 2.0%, $R_m = 11.49 \times 10^{-3}$ mol/min).

decrease of radical adsorption in the initial period of the polymerization process.[15] The concentration of oligomeric radicals in the aqueous phase increased to easily form new particles. As a result, the initial rate of polymerization was low; however, it increased gradually with the reaction time. Similar behavior was observed for the BA/PU and MMA/BA hybrid system during the first interval of the polymerization.

Rate of Polymerization

The experimental results of kinetic investigations were compared with Wessling's kinetic model, which is the most useful in highlighting the control of R_p that can be achieved under monomer-starved conditions. Wessling[11] showed that for the polymerization system which follows the Smith-Ewart mechanism, the steady-state polymerization rate is controlled by the monomer feed rate.

In the limiting Case II of the Smith-Ewart model, the total number of radicals per particle $\bar{n}$ is 0.5. Under these conditions, or in the case of fixed radical concentrations, Wessling[11] and recently Dimitratos et al.[16] predicted linear dependence of the steady-state polymerization rate, R_p, on the monomer feed rate, R_m. In their models, both monomer concentrations and total number of radicals per particles are assumed to be constant in the steady-state. Under these conditions, R_p is constant and eq. (1) may be written in the form[9]

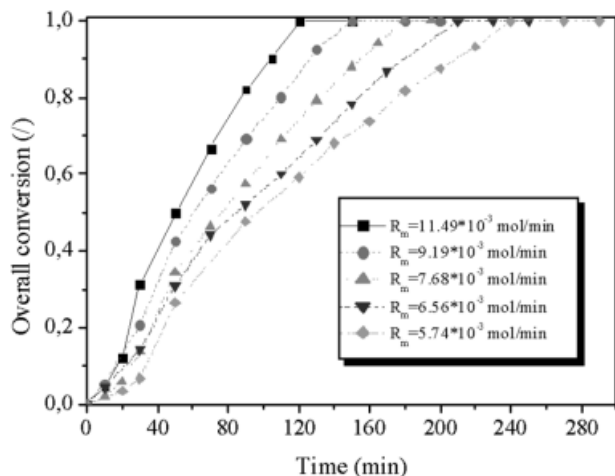$$R_p = K[M]_p V_m \tag{7}$$

Figure 3 The overall conversion curves for different monomer addition rates; (MMA/PU polymerization, concentration of emulsifier is 2.0%, initiator concentration is 0.4%).

Where

$$K = \frac{k_p N_p \bar{n}}{N_A V_m} \tag{8}$$

and V_m is the molar volume of the monomer. The product $V_m[M]_p$ is the volume fraction of monomer in the particles, Φ_m. Consequently, eq. (7) can be further simplified to

$$R_p = K\Phi_m \tag{9}$$

The reciprocal relationship between R_p and R_m has been observed by Wessling[9] in the simulation of emulsion polymerization
and

$$\frac{1}{R_p} = \frac{1}{K} + \frac{1}{R_m} \tag{10}$$

$$\Phi_p = 1 - \Phi_m \tag{11}$$

Combination of eqs. (9), (10) and (11) gives the final linear dependence of the reaction rate versus feed rate[99]

$$R_p = R_m\Phi_p \tag{12}$$

where the factor of proportionality, Φ_p, represents the volume fraction of the polymer in the monomer-swollen latex particles.

It was expected that the total number of particles, N_p, is constant for the seeded hybrid emulsion polymerization. An equal amount of PU dispersion was used as an initial charge in all experiment runs. The acrylic component added to the reactor as a preemulsion during the polymerization process was incorporated to the PU core particles.

The steady-state polymerization rates were obtained from the slope of the linear regions in the plots of overall conversion versus time. The beginning of the linear regions was determined from the instantaneous conversion versus time curves. As shown in Figure 1, the instantaneous conversion is above 0.9, shortly after the beginning of the polymerization. This confirms monomer-starved conditions during the hybrid emulsion polymerization. The molecules of added monomer are completely polymerized almost immediately upon entering the reaction vessel. A similar behavior was observed for the BA/PU and MMA/BA/PU hybrid emulsions.

Figures 3 and 4 show that in the steady-state region, the conversion curves were dependent on the monomer feed rates, R_m, during the polymerization of MMA/PU and BA/PU hybrid emulsions. Similar results were found for the MMA/BA/PU system. Different monomer feed rates were used and the addition period was specified so that the total monomer added at the end of this period was equal for every run. The conversion and R_p increased by increasing the feed rates. Figure 5 represents the linear relationship between
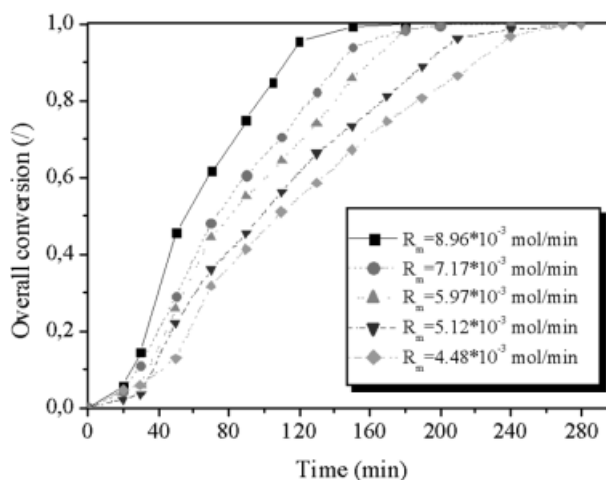

Figure 4 The influence of different monomer addition rates on the overall conversion of BA/PU hybrid emulsions; (concentration of emulsifier is 5.0%, initiator concentration is 0.4%).
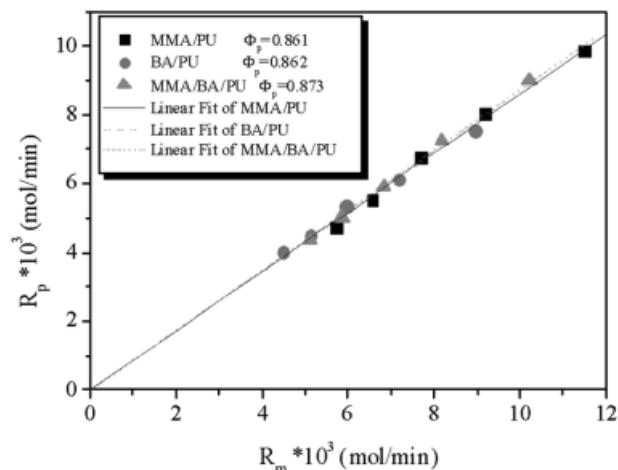
Figure 5 The rate of polymerization, R_p, dependence on the monomer addition rates, R_m, for MMA/PU, BA/PU, and MMA/BA/PU hybrid emulsions.
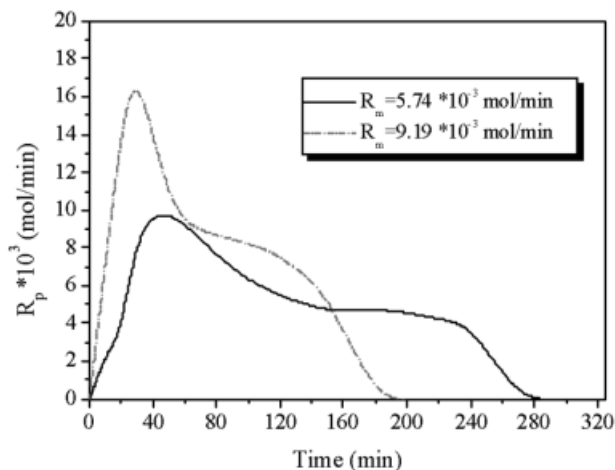

Figure 6 R_p during the polymerization of MMA/PU at two different monomer addition rates. (Concentration of emulsifier is 2.0%, initiator concentration is 0.4%.)

steady-state polymerization rates and the corresponding monomer feed rates for all three types of hybrid emulsions. The slope of the lines is the volume fraction of the polymer in monomer swollen latex particles, Φ_p.[9] The emulsions MMA/PU, BA/PU, and MMA/BA/PU have Φ_p values of 0.861, 0.862, and 0.873, respectively. These results are in agreement with Wessling's analysis of the semibatch emulsion polymerization kinetics. In practice, for semibatch emulsion polymerization operating at steady-state under monomer starved conditions, Φ_p is usually >0.8.[9] Sgard et al.[17] studied seeded semibatch emulsion polymerization of MMA. They reported Φ_p value of 0.88. Moreover, the semibatch emulsion polymerization of BA with different monomer and preemulsion feed rates was investigated by Sajjadi and Brooks.[18] The proportionality parameter, Φ_p, in monomer-starved conditions was within the range from 0.87 to 0.91. Both reports are in good agreement with the results presented here.

Figure 6 represents R_p during the polymerization of MMA/PU for two different monomer feed rates. R_p was calculated by differentiating the conversion versus time curve. The dome shape of the curve at lower conversions was a result of the autoacceleration effect, which is more obvious at higher R_m. Autoacceleration or gel effect is also present in BA/PU and MMA/BA/PU hybrid emulsions as a result of retarded translation mobility of the short-chain radical species through the viscous reaction medium. This effect leads to a dramatic reduction in the termination rate constant k_t, which causes a large increase in R_p. A similar

behavior was found by Sgard et al.[17] during the seeded semibatch emulsion polymerization of MMA.

Number of Particles

In order to study the influence of the polymerization conditions on the number of particles, the particle size was measured during the process and the N_p was calculated by equation 6. Also, the dependence of different emulsifier and initiator concentrations on the final particle size of MMA/PU, BA/PU, and MMA/BA/PU hybrid emulsions were studied.

The results indicated that neither the emulsifier nor the initiator concentrations had a significant effect on the final particle size (Table III). This is in agreement with the results of Chern and Hsu.[13] They found that the initiator had almost no influence on the particle size in the copolymerization of MMA and BA. Also, Tanrisever

Table III   The Influence of Initiator Concentrations on Particle Diameters of Final Hybrid Emulsions

Initiator Concentration (%)	PARTICLE SIZE (nm)		
	MMA/PU	BA/PU	MMA/BA/PU
0.4	136	183.1	187.4
0.8	156.7	192.8	195.5
1.2	154.3	188.7	197.2

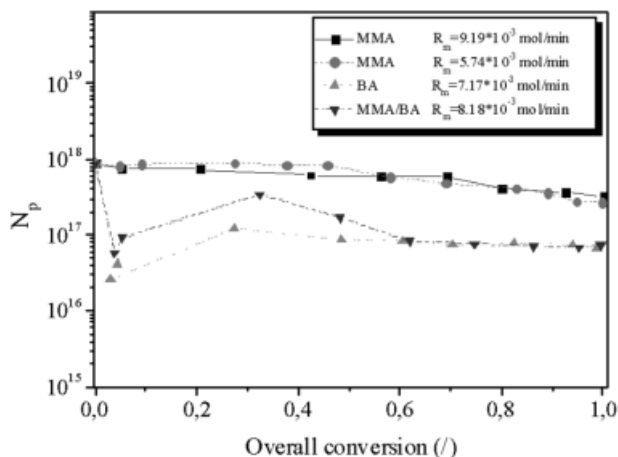**Figure 7** Number of the particles versus conversion during the polymerization of MMA/PU, BA/PU, and MMA/BA/PU hybrid emulsions.

Figure 8 The final number of particles, N_m, as a funtion of monomer addition rates, R_m, for all three hybrid systems.

et al.[19] reported that the particle size does not change much with the initiator concentration during the MMA emulsion polymerization.

Figure 7 shows the number of particles during the MMA/PU, BA/PU, and MMA/BA/PU hybrid emulsion polymerization. It may be concluded that the N_p is constant and almost the same as the number of seed PU particles for MMA/PU hybrid polymerization. The polymerization took place at a constant number of particles fixed with the amount of PU initial charge, which was equal in all runs. The result of the acrylic polymerization in the presence of PU seeds is the formation of the structured latex particles. However, coagulation between particles occurred at the beginning of the reaction in the BA/PU and MMA/BA/PU hybrid emulsions, until the polymer particles received enough surface charge. As a result, N_p decreases at the beginning of the reaction, which is pronounced in the case of BA/PU system. Later, during the cause of reaction, in the steady-state phase, N_p has a constant value. Figure 8 shows the final number of particles, which is independent on the monomer feed rates for the MMA/PU, BA/PU, and MMA/BA/PU hybrid emulsions. The final average particle diameter is in range from 136.0–156.7 nm, 183.1–199.5 nm, and 187.4–197.2 nm for the MMA/PU, BA/PU, and MMA/BA/PU hybrid emulsions, respectively.

The particle size of hybrid emulsions was also measured during the polymerization process. The results for the MMA/PU hybrids are shown in Figure 9. The larger average particle diameter during the process was caused by higher mono-
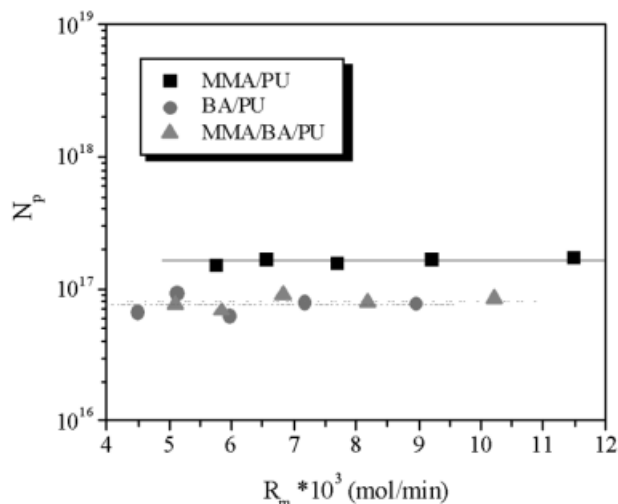
mer feed rate. However, the final particle size was almost the same for both polymerization reactions, namely 142.5 nm ($R_m = 5.74 \times 10^{-3}$ mol/min) and 137.6 nm ($R_m = 9.19 \times 10^{-3}$ mol/min).

Monomer Concentration in Polymer particles and Average Number of Radicals per Particle, $\bar{n}$

The monomer concentration in polymer particles, M_p, did not change during the Interval II in all three polymerization systems. In the steady-state region M_p was calculated using eq. (7). The values
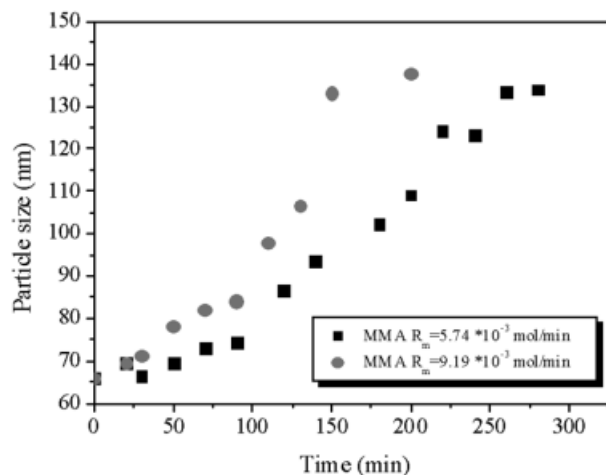

Figure 9 The average particle size diameter during the MMA/PU hybrid emulsion polymerization at two different monomer addition rates, R_m. (Concentration of emulsifier is 2.0%, initiator concentration is 0.4%.)

Table IV   Steady-State Radical Number and Concentration of Monomer in Polymer Particles for Different Monomer Addition Rates during the Polymerization of MMA/PU and BA/PU Hybrid Emulsions

	MMA/PU					BA/PU				
$R_m \times 10^3$ (mol/min)	11.49	9.19	7.68	6.56	5.74	8.96	7.17	5.97	5.12	4.48
M_p (mol/L)	2.10	1.71	1.44	1.17	1.01	1.25	1.02	0.89	0.75	0.67
$\bar{n}$	0.40	0.42	0.45	0.42	0.46	0.11	0.11	0.14	0.10	0.13

of constant K were 0.0441, 0.0419, and 0.0436 mol/min for the MMA/PU, BA/PU, and MMA/BA/PU, respectively, and have been calculated by the experimental results of plot $1/R_p$ versus $1/R_m$. As shown in Table IV, lower monomer feed rates always give lower monomer concentrations in particles. The same relation was confirmed by Li and Brooks.[20]

The steady-state $[M]_p$ values for MMA/PU hybrids were higher than the monomer concentrations in BA/PU hybrid polymer particles at the same R_p. The reason is probably a faster propagation in BA/PU particles caused by higher k_p value for BA in comparison with MMA.

From the experimentally determined rate of polymerization, R_p, $[M]_p$, and the number of particles, N_p, in the steady-state region, the number of free radicals per particle were calculated in Interval II using eq. (1).

The values of k_p, taken from the literature, are highly scattered for BA. Some research works reported in literature on BA emulsion polymerization or co-polymerization have used low value for k_p which is generally between 100–450 Lmol^{-1}s^{-1} for a temperature range of 50–80°C.[21] Recently, pulsed laser polymerization has become available. It is generally accepted as the most reliable method of estimation of k_p. Buback and Degener,[22] using the pulsed laser technique, determined the relationship between k_p and the reaction temperature during the polymerization of BA, which is:

$$\log_{10}k_p = 6.0123 - \frac{748.4}{T} \quad (\text{L mol}^{-1}\,\text{s}^{-1}) \quad (13)$$

The k_p value of 6767 Lmol^{-1}s^{-1}[22] calculated by eq. (13) at 70°C was used for BA and the value of 668 Lmol^{-1}s^{-} for MMA.[23] Equation 13 was also used by Sajjadi and Brooks[18,21,24] to calculate the values of k_p in their research on BA emulsion polymerization.

Three limiting cases were defined by Smith and Ewart for emulsion polymerization reactions

in terms of average radical number per particle.[9] Case I was defined for circumstances where $\bar{n} \ll 0.5$, which applies when the chain transfer of radicals to the monomer and termination in the aqueous phase proceed quickly relative to propagation. Case II involves instantaneous termination in the particles and a negligible desorption rate compared with the radical entry so that $\bar{n} = 0.5$. Case III describes the other extreme where $\bar{n}$ is much higher than 0.5. For case III, the termination reactions become diffusion controlled and transfer reactions and radical desorptions are slow relative to propagations.

The average number of radicals per particle calculated at each R_p is listed in Table 4. The $\bar{n}$ in the system MMA/PU are 0.40–0.46. These values are close to those predicted for Case II kinetics of Smith-Ewart theory, where it is assumed that termination takes place as soon as a new radical enters an active particle. Chen, Lee and Chiu[23] studied the $\bar{n}$ value for emulsion polymerization of MMA, which was about 0.5 at low conversion. Similar values, varying between 0.46 and 0.63, were found by Heredia et al.[25] for MMA/BA co-polymerization. Unzueta and Forcada[26] studied semibatch emulsion co-polymerization of MMA and BA. They found that in the monomer-starved conditions, the average number of radicals per particle increases slightly during the reaction, starting from the value 0.5 and achieving an end value greater than 1. During the MMA/BA co-polymerization an average number of radicals per particle of 0.4 was found by Lau et al.[27]

The $\bar{n}$ values in the BA/PU hybrid emulsions are in range from 0.10 to 0.14. Sajjadi and Brooks[18] reported the steady-state radical number between 0.08 and 0.21 during the polymerization of BA. In their recently published study,[24] a steady-state value of $\bar{n}$ was found to be around 0.13, for the experiments using emulsifier concentration of 10.0 g/L, which is in very good agreement with present results. The average radicals per polymer particles smaller than 0.5 were also

found by Xiangling at al.[28] in the study of seeded microemulsion polymerization of BA. BA/PU hybrid emulsion polymerization is a 0–1 system. This means that a particle can have one radical at the most, and on the entry of the second radical termination occurs.

Material Balance

The accumulation of monomer in steady-state region using monomer-starved conditions is defined as:[9]

$$\frac{dn}{dt} = R_m - R_p \tag{14}$$

By integration of eq. (14) the theoretical amount of unreacted monomer present in the reactor was calculated. The experimental value of unreacted monomer, n_M, was determined using eq. (15)

$$n_M = n_M^{SS} - n_M^{ov}(X_0 - X_o^{SS}) + R_m(t - t^{SS}) \tag{15}$$

where n_M^{SS} is the amount of monomer at the beginning of the steady-state region, n_M^{ov} is the overall molar amount of monomer, X_o is the overall conversion, X_o^{ss} is the overall conversion at the beginning of the steady-state region, R_m is the monomer addition rate and t_{ss} is time when the steady-state region begins.

In order for $[M]_p$ to remain constant throughout the monomer addition period, there must be

Figure 11 The agreement between predicted (lines) and experimental (symbols) values of unreacted monomer during the monomer addition period. (BA/PU hybrid emulsions, concentration of emulsifier is 5.0%, initiator concentration is 0.4%.)

an overall accumulation of monomer in the reaction vessel, because the volume of the latex particles increases with time. A good agreement between predicted accumulation of monomer, calculated by eq. (14) and experimental values are shown in Figures 10 and 11 for MMA/PU and BA/PU hybrid emulsions, respectively.

CONCLUSIONS

Aqueous acrylic–polyurethane hybrid dispersions were prepared by semibatch emulsion polymer-
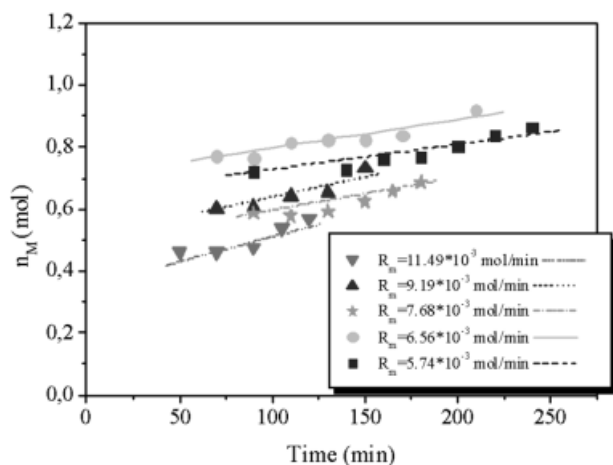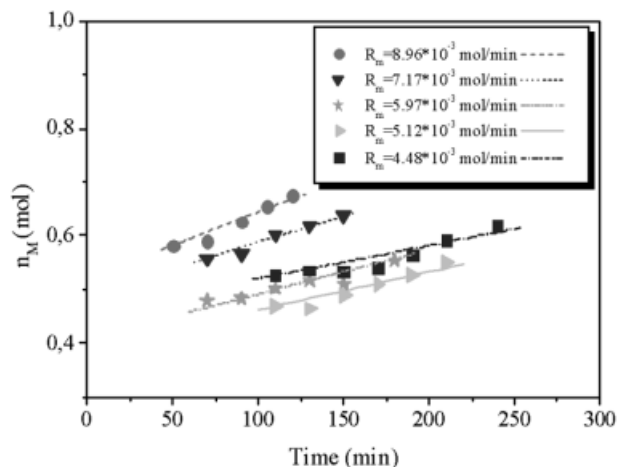

Figure 10 The predicted (lines) and experimental (symbols) values of unreacted monomer during the monomer addition period. (MMA/PU hybrid emulsions, concentration of emulsifier is 2.0%, initiator concentration is 0.4%.)
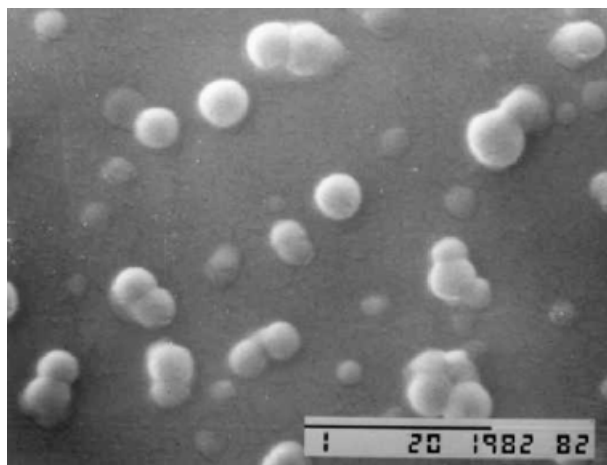

Figure 12 SEM photograph of MMA/PU acrylic–polyurethan hybrid emulsion presents structured polymer particles. Concentration of emulsifier is 2.0%, initiator concentration is 0.4%, $R_m = 9.19 \times 10^{-3}$ mol/min; scale bar is μm).

ization (Fig. 12). The particles of polyurethane dispersion were used as seeds during the polymerization of acrylic component: methyl methacrylate (MMA), butyl acrylate (BA), and a mixture of MMA and BA in ratio of 1:1. The influence of many reaction parameters, such as the emulsifier and the initiator concentrations and the monomer feed rates, on the kinetics and morphology of hybrid polymer particles was studied.

Seeded emulsion polymerizations were carried out in kinetic and morphological studies with the assumption that the monomer feed rates were so slow to keep the reactor in a monomer-starved condition and that the total number of particles would remain constant throughout the reaction.

The number of particles and the final particle size were independent on the concentration of the emulsifier, the initiator and the monomer feed rate. It was also observed that the emulsifier and the initiator concentrations did not have a significant effect on the R_p. The rate of hybrid emulsion polymerization, R_p, was controlled only by the monomer feed rate, R_m, in the steady-state. In the semibatch hybrid emulsion polymerization of MMA, BA, and a mixture of MMA/BA in the presence of PU seed particles, the polymerization rate was found to fit the Wessling's correlation of the type: $1/R_p = 1/K + 1/R_m$.

The values of the average number of radicals per particle, $\bar{n}$, during the steady-state phase of the MMA/PU hybrid emulsion polymerization agree with Smith-Ewart Case II kinetic model. On the other hand, the values of $\bar{n}$ found for the BA/PU hybrid emulsions suggest that the seeded BA/PU hybrid polymerization proceeded according to Smith-Ewart Case I kinetics.

A good agreement between the predicted values of unreacted monomer and the experimental results was observed from the material balance for all hybrid systems.

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