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ORIGINAL CONTRIBUTION

Radiation miniemulsion polymerization system with HTPB or its derivative as the costabilizer

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Abstract Miniemulsion polymerization of styrene (St) with hydroxyl-terminated polybutadiene (HTPB) or its derivative polyurethane (HPU) acting as the sole costabilizer was successfully initiated by γ-ray radiation at room temperature. Results indicated that HTPB was more efficient than its derivative HPU in retarding the diffusional degradation of monomer droplets to realize almost complete droplet nucleation. Moreover, the effects of various reaction parameters on the polymerization kinetic and the nucleation mechanism were also investigated. It was shown that the polymerization rate indicated little dependence on [HTPB] but decreased with [HPU]. Increasing the concentration of sodium dodecyl sulfate and St and the radiation dose rate would promote the polymerization in both systems.

Keywords Miniemulsion polymerization · γ-Ray radiation · HTPB · HPU

Introduction

Miniemulsions are aqueous dispersions of relatively stable oil droplets with a size in the region of 50–500 nm prepared by shearing a system containing oil, water, surfactant, and a highly water-insoluble compound (costabilizer) [1–3]. These tiny monomer droplets have an extremely large droplet surface area and most of the surfactants in miniemulsion polymerization are adsorbed onto the droplet surface. Therefore, monomer droplet nucleation mechanism predominates [4], while only few surfactants form micelle or stabilize aqueous nucleation. Hence, in an ideal miniemulsion polymerization, no monomer transport is involved, and the obtained latex particles have about the same size as the initial monomer droplets as proven by a combination of dynamic light scattering (DLS), small-angle neutron scattering, surface tension measurement, and conductometry [5].

The formation of a stable miniemulsion depends on the properties of the low-molecular-weight costabilizer. With the help of a costabilizer, a stable miniemulsion can be prepared at a low surfactant level even below its critical micelle concentration (CMC). This is because the costabilizer can provide sufficient osmotic pressure to counterbalance the diffusion of monomer from smaller to larger droplet (Ostwald ripening). This requires that the concentration of the costabilizer in the monomer droplets be high and the solubility of the costabilizer in water be low. Hexadecane and cetyl alcohol (CA) are the costabilizers most often used in publications [6]. However, these costabilizers remain in the polymer particles and may have deleterious effects on the properties of the polymer. To minimize these negative effects, several methods have been reported. One is employing the corresponding polymer to prevent the diffusional degradation. Miller and coworkers [7–9] observed enhanced droplet nucleation in the CA-containing styrene miniemulsion polymerization in the presence of predissolved polystyrene (PS) in the monomer phase. The second approach is to use reactive alkyl methacrylates such as lauryl methacrylate [10], stearyl methacrylate [11], and dodecyl methacrylate (DMA) [12] as the costabilizer. The methacrylate group may be chemically incorporated into latex particles in the subsequent miniemulsion polymerization, as shown by the

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infrared spectra. It has been demonstrated that these compounds could act similar to conventional costabilizers. Furthermore, a reactive costabilizer that also can modify the polymer may represent a more attractive alternative. Recently, Gilbert et al. [13] reported the grafting of DMA onto hydroxyl-terminated polybutadiene (HTPB; molecular weight, 8,834 g/mol) in the CA-containing miniemulsion polymerization by predissolving HTPB in the monomer phase. The miniemulsion polymerization was costabilized both by CA and the predissolved HTPB. It was found that the property of the polymer was modified by HTPB. However, the presence of the conventional costabilizer CA may cause some deleterious effects. If the low-molecular-weight HTPB can serve as the sole costabilizer, the problem will be avoided. The objective of present paper was therefore to investigate the feasibility of using HTPB as the sole costabilizer in the styrene miniemusion polymerizations. Moreover, the HTPB employed here has a lower molecular weight (about 2,100 g/mol) in comparison with the reported HTPB. In our previous work, a kind of polyurethane which was derived from HTPB (we called it HPU in this paper) had been employed as the sole costabilizer in miniemulsion polymerization of styrene (St) [14]. In this research, these two kinds of costabilizers were compared. Also, the influences of the monomer content, surfactant concentration, costabilizer, and dose rate on the polymerization rate were investigated.

Experimental part

Materials

Styrene (Shanghai Chemical Reagents Co., China) was purified to remove the inhibitor before use. The structure of hydroxyl-terminated polybutadiene (a viscous liquid, Mn=2,100, Zibo Qilong Chemical Reagents Co., China) is shown in Scheme 1. The preparation of HPU was described in our previous paper, Mn=5,000 [14]. Sodium dodecyl sulfate (SDS; Shanghai Chemical Reagents Co., China) was used as received.

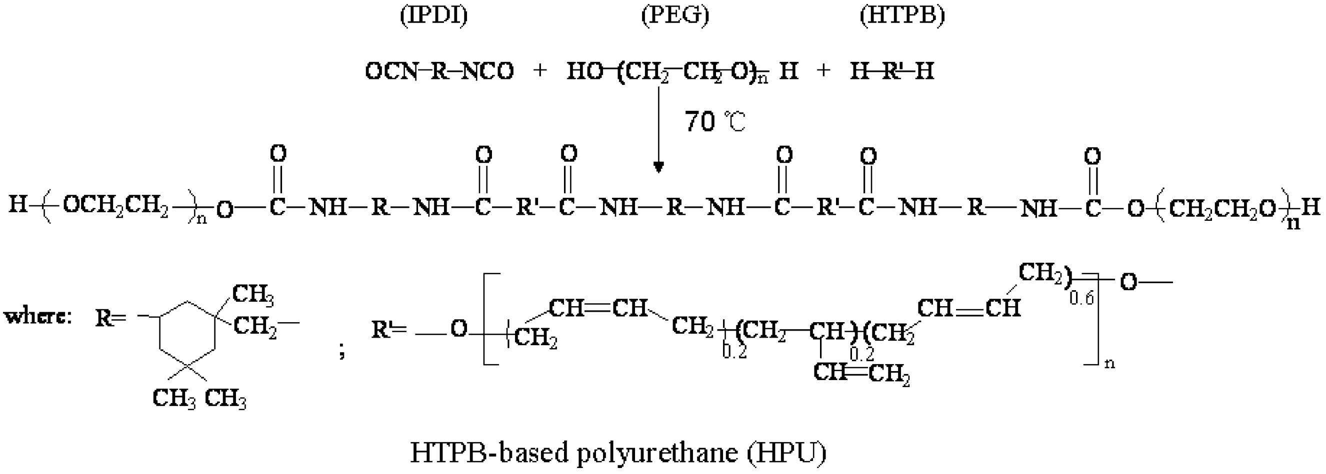
Miniemulsion polymerization of St

Step 1 emulsification: Distilled water containing SDS was mixed with St (in which HTPB or HPU was dissolved) under magnetic stirring for 30 min.
Step 2 homogenization: The mixture was ultrasonicated for 5 min (AS3120, Tianjin Automatic Science Instrument Co., Ltd.) in an ice bath to achieve a stable miniemulsion.
Step 3 radiation polymerization: The resultant miniemulsion was irradiated by ^{60}Co γ-ray (located in USTC) at a dose rate of 106 Gy/min after it was purged with nitrogen for 10 min to remove the dissolved oxygen in the system. The temperature of the system was controlled to be constant with the help of a circulating water system. The polymerization finished after 4 h.

The recipes of the miniemulsions were presented in Table 1. During the preparation and polymerization processes, it was found that the viscosity of the HTPB-costabilized system was much higher than that of the HPU-costabilized system. All the miniemulsion systems were quite stable.

Analytical methods

The shelf life of the miniemulsion was monitored by putting aside about 20 mL of the sample in the test tube at



Scheme 1 Synthesis scheme of PU dispersion, the chemical structure of HTPB was included

Table 1 The recipes of the miniemulsions and characteristics of the final PS latexes

Sample ID	Monomer[a] (wt.%)	HTPB[b] (wt.%)	HPU (wt.%)	SDS[c] (mmol/L)	Number average[d] particle diameter (nm)	Shelf life (months)
1	15	0.5	–	7	109±13	>12
2	15	1	–	7	113±15	>12
3	15	2	–	7	118±12	>12
4	15	4	–	7	121±16	>12
5	15	8	–	7	115±18	>12
6	10	2	–	7	95±13	>12
7	12	2	–	7	105±11	>12
8	18	2	–	7	130±17	>12
9	20	2	–	7	175±18	>12
10	15	2	–	5	185±15	>12
11	15	2	–	6	121±15	>12
12	15	2	–	8	102±13	>12
13	15	–	2	13	47±3	>12
14	15	–	4	13	39±4	>12
15	15	–	8	13	41±2	>12
16	15	–	2	5	52±3	>12
17	15	–	2	7	50±4	>12
18	15	–	2	10	49±5	>12
19	10	–	2	13	42±3	>12
20	12	–	2	13	46±4	>12
21	18	–	2	13	23±5	>12
22	20	–	2	13	65±6	>12

[a] The weight of St was 20 g in every recipe, and the monomer (wt.%) was based on the total weight of the miniemulsion.

[b] The weight percent was based on the monomer weight.

[c] The molar concentration of SDS was based on water.

[d] The number average particle diameter was measured by TEM.

room temperature and recording the time necessary for a visible creaming line to appear.

Surface tension was measured using the Wilhelmy plate method and a JK99B automatic surface tensiometer (Shanghai Zhongchen Co., China). Twenty-five milliliters of the miniemulsion or the latex was poured into a carefully cleaned sample vessel with a diameter of 50 mm. The surface tension was measured automatically at a constant temperature of 25 °C.

The surface analysis of latex was carried out in a VG ESCALAB MKF spectrometer (X-ray photoelectron spectroscopy—XPS) with Mg Ka X-ray source (1,253.6 eV) and with an energy analyzer set at a constant retardation ratio of 20. The miniemulsion was destabilized by adding ethanol. The precipitate was washed with water three times to remove the SDS adsorbed on the surfaces of the particles and then tested.

Size measurements of the droplets and latex particles were performed using dynamic light scattering (DynaPro MS800) at a wavelength of 824 nm, 25 °C, and the scattering angle was 90°. The variable of particle diameter during the polymerization was also detected by DLS while the irradiation was stopped at a given time and sampling was taken. The average particle size of the latex was also obtained by transmission electron microscopy (TEM) analysis using a transmission electron microscope (Japan H800) operated at 200 kV of accelerating voltage. Samples for TEM analysis were prepared at room temperature by dispersing one drop of latex into 100 mL water. Then, a drop of the solution was dripped into a holy-carbon-supported copper grid and dried. The particle number average diameter ($\overline{D_n}$) was calculated following Eq. 1 [15]:

$$\overline{D_n} = \sum N_i D_i / \sum N_i \tag{1}$$

where N_i was the number of polymer particles with diameter D_i.

And the distribution of particles was calculated by Eq. 2:

$$\sigma = \sqrt{\frac{\sum N_i \left(D_i - \overline{D_n}\right)^2}{\sum N_i - 1}}. \tag{2}$$

Results and discussions

Nucleation mechanism of radiation miniemulsion polymerization

In order to distinguish the nucleation mechanism, the average diameter of the monomer droplets ($D_{\mathrm{m},i}$) and the resultant latex particles ($D_{\mathrm{p,f}}$) were detected by DLS for both HTPB- and HPU-costabilized systems listed in Table 2. The number of monomer droplets in unit volume before polymerization ($N_{\mathrm{m},i}$) and the number of the PS latex particles produced in unit volume after polymerization ($N_{\mathrm{p,f}}$) could be consequently calculated, also shown in Table 2. Obviously, the size of the final PS latex was close to that of

Table 2 Parameters of the miniemulsions of St and PS latexes

Sample ID[a]	Costabilizer	SDS (mmol/L water)	$D_{m,i}$[b] (nm)	$D_{p,f}$[b] (nm)	$N_{m,i}$[b] ($\times10^{-16}$/L)	$N_{p,f}$[b] ($\times10^{-16}$/L)	$N_{p,f}/N_{m,i}$[b] (%)	σ_1[c] (mN/m)	σ_2[c] (mN/m)	σ_3[c] (mN/m)
10	HTPB	5	185.0	204.6	4.5	3.5	78	43.65	48.98	47.24
11	HTPB	6	136.6	145.0	11.2	10.5	94	43.12	47.87	47.12
3	HTPB	7	124.6	131.6	14.7	14.1	96	41.54	47.56	46.52
12	HTPB	8	107.4	113.6	23	22.1	96	40.35	47.12	45.96
16	HPU	5	51.1	56.3	159	102	64	42.15	46.98	45.23
17	HPU	7	49.2	50.2	178	144	81	41.67	47.02	46.53

[a] The recipes of the samples are shown in Table 1.

[b] $D_{m,i}$, $D_{p,f}$, $N_{m,i}$, $N_{p,f}$, and $N_{p,f}/N_{m,i}$ represent initial monomer droplet volume average diameter, final particle volume average diameter, the number of initial monomer droplets, the number of final particles, and the fraction of monomer droplet nucleation, respectively. $N_{m,i} = \frac{1{,}000\rho_{St}}{\frac{4}{3}\pi\left(\frac{D_{m,i}\times10^{-7}}{2}\right)^3}$; $N_{p,f} = \frac{1{,}000[\rho_{St}X+\rho_{PS}(1-X)]}{\frac{4}{3}\pi\left(\frac{D_{p,f}\times10^{-7}}{2}\right)^3\rho_{St}\rho_{PS}}$, X was the final conversion of St.

[c] σ_1, σ_2, and σ_3 represent the surface tension of miniemulsion before homogenizing, miniemulsion after homogenizing, and final PS latex, respectively.

the monomer droplets, which implied that nucleation within the droplets occurred [16]. The unchanged volume average particle diameter (see Fig. 1, detected by DLS) during the whole reaction also demonstrated that the probability of secondary nucleation was very small [17].

The results of surface tension measurement could also provide evidence on the monomer droplet nucleation mechanism. It was well known that there was equilibrium between the surfactant on water/latex surface, surfactant in solution, and surfactant on the emulsion/air interface [18]. If the latex particles were fully covered by surfactant, the rest of the surfactant could form micelles in the water phase, and the interface energy toward air would decrease and reached the value of a saturated surfactant solution. Higher surface tension, on the other hand, means that there were no free micelles in the solution, which implied that the latex particles were not completely covered with surfactant molecules. In other words, the change of the surface tension of the latex was a good measurement of whether the polymer particles were covered with enough surfactant molecules or not.

As presented in Table 2, for both miniemulsion systems costabilized by HTPB and HPU, the surface tension was 40–44 mN/m before homogenization. After homogenizing the miniemulsion, a surface tension of about 47 mN/m indicated that the surface area turned larger. Higher surface tension of the latexes in comparison to the equilibrium surface tension value (SDS: 32 mN/m) further substantiated the absence of surfactant molecules or micelles in the dispersed phase and hence ruled out micellar or homogeneous nucleation mechanism. When the polymerization finished, the surface tension only decreased slightly. This might be caused by different surface energies or by a slight change of the size in the monomer droplets and the polymer

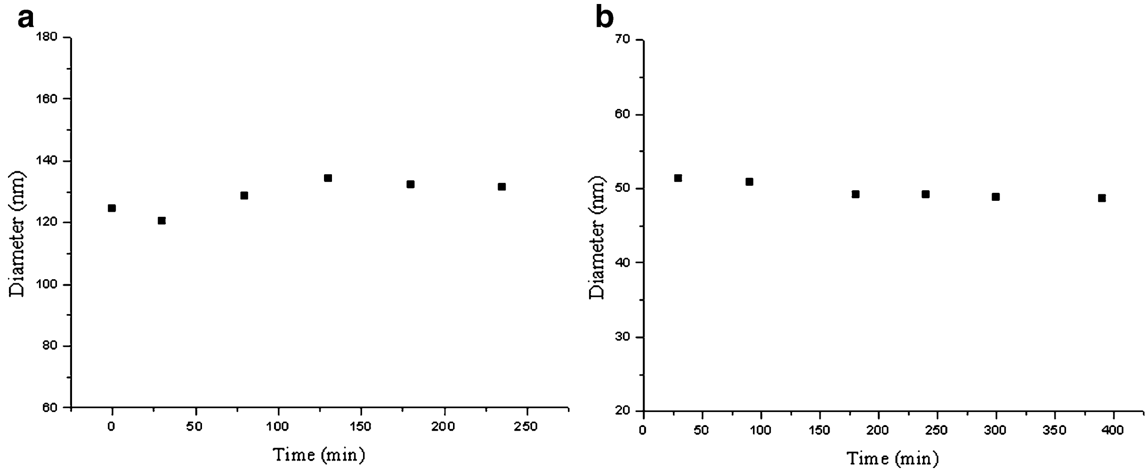


Fig. 1 Variable of volume average diameter versus time of HPU-costabilized miniemulsion (sample 3, **a**) and HTPB-costabilized miniemulsion (sample 13, **b**) during the polymerization

particles, coincident with the literature [19]. The little change in surface tension data before and after polymerization also demonstrated that the size and number of the particles almost unchanged throughout the polymerization. That is to say, the monomer droplet nucleation was the sole dominant nucleation mechanism.

Therefore, it could be concluded from the above discussion that HTPB or its derivative HPU could be used as the sole costabilizer in miniemulsion systems, in which monomer droplet nucleation predominantly occurred.

Monomer droplet nucleation efficiency

Although much research has been conducted on the miniemulsion polymerization, only limited commercial interest has been generated for this process owing to the incomplete monomer droplet nucleation. For example, Choi and El-Aasser [20] reported that only 20% of the droplets are nucleated (CA as costabilizer). Chern described that 55% (dodecyl methacrylate as costabilizer [21]) to 60% (blue dye as costabilizer [22]) are nucleated. However, Miller and coworkers [7–9] had found 95% monomer droplet nucleation when using PS coupled with CA as costabilizer. It was considered that the system consisted of small, stable-performed monomer-swollen particles which were able to efficiently capture radicals in aqueous phase. It was significant to obtain great monomer droplet nucleation efficiency since a larger fraction perhaps 100% of initial monomer droplets nucleation would result in a higher polymerization rate and production yield.

In the HTPB-costabilized systems, the initial number of miniemulsion droplets was equivalent to the final number of PS particles (see Table 2), which implied a large fraction (96%, approaching 1) of the initial number of monomer droplets captured the aqueous phase radicals and polymerized.

The approximated complete droplet nucleation could be attributed to the following respects:

1. In this study, all the miniemulsion polymerizations were conducted at the SDS content below its CMC. Micellar nucleation could be neglected. Moreover, since the water solubility of St was extremely low, and the $G(R)$ value (the yield of free radicals per 100 eV absorption of radiation energy) of St was as small as only 0.69 [16], homogeneous nucleation was a relatively inefficient process. Thus, the large number of monomer droplets was the main nucleation loci. Owing to the strong non-selectivity interaction between high-energy ^{60}Co γ-ray ($E\gamma = 1.25$ MeV) and the substances, free radicals can be generated in both the dispersed phase and continuous phase. At the same time, not only the monomer but also the nucleated particles could produce free radicals themselves in the oily phase. These radiation-induced free radicals were accompanied with high energy [23]. So they were very active to initiate polymerization. As a result, the average number of radicals per particle was thought to be higher in radiation miniemulsion polymerization. All this will increase the monomer droplet nucleation efficiency and the polymerization rate.
2. The composition on the particles surface was analyzed by XPS, which used X-rays to irradiate the particles' surface and generated photoelectron whose energy was characteristic of each element. As shown in Fig. 2, an oxygen peak together with a carbon peak in the XPS spectrum of the final polymer indicated the presence of HTPB on the surface of the particles. That is to say, not only the surfactant SDS but also the HTPB polymer existed at the surface of the St droplets. As a result, the stability of the monomer droplets was expected to be enhanced for that HTPB could create an osmotic pressure opposing Ostwald ripening, as reported by Gilbert et al. [13]. Additionally, this was in favor of complete droplet nucleation since polymers were more efficient than droplets in capturing radicals [7–9].
3. The presence of viscous HTPB increased the interior viscosity thereby increased the probability of a radical to propagate rather than desorb from the monomer droplets [24].

On the other hand, as to the HPU-costabilized systems, the monomer droplet nucleation efficiency was more than 60%, but relatively lower in comparison with that of HTPB-costabilized systems at an identical surfactant level (see Table 2). That is to say, HTPB was more efficient in enhancing monomer droplet nucleation. According to the LSW theory [25], the rate of Ostwald ripening [$d(D_m^3)/dt_a$]

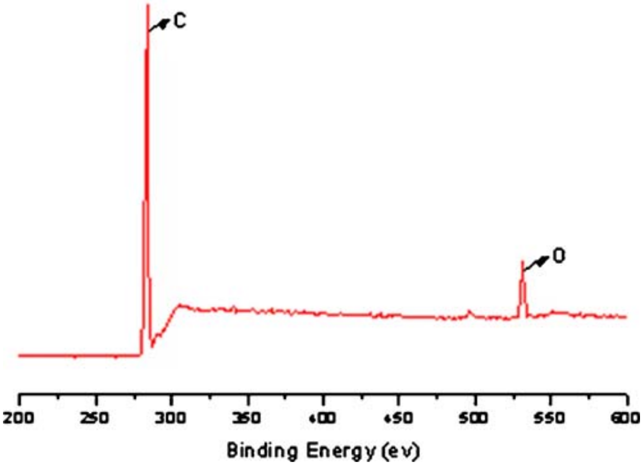


Fig. 2 XPS spectrum of sample 4

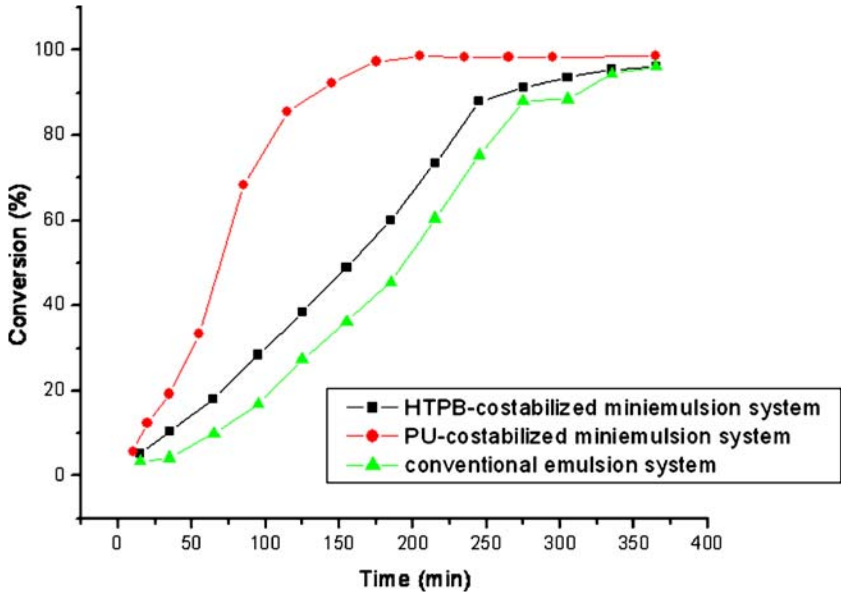


Fig. 3 Conversion–time curves for comparison between miniemulsion and emulsion polymerization. St wt.%=15%, [SDS]=15 mmol/L H_2O, [costabilizer]=2 wt.% based on monomer

for the miniemulsion could be predicted by the following equation (Eq. 3):

$$\left(\mathrm{d}\left(D_{\mathrm{m}}^{3}\right)/\mathrm{d}\,t_{\mathrm{a}}\right) = 64\sigma D_{\mathrm{co}} V_{\mathrm{m}} C_{\mathrm{co}}(\infty)/(9RT\Phi_{\mathrm{co}}) \qquad (3)$$

where t_a was the aging time, σ the oil droplet–water interfacial tension, D_m the average oil droplet size, D_{co} the molecular diffusivity of costabilizer, V_m the molar volume of the oil phase, $C_{co}(\infty)$ the solubility of the bulk costabilizer in water, and Φ_{co} the volume fraction of costabilizer in the oil droplet. As the hydrophilic PEG was introduced to the chain of HPU, it could be assumed that the values of D_{co} and $C_{co}(\infty)$ of HPU were larger than HTPB, so the Ostwald ripening was more notable in HPU-costabilized miniemulsions correspondingly. The molecular weight was another parameter to determine the efficiency of the costabilizer [26]. Low-molecular-weight costabilizer generated a higher osmotic pressure to suppress Ostwald ripening. From this point of view, HTPB (Mn=2,100) should costabilize the miniemulsion systems better than its derivative HPU (Mn=5,000). In addition, the presence of HPU might prevent some of the free radicals from entering into the monomer droplets to initiate polymerization due to the steric obstacle [14], which did not happen in the case of HTPB.

Polymerization rate for miniemulsions and conventional emulsions

As presented in Fig. 3, the polymerization of radiation-induced miniemulsion was much faster than that of classical emulsion polymerization. It might be related with the fact that the particles produced were smaller in miniemulsions than that in classical emulsions. Thus, the higher

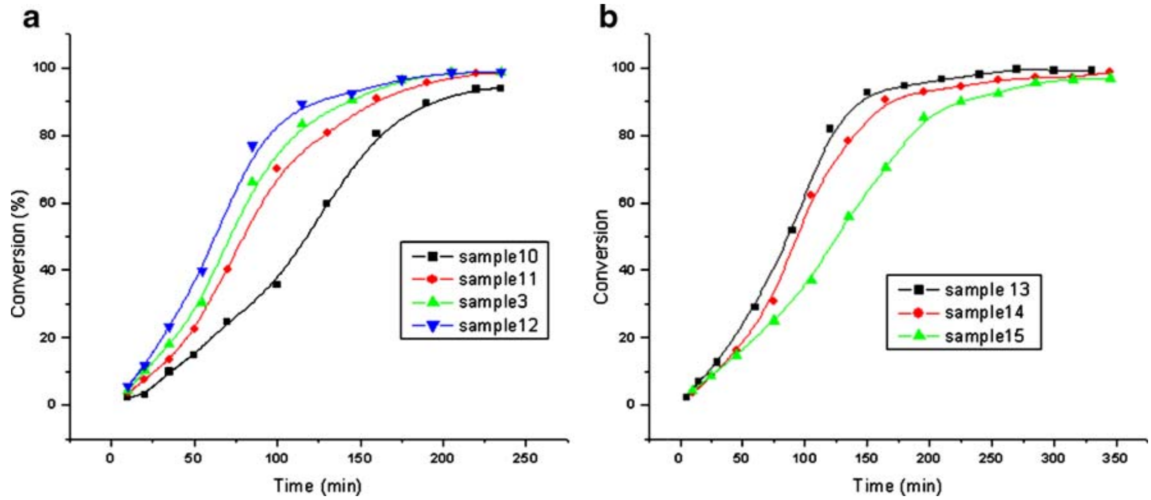


Fig. 4 Effect of the concentration of costabilizer for miniemulsion costabilized by **a** HTPB and **b** HPU, respectively

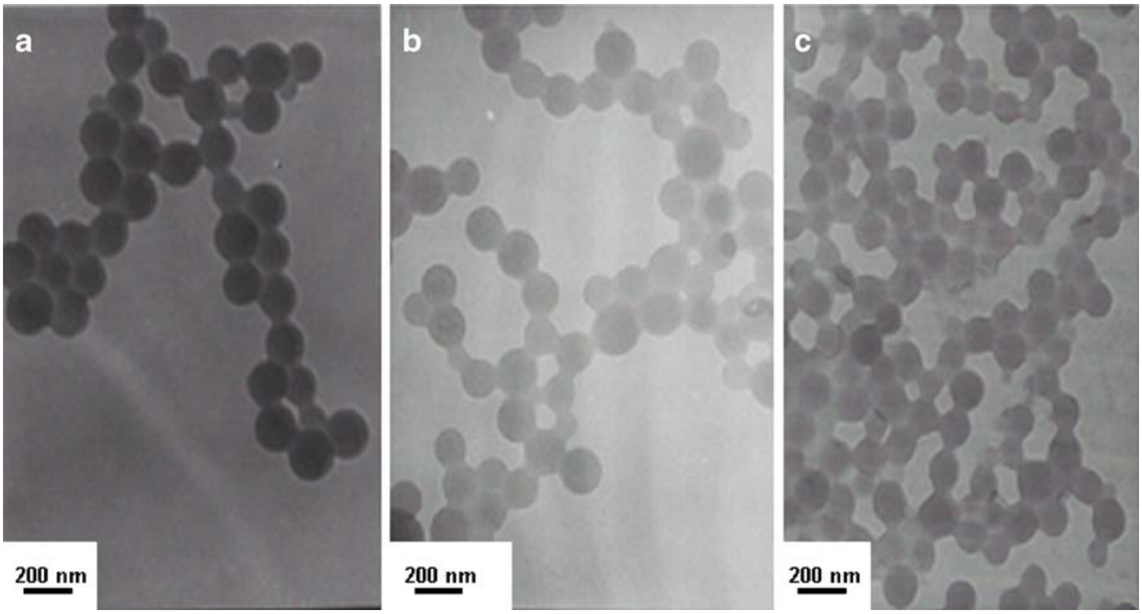


Fig. 5 TEM images for the HTPB-costabilized system: **a** sample 3 ($\overline{D_n}$=118±12 nm); **b** sample 4 ($\overline{D_n}$=121±16 nm); **c** sample 5 ($\overline{D_n}$=115±18 nm)

particle number led to faster polymerization rate. Under certain circumstances, it would represent a significant practical advantage for utilizing miniemulsions instead of conventional emulsions for production of latex particles.

Effect of costabilizer

The polymerization kinetic of different amounts of costabilizer was shown in Fig. 4a,b. Combining with the data of the particle sizes in Table 1, it could be found that the concentration of HTPB had almost no influence on the polymerization rate and particle size within the experimental range from 0.5 to 8 wt.% (based on the monomer), as shown in the TEM images in Fig. 5. This result suggests that the Ostwald ripening was effectively counterbalanced, and the miniemulsion polymerization was successfully carried out even at a low HTPB level of 0.5 wt.%. Therefore, it could further demonstrate that HTPB was an effective costabilizer to retard the diffusional degradation of monomer droplets in the miniemulsion system. However, as to the HPU-costabilized system, the polymerization rate decreased as [HPU] increased. The slower polymerization rate was explained to be owing to two possibilities: the presence of more HPU might prevent free radicals from entering into the monomer droplets to initiate polymerization due to the steric obstacle. This had also been demonstrated in our previous paper [14] by the fact that the average number of radicals per particle n_b calculated decreased when the amount of HPU increased. In addition, when more HPU was added and dissolved into the

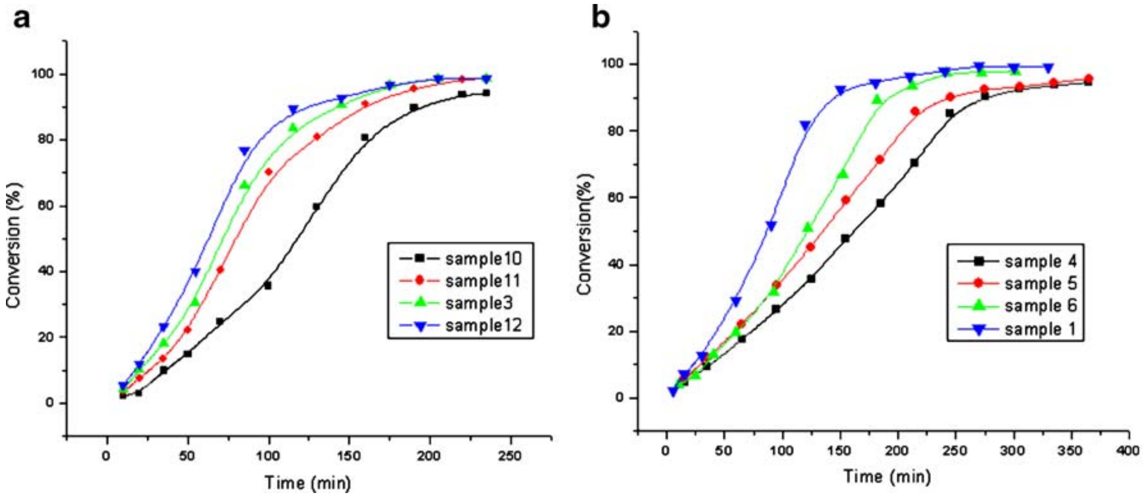


Fig. 6 Effect of SDS content for miniemulsion costabilized by **a** HTPB and **b** HPU, respectively

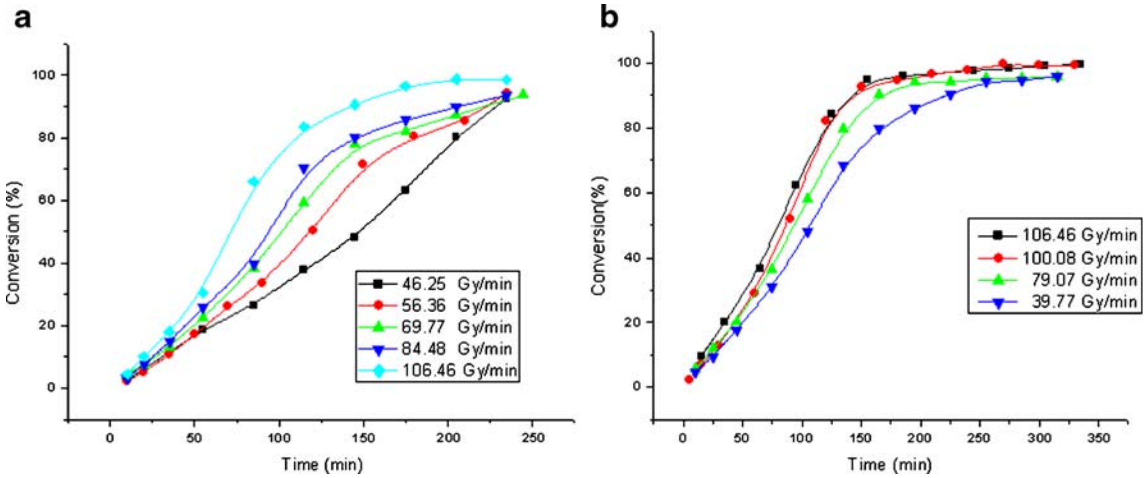


Fig. 7 Effect of dose rate for miniemulsion costabilized by **a** HTPB (sample 3) and **b** HPU (sample 13), respectively

monomer droplets, the monomer concentration in the nucleated polymer particles would decrease.

Effect of surfactant concentration [SDS]

In this series, the influence of surfactant concentration on the polymerization rate was studied. Table 1 showed that when [SDS] increased, the particle diameter decreased for both the two systems. As expected, the reaction accelerated accordingly as illustrated in Fig. 6, which was coincident with the usual responses to the increase of the surfactant amount [27]. The higher the SDS concentration, the larger the number of latex particles formed during the reaction and the greater the polymerization rate.

Effect of radiation dose rate

In this series of experiments, the miniemulsions of samples costabilized by HTPB or HPU were initiated at different dose rates, respectively. The polymerization was accelerated at a higher dose rate. However, it was found that the particle size was almost not influenced for both systems. As we know, miniemulsion polymerization velocity (R_p) increased with the amount of the initiator. In the radiation-induced miniemulsion polymerization process, the dose rate $\dot{D}$ corresponded to the concentration of the initiator [28]. Thereby, the results that $D_{p,f}$ was rather insensitive to changes in dose rate might be the most compelling evidence for the dominant monomer droplet nucleation [2]. At the same time, more free radicals would be produced at a higher dose rate, and the reaction rate increased correspondingly as illustrated in Fig. 7.

Effect of monomer content [St]

The influence of monomer content on the reaction rate was shown in Fig. 8. When the monomer content increased, the concentration of St in the nucleated particles would increase and thereby lead to faster polymerization rate in both systems costabilized by HTPB and PU, respectively.

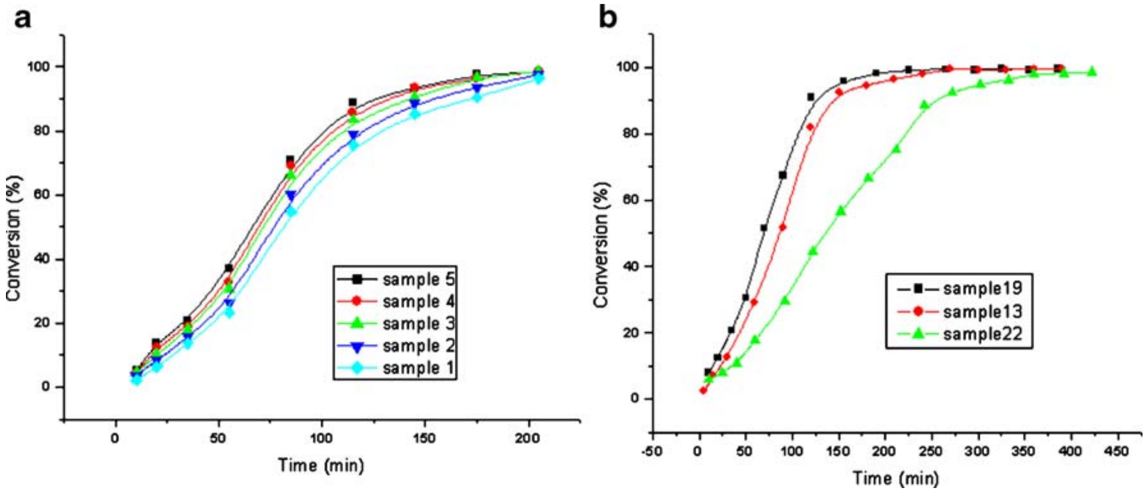


Fig. 8 Effect of monomer content for miniemulsion costabilized by **a** HTPB and **b** HPU, respectively

Conclusion

Polymeric costabilizer HTPB and its derivative HPU were successfully used as the sole costabilizer in the miniemulsion polymerization of styrene initiated by γ-ray radiation. Monomer droplet nucleation mechanism was confirmed in both systems. In the HTPB-costabilized miniemulsion system, high nucleation efficiency could be reached. On the other hand, in the HPU-costabilized system, the viscosity of the system was reduced in contrast to that of the HTPB-costabilized system. As a result, polystyrene nanoparticles with relatively small diameter (40–70 nm) and narrow particle size distribution could be easily prepared. The polymerization rate indicated little dependence on [HTPB] but decreased with [HPU]. Increasing [SDS], [St], and radiation dose rate would accelerate the polymerization in both systems.

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