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ORIGINAL CONTRIBUTION

Miniemulsion polymerization of styrene costabilized with polyurethane via ^{60}Co γ-ray radiation initiation

Hua Wang · Xuewu Ge · Linyong Song · Huarong Liu

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Abstract Polyurethane (PU) was successfully synthesized and used as costabilizer in the miniemulsion polymerization of styrene (St) initiated by ^{60}Co γ-ray radiation at room temperature. Only 2 wt% PU based on the monomer was enough to prepare a stable miniemulsion with a shelf life of more than 12 months. Preservation of original particle size and distribution throughout the polymerization observed from dynamic light scattering measurements indicates the predominance of monomer droplet nucleation. Kinetic analysis shows that there is no constant rate stage, which also suggests a droplet nucleation mechanism. Polystyrene (PS) nanoparticles with relatively small diameters (40–70 nm) and narrow size distribution could be easily prepared. The effects of surfactant, costabilizer, and absorbed dose rate on the miniemulsion polymerization were discussed.

Keywords Styrene · Miniemulsion polymerization · γ-Ray radiation · Costabilizer · Polyurethane · Kinetics

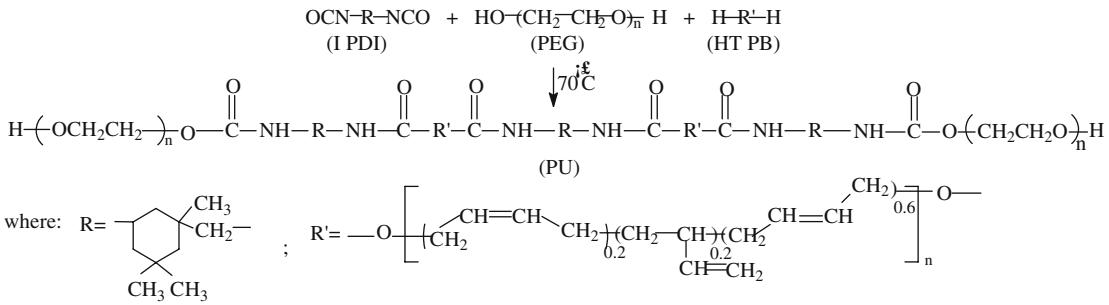
Introduction

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]. The droplet nucleation mechanism predominates in miniemulsion polymerization [4], as most of the surfactant is adsorbed onto the droplet surface with few surfactants to 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), surface tension, and conductivity measurements [5]. To discuss a typical calorimetric curve for a miniemulsion polymerization, Bechthold et al. [6] observed many miniemulsions and proved that there was no interval of constant reaction rate, which is one of the big differences with emulsion polymerization, as the diffusion of monomer does not contribute to the rate-determining step. Recently, miniemulsion polymerization have attracted much attention because of their wide applications in the production of latexes with special particle morphology, controlled radical polymerization in dispersed media, encapsulation of inorganic solids, and so on [7–9]. It opens the possibilities of expanding the application of emulsion polymerization and provides many advantages. Especially, only a small surfactant concentration is needed to stabilize the miniemulsion droplets, which represents significant practical cost.

However, some low molecular weight chemical compounds, such as long-chain alkane (hexdecane, HD) and fatty alcohol (cetyl alcohol), as typical costabilizers [10, 11] used in the miniemulsion polymerization to retard the diffusion of monomer from small droplets to large ones (Ostwald ripening), will remain in the particles after polymerization and reduce the mechanical properties of the final product. Moreover, the slow evaporation of these costabilizers will pollute the atmosphere. To avoid these negative effects, polymers have been introduced to costabilize miniemulsions [12]. It had been demonstrated that they would possibly delay Ostwald ripening sufficiently to allow nucleation of the monomer droplets by water-phase

H. Wang · X. Ge (✉) · L. Song · H. Liu
Department of Polymer Science and Engineering,
University of Science and Technology of China,
Hefei, Anhui 230026, People's Republic of China
e-mail: xwge@ustc.edu.cn

Scheme 1 Synthesis scheme of PU dispersion



radicals. The latex produced from a polymer-costabilized miniemulsion has all the characteristics of conventional miniemulsion. In addition, they are totally innocuous in the final products [13, 14]. Tsavalas et al. [15] successfully prepared stable cross-linkable coatings via hybrid miniemulsion polymerization costabilized by polyester resin. However, the weight ratio of resin to monomer was as high as 1:3 or even 1:1. Yu ZQ [16, 17] had synthesized a kind of carboxylated polyurethane and used it as costabilizer in the miniemulsion of styrene. The polymerization results showed that homogeneous nucleation and droplet nucleation coexisted, and the miniemulsions were not very stable with shelf lives of only several days.

Γ-ray radiation has been widely used to initiate emulsion polymerization [18], microemulsion polymerization [19], and dispersed polymerization [20]. However, there are only a few studies related to γ-ray radiation-induced miniemulsion polymerization. But, in fact, γ-ray radiation is an efficient way to initiate miniemulsion polymerization for preparing novel materials with unusual properties because of its unique advantages such as no need of additional initiators, temperature independence, and strong penetrability. In addition, the initiation and polymerization can take place at room temperature. Obviously, low temperature is in favor of the stability of miniemulsion.

In this study, one kind of polyurethane (PU) based on isophorone diisocyanate (IPDI) with a molecular weight of about 5,000 (the molecular weight of PU can be calculated from the recipe theoretically [21]) was synthesized and successfully used as costabilizer in the miniemulsion polymerization of St initiated by ^{60}Co γ-ray radiation at room temperature. Just 2 wt% polyurethane based on St was enough to prepare a quite stable miniemulsion. The nucleation mechanism and kinetics were investigated.

Experimental part

Materials

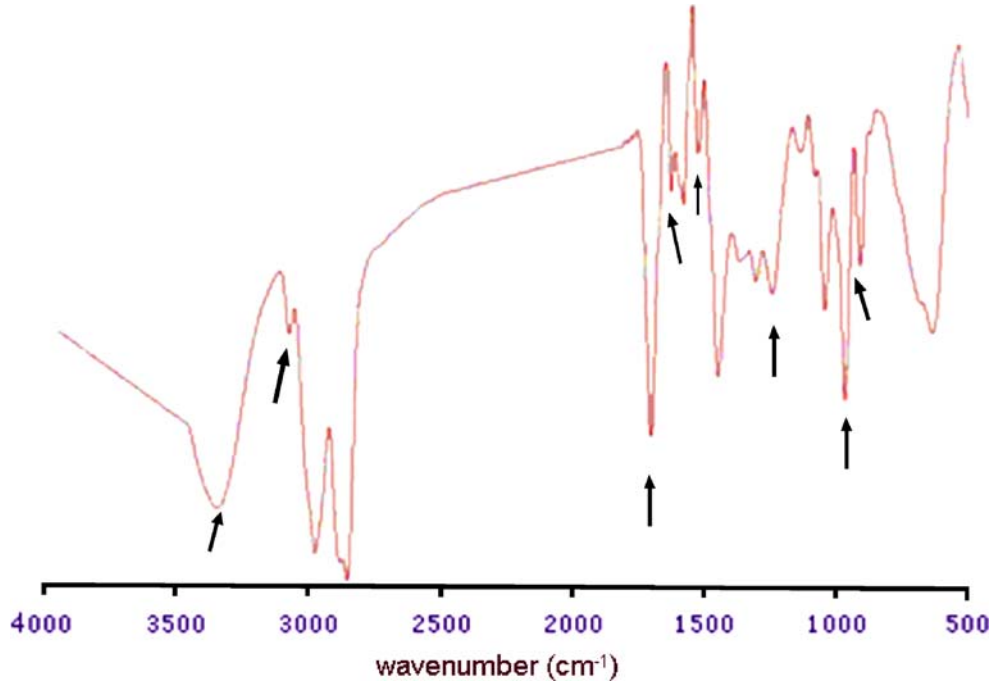
Styrene (Shanghai Chemical Reagents) was purified to remove the inhibitor by passing it through a basic alumina column and stored in a refrigerator before use. Kerosene (Shanghai Chemical Reagents), Hexdecane (HD, Aldrich),

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

Sample no.	Monomer[a] wt%	PU (g)	HD (g)	Water (g)	SDS (mmol l^{-1})[b]	D[c] (nm)	Shelf life (months)	N× 10^{-18} (particles/l)[d]	R_{pmax}[e] (mol/l/min)
1	15	0.40	/	112	13	47.1	>12	2.61	0.91
2	15	0.80	/	111	13	39.5	>12	4.42	0.84
3	15	1.60	/	109	13	41.3	>12	3.87	0.57
4	15	0.40	/	112	5	52.3	>12	1.91	0.43
5	15	0.40	/	112	7	50.3	>12	2.14	0.50
6	15	0.40	/	112	10	49.2	>12	2.29	0.67
7	10	0.40	/	178	13	41.9	>12	3.71	0.99
8	12	0.40	/	144	13	45.6	>12	2.30	0.95
9	18	0.40	/	89	13	52.6	>12	2.25	0.81
10	20	0.40	/	78	13	65.3	>12	1.31	0.65
11	15	/	0.40	112	13	59.7	>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 molar concentration of SDS was based on water.
[c] D represented particle diameter, and it was measured by TEM.
[d] N represented the number of the particles.
[e] R_{pmax} represented the maximum rate of the polymerization, and it could be obtained from the polymerization rate-time curve, which was the derivation of the conversion-time curve.

Fig. 1 FTIR spectra of PU



isophorone diisocyanate (IPDI, Aldrich), polyethylene glycol 200 (PEG 200, Shanghai Chemical Reagents), hydroxyl-terminated polybutadiene (HTPB, M_w=2,100, Zibo Qilong Chemical Reagents), sodium dodecyl sulfate (SDS, Shanghai Chemical Reagents) were used as received.

Synthesis of polyurethane dispersions

Four grams (0.02 mol) PEG and 41 g (0.02 mol) HTPB were introduced into a 500-ml four-necked, round-bottom flask equipped with a mechanical stirrer, condenser, nitrogen inlet, and thermometer. Kerosene (140 g) was used as a solvent. The mixture was stirred for 30 min at 70 °C to obtain a homogeneous solution. Then, 6.66 g (0.03 mol) IPDI was added and the reaction continued for 4 h. The resulting product was a stable dispersion with a solid content of about 35%. Scheme 1 shows the PU dispersion synthesis process.

Preparation of the miniemulsion

Miniemulsion was prepared by dissolving SDS in water and PU in St, respectively. Oily and aqueous phases were mixed and stirred for 30 min with a magnetic stirrer. The pre-emulsion was then sonicated in pulse mode for 5 min (AS 3120 Ultrasonic Cleaner). After that, the resultant miniemulsion was purged with nitrogen for 10 min to remove the dissolved oxygen in the system and then irradiated by ^{60}Co γ-ray at a dose rate of 106.46 Gy/min for 4 h at room temperature. The recipe of the miniemulsion was presented in Table 1.

Analytical methods

The shelf life of the miniemulsion was monitored by sitting aside about 20 ml of the sample in the test tube at room temperature and observing the time necessary for a visible

Table 2 Characteristic FT-IR absorptions present in the spectra of the PU

Wavenumbers (cm^{-1})	Bonds	Vibrational modes [22–24]
3,345	N–H urethane in hydrogen bond	Stretching vibration
3,074	C–H vinyl group	Stretching vibration
1,703	C=O urethane free and forming hydrogen bonds	Stretching vibration
1,629	C=C vinyl group (HTPB)	Stretching vibration
1,529	C–N–H urethane	Stretching vibration (C–N) Bending vibration (N–H)
1,245	C–O–C	Asymmetrical stretching
968 and 913	C–H vinyl group (HTPB)	Out-of-plane bending vibrations

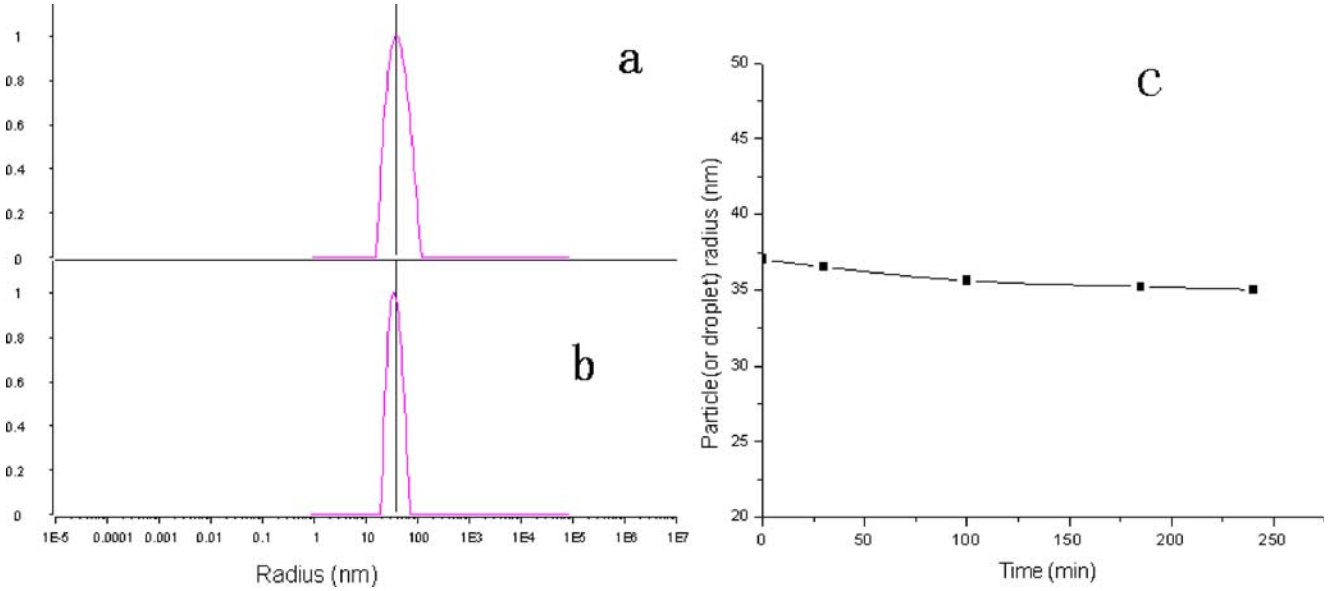


Fig. 2 Size and distribution of sample 5 from DLS measurements: **a** Monomer droplets (R=37 nm; PDI=0.152); **b** PS particles (R=35 nm; PDI=0.076) **c** variable during the polymerization

creaming line to appear. The conversion was determined by the gravimetric method. Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a VECTOR22 FTIR spectrometer using a KBr pellet. Size measurements of the monomer droplets and latex particles were performed by DLS (ALV/DLS/SLS-5022F) equipped with a multi-tau digital time correlator (ALV5000) and a cylindrical 22-mW UNIPHASE He–Ne laser (λ_0=632 nm) as the light source. Transmission electron microscopy (TEM) analysis was performed with a Hitachi H-800 operating at 200 kV. The diluted samples were mounted on the copper grids and left to dry. The particle number average diameter $(\overline{D_n})$ is calculated following the Eq. 1:

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

Where N_i is the number of polymer particles with diameter D_i

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

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

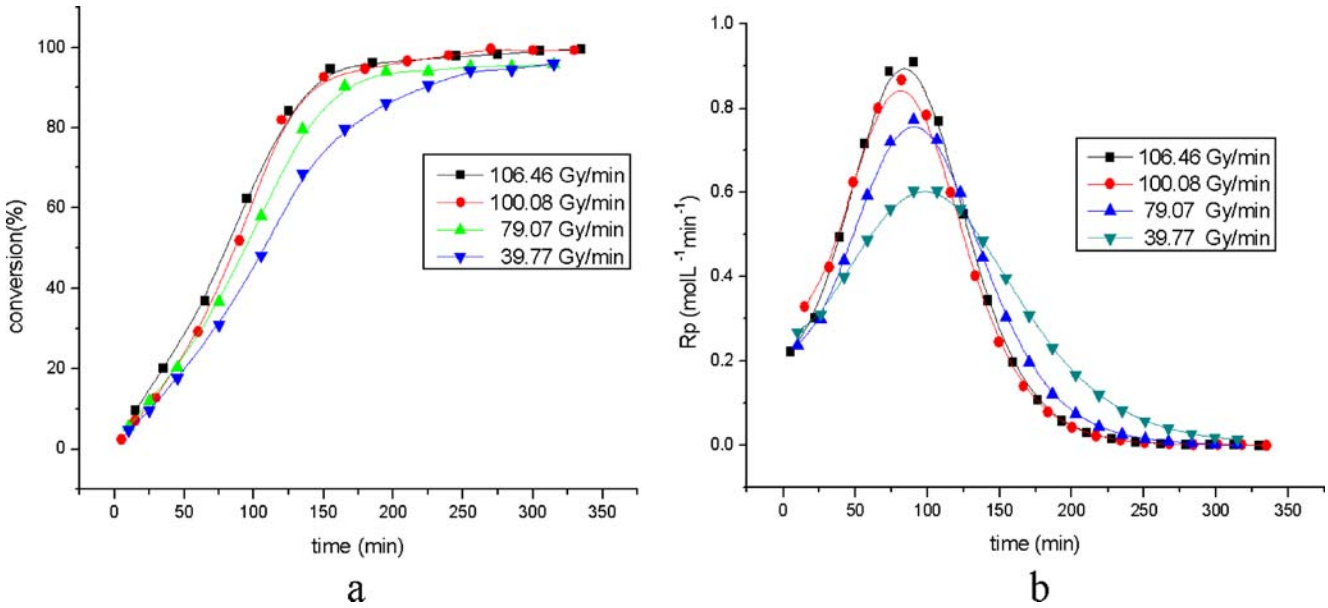


Fig. 3 Effect of dose rate on miniemulsion polymerization of sample 1: **a** Conversion; **b** polymerization rate

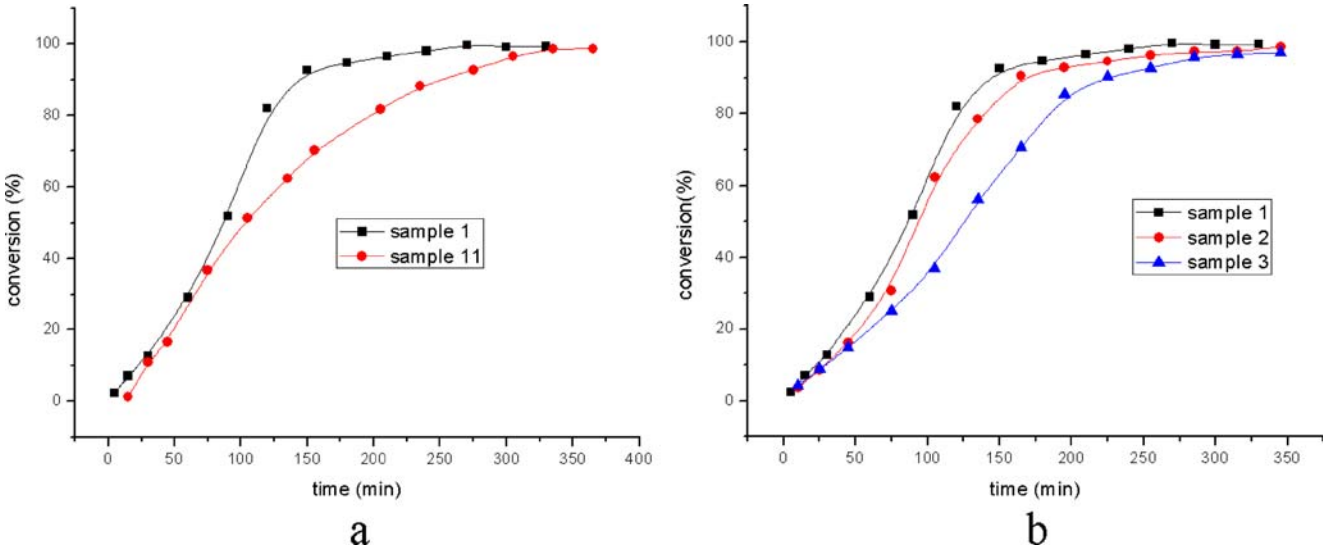


Fig. 4 Effect of costabilizer on conversion: **a** Miniemulsions with different kinds of costabilizer; **b** miniemulsions costabilized by various amounts of PU

Result and discussion

PU characterization by FT-IR

PU was characterized by infrared spectroscopy as shown in Fig. 1. The main characteristic group absorptions in the spectra were summarized in Table 2, which suggested that PU was successfully synthesized.

Nucleation mechanism

Serials of DLS measurements were performed to study the size and distribution of the monomer droplets and latex particles. Comparing the monomer droplet radius and the particle radius (shown in Fig. 2a,b), only very small difference was observed. The preservation of size was an evidence of monomer droplet nucleation [5]. Figure 2c shows the variable in size from monomer droplets to polymer particles during the polymerization. The miniemulsion was so stable that the particle size almost did not change during the whole reaction process (the little decrease was because of volume shrinkage). This result also indicated that nucleation and polymerization took place in the monomer droplets themselves [25]. After polymerization, a narrow and symmetric size distribution of PS particles with an average radius of 35 nm was obtained.

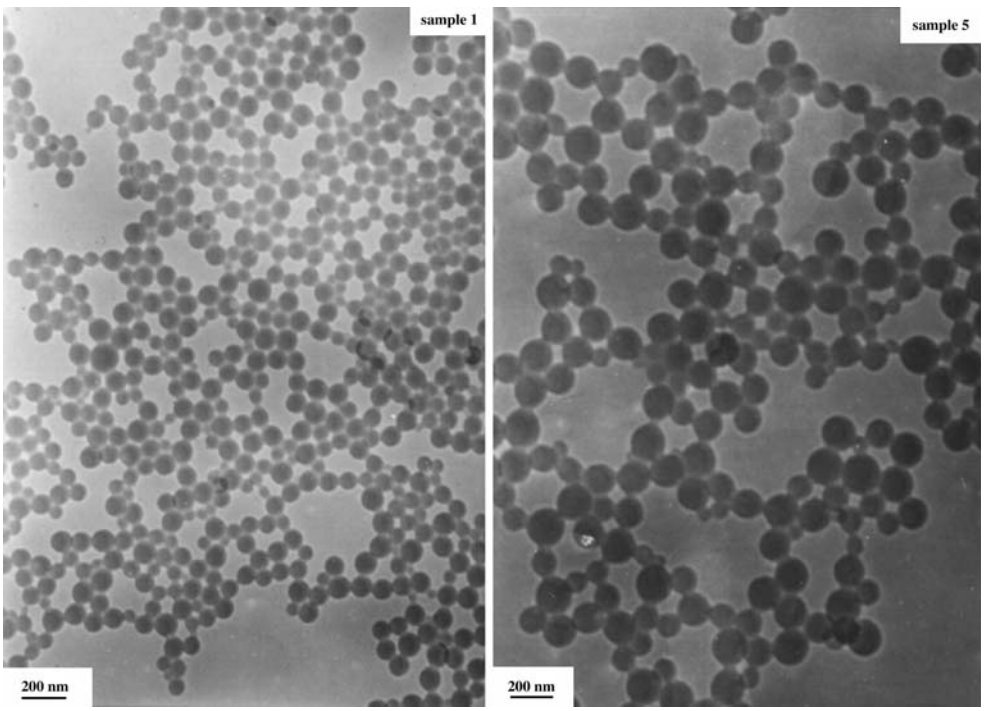


Fig. 5 TEM images of PS particles prepared from sample 1 $\left(\overline{D_n} = 47 \pm 5\ \text{nm}\right)$ and sample 5 $\left(\overline{D_n} = 50 \pm 5\ \text{nm}\right)$, respectively

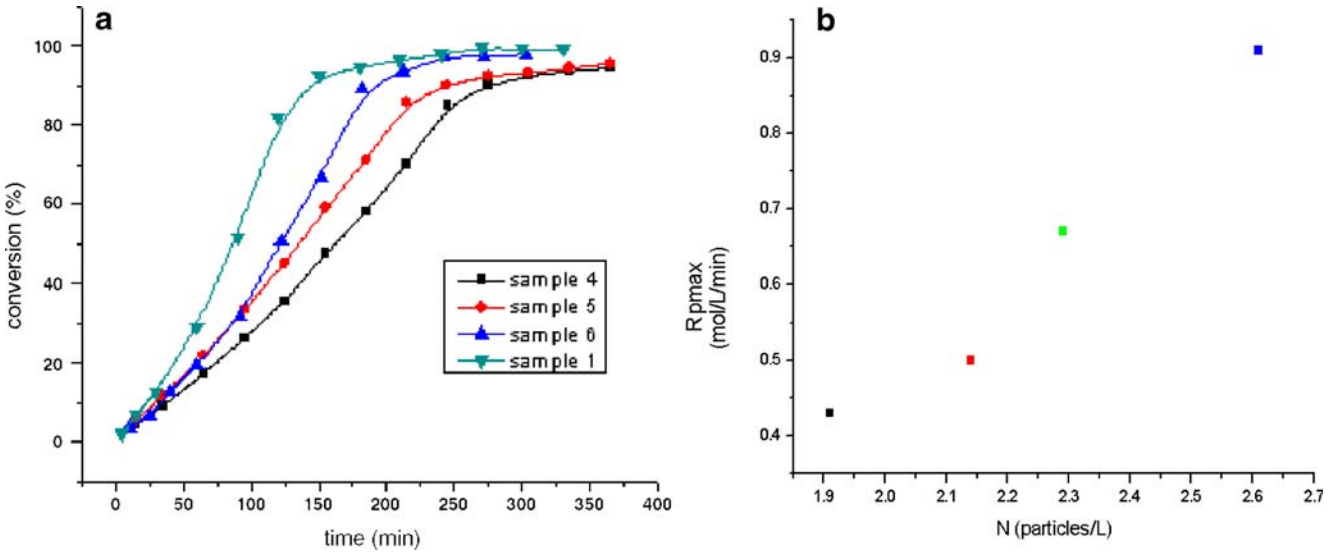


Fig. 6 **a** Effect of SDS content on conversion; **b** the relationship between R_{pmax} and N (the *black*, *red*, *green*, and *blue plot* represent the latex of samples 4, 5, 6, and 1, respectively)

(there were differences between DLS and TEM results as what they measured were water-swollen particles and dried particles, respectively).

About emulsion polymerization mechanism, Harkins et al. [26] depicted three major intervals which played an integral part in the reaction course: interval I (increasing rate stage), interval II (constant rate reaction stage), and interval III (decreasing rate stage). As a comparison, many kinetic measurements were taken. Figure 3b gives polymerization rate curves for the styrene miniemulsion systems initiated at different dose rates. The first interval was the particle nucleation interval (interval I). This interval ended at the reaction rate maximum of about 50% conversion. After the maximum rate, the reaction went into the rate-decreasing period directly. No interval with constant reaction rate could be found, which coincided with the kinetic mechanism of the typical miniemulsion polymerization [6]. It could be also found that if the miniemulsion was initiated at a higher dose rate, the nucleation period would be shortened, as more free radicals were produced, and more particles were nucleated at the same time.

As $R_p = k_p \times n_b \times [M] \times \frac{N}{N_A}$, in which k_p, n_b, $[M]$, and N represented propagation rate constant, the average number of radicals per particle, monomer concentration in the particles, and the number of particles, respectively, and k_{pSt}=1.2E4 mol/l/min, $[M]$=8.7 mol/l (the initial value could be regarded as that of the bulk phase). Combining with the data of N in Table 1, n_b could easily be calculated. For example, for the run with a minimum dose rate of 39.77 Gy/min in Fig. 3, a value of n_b as 2.22 could be estimated. This value was awfully high for such a small droplet (47.1 nm diameter) to confine, and it suggested that the entry of radicals was so frequent in radiation miniemulsion polymerization. Under high-energy radiation ($E_\gamma = 1.25$ Mev), there were non-selectivity interactions between γ-ray and the substances. ·H and ·OH were mainly produced from the radiolysis of water in the aqueous phase. These radicals were accompanied with high energy, so they were very active and easy to diffuse into the monomer droplets and initiated polymerization. At the same time, not only the monomer but also the nucleated particles could produce free radicals themselves in the oily phase. Besides these, the termination in the droplets was so limited because of the enhanced gel effect due to the increasing viscosity.

Kinetics

To observe the effects of recipe and dose rate on the polymerization kinetics, the relationship between monomer

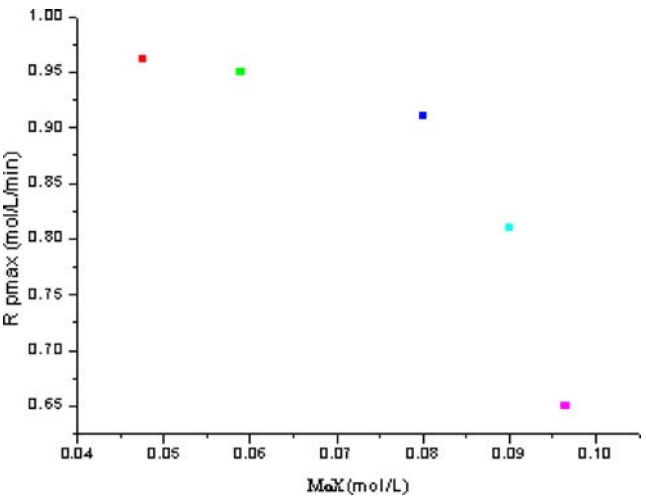


Fig. 7 Effect of St content on R_{pmax} (M_0 and X mean the initial monomer concentration based on the total reaction mixture and the monomer conversion, respectively. The plots from *left* to *right* correspond to samples 7, 8, 1, 9, and 10, respectively)

conversion and time of different samples was studied. All the polymerizations were initiated at room temperature. Conversion-time curves of the miniemulsion polymerization costabilized by PU and HD was shown in Fig. 4a. It was apparent from the figures that the polymerization of the miniemulsion costabilized by PU was faster than that by HD. The higher polymerization rates may be attributed to the effect of vinyl group in the chain of HTPB (see Scheme 1) which didn't exist in HD. When the miniemulsion was irradiated by high-energy γ-ray, the monomer St would react with the vinyl group, and PS may be grafted onto PU chain. The polymerization would be accelerated. In addition, the latex particles prepared from PU-costabilized miniemulsion were smaller (see Table 1).

Table 1 showed that when the surfactant content increases from 5 to 7, 10, 13 mM, the particle diameters decreased from 52.3 to 50.3, 49.2, and 41.9 nm (the TEM images of samples 1 and 5 could be seen in Fig. 5). As expected, the reaction accelerated accordingly as illustrated in Fig. 6, which was coincident with the usual response to the increase of the surfactant content [27, 28]. The higher the SDS concentration, the larger was the number of latex particles (see Fig. 6b) formed during the reaction and the greater was the polymerization rate (n_b calculated was not drastically different).

The conversion-time curves of varying amounts of costabilizer were shown in Fig. 4b. It could be seen that the polymerization rates decreased when the amount of PU increased, in accord with the results reported by Miller et al. [29] for St miniemulsion polymerization with polystyrene as the sole costabilizer and the miniemulsion of Yu et al. [16] costabilized by waterborne PU. The slower polymerization rate was due to two possibilities: The presence of more PU might prevent free radicals from entering into the monomer droplets to initiate polymerization due to the steric obstacle. This had been demonstrated by the fact that the average number of radicals per particle n_b calculated as explained before was decreased from 4.52 to 2.38 and 1.54 when the amount of PU increased from 2 to 4 and 8 wt% based on the monomer. In addition, when more PU was added and dissolved into the monomer droplets, the monomer concentration in the nucleated polymer particles would decrease.

Monomer content affected the reaction rate as shown in Fig. 7. When monomer content increased, the number of monomer droplets would decrease, and their diameter would increase owing to the lack of surfactant. Therefore, the number of nucleated particles decreased [30] (see Table 1), leading to the slower polymerization rate and the larger polymer particles, coincident with the diameter results.

As we know, miniemulsion polymerization velocity increases with the amounts of the initiator [31]. In the γ-ray radiation-induced miniemulsion polymerization process, radiation dose rate corresponds to the concentration of initiator. As a result, higher dose rate would promote the polymerization, as illustrated in Fig. 3.

Conclusion

In summary, we have reported a novel route to produce PS latex with relatively smaller size via γ-ray radiation-induced miniemulsion polymerization using PU as costabilizer at room temperature. The miniemulsions were quite stable with a shelf life of more than 12 months, and the polymerization rate was faster than that of the miniemulsion costabilized by classical costabilizer HD. The entry of radicals was quite frequent in radiation miniemulsion polymerization, and higher absorbed dose rate could accelerate the reaction. DLS and kinetic measurements demonstrated the predominant mechanism of monomer droplet nucleation. The particle size of PS was affected by the contents of monomer, surfactant, and costabilizer.

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