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ORIGINAL PAPER

Kinetics and latex particles analysis on styrene emulsion polymerization induced by ^{60}Co γ rays in presence of anionic polymerizable emulsifier

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Abstract ^{60}Co γ rays induced styrene emulsion polymerizations were carried out with sodium undec-10-enoate (UDNa) as emulsifier at room temperature and the different kinetics was discussed. The influence of absorbed dose rate, monomer concentration and emulsifier concentration on kinetics and latex particles was studied. The polymerization kinetics relation was found as $R_P \propto D^{0.37} \cdot M^{0.75} \cdot E^{0.70}$ (R_P, maximum polymerization rate; D, absorbed dose rate; M, monomer concentration; E, emulsifier concentration). The particles' diameter increases and particle size distribution (*PSD*) becomes narrower with the decrease of absorbed dose rate and increase of monomer content. The effect of UDNa content on particles' diameter and particle size distribution is the same as that of emulsifier in conventional emulsion system. This type of emulsion polymerization can easily form monodisperse particles.

Keywords ^{60}Co γ rays induced emulsion polymerization · Polystyrene · Particle size distribution · Kinetics · Polymerizable emulsifier

Introduction

Emulsion polymerization has been used widely in industry and its products have many advantages. But the conventional emulsifiers often desorbs from the surface of the latex particles during its shelf life or under conditions of high shear and freeze-thaw etc. [1, 2] This can cause environment pollution and create a problem in treatment of the latter. [3, 4] All problems can be owing to emulsifiers' physical adsorption on surface of polymer latexes. Based on the above problems, polymerizable emulsifiers emerge. Polymerizable emulsifier molecule contains not only hydrophilic and hydrophobic segments but also reactive groups which can copolymerize with primary monomer [5, 6]. The desorption of the emulsifier from the latex particle surface or migration in the polymer film is eliminated by chemical incorporation of the emulsifier into the polymers. As an initiated polymerization method, ^{60}Co γ rays have many advantages over chemical initiators. [7–9]

Many polymerizable emulsifier systems have been deeply studied [10–15] and research about ^{60}Co γ rays induced emulsion polymerization were also found. [16–18] But there were few articles about kinetics of ^{60}Co γ rays induced emulsion polymerization with ionic comonomer as emulsifier.

This article paper focuses on the kinetics and latex particles of the ^{60}Co γ rays induced emulsion of styrene using another anionic polymerizable emulsifier UDNa.

Experimental

Synthesis of polymerizable emulsifiers

UDNa (sodium undec-10-enoate, $CH_2=CH(CH_2)_8COO^-Na^+$) was synthesized by reaction of undec-10-enoic acid and sodium hydroxide in absolute ethanol; the light yellow precipitation was collected, washed three times by absolute ethanol and freeze dried 12 h.

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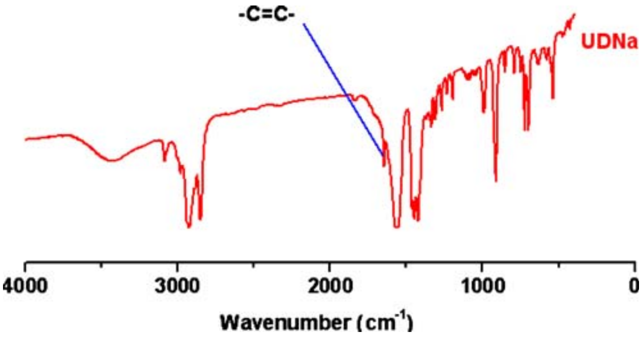


Fig. 1 FT-IR spectra of UDNa

Characterization

Monomer conversions were determined gravimetrically (see polymerization part). The polymerization rate Rp was obtained by derivation of the conversion versus time curves as followed equation:

$$R_p = \frac{W \cdot C_m \cdot D_L}{M_{St} \cdot V}, \mathrm{mol} \cdot \mathrm{L}^{-1} \cdot \mathrm{min}^{-1} \tag{1}$$

where W (g) is the weight of all mixture, C_m (=10%) is monomer content, D_L (% /min) is maximal vertical ordinate value of differential curve from conversion~time curve, M_{St} (=104 g/mol) is mole mass of styrene, V (L) is the volume of all mixture. Since the monomer content is very low, the density of all mixture is approximatively regarded as that of pure water.

FT-IR spectra of were recorded with a VECTOR22 spectrometer. Particle size and morphology of polystyrene latex were examined by a Hitachi-H800 transmission electron microscope with 200 kV accelerating voltage. The particle size distribution and the average number of polymer particles per unit of aqueous phase were calculated according to the reference with use of Eqs (2 and 3). [19]

$$D_n = \sum n_i D_i / \sum n_i \tag{2}$$

$$D_w = \sum n_i D_i^4 / \sum n_i D_i^3$$

$$D_v = \left(\sum n_i D_i^3 / \sum n_i\right)^{1/3}$$

$$PSD = D_w / D_n$$

$$N_p = 6mx / \left(\pi \rho_P D_v^3 V\right) \tag{3}$$

where D_n is number average diameter, D_w is weight average diameter, D_v is volumer average diameter, n_i is the number of polymer particles with diameter D_i and PSD is the particle size distribution, m is the weight of monomer per unit volume of water, x is the fractional conversion, ρ_p is the density of polystyrene at 60°C.

Emulsion polymerization in presence of polymerizable emulsifiers

Monomer, UDNa and water were mixed together in a round bottom flask and stirred with high speed; then the mixture was divided into a certain amount of little glass bottles with same volume and each glass bottle can contain 5 g mixture; purified nitrogen was bubbled through every glass bottle for about 45 min to get rid of oxygen and sealed immediately; the system was subjected to the field of a 2.22×10^{15} Bq ^{60}Co γ rays source at room temperature; a glass bottle was taken out at different time to calculate monomer conversion.

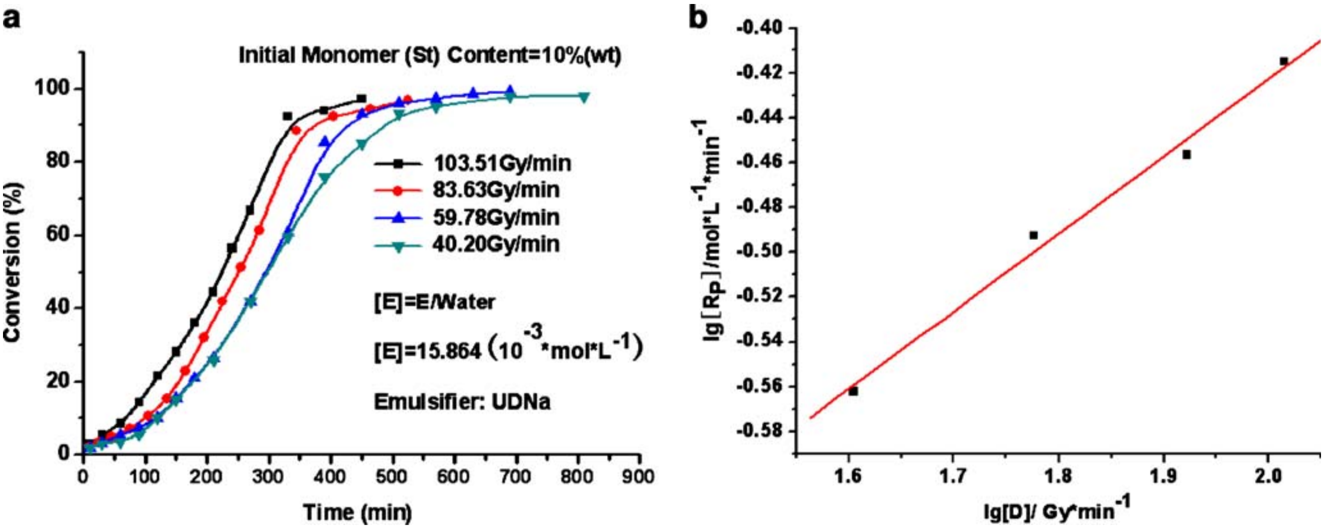


Fig. 2 **a** Conversion vs time curve at different absorbed dose rates; **b** effect of absorbed dose rate on R$_P$

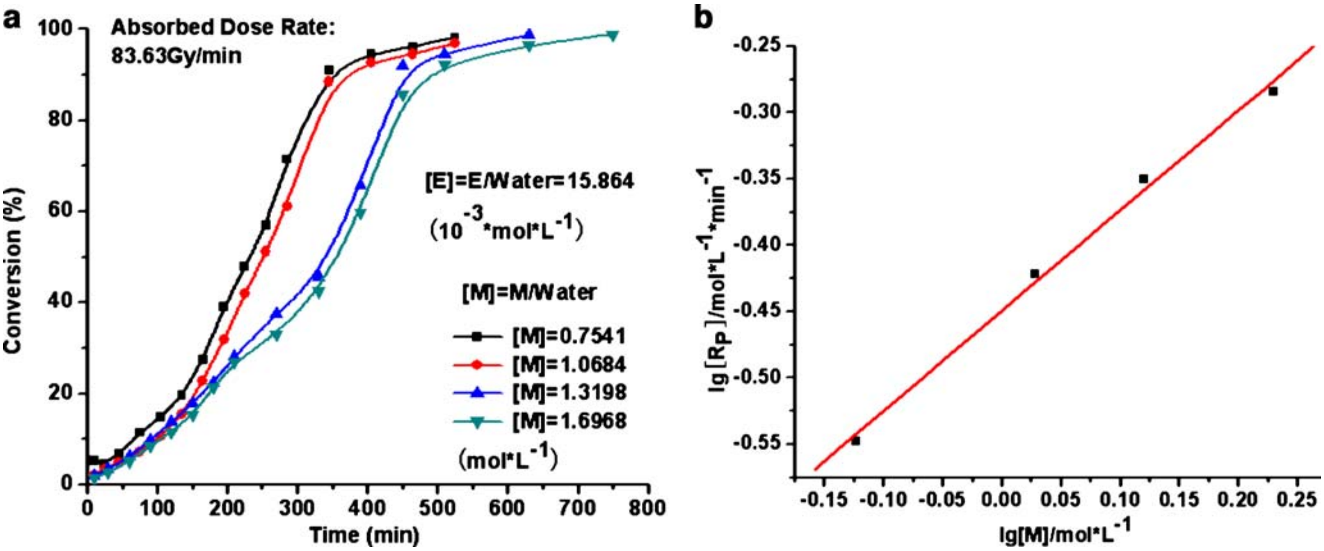


Fig. 3 **a** Conversion vs time curve at various monomer concentrations; **b** effect of monomer concentration on R_P

Results and discussion

Characterization of surfactant monomer

From the FT-IR spectra of UDNa we can see that double bond obviously appears at the wavenumber 1640 cm^{-1} in Fig. 1.

As is known that undec-10-enoic acid (CH_2=CH $(CH_2)_8COOH$) is the deep processing product of castor oil, it not only has surface activity but also can inhibit fungus. Sodium undec-10-enoate resulted from undec-10-enoic acid has both polymerization activity and emulsifying function (CMC=43 mM). [20] So it is an environment-friendly emulsifier.

Polymerization kinetics

Effect of irradiation dose rate

The dependence of the conversion on the reaction time at different absorbed irradiation dose rates is shown in Fig. 2a. The correlation between the absorbed irradiation dose rate and the polymerization rate (Rp) is displayed in Fig. 2b and can be expressed as $R_P \propto \dot{D}^{0.37}$ which is similar to that of conventional emulsion polymerization $R_P \propto \dot{D}^{0.40}$. The higher the absorbed irradiation dose rate is, the faster the rate of formation free radicals is; hence higher polymerization rate appears.

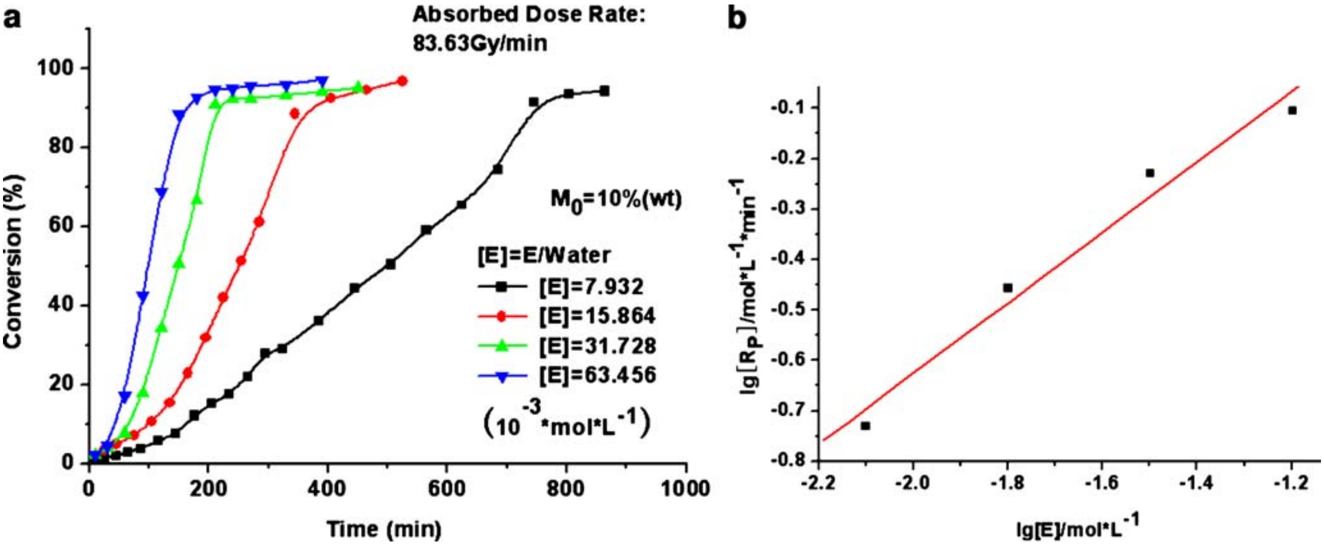


Fig. 4 **a** Conversion vs time curve at various UDNa contents; **b** effect of UDNa content on R_P

Table 1 The effect of absorbed dose rate on the latex particles according to Fig. 5

Run(different dose rate, Gy/min)	D_n (nm)	D_w (nm)	D_v (nm)	*PSD*	N_p ($\times 10^{15}$/ ml)
D1 (130.32)	62.17	63.17	62.52	1.016	1.24
D2 (83.63)	85.46	86.15	85.69	1.008	0.48
D3 (45.36)	90.47	90.92	89.30	1.005	0.41
D4 (31.20)	94.23	94.63	94.36	1.004	0.36

Effect of monomer concentration

Figure 3a shows the polymerization rate~conversion curves obtained at various monomer concentrations. The effect of monomer content on polymerization kinetics can be calculated as$R_P \propto M^{0.75}$ from Fig. 3b.

Effect of UDNa concentration

Figure 4a is conversion~time curves obtained at various UDNa contents. The effect of UDNa content on polymerization kinetics is displayed as$R_P \propto E^{0.70}$ from Fig. 4b. A higher UDNa concentration means more reaction centers and causes faster UDNa adsorption which result in higher polymerization rate. In dispersion polymerization, the impact exponent of stabilizer concentration on R_P is often lower than 0.7 with the reason that the system is homogeneous phase in early reaction while that of microemulsion is greater than 1 with the use of much emulsifier. [21, 22]

Diameters of latex particles

Effect of dose rate

We can see that the average particles' diameter increases and *PSD* becomes narrower with the decrease of absorbed dose rate from Table 1 and Fig. 5. More reactive radicals generated in water at higher absorbed dose rate result in faster nucleation and congregation; furthermore this will lead to more polymer particles and increase of N_P which is similar to that of chemical initiators' systems [23]. Under this condition, smaller polymer particles will form with the same weight monomers. But large number of particles will collide and congregate each other and this makes *PSD* become narrow.

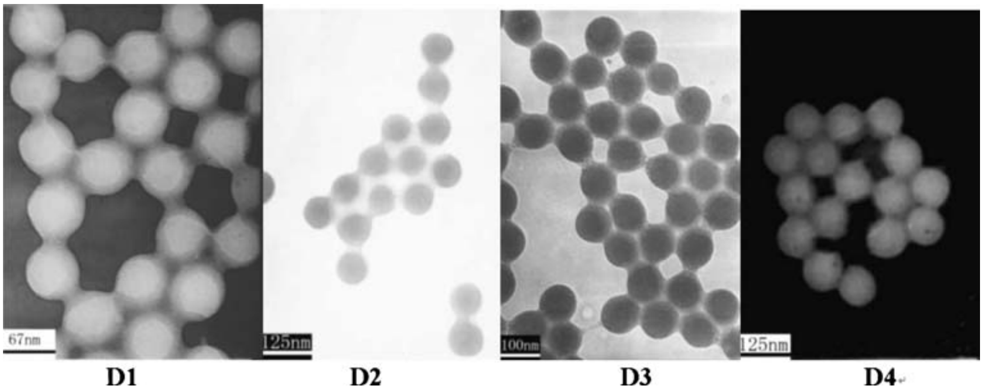
Effect of monomer content

Figure 6 and Table 2 show that particle diameter increases and *PSD* becomes narrow as monomer increases. Since the number of oligomers derived from the reaction between styrene and UDNa at early polymerization is constant because of stable UDNa's concentration, the number of oligomers that stabilize monomer will decrease with increase of monomer, which leads to less chance of smaller particles' formation and narrow *PSD*; that the oligomers is constant makes the number of generated latex particles keep invariable, so the monomer addition has no effect on nucleation and then N_P in Table 2 keeps nearly constant.

Effect of UDNa concentration

The effect of UDNa concentration on the latex particles is the same as that of emulsifier in conventional emulsion system which can be seen in Table 3 and Fig. 7.

The essential role of the ionic comonomer UDNa in the emulsifier-free emulsion polymerization is that it can be chemically bonded onto the particles' surface to provide better electrostatic stability, but different comonomers usually provide different reactivities and hydrophilic properties which lead to different polymerization behaviors in the aqueous phase and nucleation behaviors. [24] That the —COO$^-$ groups chemically bonded on particle surface increased with increase of UDNa content explained the relationship with particles' diameter. Because the ionized comonomer reacted with radicals generated by γ rays to



D1 D2 D3 D4

Fig. 5 TEM images of St latex particles at different dose rates: D1, 130.32Gy/min, 58644Gy, 97.09%; D2, 83.63Gy/min, 43905.75Gy, 96.86%; D3, 45.36Gy/min, 31298.4Gy, 99.24%; D4, 31.20 Gy/min, 25272Gy, 98.04%

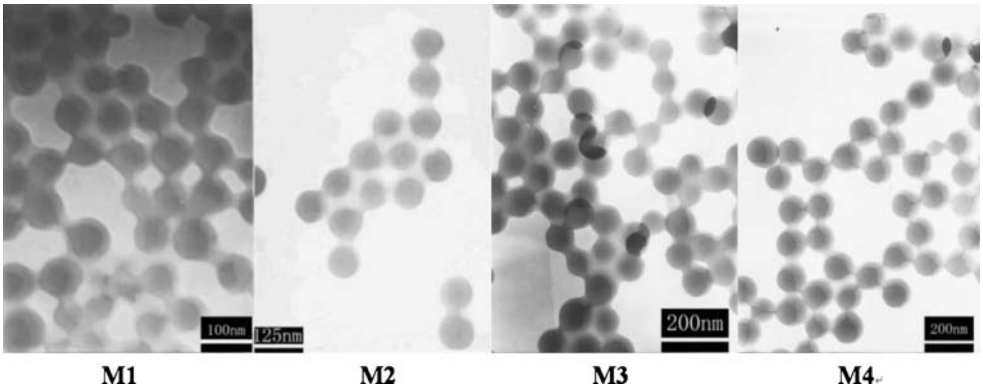


Fig. 6 TEM images of St latex particles at different monomer concentrations (monomer/water, mol/L): M1, 0.7541; M2, 1.0684; M3, 1.3198; M4, 1.6968

Table 2 The effect of monomer concentration on the latex particles according to Fig. 6

Run (different monomer/water ratio, mol/L)	D_n (nm)	D_w (nm)	D_v (nm)	*PSD*	N_p ($\times 10^{15}$/ ml)
M1 (0.75)	79.24	84.51	81.05	1.066	0.40
M2 (1.07)	85.46	86.15	85.69	1.008	0.48
M3 (1.32)	103.85	106.03	104.57	1.021	0.33
M4 (1.70)	117.02	118.02	117.36	1.007	0.30

Table 3 The effect of UDNa concentration on the latex particles according to Fig. 7

Run(different UDNa/water ratio, $\times 10^{-3}$mol/L)	D_n (nm)	D_w (nm)	D_v (nm)	*PSD*	N_p ($\times 10^{15}$/ ml)
E1 (7.93)	123.93	124.01	123.96	1.001	0.15
E2 (15.86)	85.46	86.15	85.69	1.008	0.48
E3 (31.73)	62.61	63.32	62.85	1.011	1.19
E4 (64.46)	50.57	53.29	51.57	1.054	2.19

form many oligomer radicals, the primary particle formation was accelerated with increasing UDNa concentration and resulted in decreasing diameter and increasing N_P. Meanwhile, numerous primary particles are likely to collide which causes increasing *PSD*. Moreover, UDNa is a soluble-water monomer; the —COO$^-$ groups were at the surface of the latex particle as far as possible after UDNa copolymerized with St. [25] This can be seen carefully from the TEM images.

The particles of all the TEM images have good monodispersity. The monodispersity is only obtained when the initiation and nucleation stage is very short compared with the overall reaction period. At the same time, the period of repetitive nucleation must be made so short that monodispersity arise from subsequent uniform growth on the existing nuclei. [26] For our work, ^{60}Co γ rays produce a higher rate of free radicals formation and initiation and the formation of nuclei is a quite short time (about 10^{-6} s) after radiation. [27] The number of the particles becomes constant as soon as the nuclei form, which results in monodisperse particles.

Shell life of the prepared emulsions

Table 4 shows shell life of the prepared emulsion samples. All samples can keep being not stratified for at least 3 months and almost no coagulum was found, indicating

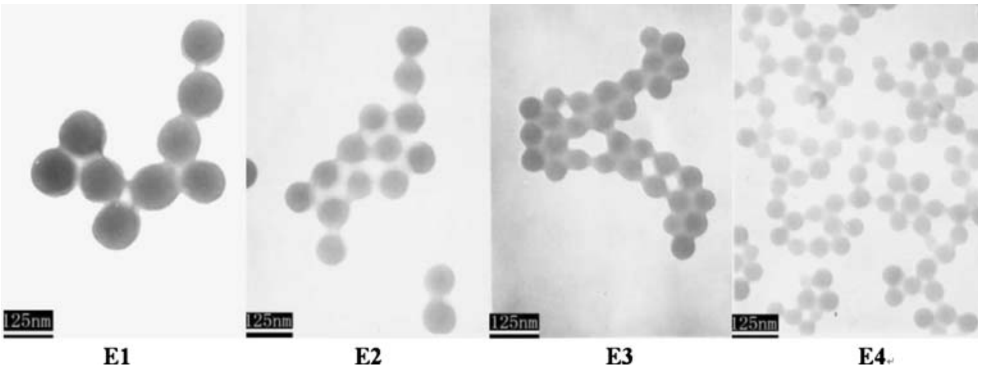


Fig. 7 TEM images St latex particles at different UDNa concentrations (UDNa/water, 10^{-3}mol/L): E1, 7.932; E2, 15.864; E3, 31.728; E4, 63.456

Table 4 Shell life of the prepared emulsions

Sample	Shell life/ days (not stratified)	Sample	Shell life/ day (not stratified)	Sample	Shell life/ days (not stratified)
D1	>360	M1	>360	E1	120
D2	300	M2	300	E2	300
D3	200	M3	240	E3	>360
D4	150	M4	120~150	E4	>360

better stability of prepared latexes than that of conventional emulsion products.

Since our system is essentially emulsifier-free emulsion copolymerization of styrene with anionic monomer which follows oligomer micellar nucleation mechanism and ^{60}Co γ rays induced polymerization is adopted, more complicated mechanism for particle formation exists. UDNa acts as not only a comonomer but also an emulsifier. It copolymerizes with the main monomer and becomes covalently bound to integrate with the main polymer chains. This makes the microlatexes possess firm surface-active groups which provide the electrostatic stabilization for the microparticles. The presence of more ionic groups at particle surfaces certainly enhances the electrostatic repulsive forces between the particles and hence, the coagulation of primary particles would be restricted. Meanwhile, the charged particles generated by water under the irradiation of ^{60}Co γ rays can also stabilize latex particles. The aforesaid two effects cause almost no coagulum in the final emulsion. In polymerizable surfactant emulsion system, fast particle nucleation and the rapid depletion of monomer are apt to occur. [28] So it can easily lead to monodisperse latex particles.

Conclusions

In this work, the specific kinetics features of the ^{60}Co γ rays induced styrene emulsion polymerization have been studied. This method had both the advantages of irradiation induction and emulsifier-free polymerization. At the same time, uniform polymer particles were obtained. Polymerization rate increases with the increase of dose rate, stabilizer concentration and monomer concentration. While the particle size increases with decrease of dose rate, increase of monomer and decrease of stabilizer concentration. Generally, the latex particles have good monodispersity. The colloidal stability of γ rays induced latex prepared with a surfmer is better than that of prepared with a conventional surfactant. Further study of the different monomers and other ionic polymerizable surfactant systems are in progress.

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References

1. Greene BW, Sheetz DP (1970) J Colloid Interface Sci 32:96. doi:10.1016/0021-9797(70)90106-2
2. DiGioia FA, Nelson RE (1953) Ind Eng Chem Res 45:745. doi:10.1021/ie50520a028
3. Holmberg K (1992) Prog. Org. Coat. 20:325. doi:10.1016/0033-0655(92)80022-O
4. Mobarakeh HS, Roudboneh MH (2006) J Polym Res 13:421. doi:10.1007/s10965-006-9062-x
5. Guyot A (1996) Curr Opin Colloid Interface Sci 1:580
6. Urquiola MB, Dimonie VL, Sudol ED, El-Aasser MS (1992) J. Polym. Sci. Polym. Chem. Ed. 30:2619. doi:10.1002/pola.1992.080301216
7. Dai Q, Wu DZ, Zhang ZC, Ye Q (2003) Polymer (Guildf) 44:73. doi:10.1016/S0032-3861(02)00728-0
8. El-Mohdy HLA, Ghanem S (2009) J Polym Res 16:1. doi:10.1007/s10965-008-9196-0
9. El-Mohdy HLA, El-Rehim HAA (2009) J Polym Res 16:63. doi:10.1007/s10965-008-9203-5
10. Chen SA, Chang HS (1985) J. Polym. Sci. Polym. Chem. 23:2615
11. Wang X, Sudol ED, El-Aasser MS (2001) J. Polym. Sci. Polym. Chem. Ed. 39:3093. doi:10.1002/pola.1290
12. Wang X, Sudol ED, El-Aasser MS (2001) Langmuir 17:6865. doi:10.1021/la010641n
13. Guyot A, Âbele S, Sjöberg M, Hamaide T, Zicmanis A (1997) Langmuir 13:176. doi:10.1021/la960577n
14. Guyot A, Âbele S, Zicmanis A, Graillat C, Monnet C (1999) Langmuir 15:1033. doi:10.1021/la980562k
15. Guyot A, Soula O (1999) Langmuir 15:7956. doi:10.1021/la9817009
16. Larrabee CE, Sprague ED (1979) J. Polym. Sci. Polym. Let. Ed. 17:749. doi:10.1002/pol.1979.130171201
17. Ye Q, Ge XW, Zhang ZC (2003) Radiat Phys Chem 66:11. doi:10.1016/S0969-806X(02)00307-9
18. Xu XL, Ge XW, Zhang ZC, Zhang MW (1998) Polymer (Guildf) 39:5321. doi:10.1016/S0032-3861(97)10205-1
19. Zaragoza-Contreras EA, Navarro-Rodríguez D (2003) Polymer (Guildf) 44:5541. doi:10.1016/S0032-3861(03)00621-9
20. Larrabee CE Jr, Estel D (1979) J. Polym. Sci. Polym. Lett. 17:749
21. Ye Q, Ge XW, Zhang ZC (2003) Radiat Phys Chem 66:11. doi:10.1016/S0969-806X(02)00307-9
22. Xu XL, Fei B, Zhang ZC, Zhang MW (1996) J. Polym. Sci. Polym. Chem. 34:1657. doi:10.1002/(SICI)1099-0518(19960715)34:9<1657::AID-POLA2>3.0.CO;2-P
23. Ober CK, Hair ML (1987) J. Polym. Sci. Pol. Chem. Ed. 25:1395. doi:10.1002/pola.1987.080250516
24. Xu ZS, Yi CF, Cheng SY, Zhang JZ (1997) J Appl Polym Sci 66:1. doi:10.1002/(SICI)1097-4628(19971003)66:1<1::AID-APP1>3.0.CO;2-X
25. Xu ZS, Lu GH, Cheng SY, Li JZ (1995) J Appl Polym Sci 56:575. doi:10.1002/app.1995.070560506
26. Lamer VK, Dinegar RH (1975) J Am Chem Soc 72:4847. doi:10.1021/ja01167a001
27. Naka Y, Kaetsu I, Yamamoto Y, Hayashi K (1991) J. Polym. Sci. Polym. Chem. 29:1197. doi:10.1002/pola.1991.080290814
28. Liu J, Chew CH, Gan LM, Teo WK, Gan LH (1997) Langmuir 13:4988. doi:10.1021/la970252m