

Kinetic and size control of polystyrene and polyacrylic octadecyl ester lattices via polymerization in O/W microemulsions

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Abstract

The kinetic studies of the acrylic octadecyl ester and styrene polymerization in microemulsion systems, (1) cetyl pyridine bromide (CPDB)/*t*-butanol/styrene/water; (2) CPDB/*t*-butanol/toluene + acrylic octadecyl ester (1:1, w/v)/water; (3) cetyl pyridine bromide/styrene/formamide, were made by using dynamic laser light scattering techniques (DLS). The mechanisms of nucleation of latex particles were discussed. The most possible nucleation location of the styrene and acrylic octadecyl ester microlatex particles in aqueous microemulsion system is in aqueous phase via homogeneous nucleation. Meanwhile, parts of microlatex particles are possibly produced via swollen micelles (microemulsions) and monomer droplets nucleation. On the other hand, the most possible nucleation location of the styrene microlatex particles in nonaqueous microemulsion system is inside monomer droplets. The relationship between the amount of monomer and the size of microlatex was also investigated. It has been found that the size of microlatex particles could be controlled by changing the amount of monomer. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The study of emulsion polymerization was started from the beginning of this century. The ethylene monomer was found by Hoffman in 1909

and could be polymerized in emulsion. There has been a steadily increasing number of investigations on emulsion polymerization, and several kinds of theory and kinetic models were put forward. After intensive study of the emulsion polymerization, the attention of the scientists was shifted to the microemulsion polymerization. During the past few years, tremendous advances have

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been reported on polymer synthesis in microemulsions [1–4].

Microemulsions are transparent, isotropic and thermodynamically stable mixtures of oil and water stabilized by surfactant and usually with a cosurfactant [5]. There are three structures: O/W, B.C and W/O. The size of the liquid droplet is equal to that of tens of nanometers up to hundreds of nanometers. The goal of polymerization in microemulsions is to control the structural properties of the resulting polymers on a mesoscopic scale. Polymerization of the oil component in globular O/W type microemulsion leads to ultrasmall latex particles with narrow particle size distribution [6–8]. Atik and Thomas reported microemulsion polymerization of styrene with azobis (isobutyronitrile) (AIBN) as an initiator and obtained narrowly distributed latex particles with diameters on the order of 20–30 nm [9,10]. Turro and El-Aasser et al. examined the photoinitiated polymerization of styrene in microemulsion, using pentanol as a cosurfactant and toluene as a mediator [11]. Jayakrishnan and Shah first demonstrated that the polymerization of styrene in microemulsion can be performed by surfactants alone, without a cosurfactant [12]. Styrene polymerization in nonaqueous microemulsion system has also been reported [13,14].

During the polymerization, monomers are located possibly in the following locations: (1) monomer droplets; (2) monomer-swollen micelles (microemulsions); (3) aqueous phase. In our research, the kinetic study of acrylic octadecyl ester and styrene polymerization in aqueous microemulsion system and styrene polymerization in nonaqueous microemulsion system have been made by checking the size changes of the microlatex particles using the dynamic laser light scattering technique. The mechanisms of nucleation of microlatex particles are also investigated. One conclusion is that the most possible nucleation location of the microlatex particles in aqueous microemulsion system is in aqueous phase via homogenous nucleation. Another possibility is that parts of microlatex particles are produced via monomer-swollen micelles (microemulsions) and monomer droplets nucleation. On the other hand, the most possible nucleation location of the sty-

rene latex particles in nonaqueous microemulsion system is inside monomer droplets. From the investigation on the relationship between the amount of monomer and the size of microlatex particles, we come to the conclusion that the sizes of the microlatex particles can be controlled by changing the amount of monomer.

2. Experimental section

2.1. Materials

Styrene (A.R.) was first washed with 10% aqueous sodium hydroxide to remove the inhibitor, and then with distilled–deionized water to remove residual base. After being dried with anhydrous sodium sulfate, the styrene was vacuum distilled under nitrogen at 20 torr and 40 °C. The acrylic octadecyl ester was synthesized by our group. The same method described in the literature was used [15]. The cetylpyridine bromide was recrystallized twice from acetone–ethanol (3:1, v/v). Other chemicals used in this work are used as they are without further purification.

2.2. Dynamic laser light scattering

Particle size and size distribution were measured by the dynamic laser light scattering with 400 W solid laser. The wavelength is 532 nm. (ALV/SP—125, Germany); the correlator is ALV—5000. The single-phase region of the microemulsion system was determined visually by titrating a specific amount of CPDB and *t*-butanol or CPDB and *t*-butanol or CPDB and styrene with water or formamide in a screw-capped tube at room temperature. Each titration was thoroughly mixed by using a magnetic stirrer. The clear-turbid boundaries were established from the systematic titrations. The transparent microemulsion regions are shown in Figs. 1 and 2 for an aqueous microemulsion and a nonaqueous, respectively.

The samples were prepared according to the points A, B and C selected from the microemulsion regions in the phase diagram (Figs. 1 and 2). In these microemulsion regions, the sample is

transparent and fluid. With addition of initiator system $((\text{NH}_4)_2\text{S}_2\text{O}_8 : \text{NaHSO}_3 = 2:1, \text{ w/w})$, the droplet size and the size distribution of the microemulsion polymerization system were immediately measured by using the dynamic laser light scattering technique. The size and the distribution of the selected samples were determined as a function of time. The method is based on the measurement of the particles' diffusion coefficient by measuring the intensity of fluctuation of the scattered light as they undergo Brownian motion. As a very detailed analysis of the theory has been made by Pusey [16], only a very brief summary is given here: when a light beam passes through a colloidal dispersion that undergoes Brownian motion, the intensity will fluctuate in such a way that the time taken for intensity maximum to go to the minimum (i.e. the coherence time) corresponding to the time required for moving one wave length.

By using a photomultiplier of active area about the size of the diffraction maximum, this intensity fluctuation can be measured. The normalized autocorrelation function $[g^{(1)}(\tau)]$ is given by:

$$[g^{(1)}(\tau)] = \exp - (\Gamma \tau) \quad (1)$$

where Γ is the decay rate or inverse coherence time and τ is the correlation delay time. Γ is related to the transnational diffusion coefficient D by:

$$\Gamma = DK^2 \quad (2)$$

where K is the scattering vector given by:

$$K = \left(\frac{4 \pi n}{\lambda_0} \right) \sin \left(\frac{\theta}{2} \right) \quad (3)$$

where λ_0 is the wavelength of the incident light in vacuum, n is the refractive index of the solution and θ is the scattering angle.

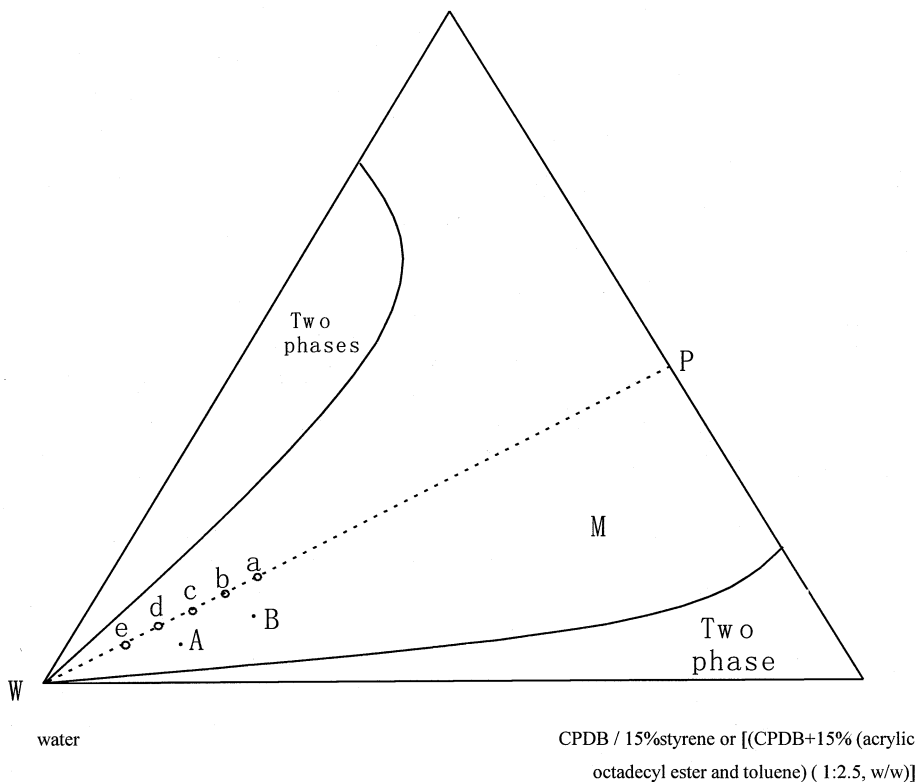


Fig. 1. The pseudo-ternary phase diagram of CPDB/*t*-butanol/15% styrene/water system or [CPDB + *t*-butanol/15% (acrylic octadecyl ester and toluene) (1:2.5, v/v) system.

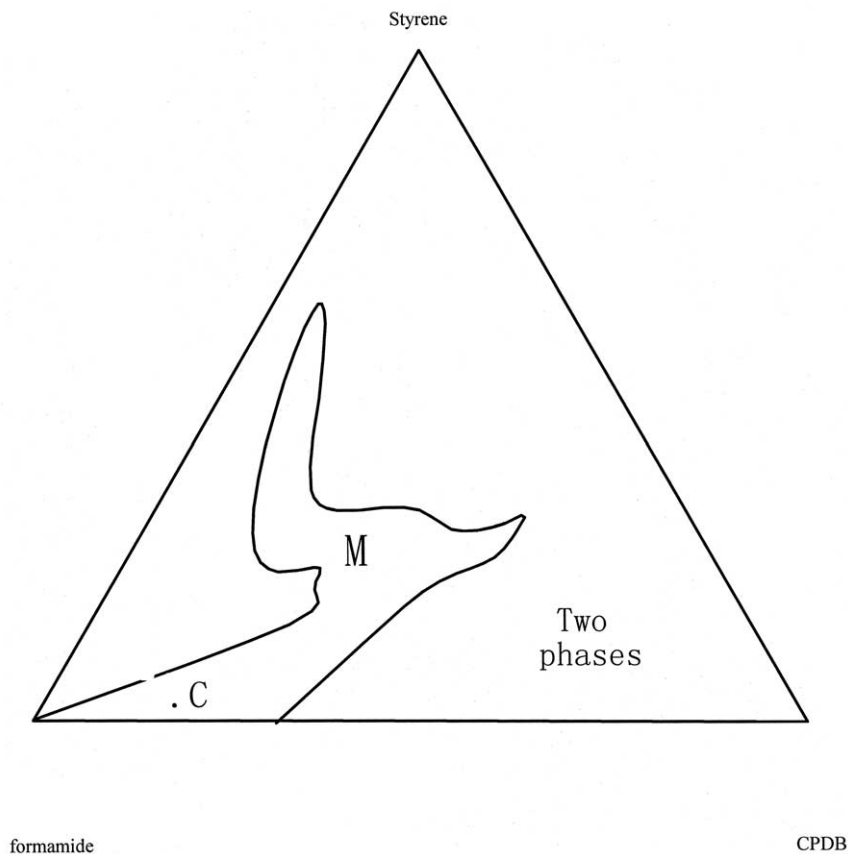


Fig. 2. The tertiary phase diagram of the CPDB/styrene/formamide nonaqueous system.

The hydrodynamic particle radius R_h can be calculated from D by using the Stokes–Emulsion equation:

$$R_h = \frac{kt}{6\pi\eta_0 D} \quad (4)$$

where k is the Boltzmann constant, T is the absolute temperature and η_0 is the viscosity of the continuous medium.

With monodisperse systems, plots of $[g^{(1)} \Gamma]$ versus τ can be represented by a single exponential, and hence R can be calculated from D . With polydisperse systems, such as those encountered in the present microemulsion, the plot can not be represented by a single exponential. In this case, a proper method is used to deal with the data to attain a z -average diameter and a polydispersity index. This is automatically done by using the

computer software provided with the ALV-5000. Therefore, all results for droplet or particle size given in this paper show a z -average.

When the size of particles is $\leq \lambda/10$, here λ is the wavelength of incident light, the theory of Rayleigh Scattering can be used [17].

$$I = \frac{I_0 - 16\pi^4 R^6 (n^2 - 1)^2}{(n^2 + 2)^2 r^2 \lambda^4} \quad (5)$$

where I , I_0 are the intensity of the scattered light and incident light; R is the geometric radius of the particle; n is the refractive index of the sample solution; r is the distance from the light source to the visible point of the sample solution.

The Rayleigh ratio R_θ is defined as:

$$R_\theta = \frac{16\pi^4 R^6 (n^2 - 1)^2}{(n^2 + 2)^2 \lambda^4} \quad (6)$$

From the Eqs. (5) and (6), this expression reduces to:

$$\frac{I}{I_0} = \frac{R_\theta}{r^2} \quad (7)$$

In addition [18]:

$$R = \left(\frac{5}{3}\right)^2 R_g = 3.60 R_h \quad (8)$$

Here R_g , R_h are the particle radius of gyration and hydrodynamic.

The ratio of the numbers for the different size particles in the same system can be obtained from the Eq. (7) [19]:

$$\frac{N_1}{N_2} = \frac{W_1 R_{h2}^6}{W_2 R_{h1}^6} \quad (9)$$

Where N_1 , N_2 are numbers of the particle 1 and 2; w_1 , w_2 are the weighting function of the scattering intensities for the particle 1 and 2 in the sample system.

3. Results and discussion

3.1. Polymerization in aqueous microemulsion system

The first sample was selected from at point A in the microemulsion region of the Fig. 1 which is composed of cetylpyridine bromide/*t*-butanol/styrene/water. The content of the monomer for the sample is 0.14 and 0.03% for an initiator; the temperature is 40.0 °C. At the different time, the droplet size and its distribution of the droplets in the selected sample were measured and the results were shown in Fig. 3 and Table 1.

The second sample was selected from at point B in the microemulsion region of the Fig. 1 which is composed of cetylpyridine bromide/*t*-butanol/acrylic octadecyl ester and toluene (1:2.5, v/v)/water. The contents of the monomer for the second sample is 0.145%, while for initiator is 0.03%. The temperature is 40.0 °C. The droplet size and its distribution were measured as a function of time during the polymerization and the results were shown in Table 2. These curves of its size and size distribution at different time are similar to those

of sample 1. Due to limited space, these curves had been deleted.

From Fig. 3, it is seen that there are three kinds of particle existing in the system before polymerization: they are possibly micelles, swollen-micelles (microemulsions) and monomer droplets and their sizes are 0.1–1, 2–8 and 15–300 nm, respectively. When the polymerization starts soon after, the peaks of micelles and swollen-micelles disappeared and a new peak is produced. Which represents the new microlatex particles with diameter about 1 nm. The intensity of the peak increases when the polymerization continues. The peak of the monomer droplet also disappears when the polymerization is finished. Only the new polymerized microlatex particles exist in the system. From Table 1, it is also seen that the number of the swollen micelle is 1.5×10^6 times that of the monomer droplets before polymerization. When the polymerization time of 8.5 min, the number of the new microlatex particles is 4.3×10^{10} times that of the monomer droplets and the number of new microlatex particles changes bigger with the polymerization proceeding. In the end of the number of the monomer droplet disappears. From Fig. 3 ($t = 465$ min), the polydispersity of the microlatex particles is obtained such as 1.17 nm, 12.16%; 1.33 nm, 21.43%; 1.5 nm, 34.26%; 1.67 nm, 21.16% and 1.83 nm, 11.09%, respectively. The results of sample 2 is similar to those of sample 1, however, the difference is that monomer droplets do not disappear completely for there is toluene contained in sample 2.

When the soluble initiator is added to the system, the radicals are formed in the aqueous phase at the reaction temperature. There is also a small amount of monomers existing in the aqueous phase, so the polymerization can be initiated. The solubility of the polymer is very small in aqueous phase and the amount of monomers is also very small. So the polymer separates out in aqueous phase when the polymerization continues, the surfactant molecules not only can be adsorbed on the surface of the separation polymer; the monomers and radicals can also be adsorbed on the surface of the polymer and form new microlatex particles. This is the mechanism called homogeneous low polymer nucleation [20]. The radicals can also be

diffused inside the monomer droplet and swollen micelles with initiate the polymerization, however, it can be from the Table 1 that is the amount of the swollen micelles is very bigger than that of the monomer droplets ($1.5 \times 10^6:1$), so normally most radicals entered the former. When one radical enters one swollen micelle and initiates polymer-

ization and forms one polymer chain, and then may be some polymer chains composing one microlatex particle which is changed from the swollen micelle. This is the mechanism called the swollen micelle nucleation. The monomer used in this work is almost insoluble in water, so the polymerization can not be completed by the ho-

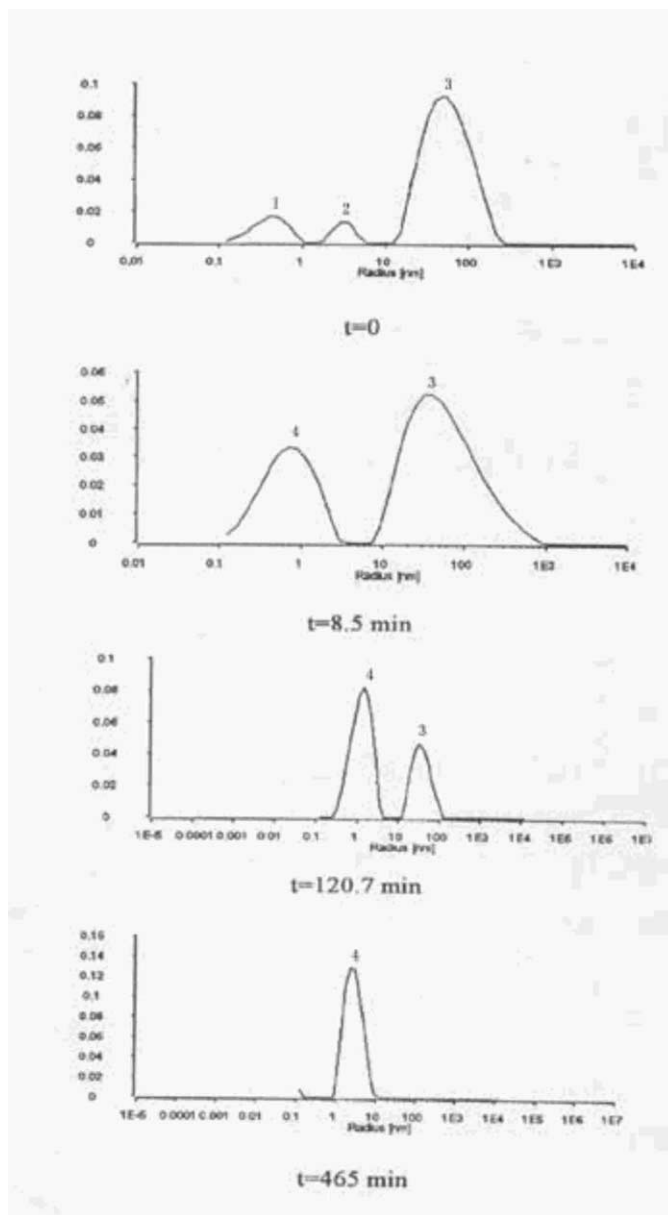


Fig. 3. The size and size distribution of styrene polymerization in aqueous microemulsion system at different time by DLS.

Table 1

The experimental results of the styrene polymerization in aqueous microemulsion system of CPDB/*t*-butanol/Styrene/H₂O at 40 °C

Number	Time (min)	Peak	Particles size (nm)	Weighting of particle	Ratio of the number for different particle
1	0	1	0.3957 ± 1.026	0.08326	$N_1/N_3 = 7.4$ E11
		2	3.085 ± 1.151	0.039	$N_2/N_3 = 1.5$ E6
		3	52.96 ± 3.077	0.6491	
2	8.5	4	0.8198 ± 0.8391	0.2813	$N_4/N_3 = 4.3$ E10
		3	53.68 ± 3.499	0.5106	
3	120.7	4	1.212 ± 0.565	0.5108	$N_4/N_3 = 1.6$ E10
		3	53.98 ± 3.49	0.2541	
4	143.0	4	1.722 ± 0.7175	0.6268	$N_4/N_3 = 2.4$ E10
		3	78.32 ± 4.317	0.227	
5	465.0	4	3.349 ± 1.080	0.8791	

Note: the initiator composed of (NH₄)₂S₂O₈ and NaHSO₃ (2:1, w/w); 1, 2, 3 and 4 refer to the peak number in each figure; N_1 , micelles; N_2 , swollen micelles; N_3 , monomer droplets; N_4 , microlatex particles amount; and its sub-digit refers to the peak number.

homogeneous low polymer mechanism. When the polymerization is in the process of 8.5 min, the swollen micelle disappears which implies part of the microlatex particles are formed via swollen-micelle nucleation mechanism. It can be concluded from Tables 1 and 2 that the final amount of microlatex particles are much bigger (first sample: 2.87×10^4 times; second sample: 2.01×10^3 times) than those of swollen-micelles and the amount of monomer droplets at the beginning of the polymerization. This means that microlatex particles polymerized in the aqueous microemulsion system must be partly formed in homogeneous low polymer nucleation. It can be concluded that the nucleate amounts of the microlatex particles in the microemulsion system are three partial contribution which included homogeneous low polymer, swollen micelles and monomer droplets in the aqueous microemulsion systems.

There is a dynamic equilibrium among surfactants, monomers and micelles, swollen-micelles, monomer droplets and microlatex particles in the system. When the polymerization starts, the dynamic equilibrium of monomers is shifted continuously from the monomer droplet to the aqueous phase and swollen micelles to microlatex particles or directly to the microlatex particles. At the same time, the dynamic equilibrium of surfactant is shifted from micelles to aqueous phase to microlatex particles. The size of the microlatex particles is

growing from 1 to 5 nm during the polymerization process and the area of the peak is also enlarged. More and more surfactant molecules are adsorbed onto the surface of the microlatex particles, so the peaks of micelles disappear after the polymerization, the monomer droplet also disappears when the polymerization is finished. There is toluene in the second system, so the peak of monomer droplet does not disappear completely until the polymerization is finished. From the Fig. 3, it is also seen that there are two aspects contributing to the increase of the microlatex particles. One is from homogeneous and swollen micelles nucleation mechanism, the other is from the collision of the small microlatex particles, so the coagulation of microlatex particles occurs while the size of microlatex particles increases.

3.2. Polymerization in a nonaqueous microemulsion system

The sample was selected from at point C the nonaqueous microemulsion region in Fig. 2 which is composed of cetyl bromide/styrene/formamide. The content of monomer of the sample is 0.25 and 0.05% for the initiator, the temperature is 25.4 °C. The sizes and the size distribution of polymerized particles were measured by the dynamic light scattering as a function of time. The results were shown in Table 3. These curves of its size and size distribution at different time are

similar to those of sample 1 and had also been deleted.

From Table 3, it is seen that there are three peaks of micelle (1) swollen micelle; (2) and monomer droplet; (3) before the polymerization. When the polymerization begins, the position of new microlatex particles' peak overlaps with that of monomer droplet, then these peaks of micelle and swollen micelle change small before 115 min then do not change until the end. In addition, the amount of microlatex particle in the end of reaction is much less than that of monomer droplet about 8.4×10^4 times before the polymerization. The result to obtain the nucleation location of the styrene microlatex particles in formamide microemulsion is inside monomer droplets. The phenomenon has been illustrated the polarity of formamide is weaker than that of water. So the ions of initiations gather onto the surface of the monomer droplet and enter it by diffusing to mitigate the polymerization. But the monomer droplet in aqueous is supplied monomer as 'store-house' in progress and does not polymerize as the

reaction starts. The size of microlatex particles (200–300 nm) from the aqueous system (1–15 nm).

3.3. The control of the size of microlatex particles by microemulsion polymerization

The wp line in Fig. 1 which the weight ratio of styrene, CPDB and *t*-butanol is 3:9:8 such as a, b, c, d and e points. These different O/W microemulsion samples are prepared with addition of different amount of water. The content of initiator is 0.05% and the temperature is 25.4 °C. By using the above samples, the effect on the size of microlatex particles by addition of different amount of water has been studied. The results are shown in Fig. 4.

From Fig. 4, it is seen that the concentration of styrene monomer has a good linear relationship from 4 to 15 nm for the size of microlatex particles. When the experiment was arranged in e, d, c, b, a sequence for Fig. 1, the concentration of styrene increased and the radius of particles also increased. This means that the size of microlatex particles can be controlled by changing the concen-

Table 2

The nucleation process of monomer-swollen micelles in the CPDB/*t*-butanol/acrylic octadecyl ester + styrene/H₂O at 25.4 °C

Time (min)	Experimental results			
	Peak number	Particle size (nm)	Weighting of particles	Ratio of the number for different particle
0	1	0.5897 ± 0.5574	0.03096	$N_1/N_3 = 2.8$ E10
	2	7.409 ± 2.006	0.01711	$N_2/N_3 = 3.9$ E3
	3	55.90 ± 2.371	0.8141	
12.5	1	0.3576 ± 1.208	0.0017	$N_1/N_3 = 2.6$ E10
	4	2.417 ± 0.9135	0.2836	$N_4/N_3 = 4.5$ E7
	3	51.58 ± 3.213	0.5905	
18.0	4	2.628 ± 0.9886	0.3427	$N_4/N_3 = 2.8$ E7
	3	49.35 ± 3.337	0.5335	
23.67	4	2.883 ± 1.037	0.3865	$N_4/N_3 = 1.9$ E7
	3	48.80 ± 3.437	0.4844	
48.0	4	3.477 ± 1.135	0.5033	$N_4/N_3 = 1.1$ E7
	3	49.13 ± 3.661	0.3591	
95.0	4	3.547 ± 1.153	0.5433	$N_4/N_3 = 1.9$ E7
	3	53.42 ± 3.787	0.3288	
130.0	4	3.54 ± 1.138	0.5515	$N_4/N_3 = 1.7$ E7
	3	51.71 ± 3.761	0.3223	
1878	4	4.413 ± 1.232	0.6032	$N_4/N_3 = 8.0$ E6
	3	52.70 ± 3.914	0.2175	

Note: the initiator composed of (NH₄)₂S₂O₈ and NaHSO₃ (2:1, w/w); 1, 2, 3 and 4 refer to the peak number in each figure; N_1 , micelles; N_2 , swollen micelles; N_3 , monomer droplets; N_4 , microlatex particles amount; and its sub-digit refers to the peak number.

Table 3

The experimental results of the styrene polymerization in nonaqueous microemulsion system of CPDB/styrene/formamide at 25.4 °C

Number	Time (min)	Peak	Particle size (nm)	Weighting of particles	Ratio of N value
1	0	1	0.2372 ± 1.501	0.0002	
		2	0.8023 ± 1.248	0.04125	$N_1/N_3 = 3.920 \text{ E15}$
		3	229.1 ± 5.456	0.1404	$N_2/N_3 = 1.593 \text{ E14}$
2	18.0	1	0.2372 ± 1.501	0.019	
		2	4.2301 ± 1.493	0.03	$N_1/N_4 = 3.894 \text{ E15}$
		4	169.6 ± 4.073	0.6520	$N_2/N_4 = 1.912 \text{ E8}$
3	32.0	1	0.9321 ± 0.0702	0.0197	
		2	5.879 ± 1.7	0.024	$N_1/N_4 = 3.610 \text{ E12}$
		4	146.7 ± 2.0	0.083	$N_2/N_4 = 6.981 \text{ E7}$
4	115.0	1	1.092 ± 1.129	0.002078	
		2	11.69 ± 2.462	0.007113	$N_1/N_4 = 4.521 \text{ E10}$
		4	177.9 ± 2.711	0.8592	$N_2/N_4 = 1.028 \text{ E5}$
5	130.0	1	0.9507 ± 0.08748	0.003	
		2	9.317 ± 2.235	0.00616	$N_1/N_4 = 1.658 \text{ E11}$
		4	181.0 ± 2.704	0.8617	$N_2/N_4 = 3.843 \text{ E5}$
6	182.3	1	1.163 ± 2.155	0.0088	
		2	5.304 ± 1.676	0.0058	$N_1/N_4 = 2.086 \text{ E11}$
		4	192.3 ± 2.746	0.8621	$N_2/N_4 = 1.528 \text{ E7}$
7	343.7	1	1.121 ± 2.190	0.0004	
		2	4.066 ± 1.417	0.00961	$N_1/N_4 = 2.352 \text{ E10}$
		4	213.6 ± 3.227	0.8139	$N_2/N_4 = 2.482 \text{ E8}$
8	352.5	1	0.076 ± 2.229	0.00053	
		2	6.603 ± 1.895	0.009	$N_1/N_4 = 5.681 \text{ E10}$
		4	225.7 ± 3.189	0.8237	$N_2/N_4 = 1.743 \text{ E7}$

Note: the initiator composed of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and NaHSO_3 (2:1, w/w); 1, 2, 3 and 4 refer to the peak number in each figure; N_1 , micelles; N_2 , swollen micelles; N_3 , monomer droplets; N_4 , microlatex particles amount; and its sub-digit refers to the peak number.

tration of the monomer by using its pseudo-tertiary phase diagram.

For the acrylic octadecyl ester, the same procedure was followed to check the size changes when the different amount of water is added because the weight ratio amount acrylic octadecyl ester, CPDB and *t*-butanol is 1:10.5:9.3. The content of initiator is 0.05% and the temperature is 25.4 °C. The results are shown in Fig. 5.

From Fig. 5, it can be seen that the amount of acrylic octadecyl ester monomer has a good linear relationship with the radius of microlatex particles in the concentration range of 0.313–0.152%. The radius of the microlatex particles can be controlled in this concentration range, while in the concentration range of 0.042–0.152%, the size of microlatex particles are almost the same.

3.4. How many single-chain polystyrene in a microlatex particles

The molecule weight of the microlatex particles were measured by the static light scattering when the content of styrene monomer was 0.141%. The single-chain polystyrene was got in the same condition. It was precipitated and purified from microemulsion by adding benzyl, then was dried and made up toluene solution. Its molecule weight was also measured by the static light scattering. For microlatex particles ($\text{dn}/\text{dc} = 0.229 \text{ g ml}^{-1}$, n , refrangibility; c , concentration) $M_w = 2.7 \times 10^5 \text{ g mol}^{-1}$, for single-chained polystyrene ($\text{dn}/\text{dc} = 0.110 \text{ g ml}^{-1}$) $M_w = 1.6 \times 10^5 \text{ g mol}^{-1}$, so there are two single-chained poly styrene in one microlatex particle.

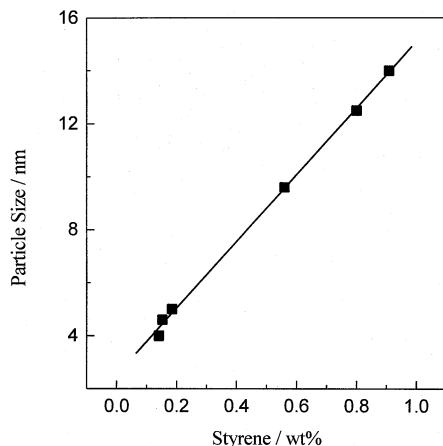


Fig. 4. The size change of the microlatex particles as a function of the concentration of styrene monomer.

4. Conclusion

With the polymerization of styrene and acrylic octadecyl ester in aqueous microemulsions, the nucleation occurs mostly in the aqueous phase via homogeneous nucleation mechanism, while a part of microlatex particles of styrene or acrylic octadecyl ester are formed by swollen micelle and monomer droplet nucleation mechanism.

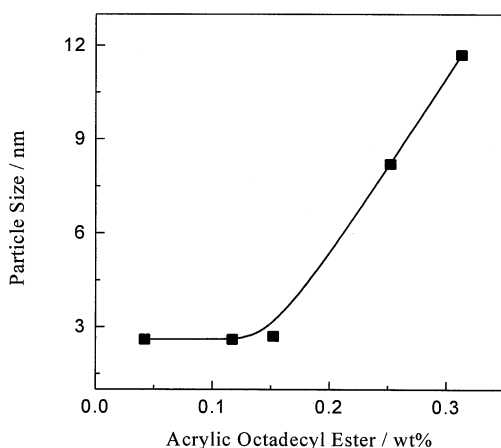


Fig. 5. The size change of the microlatex particles as a function of the concentration of acrylic octadecyl ester.

With the polymerization of styrene in non-aqueous microemulsion system, the nucleation occurs inside monomer droplets.

The sizes of the microlatex particles can be controlled by changing the amount of monomer, when fixing the weight ratio among monomer, surfactant and cosurfactant. For styrene and acrylic octadecyl ester polymerization in O/W microemulsion, and for styrene polymerization is O/W nonaqueous microemulsion, the microlatex particles with diameter about 3.0 ± 1 , 4.5 ± 1 , 226 ± 3 nm, respectively.

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