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Stabilizing effect of the cationic surfactant (CPB) in emulsion polymerization

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SUMMARY

Stable latices were prepared from the emulsion polymerization of styrene, using 2,2′-azobis(2-amidinopropane) dihydrochloride as the initiator and cetylpyridinium bromide (CPB), or a mixture of CPB and a nonionic surfactant as the emulsifier. The latices prepared with CPB exhibits extraordinarily low surface coverage values. The outstanding stabilizing effect of CPB outweighs the mixed-surfactant effect. However, the initiation was promoted by using the mixed surfactants. Increasing the initiator content, the initiation efficiency decreases and the kinetic moves toward the ideal case. The hydrodynamic layer thickness of latices have also been investigated.

INTRODUCTION

Latex protected by the cationic surfactant can find a potential use in the construction applications, where the coagulation of latex in an alkaline situation favors the formation of coating layer. However, using the cationic surfactant in emulsion polymerization (1-6) can be relatively rare compared to using the anionic surfactant. Different types of initiators are required in facilitating the emulsion polymerization owing to the opposite charges the surfactants bearing. Sometimes the polymerization conditions were pretty different that photoinitiators (1, 3) (or redox initiator (2)) rather than the commonly used initiators were used, and extra components (such as CCl_4) might be present to accelerate the polymerization (3).

Among the articles, one (6) has investigated the dependence of the number of polymer particles and of the rate of polymerization on emulsifier concentration for the emulsion polymerization of acrylonitrile initiated by γ-radiation. On the other articles (4, 5), higher concentrations of cationic surfactants such as cetyltrimethyl ammonium chloride (CTMA) and dodecyltrimethyl ammonium chloride (DTMA) have been used in microemulsion polymerization to prepare latex particles with a well-defined size and surface structure.

In this study, stable polystyrene latex was prepared by using a cationic surfactant, cetylpyridinium bromide (CPB), or a mixture of CPB and a nonionic surfactant as the emulsifier and 2, 2′- azobis(2-amidinopropane) dihydrochloride (AAP) as the initiator in the emulsion polymerization.

It is interesting to know that the latex prepared with the cationic surfactant exhibits a surprisingly low surface coverage, compared with the latex prepared with an anionic one (i.e., sodium dodecyl sulfate (SDS)). Furthermore, the synergistic stabilizing effect was not found for using a mixture of ionic and nonionic surfactants (i.e., CPB and Pannox (polyoxyethylene nonylphenyl ether)) and overshadowed by the distinguishing stabilizing effect of CPB.

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The synergistic stabilizing effect is usually found for the latex using a mixture of ionic and nonionic surfactants and the resulting latex has a smaller particle size (7-9). But this was not applicable for the system of CPB and Pannox.

An attempt was also made in this study to investigate the steady effective initiation in emulsion polymerization for runs differing in emulsifier compositions or initiator amount. With the increase of initiator content, the effective initiation decreases and levels off to approach the ideal free-radical polymerization kinetics (i.e., 1/2 order dependence of polymerization rate on initiator content). On the other hand, with the increase of surfactant content, the steady effective initiation tends to increase.

All of these results may ignite some more sparkles to future explorations.

EXPERIMENTAL

Materials

The styrene (SM) monomer was purified by prewashing and vacuum distillation. The cationic surfactant, cetylpyridinium bromide ($C_{21}H_{38}BrN$) (CPB) (critical micelle concentration (cmc) of CPB in water is 5.75×10^{-4} mol/L), and the initiator, 2,2'-azobis(2-amidinopropane) dihydrochloride (AAP), are both of reagent grade and used without further purification. Nonionic surfactant, Pannox (polyoxyethylene nonylphenyl ether, C_9H_{19}-C_6H_4-O-$(CH_2CH_2O)_n$-H) (PA) was treated by heating at 70°C overnight under vacuum to decompose thermally unstable peroxides.

Polymerization and Parameter determinations

The recipe series are shown in Table 1. Polymerizations were conducted in 250 ml fourneck round-bottom flasks at 50°C in a thermostatted water bath. Samples were withdrawn several times during the polymerization. The conversion of monomer to polymer was determined gravimetrically.

The particle size was measured with a Photal 3000/3100 dynamic light scattering spectrophotometer (DLS). The various average diameter data, such as number-(D_n), weight-(D_w) and volume-average (D_v) diameters, and the particle number per cm^3 of aqueous phase (N) are defined as usual (7). Note that D_{vi} and D_{vf} are the D_v at conversions of about 50% and 95%, respectively

The measurements of kinetics data such as the radical number per particle ($\bar{n}$) followed the same procedures as mentioned elsewhere (10). The formula of $\bar{n}$ is shown as

$$\bar{n} = R_p N_A / k_p N [M] \qquad (1)$$

where R_p is the rate of polymerization, k_p the propagation rate coefficient, N_A the Avogadro's number, and [M] the monomer concentration in particle. Important parameters are assigned as : [M]=5.55 (mol/L), (and $\phi_m = 0.60$), $k_p = 123$ (L/mol-s), $d_m = 0.91$ (g/cm^3) and $d_p = 1.053$ (g/cm^3).

The steady effective initiation (f_i) is defined as the steady-state instant active radical number per initiator molecule fed and can be calculated as follows:

$$f_i = (\bar{n}\, N/N_A)(W/d_w)/([I]/M_I) \qquad (2)$$

where W, d_w, [I] and M_I are the weight and density of water, the initiator weight (g), and the molecular weight of initiator (271.19 for AAP), respectively.

The hydrodynamic layer thickness (δ) is calculated from the specific viscosity (η_s) (11-13).

$$\eta_s = 2.5\,\Phi\,(1+\delta/r)^3 \qquad (3)$$

where Φ is the volume fraction of polymer in the latex and r is the radius of the particle. The η_s was determined at 30.0 ± 0.1°C, using the Ostwald-Fenske viscometer, with a solid content fraction of 0.25.

The method of soap titration (14) was utilized to determine the molecular area (A_m), which is defined as the area occupied by the surfactant molecule on polymer particle surface at saturation adsorption. The A_m was calculated by using the equation as

$$A_m = 6 / ((q/p)\, D_v\, N_A\, d_p) \qquad (4)$$

where q is the total moles of surfactant required to cover p grams of polymer particles.

The total particle surface area per recipe (TS) and the surface coverage (SC) were calculated as follows:

$$TS = 6\, m\, (\%\ \text{conv.}) / (D_v\, d_p \cdot 100) \qquad (5)$$

$$SC = A_m\, (E/M_E)\, N_A / TS \qquad (6)$$

where m is the weight of monomer per recipe, d_p is the density of polymer, and E and M_E are the amount (g) and the molecular weight of surfactant used in each recipe.

RESULTS AND DISCUSSION

Special stabilizing effect of CPB

Remarkable stabilizing effect was found for cationic surfactant, CPB, with extremely low SC values (Fig. 1). The SC value represents that the proportion of particle surface area actually occupied by surfactant molecule. That is, a low SC value means that fewer surfactants are required in occupying a certain surface area. The SC values of CPB system are much smaller than those of sodium dodecyl sulfate (SDS), an anionic surfactant, usually used in emulsion polymerization (EP), as shown in Fig. 1. Despite the CPB has the lower values in SC than the SDS, the differences both in the D_v data (Table 2 and Fig. 2) and A_m values are not large. The A_m values of SDS and CPB are 47 and 55 (Å^2), respectively. The latter was obtained in this study, while the former was reported elsewhere (15, 16).

It shows that the SC values do not decrease with increasing the initiator (AAP) content (i.e., [AAP]), as shown in Table 3, and this proves that the effect of [AAP] can not be the dominating effect to the small SC value. Note that the SC value is counted based on the surfactant content, but the basis does not include initiator content.

The outstanding stabilizing effect of the CPB outweighs the mixed-surfactant effect.It has been reported (7-9,16) that using a mixture of ionic and nonionic surfactants has a synergistic stabilizing effect, at least found for the mixtures of SDS and nonionic surfactants (e.g., Emulphogen BC-840 (7-9), or Pannox series (16)). This has been illustrated by the fact that the particle size data for the mixed-surfactant system with the synergistic stabilizing effect

Table 1
Polymerization recipe series (unit, g)

	A	B	C
St	50	50	50
H_2O	150	150	150
AAP	Variable	0.50	0.50
CPB	0.45	Variable	Variable
PA	--	--	3.0

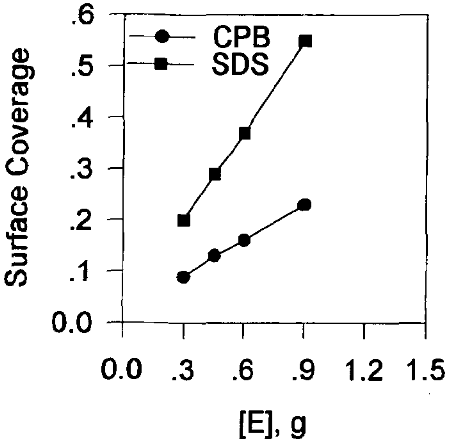

Fig. 1. Surface coverage data for CPB and SDS

Table 2
Values of Dvf and SC for the system of SDS ($K_2S_2O_8$/SM/H_2O = 0.19/25.0/75.0)

SDS(g)	Dvf (Å)	SC
0.30	906	0.20
0.45	859	0.29
0.60	835	0.37
0.90	823	0.55

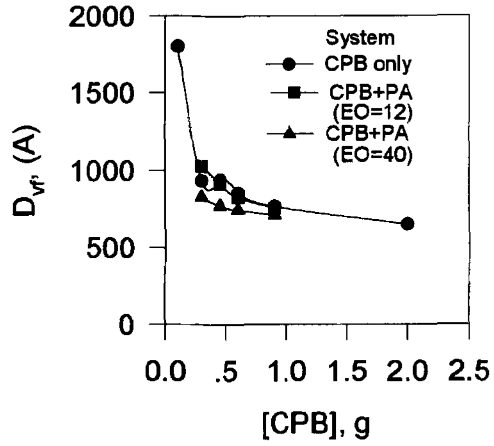

Fig. 2. Volume-average particle size for each recipe

Table 3
Initiator content effect on surface coverage (Recipe series A) (Data at 95.0±3.0 % conv.)

AAP (g)	D_{vf} (Å)	TSx 10^{-23} (Å^2)	A_m (Å^2)	SC	δ nm
0.1	985	2.79	51	0.13	47.4
0.3	951	2.87	52	0.13	26.5
0.5	940	2.95	54	0.13	21.3
0.7	881	3.11	57	0.13	18.1
1.0	877	3.13	57	0.13	15.9

are much smaller than those of single-surfactant system and the TS values of the mixture (TS_m) are rather close to the summation for those of component ones (TS_i and TS_n). However, in this study, we found that the additional use of nonionic surfactant (Pannox) does not impart the synergistic stabilizing effect to the mixed-surfactant system. In other words, the particle size data are not much smaller, as shown in Fig. 2, and the TS_m values are even much smaller than the summations of TS_c and TS_p, as shown in Table 4. As a consequence, the higher SC values were found for the mixed-surfactant systems, as shown in Fig. 3. Comparing the two mixed-surfactant systems, we can also found that the mixture containing PA of EO number (no.) of 40 has the smaller SC values than the mixture containing PA of EO no. of 19. This is owing to that the former has the better stabilizing efficiency than the latter so that the former can form the larger total particle surface area by forming the smaller size particles.

The higher surface coverage means that the more surfactant molecules are packed in a certain surface area. This naturally forces the surfactant chains to push outwards, and, therefore, leads to the larger hydrodynamic layer thickness (δ), as shown in Tables 4 and 5.

Increasing the CPB content ([CPB]), the latex particle size decreases rapidly then levels off, as shown in Table 5. The variations of other related data, such as N, Rp and $\bar{n}$ follow the similar pattern as usually shown in ordinary emulsion polymerization, i.e., the N and Rp increase and $\bar{n}$ decreases with increasing the surfactant content.

The steady effective initiation (f_i) can reflect the initiation efficiency of an initiator in the reaction. The formula of f_i is shown in Eq. 2.

The f_i value increases with both CPB and total surfactant contents, as well as the EO no. of PA, as shown in Fig. 4. Although the use of extra amount of either CPB or PA does not reduce the D_{vf} much (Fig. 2), the f_i increases quite apparently (Fig. 4). This reveals that the increase of surfactant content should have a favorable effect on the initiation. This may be due to that the initiated radicals can form the polymer chains more effectively and eliminate possible early termination by either (i) forming the more micelles, or (ii) giving the better stabilization of particles during the emulsion polymerization. The former is easier to be accepted since the initiating species get more chances to grow in the micelles. Meanwhile, the latter can not be neglected since if the particles remain stable, the chance for early recombination between initiating species may be reduced.

Extra stabilizing effect of the Initiator

Extra stabilizing effect of using higher amount of initiator ([AAP]) was found that the particle size decreases, and both the TS and the Am increase (Table 3). The effect is quite similar to the effect of increasing the surfactant content, but not so evident as that of the latter effect, otherwise the SC values (Table 3) may decrease considerably with the [AAP].

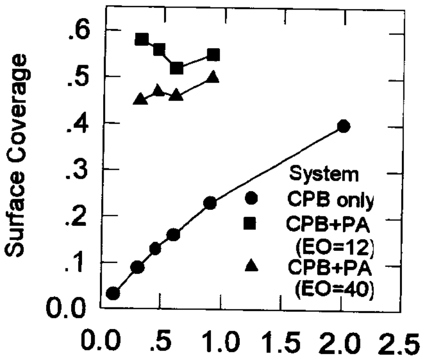

Fig. 3. Surface coverage versus CPB content

Table 4
Mixed surfactant effect (Recipe series C)
(Data at 95.0±3.0 % conv.)

EO No. PA	CPB (g)	Dvf (Å)	TSm ($Å^2$)	TSc ($Å^2$)	TSp ($Å^2$)	δ/r
12	0.30	1030	2.64	2.81	-	0.45
12	0.45	916	3.00	3.04	-	0.51
12	0.60	826	3.34	3.23	-	0.52
12	0.90	757	3.60	3.54	-	0.61
19	0.45	785	3.50	3.04	-	0.51
40	0.30	827	3.20	2.81	2.09	0.55
40	0.45	772	3.43	3.04	2.09	0.57
40	0.60	743	3.60	3.23	2.09	0.59
40	0.90	710	3.73	3.54	2.09	0.61
50	0.45	732	3.66	3.04	2.34	0.60

δ/r at a solid fraction of 0.223 ± 0.003

Table 5

Cationic surfactant content effect (Recipe series B)

CPB (g)	Dvi (Å)	N x 10^{-14} ml^{-1}	Rp× 10^5 mol ml^{-1} min^{-1}	$\bar{n}$	δ/r
0.10	1090	2.81	2.32	1.22	0.38
0.30	847	5.28	2.63	0.74	0.49
0.45	768	7.49	2.67	0.38	0.48
0.60	470	31.0	2.91	0.14	0.55
0.90	462	31.6	3.91	0.18	0.53
2.0	338	81.6	7.42	0.13	0.58

δ/r has a solid fration of 0.23 and at 95.0±3.0 % conv.

Dvi, N and $\bar{n}$ are at 55.0 ±4.0 % conv.

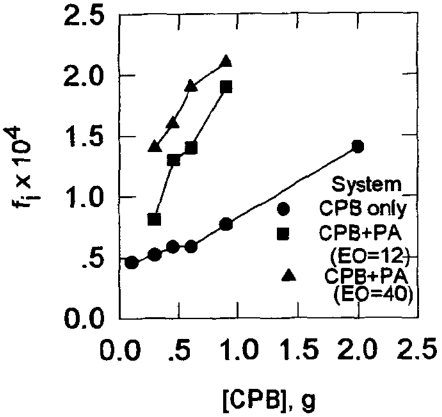

Fig. 4. Values of steady effective initiation versus CPB content

With increasing [AAP](Table 6), the initiation efficiency decreases and the steady effective initiation (f_i) decreases. Localized crowded situations for radicals arising from the increase in [AAP] leads to the more early mutual termination between radicals.This may be the cause for the decrease in f_i. However, at the higher [AAP], the situation may become more closer to that of the ideal free-radical polymerization kinetics (i.e., $Rp \sim [I]^{0.5}$). This can be illustrated by the fact that the ratio of (fkd/kt or $[M \cdot]^2/([I]/M_I)/(W/d_w)$) (i.e., $[(Rp^2/[I])(M_I(d_w/W)/kp^2[M]^2]$) decreases and levels off to approach a constant value, as shown in Fig. 5.

The generation of more particles is obvious. It can be expected that the total number of radicals increases with increasing the total amount of initiator fed since AAP is water-soluble. The fact that the Rp increases but the $\bar{n}$ decreases (Table 5) with increasing the [AAP] may be attributed to the increase in the particle number (N), as can be deduced from Eq.1. This is true that the N increases with increasing [AAP], as shown in Fig. 6. This is consistent with the argument (17,18) that more polymerization may occur if the more radicals are generated in the aqueous phase during the EP. The polymeric chains may exhibit some surface activity due to the charged chain ends they carried, so that this favors the formation of more latex particles. Furthermore, the charged end groups of polymer chains will stay on the particle surface and contribute a stabilizing effect to latex particles (19,20).

As shown in Table 3, the hydrodynamic layer thickness (δ) of CPB on Polystyrene (PS) particles decreases with the [AAP]. This may be elucidated as that more charged end-groups of PS chains on particle surface leads to the depletion of surfactant molecules, and, therefore, the smaller δ. In some situation, the δ indeed decreases with increasing surfactant content in the EP recipes (13,16).

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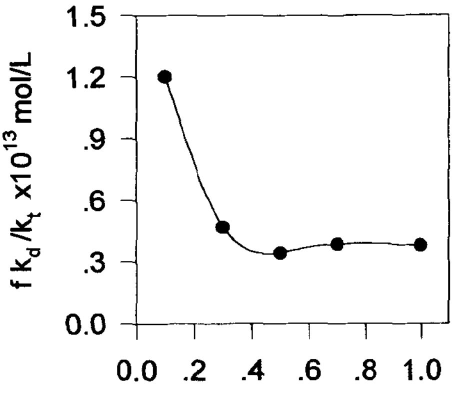

Fig. 5. Values of (f k_d/k_t) versus AAP amount

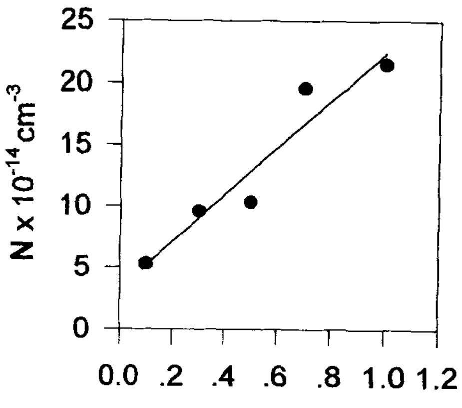

Fig. 6. Particle number versus AAP amount

Table 6

Initiator content effect on $\bar{n}$ and f_i (Recipe series A)

AAP (g)	% Conv	Dvi (Å)	Rp × 10^5 (mol ml^{-1} min^{-1})	$\bar{n}$	f_i x 10^4
0.1	46.3	810	2.19	0.62	2.2
0.3	47.0	667	2.40	0.37	0.80
0.5	44.8	641	2.67	0.38	0.52
0.7	42.3	507	3.31	0.25	0.47
1.0	44.1	499	3.86	0.27	0.39

REFERENCES

1. Patsiga RA, Lerdthusnee W, Marawi I (1983) Org Coat Appl Polym Sci Proc. 48: 790
2. Smirnov AM, Lukhovitskii VI, Karpov VL (1972) Vysokomol Soedin, Ser B 14(1): 6
3. Shimada S, Nakagawa K, Tabuchi K (1993) Polym. J 25(10): 1033
4. Antonietti M, Bremser W, Müschenborn D, Rosenauer C, Schupp B, Schmidt M (1991) Macromol 24: 6636
5. Antonietti M, Lohman S, Niel CV (1992) Macromol 25: 1139
6. Polikarpov VV, Lukhovitskii VI, Pozdeyeva RM, Karpov VL (1974) Vysokomol Soedin A16 (10) : 2207
7. Chu H-H, Piirma I (1989) Polym Bull 21: 301
8. Wang H-H, Chu H-H (1990) Polym Bull 24: 207

9. Chu H-H, Lin C-C (1992) Polym Bull 28: 419
10. Chu H-H, Gau J-H (1995) Macromol Chem Phys 196: 2251
11. Saunders FL (1961) J Colloid Sci 16: 13
12. Garvey MJ, Tadros ThF, Vincent B (1976) J. Colloid Interface Sci 55 (2): 440
13. Chu H-H, Hsu X-C (1994) J Appl Polym Sci 51: 1653
14. Maron SH, Elder ME, Ulevitch IN (1954) J Colloid Interface Sci 9: 89
15. Piirma I, Chen SR (1980) J Colloid Interface Sci 74: 90
16. Chu H-H, Cheng H-C J Macromol Sci-Pure, submitted
17. Alduncin JA, Forcada J, Barandiaran MJ (1991) J Polym Sci: Part A, Polym Chem 29:1265
18. Nomura M, Ikoma J, Fujita K (1993) J Polym Sci: Part A, Polym Chem 31: 2103
19. Ali SI, Steach JC, Zollars RL (1987) Colloid Surf 26: 1
20. Hawkett BS, Gilbert RG, Napper DH (1980) Royal Soc Chem J: Faraday Trans I 76: 1323