Effect of water-soluble cosurfactants on microemulsion polymerization of styrene

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The polymerization of styrene has been studied in microemulsions which were stabilized by cetyltrimethylammonium bromide and different water-soluble cosurfactants such as 2-ethoxyethanol, 2-butoxyethanol, 2-(2-ethoxyethoxy)ethanol and 2-(2-butoxyethoxy)ethanol. The activation energy of polymerization and molecular weight of polystyrene were affected by the molar ratio of cosurfactants to surfactant in the dispersed phase. No particular trend was observed for the effect of the cosurfactant on the particle sizes of latexes. A plausible mechanism of radical chain termination for the polymerization is discussed in relation to the interfacial fluidity of a microemulsion particle.

(Keywords: polymerization; styrene; microemulsion; cosurfactants)

INTRODUCTION

A microemulsion is viewed to consist of microdroplets of either water or oil pools dispersed in an oil-continuous phase (w/o) or a water-continuous phase (o/w), respectively. The intermediate structure of microemulsions is likely to be a bicontinuous one, in which both water and oil span the sample[1]. They are all stabilized by interfacial layers of surfactant with or without a cosurfactant. Hydrophilic surfactants may be anionic, cationic, non-ionic or a mixture of these, while a hydrophobic cosurfactant is usually an alcohol of medium chain length. Optically isotropic microemulsions are generally formed spontaneously when appropriate amounts of components are brought into contact. Though the overwhelming majority of microemulsions are thermodynamically stable[2], some of them may be only kinetically stable[3].

Stoffer and Bone[4,5] published their papers on microemulsion polymerizations of methyl methacrylate (MMA) and methyl acrylate in 1980. They encountered phase separation during the polymerizations. On the other hand, Leong and Candau[6] and Candau *et al.*[7] successfully polymerized acrylamide in stable water-in-oil microemulsions. Atik and Thomas[8] also reported the polymerization of styrene in an o/w microemulsion, producing spherical, monodisperse latex particles. Several other researchers have also studied polymerizations of styrene and MMA in various o/w microemulsions with[9–16] and without[17–19] a cosurfactant. Very small polymer particles of the order of 10–30 nm in diameter have been obtained from these stable microemulsion polymerizations.

The most commonly used cosurfactant in the above cited systems was pentanol; other cosurfactants used were hexanol[8] and butyl carbitol[16]. It has been a concern that the alcohol cosurfactant may act as a destabilizer for latex particles by desorbing surfactant from the surfaces of polymer–monomer particles, in addition to its function as a potential chain-transfer agent[10]. It is also known that the high solubility of polystyrene in the butyl cellosolve used as a cosurfactant gives rise to greater stability for the polymerization of styrene in surfactant solutions[20].

Due to differences in the equilibrium partitioning of an alcohol between different phases, the stability of a polymerized microemulsion may vary according to the alcohol used. The effects of four water-soluble cosurfactants on styrene polymerization in microemulsions stabilized by cetyltrimethylammonium bromide (CTAB) are discussed in this paper.

EXPERIMENTAL

Materials

2-Ethoxyethanol (cellosolve, Ce), 2-butoxyethanol (butyl cellosolve, BCe), 2-(2-ethoxyethoxy)ethanol (carbitol, Ca) and 2-(2-butoxyethoxy)ethanol (butyl carbitol, BCa) from TCI (Japan) were vacuum distilled at 10 torr (25°C), 10 torr (48–50°C), 1.0 torr (39–40°C) and 0.1 torr (60°C), respectively. Styrene from Fluka was purified by vacuum distillation under a nitrogen atmosphere at 5–6 torr (25–26°C). Cetyltrimethylammonium bromide (CTAB) from TCI (Japan) was recrystallized from an ethanol–acetone mixture (1:3 by volume). Potassium persulfate (KPS) from Fluka and 2,2′-azobisisobutyronitrile (AIBN) from TCI were recrystallized from distilled water and methanol, respectively. Water was distilled twice.

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Polymerization

Polymerization of styrene in an o/w microemulsion was carried out in a glass dilatometer. After degassing at 10 torr with two freeze–thaw cycles, the microemulsion was introduced directly into a dilatometer through a special joint attachment. The change of liquid level in the capillary of the dilatometer was monitored as a function of time by a cathetoscope. The fractional conversion of styrene was determined from the volume change which was calculated from the height of the capillary.

After polymerization, the polystyrene was precipitated in a large quantity of ethanol. The polymer was washed repeatedly with ethanol and water in order to remove CTAB. The conductivity of the final washing was measured in order to determine the purity of the polystyrene obtained.

Molecular weight determination by gel permeation chromatography

The molecular weights of the polystyrenes were determined on a Varian 5500 liquid chromatography system equipped with an RI-3 detector. The column used was Varian MicroPak TSK GMH6 gel and the eluent was tetrahydrofuran (THF). Polystyrene standards (Polyscience; 0.2 mg ml^{-1} in THF) were used for the calibration. The flow rate was maintained at 0.8 ml min^{-1}.

Characterization of microlatexes

Microemulsion latexes were examined on a JEOL JEM-100CX electron microscope. One drop of the neat microemulsion latex was added to 2 ml of 0.2% phosphotungstic acid (PTA) and the mixture was well mixed with a Vortex blender. A drop of this mixture was then put on a copper grid coated with a thin layer of Formvar®.

RESULTS AND DISCUSSION

Phase compositions of o/w microemulsions

Water-soluble butyl carbitol ($C_4H_9OCH_2CH_2OCH_2CH_2OH$, BCa) has been successfully used as a cosurfactant in CTAB microemulsions for the polymerization of styrene[16]. The present study included three other water-soluble cosurfactants, i.e. carbitol ($C_2H_5OCH_2CH_2OCH_2CH_2OH$, Ca), butyl cellosolve ($C_4H_9OCH_2CH_2OH$, BCe) and cellosolve ($C_2H_5OCH_2CH_2OH$, Ce). The basic compositions of the microemulsions studied were 85.1 wt% H_2O, 7.45 wt% CTAB and 7.45 wt% of the various cosurfactants. It was found that the maximum solubilizations of styrene in these microemulsions decreased from 9.5 to 5.5 wt% as the cosurfactant was varied through the sequence BCa, Ca, BCe, Ce. These maximum solubilizations of styrene are relatively large compared to the mere 0.2 wt% styrene which could be dissolved in a similar microemulsion containing pentanol as a conventional cosurfactant. All the microemulsions became turbid when the styrene concentration exceeded their respective maximum solubilizations.

The distributions of styrene and cosurfactants in the continuous (aqueous) phases and the dispersed phases of the microemulsions were analysed by dialysis[21]. A dispersed phase of a microemulsion is considered to consist of an oil core and a membrane phase (interface).

Table 1 Distributions of styrene (St) and cosurfactant (CoS) in the continuous phases (ϕ_c) and dispersed phases (ϕ_d) of o/w microemulsions[a]

CoS	Maximum solubilization of St (wt%)	Distribution of St (wt%)		Distribution of CoS (wt%)		Molar ratio CoS/CTAB
		ϕ_c	ϕ_d	ϕ_c	ϕ_d	ϕ_d
BCa	9.5	4.80	95.2	42.0	58.0	1.08
Ca	6.5	2.10	97.9	43.6	56.4	1.54
BCe	5.8	2.30	97.0	43.6	56.4	1.75
Ce	5.5	1.40	98.6	35.4	64.6	2.63

[a] Basic compositions: 85.1% H_2O, 7.45% CTAB and 7.45% CoS

As shown in *Table 1*, over 95% added styrene was distributed in the dispersed phase of each system. The remaining styrene distributed in the continuous phase varied from 1.4 to 4.8%. The microemulsion containing BCa had the highest styrene solubilization (4.8%) in the continuous phase, while the Ce microemulsion system had the lowest solubilization (1.4%). Distributions of the cosurfactants (56–65%) in the dispersed phases were higher than those in the continuous phases (35–44%). The relatively high percentages of the cosurfactants distributed in the continuous phases were due to their good solubilities in water. As for the less water-soluble pentanol, it has been reported[22] that more than 60% pentanol partitions into the interface of a styrene microemulsion while only about 20% is in the continuous phase. The remaining 10 to 15% pentanol is mixed with styrene in the core phase. If we also assume that about 10 to 15% of each type of the carbitols or the cellosolves will dissolve in the styrene core phase, we can estimate that about 40 to 50% of each cosurfactant would be present at the interface of each microemulsion.

The existence of a cosurfactant in an interface is important in determining the stability of a microemulsion. Increasing the amount of alcohol partitioning at an interface will increase the fluidity and natural curvature of the interface[23,24]. Since we are unable to obtain the exact compositions of the cosurfactants at the interfaces of the microemulsions by the dialysis method, we present our results in the form of the molar ratio of cosurfactant (CoS) to CTAB based on the total dispersed phase (ϕ_d) of each system, rather than the interface. As can be seen from the last column of *Table 1*, the molar ratio of CoS/CTAB in ϕ_d increased from about 1 to about 2.6 in the sequence BCa, Ca, BCe, Ce. This implies that the fluidity of the interface of the microemulsion is increasing, resulting in a lower maximum styrene solubilization, as we move from BCa to Ce. The trend on the maximum styrene solubilization is similar to that of the maximum water solubilization, which decreases with increasing interfacial fluidity of the w/o microemulsion[25,26].

Kinetics of polymerization

The compositions used for the kinetic study are listed in *Table 1*, in which the concentration of styrene was varied from 2 to 6%. Potassium persulfate (KPS) was at 0.6 mM (based on water content) and most of the polymerizations were carried out at 50°C. The rate of polymerization did not seem to vary significantly with respect to the different cosurfactants. Hence, the rates of polymerization for the system using Ca only are shown in *Figure 1*. The rate increased with increasing concentration of styrene and polymer conversion. It reached the maximum at about 20% conversion and then decreased on further polymerization. Only two polymerization rate intervals were observed for all systems, i.e. interval I and interval II (*Figure 1*). There was no apparent plateau region as would be expected from a conventional emulsion polymerization. In interval I (nucleation period), the increasing rate of polymerization was due to the increasing number of polymerization loci formed. Interval I ended after the rate had reached the maximum. The rate then decreased in interval II (particle growth) because the monomer concentration in the growing particles was diminishing.

The concentration dependences of styrene ($a \cong 1$) and KPS ($b \cong 0.4$) on the rate of polymerization were similar among the systems, as shown in *Table 2*. However, the activation energies E_a of the polymerizations, obtained from Arrhenius plots, were significantly different for these systems. E_a decreased steadily from 92.1 to 54.1 kJ mol^{-1} as the cosurfactant in the microemulsion was changed from BCa to Ce. This is attributed to the increasing fluidity of the interface, as discussed earlier. It is highly probable that a fraction of the dissolved styrene in the continuous phase would first be initiated by KPS radicals to form oligomeric anion radicals of higher hydrophobicities. These radicals might then diffuse into microemulsion droplets to continue the polymerization. The direct entry of KPS free radicals into microemulsion droplets is also possible. In any case, the more fluid the interface, the easier the radicals can diffuse into the microemulsion droplets. Consequently, E_a decreased steadily as the ratio of CoS to CTAB increased, according to the sequence of CoS listed in *Table 1*.

Table 2 Kinetic parameters of styrene polymerization in o/w microemulsions with different cosurfactants (CoS)

CoS	[Styrene]^a a	[KPS]^b b	E_a (kJ mol^{-1})
BCa	1.03	0.45	92.1
Ca	1.03	0.39	85.7
BCe	1.01	0.43	61.9
Ce	0.99	0.48	54.1

Table 3 Molecular weights of polystyrene

Microemulsion^a (0.6 mM KPS)	Polymerization temperature (°C)	$10^{-6}\bar{M}_n$	$10^{-6}\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
Butyl carbitol				
Styrene 2%	40	1.40	5.08	3.63
4%	40	2.52	8.10	3.21
6%	40	4.08	10.10	2.48
2%	50	0.62	2.88	4.64
4%	50	1.06	4.37	4.12
6%	50	1.48	5.52	3.72
Cellosolve				
Styrene 2%	50	0.52	1.67	3.21
4%	50	0.74	2.26	3.05
5.5%	50	0.99	2.86	2.91

^{a} Same basic compositions as in *Table 1*

Molecular weights of polystyrenes

The concentration of styrene, different cosurfactants and temperature were found to affect the molecular weights ($\bar{M}_w > 10^6$) of the polystyrenes produced, as shown in *Table 3*. The general trend was that higher molecular weights of polystyrene were obtained from systems with higher styrene concentrations. This is the consequence for a radical polymerization system with a relatively low rate of termination. The monomer concentration effect was especially pronounced in the system containing BCa. This system also produced much higher molecular weights compared to those from the Ce system. A greater amount of Ce present in the dispersed phase of the microemulsion would give rise to a more fluid interfacial layer, and this would facilitate the diffusion of KPS radicals and oligomeric radicals into the microemulsion droplets. This would increase the rate of radical termination and produce lower molecular weights of polystyrene. On the other hand, a less fluid interface due to a smaller amount of BCa in the dispersed phase might relatively reduce the rate of radical entry to the microemulsion droplets and retard the rate of radical termination by incoming radicals. As a result, polystyrenes with higher molecular weights would be obtained if terminations were not dominated by chain-transfer reactions.

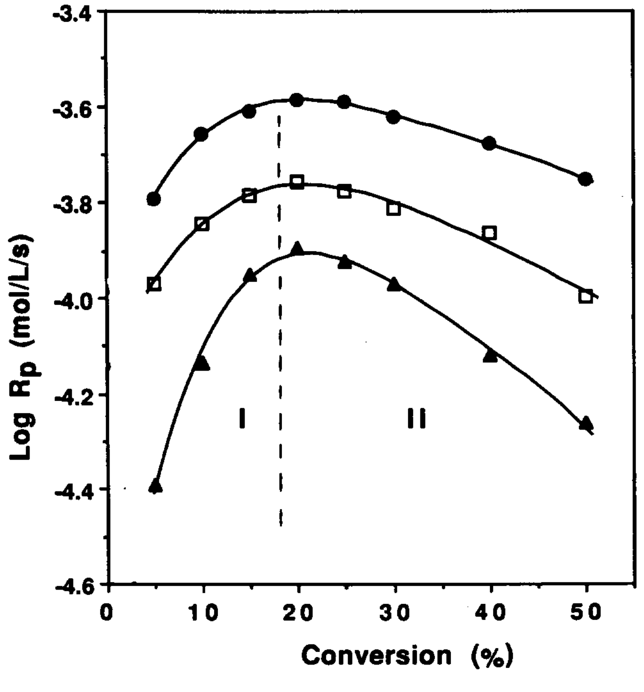

Figure 1 Effect of styrene concentration on polymerization using 0.6 mM KPS and carbitol cosurfactant at 50°C: (▲) 2% styrene; (□) 4% styrene; (●) 5.5% styrene

Radical chain terminations might occur not only by combination/disproportionation but also through chain-transfer reactions with monomer, initiator, surfactant and cosurfactant. Since the polymerization systems contained the same components except for the cosurfactants, the variation in the molecular weights of the polystyrenes was first suspected to be due to chain-transfer reactions with the different cosurfactants. No chain-transfer constants for these cosurfactants are available for direct comparison, but the discussion may be based on the chain-transfer constants of some alcohols which possess a similar functional group (CH_2CH_2OH). The chain-transfer constants at 60°C for styrene radical to ethanol,

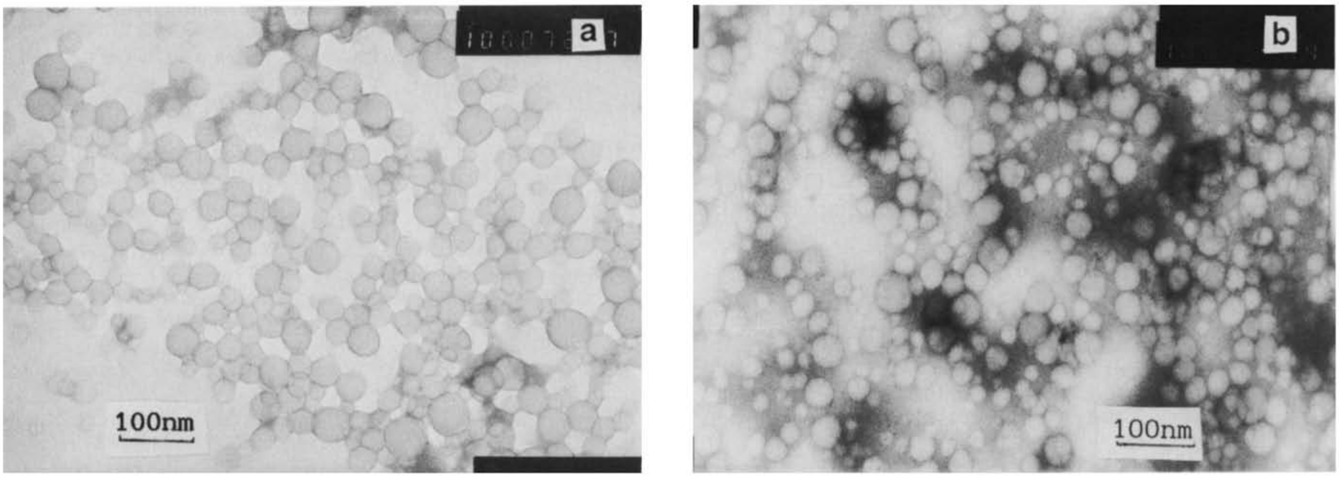

Figure 2 Transmission electron micrographs of polystyrene obtained from microemulsions using (a) BCa and (b) Ce

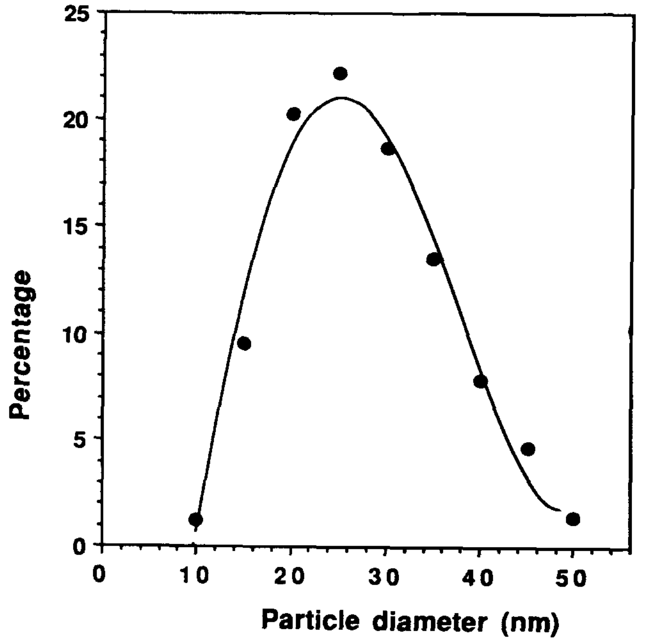

Figure 3 The size distribution of polystyrene particles obtained from the BCa microemulsion

Table 4 Particle sizes of polystyrene microlatexes

Microemulsion[a] CoS	Styrene (%)	$\bar{d}_n$	$\bar{d}_w$	$\bar{d}_w/\bar{d}_n$
BCa	4	23.3	32.4	1.39
	6	27.8	36.1	1.29
Ca	4	29.2	43.2	1.50
BCe	4	27.2	39.3	1.45
Ce	4	21.4	30.4	1.42

[a] Same basic compositions as in *Table 1*

n-propanol, n-butanol and 1,2-ethanediol are 1.6, 2.0, 1.6 and 1.4×10^{-4}, respectively[27]. The indication is that the chain-transfer constants for these alcohols are not much affected by different alkyl chain lengths or even the presence of a diol. Based on this observation, we can assume that the chain-transfer constants for BCa and Ce would be similar because of a common CH_2CH_2OH group. Thus, the large differences in the molecular weights of the polystyrenes obtained from the BCa and Ce systems cannot simply be attributed to different chain-transfer reactions. They are more likely due to an indirect effect of the cosurfactant on the interfacial fluidity, affecting the rate of radical termination in particles.

Though we are unable to predict the extent of chain-transfer reactions for these cosurfactants, it might be quite significant judging from the values of $\bar{M}_w/\bar{M}_n$ for the BCa system at the higher temperature shown in *Table 3*. As the polymerization temperature was increased from 40 to 50°C, $\bar{M}_w$ reduced by almost half and $\bar{M}_w/\bar{M}_n$ increased significantly. Since the $\bar{M}_w/\bar{M}_n$ values for the BCa system are larger than those from the Ce system at a given temperature, it appears that chain-transfer reactions in the Ce system might be less significant. Hence, polystyrenes of lower molecular weights obtained from the Ce system might mainly be due to a fast rate of termination arising from the effect of interfacial fluidity.

Particle sizes of microlatexes

Figure 2 shows two transmission electron micrographs (TEMs) of polystyrene particles obtained from BCa and BCe microemulsions. Their particle sizes ranged from about 10 to 50 nm in diameter. The particle size distribution for the BCa system is shown in *Figure 3*. The number average $\bar{d}_n$ and weight average $\bar{d}_w$ of the particle sizes were calculated from the following equations[28]

$$\bar{d}_n = \Sigma \frac{N_i d_i}{N_i} \qquad \bar{d}_w = \Sigma \frac{N_i d_i^4}{N_i d_i^3}$$

where N_i is number of particles of diameter d_i. Based on about 300 to 500 particle counts for each sample, the calculated $\bar{d}_n$, $\bar{d}_w$ and polydispersity index $\bar{d}_w/\bar{d}_n$ are summarized in *Table 4*. There is no particular trend that indicates the decisive effect of different cosurfactants on the average particle size and the size distributions. It seems that microemulsions containing Ca or BCe produced slightly larger particles ($\bar{d}_n = 27$–29 and $\bar{d}_w = 39$–43 nm) than the other two systems. The effect of styrene concentration on particle size was also examined for the BCa system. *Table 4* shows that $\bar{d}_n$ increases from 23 to 28 nm with increasing styrene concentration from 4 to 6%. This is expected because more monomer is available for the continuing growth of particles to larger sizes.

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