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EFFECT OF SURFACTANT CONFIGURATIONS ON MINIEMULSION POLYMERIZATION*

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ABSTRACT

In the adsorbed state, the molecular area (A_c) of fatty alcohol (FA) decreases and the hydrodynamic layer thickness (δ) of mixed-surfactant (FA + sodium dodecyl sulfate, SDS) increases with increasing alkyl chain length of FA. In bulk solution, the hydrodynamic volume of mixed-surfactant (FA + SDS) increases with increasing alkyl chain length of FA. In both states the FAs were solubilized by SDS. These results reflect that a FA with a shorter alkyl chain length can stabilize a larger total particle surface area on latex and form smaller particles. The increase in the content of FA leads to increases in δ and particle size, and a decrease in polymerization rate. It may be plausible to consider that the FA has a rather rigid configuration in water. The degree to which the size of monomer droplets can be reduced may be related to the rigidity of the FA.

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INTRODUCTION

The low molecular weight fatty alcohols (or hydrocarbons) have been used in miniemulsion to retard the diffusion of monomer out of monomer droplets [1] and, therefore, to attain stable dispersion. The particle diameter of monomer droplets can be as small as 100–400 nm in miniemulsions [2, 3], so that the monomer droplets become the dominating nucleation site. The thermodynamic principle behind the miniemulsion has been studied rather extensively [1, 4, 5].

The use of a mixture of cetyl alcohol (CA) and sodium dodecyl sulfate (SDS) was found to improve effectively the stability of styrene emulsion [2]. This surfactant combination has been applied in the miniemulsion polymerization [1–3, 6, 7] and the direct emulsification of polymers [8, 9].

When low molecular weight fatty alcohols (i.e., partially miscible polar substances) such as CA are solubilized in water in the presence of SDS, it is believed that the polar component is on the micelle surface with the hydrocarbon chain pointing inward [10, 11].

It has been reported [12] that the addition of low molecular weight hydrocarbons or alcohols to aqueous solutions of ionic surfactants decreases the critical micelle concentration (CMC) and increases the micellar size. The increase in micellar size may be attributed not only to the incorporation of solubilizate molecules but also to the increase of the aggregation number of the surfactant itself in micelles [13].

In a miniemulsion copolymerization [6], using hexadecane (HD) as a cosurfactant, the amount of adsorbed sodium hexadecyl sulfate (SHS) on the monomer droplets was found to increase rapidly with the amount of HD added.

In addition, styrene emulsion prepared by using SDS together with a fatty alcohol (C_{10}–C_{18}) was found to have its stability decrease in the following order: $C_{16} > C_{18} > C_{14} > C_{12} > C_{10}$, where the stability was measured by ultracentrifugation [14]. Hence, the extension of the surfactants (SDS and solubilizate) both in bulk solution and at the adsorbed state seems important to an understanding of the stabilizing effect of the surfactant systems.

To understand the extension of surfactant molecules at the adsorbed state, attempts were made to investigate the saturated molecular area and the hydrodynamic layer thickness (δ) of surfactant molecules. The soap titration method [15, 16] was used to determine the saturated molecular areas of surfactant (A_m or A_c), where the assumption made by Maron [15] of constant effective molecular area of a surfactant on a particle surface at the saturation adsorption was adopted. It has also been demonstrated [17] that within a range of particle diameter (700 to 1500 Å), a constant A_m can be obtained for a surfactant adsorbing on a specific polymer particle. Values of A_c of fatty alcohols (FA) in the mixture (SDS + FA) were evaluated by an additive rule. Values of the δ [18–20] of the mixed surfactants were determined by modifying Einstein's law.

By adopting the concept of an equivalent hydrodynamic sphere [21], the effective hydrodynamic volume (V_e) of a mixed surfactant in bulk solution (i.e., using the SDS aqueous solution of 10 mM as the diluent) was determined from the intrinsic viscosity. The mixture of (SDS + FA) was then applied to the miniemulsion polymerization of styrene.

The results may be helpful to an understanding of the stabilizing effects of (SDS + FA) on both the oil droplets and the particles.

EXPERIMENTAL

Materials

Styrene (SM) was purified by washing with aqueous NaOH solution, followed by extra-pure water, dried over anhydrous $MgSO_4$, and stored at −10°C until used. Other chemicals were reagent grade and used as received. The emulsifier used was sodium dodecyl sulfate (SDS). Cosurfactants (fatty alcohols) used included *n*-decanol (C_{10} or DA), lauryl alcohol (C_{12} or LA), cetyl alcohol (C_{16} or CA), and octadecyl alcohol (C_{18} or OA). The initiator was potassium persulfate ($K_2S_2O_8$). Water was from the Ultra-pure Water System (Kintech Co.) with a conductivity of 2 μmho.

Emulsion Polymerization

The polymerization recipe is shown in Table 1. Emulsion polymerizations were conducted in 120 mL glass bottles. The capped bottles with their contents were rotated end-over-end at 45 rpm and 60 ± 0.5°C in a thermostated water-bath. The mixed surfactant was predissolved in water at 65°C 1 hour beforehand. The conversion of monomer to polymer was determined gravimetrically. The polymerization rate was determined from the slope of the conversion–time curve in the constant rate region. The particle size was determined with a Photal DLS 3000/3100 dynamic light-scattering spectrophotometer. The volume-average diameter (D_v, in Å), the number of particles per liter of aqueous phase (N), and the total particle surface area per cm^3 of aqueous phase (TS, in Å $^2/cm^3$) were computed as follows:

$$D_v = [\Sigma N_i D_i^s / \Sigma N_i D_i^3]^{1/3} \qquad (1)$$

$$N = \frac{10(\mathrm{M/W})\,(\%\ \mathrm{conversion})\,d_w}{d_p(\pi/6)(D_v \times 10^{-8})^3} \qquad (2)$$

$$TS = \frac{(\mathrm{M/W})\,(\%\ \mathrm{conversion})\,d_w}{d_p(1/6)(D_v \times 10^{-22})} \qquad (3)$$

where N_i is the number of particles with diameter D_i, (M/W) is the weight ratio of monomer to water in the recipe, d_w is the density of water (= 1.00 g/cm^3), d_p is the density of polystyrene (PS) (= 1.053 g/cm^3), and π = 3.14.

TABLE 1. Polymerization Recipe

Styrene	= 25 g
H_2O	= 75 g
$K_2S_2O_8$	= 0.188 g
SDS	Variable
Fatty alcohol	Variable

The average radical number per particle ($\bar{n}$) was calculated by using

$$R_p = k_p N \bar{n} [\mathrm{M}]/N_a \tag{4}$$

where k_p is the propagation rate constant ($\mathrm{L \cdot mol^{-1} \cdot s^{-1}}$), N_a is Avogadro's number, and [M] is the monomer concentration within the particles ($\mathrm{mol \cdot L^{-1}}$) and was determined from Eq. (5):

$$[\mathrm{M}] = \frac{d_p}{(M_0/1000)[(d_p/d_m) + (1/\phi_m) - 1]} \tag{5}$$

where M_0 is the molecular weight of monomer (= 104 $\mathrm{g \cdot mol^{-1}}$ for SM), ϕ_m is the weight fraction of monomer in the particle, and d_m is the density of SM (0.91 $\mathrm{g/cm^3}$). The fractional conversion (ϕ_p) is related to ϕ_m by

$$\phi_m = 1 - \phi_p$$

Viscosity

Viscosities of the surfactant solution and the latex were measured by using the Ostwald–Fenske capillary viscometer at 30 ± 0.1°C in a thermostated water-bath.

Determination of the Hydrodynamic Layer Thickness

The hydrodynamic layer thickness (δ) is related to the specific viscosity (η_s) (18–20) as

$$\eta_s = 2.5\phi(1 + \delta/r)^3 \tag{6}$$

where ϕ is the volume fraction of polymer in the latex and r is the radius of the particle.

Determination of the Effective Hydrodynamic Volume of the Surfactant in Bulk Solution

The specific viscosity (η_{sp}) of mixed surfactants with a fixed molar ratio in an SDS aqueous solution of 10 mM (i.e., 10^{-3} mol/L) was measured at various dilute concentrations. Note that SDS in the diluent was considered separately from that in the solute. The values of η_{sp}/c were plotted against c, where c is the solute concentration (i.e., original mixture of FA and SDS) in g/dL. The intrinsic viscosity, $[\eta]$, is obtained by extrapolating the data to infinite dilution [21].

The effective hydrodynamic volume (V_e) [21] of the mixed surfactant (SDS/CA) was calculated by using Eq. (7):

$$[\eta] = 2.5V_e/M \tag{7}$$

where M is the average molecular weight (MW) of solute (i.e., the number-average MW of the fatty alcohol-SDS in each solute system).

Surface Tension Measurements

Surface tension was measured by using the duNoüy tensiometer and a platinum-iridium ring.

Determination of Molecular Area of Surfactant

The method of soap titration presented by Maron et al. [15] was utilized to determine the area occupied by the surfactant molecule on the polymer (polystyrene, PS) particle surface at saturation adsorption.

Latices were titrated with an SDS aqueous solution of 30 mM until the critical micelle concentration (CMC) was reached (i.e., the saturation point). The molecular area (A_m) of the surfactant (SDS) was calculated by using

$$A_m = 6/((q/m)D_v N_a \rho) \tag{8}$$

where N_a is Avogadro's number and A_m represents the molecular area of the surfactant on the latex particle of a volume-average diameter, D_v, and density, ρ. The q is the total moles of SDS required to cover m grams of polymer particles; i.e., q is the mole number of SDS presented originally plus that added during the titration, subtracting that dissolved in the aqueous phase.

For latices covered with the mixed surfactant (FA + SDS), the same procedure was used to determine $[A_m]_{mix}$ (i.e., the molecular area of SDS when FA was present). The latices were soap-titrated with 30 mM of the SDS aqueous solution to determine how many moles of SDS were required to cover the whole particle surface area, and $[A_m]_{mix}$ was then calculated by using Eq. (8). An assumption was made that all the particle surface area can be occupied by SDS regardless of the presence of FA. Therefore, the difference between the value of $[A_m]_{mix}$ and that of A_m of SDS (single surfactant) should be attributed to the presence of FA.

The molecular area (A_c) of fatty alcohol was obtained by subtracting the A_m of SDS from the $[A_m]_{mix}$ as follows:

$$([A_m]_{mix} - A_m)C_s/C_f = A_c \tag{9}$$

where C_s is the moles of SDS covering a unit weight of polymer and C_f is the moles of fatty alcohol covering the same weight of polymer.

RESULTS AND DISCUSSION

Hydrodynamic Volume of Mixed Surfactant in the Bulk Solution

Fatty alcohol can be solubilized in water by SDS. It was found that the hydrodynamic volume (V_e) increases with the alkyl chain length of FAs, as shown in Table 2. The reduced viscosity is plotted against the concentration of solute (i.e., SDS + FA), as shown in Fig. 1. Both the slope and intercept (i.e., $[\eta]$) increase with the alkyl chain length of FAs. The increasing slope reflects the decreasing interaction between the solute and solvent [22, 23], while the increasing $[\eta]$ indicates the increasing rigidity of FAs in the solution.

TABLE 2. Data of the Number-Average Molecular Weight (M) of a Mixed Surfactant and the Intrinsic Viscosity ($[\eta]$) and Effective Hydrodynamic Volume (V_e) for the Mixture (SDS + FA) at 30°C with [SDS] = 10 mM as the Diluent

Surfactant	Molar ratio	M	$[\eta]$, dL/g	V_e, nm^3
SDS/DA	1.0/3.0	191	0.50	6.34
SDS/LA	1.0/3.0	212	1.15	16.2
SDS/CA	1.0/3.0	254	1.32	22.3
SDS/OA	1.0/3.0	275	1.59	29.0

Spatial Extension of Mixed Surfactant in the Attached State

The molecular area (A_c) for FAs on PS particle surface in the presence of SDS decreases with an increase in the alkyl chain length of FA, as shown in Table 3. The value represents the saturated area occupied by a FA molecule, and its computation has been given in the Experimental Section. Note that the average values were obtained for A_c for each FA from a series of soap titrations to latices with varied FA/SDS ratios. The deviation for each A_c was mostly 10% except that of the OA.

The molecular area (A_m) of SDS on PS latices has been reexamined by using soap titration. The obtained value is 47 (Å^2), which is consistent with the reported value [17].

The increase in the concentration of CA does not increase the total particle surface area per cm^3 of aqueous solution (TS), as shown in Table 4. Consider also that the unsaturated molecular area should be much larger than the A_m or A_c. For instance, the value could be as large as 302 Å^2 for a recipe containing a single surfactant of SDS (0.22 g). Consequently, the addition of CA seems to pack at the interspace between SDS molecules. This leads to an arrangement in which molecules of SDS and FA pack side by side, similar to the schematic diagram depicted by some investigators [10, 11]. This may lead to the formation of a compact envelope on the

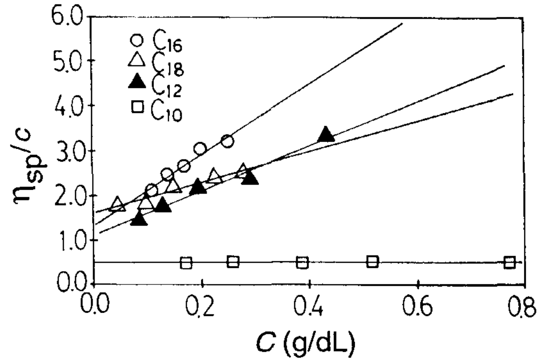

FIG. 1. Huggins plot for each combination of (FA + SDS) as solute, diluted with an SDS aqueous solution of 10 mM.

TABLE 3. The CMC of Fatty Alcohols (FA) in Water and the Molecular Area (A_c) for Fa on the Polystyrene Particle Surface, Both in the Presence of SDS

Fatty alcohol	CMC, mM	A_c, Å^2
Decanyl alcohol	24.0	34 ± 5.0%
Lauryl alcohol	23.1	31 ± 5.1%
Cetyl alcohol	20.0	24 ± 9.7%
Octadecyl alcohol	21.4	19 ± 19%

surface of a particle (and on the surface of monomer droplets) and, therefore, impart significant stabilization to the monomer droplets [24].

It has been found that increasing the alkyl chain length of a surfactant decreases the effective molecular area for such surfactants as sodium alkyl sulfate [17], fatty acids [15], and cationic alkyl ammonium [25]. It was interpreted [17] that longer alkyl chain may increase hydrophobic interactions and, therefore, a larger number of surfactant molecules can be packed onto a fixed area of particle surface. Others [26] suggested that the adsorbed surfactant does not lie flat on the particle surface but instead forms some type of ordered structure when adsorbed.

The δ increases with both alkyl chain length and CA content, as shown in Table 5, where the same seed latex was used. Since the FA is rather insoluble in water and can be solubilized in the presence of SDS, it may be plausible to consider that FA has a rather rigid configuration in water and that the rigidity may be decreased by increasing the SDS content or by decreasing the alkyl chain length of FA so that δ decreases. A thicker hydrodynamic layer may lead to the formation of larger particles [20] or larger monomer droplets in miniemulsion.

Miniemulsion Polymerization

By increasing the CA content, the latex particle size increases (or the particle number decreases), and the polymerization rate (R_p) decreases when the content of SDS is kept constant, as shown in Fig. 2. As the alkyl chain length (i.e., carbon number) of FA increases, D_v increases and R_p decreases, as shown in Fig. 3. Recall that an increase in CA content will increase δ, and an increase in the alkyl chain length of FA will increase δ but decrease A_c. Therefore, both an increase in δ and a

TABLE 4. The Variation of the Volume-Average Diameter (D_v) and the Total Particle Surface Area per cm^3 Aqueous Phase (TS) for Latex Using a Fixed Amount (0.22 g) of SDS and Various Amounts of CA

CA (g)	0	0.09	0.18	0.54	0.90
% Conversion	94.8	95.7	93.9	94.4	97.5
D_v (nm)	82.6	136	142	153	159
$TS \times 10^{-21}$ (Å^2/cm^3)	2.18	1.34	1.26	1.17	1.16

TABLE 5. The Specific Viscosity (η_{sp}) and Hydrodynamic Layer Thickness (δ) of Surfactants on PS Latex of a Fixed D_v of 79.7 nm, Measured at a Given Volume Fraction (ϕ) ([SDS] = 20 mM)

Surfactant	Molar ratio	η_{sp}	ϕ	δ/r	δ, nm
SDS	1.0/0.0	0.617	0.116	0.286	11.4
SDS/CA	1.0/0.5	0.708	0.118	0.338	13.5
SDS/CA	1.0/1.0	1.27	0.121	0.613	24.4
SDS/CA	1.0/3.0	1.71	0.133	0.726	28.9
SDS/CA	1.0/5.0	1.98	0.145	0.763	30.4
SDS/DA	1.0/3.0	0.777	0.127	0.348	13.9
SDS/LA	1.0/3.0	1.06	0.129	0.486	19.4
SDS/CA	1.0/3.0	1.71	0.133	0.726	28.9
SDS/OA	1.0/3.0	2.26	0.135	0.883	35.2

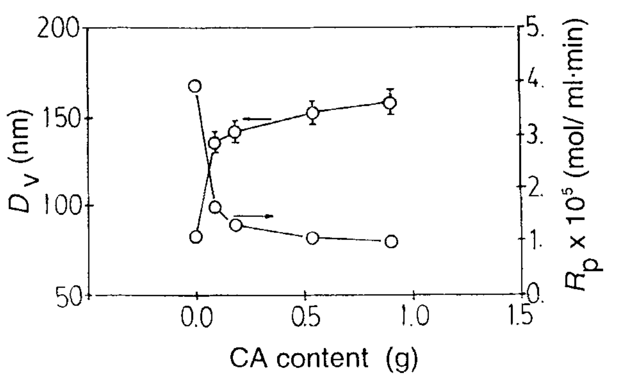

FIG. 2. Volume-average particle diameter (D_v, at about 90% conversion) and polymerization rate (R_p) vs CA content with a constant [SDS] of 0.22 g.

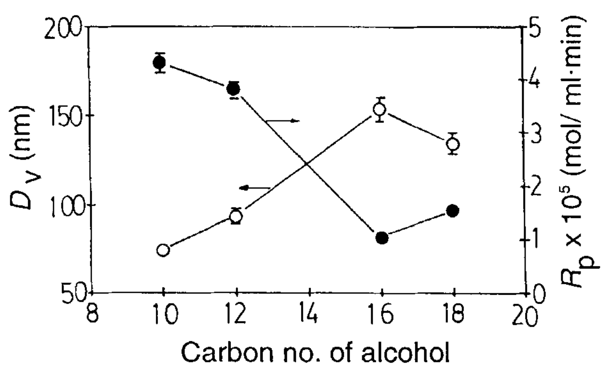

FIG. 3. Volume-average particle diameter (D_v, at about 90% conversion) and polymerization rate (R_p) vs the alkyl chain length of fatty alcohol ([SDS] = 0.22 g and [FA] = 30 mM).

TABLE 6. The Average Radical Number per Particle ($\bar{n}$) at about 50% Conversion Increases with the Content of CA (N = particle number per liter aqueous phase and [M] = monomer concentration within the particles)

CA (g)	0	0.09	0.18	0.54	0.90
% Conversion	54.8	54.9	54.9	52.4	49.6
$R_p \times 10^5$ (mol/L·s)	56.8	35.3	18.0	14.0	17.7
$N \times 10^{-17}$ (L^{-1})	9.2	2.9	1.7	1.0	1.1
[M] (mol/L)	4.24	4.23	4.23	4.45	4.69
$\bar{n}$	0.49	0.98	0.85	1.1	1.2

decrease in A_c lead to a decrease in the stabilizing efficiency of the mixed-surfactant system.

It has been pointed out that monomer droplets are the dominant reaction sites [2, 3] in miniemulsion polymerization. Ugelstad et al. [2] showed that when the monomer droplet size is greatly reduced (to 0.7 μm or smaller), the principal nucleation sites are the droplets since most of the SDS molecules may pack on the droplets. Therefore, an increase of FA content will decrease the amount of free SDS in the aqueous phase and leave less chance for micellar nucleation [27] to occur.

Note that Delgado [6] has shown that in the presence of hexadecane, the amount of sodium hexadecyl sulfate adsorbed on monomer droplet increases rapidly. The same situation may make the free SDS rare in the aqueous phase, reduce the amount of solubilized monomer, and change the dependence of R_p on [SDS].

It has been reported [28, 29] that the kinetics of emulsion polymerization in monomer droplets follow Smith-Ewart Case 3 [30], where the average radical number per particle ($\bar{n}$) > 1.0 and the kinetics are like those of bulk polymerization. Computation of $\bar{n}$ at about 50% conversion has been performed in this study. In the absence of CA, $\bar{n}$ is 0.5, where k_p is 176 (L/mol·s) [31]. Note that it would be better to use the K_p data recommended by the IUPAC Working Party [32]. However, adequate data are not available for k_p at 60°C, except for the value of 161 (L/mol·s) at 40°C [33] (which is close enough to 176 L/mol·s). In the presence of CA, values of $\bar{n}$ are larger than 0.5 and increase with the CA content, as shown in Table 6.

CONCLUSIONS

An increase of FA content in miniemulsion polymerization will decrease the free SDS content in the aqueous phase and leave less chance for micellar nucleation to occur, while the droplet size may become larger because of the formation of a thicker hydrodynamic film on the droplet surface. This leads to an increase in D_v and a decrease in R_p. Increasing alkyl chain length may have the same effect as increasing FA content due to an increase of the hydrophobic portion (and, therefore, the rigidity) of the chain.

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REFERENCES

[1] P. L. Tang, E. D. Sudol, C. A. Silebi, and M. S. El-Aasser, *J. Appl. Polym. Sci., 43*(6), 1059 (1991).

[2] J. Ugelstad, M. S. El-Aasser, and J. W. Vanderhoff, *J. Polym. Sci., Polym. Lett. Ed., 11*, 503 (1973).

[3] Y. T. Choi, M. S. El-Aasser, E. D. Sudol, and J. W. Vanderhoff, *J. Polym. Sci., Polym. Chem. Ed., 23*, 2973 (1985).

[4] W. I. Higuchi and J. Misra, *J. Pharm. Sci., 51*, 459 (1962).

[5] C. N. Lewis and M. Randall, *Thermodynamics and the Energy of Chemical Substances*, McGraw-Hill, New York, 1923, p. 252.

[6] J. Delgado, M. S. El-Aasser, and J. W. Vanderhoff, *J. Polym. Sci., Polym. Chem. Ed., 24*, 861 (1986).

[7] R. C. Dewald, L. H. Hart, and W. F. Carroll Jr., *Ibid., 22*, 2923 (1984).

[8] M. S. El-Aasser, J. W. Vanderhoff, and G. W. Poehlein, *Prepr., Am. Chem. Soc., Div. Org. Coat. Plast. Chem., 37*, 92 (1977).

[9] J. W. Vanderhoff, M. S. El-Aasser, and J. S. Ugelstad, US Patent 4,177,177.

[10] W. D. Harkins, R. Mittlemann, and M. L. Corria, *J. Phys. Colloid Chem., 53*, 1350 (1949).

[11] A. E. Alexander and P. Johnson, *Colloid Science*, Vol. II, Oxford University Press, 1949.

[12] B. A. Mulley and A. D. Metcalf, *J. Pharm. Pharmacol., 8*, 774 (1956).

[13] T. Nakagawa, K. Kuriyama, and H. Inoue, *J. Colloid Sci., 15*, 268 (1960).

[14] M. S. El-Aasser, C. D. Lack, Y. T. Choi, T. I. Min, J. W. Vanderhoff, and F. M. Fowkes, *Colloids Surf., 12*, 79 (1984).

[15] S. H. Maron, M. E. Elder, and I. N. Ulevitch, *J. Colloid Interface Sci., 9*, 89 (1954).

[16] T. R. Paxton, *Ibid., 31*, 19 (1969).

[17] I. Piirma and S.-R. Chen, *Ibid., 74*(1), 90 (1980).

[18] F. L. Sauders, *J. Colloid Sci., 16*, 13 (1961).

[19] W.-D. Hergeth, W. Lebek, E. Stettin, K. Witkowski, and K. Schmutzler, *Makromol. Chem., 193*, 1607 (1992).

[20] H.-H. Chu and X.-C. Hsu, *J. Appl. Polym. Sci., 51*, 1653 (1994).

[21] T. K. Kwei, in *Macromolecules—An Introduction to Polymer Science* (F. A. Bovey and F. H. Winslow, Eds.), Academic, New York, 1979, Ch. 4.

[22] M. L. Huggins, *J. Am. Chem. Soc., 64*, 2716 (1942).

[23] H. Morawetz, *Macromolecules in Solution*, Wiley-Interscience, New York, 1966, p. 309.

[24] M. K. Sharma, S. Y. Shiao, V. K. Bansal, and D. O. Shah, *ACS Symp. Ser., 272*, 7 (1985).

[25] P. Connor and R. H. Ottewill, *J. Colloid Interface Sci., 37*, 642 (1971).

[26] S. I. Ali, J. C. Steach, and R. L. Zollars, *Colloids Surf., 26*, 1 (1987).

[27] W. D. Harkins, *J. Am. Chem. Soc.*, *69*, 1428 (1947).

[28] J. Ugelstad, F. K. Hansen, and S. Lange, *Makromol. Chem.*, *175*, 507 (1974).

[29] A. R. M. Azad, J. S. Ugelstad, R. M. Fitch, and F. K. Hansen, *ACS Symp. Ser.*, *24*, 1 (1976).

[30] W. V. Smith and R. H. Ewart, *J. Chem. Phys.*, *16*, 592 (1948).

[31] M. S. Matheson, E. E. Auer, E. B. Bevilacqua, and E. J. Hart, *J. Am. Chem. Soc.*, *73*, 1700 (1951).

[32] M. Buback, R. G. Gilbert, G. T. Russell, D. J. T. Hill, G. Moad, K. F. O'Driscoll, J. Shen, and M. A. Winnik, *J. Polym. Sci.*, *A30*, 851 (1992).

[33] O. F. Olaj, P. Kremminger, and I. Schnöll-Bitai, *Makromol. Chem., Rapid Commun.*, *9*, 771 (1988).

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