Emulsion copolymerization of acrylonitrile and butyl acrylate
6. Effect of free radical desorption on the polymerization process

I. CAPEK

Polymer Institute, Centre for Chemical Research,
Slovak Academy of Sciences, CS-842 36 Bratislava

Dedicated to Professor Ing. J. Beniska, DrSc., in honour of his 60th birthday

This paper shows that the Smith—Ewart kinetic model developed so far for emulsion polymerization of water-insoluble monomer is applicable to the prediction of the average number of radicals per particle. The classical model is not applicable for emulsion copolymerization of monomers highly soluble in water to the prediction of kinetic parameters. It is reported that the radical desorption is governed by the chain transfer step and the copolymerization process is significantly influenced by the desorption of oligomer radicals.

The equilibrium monomer concentration within monomer swollen polymer particles is constant and independent of the emulsifier concentration and increases with increasing acrylonitrile content in the monomer feed.

The average number of radicals per particle is estimated to increase with decreasing emulsifier concentration and butyl acrylate content in the feed. In the presence of a radical scavenger low values of both the radical concentration and the average number of radicals per particle are estimated.

В работе показывается, что кинетическая модель Смита—Эварта, разработанная для эмульсионной полимеризации водонерастворимого мономера, пригодна для предсказания среднего числа радикалов на частицу. Классическая модель не приложима для предсказания кинетических параметров эмульсионной сополимеризации мономеров, хорошо растворимых в воде. Сообщается, что десорбция радикалов управляется стадией переноса цепи, и процесс сополимеризации в значительной мере зависит от десорбции олигомерных радикалов.

Равновесная концентрация мономера внутри набухших мономером полимерных частиц постоянна и не зависит от концентрации эмульгатора. Она возрастает при увеличении содержания акрилонитрила в исходном мономерном сырье.

Определяется, что среднее число радикалов на частицу увеличивается при снижении концентрации эмульгатора и содержания бутилакрилата в сырье. В присутствии акцептора радикалов отмечаются низкие

значения как концентрации радикалов, так и среднего числа радикалов
на частицу.

Although emulsion copolymerization is industrially more important than the emulsion homopolymerization, the kinetic study of the emulsion copolymerization systems has so far received only little attention compared to the emulsion homopolymerizations and bulk or solution polymerizations. This is mainly due to the complicated character of the emulsion copolymerization. It is also important to verify the accepted kinetic theories developed so far for emulsion polymerization for a comonomer system in which at least one of the monomers has high water solubility, since it may significantly influence the polymerization kinetics.

The characteristic features of the emulsion polymerization are due to the fact that each polymer particle where polymerization takes place should have at most one polymerizing radical. With increasing the average number of radicals per particle ($\bar{Q}$) from 0.5, the characteristics of this system gradually change from those of emulsion to bulk high conversion polymerizations.

The radical concentration within polymer particles is reported to be affected by the radical desorption from the particles [1]. It seems that the exit of radicals from latex particles depends on quantities such as the initiator concentration, the mass fraction of polymer within particles, the surface properties of polymer particles, and the water solubility of monomers [2].

Ballard et al. [3] proposed a mathematical model for emulsion copolymerization systems which is essentially applicable in all range of $\bar{Q}$. With increasing the value of $\bar{Q}$, however, estimation *via* this model becomes more and more complex.

Nomura et al. [4] have proposed a simple method predicting the average number of radicals per particle and their kinds in emulsion polymerization systems.

In this paper, therefore, a simple model predicting the average number of radicals per particle for emulsion copolymerization is developed by extending emulsion homopolymerization theory [4].

The authors [5] studied the emulsion polymerization of methyl methacrylate which has relatively high water solubility. They found, however, that the average number of radicals per particle is much higher than 0.5.

The effect of the radical desorption from the polymer particles on the emulsion polymerization process is thus still open to both experimental and theoretical verifications.

In this paper the emulsion copolymerization of water-insoluble butyl acrylate and high water-soluble acrylonitrile has been studied. The data are quantitatively interpreted using the generalized *Smith—Ewart* [6] and *Nomura* [4] models.

Theory

The rate of emulsion polymerization of monomer A is expressed by

$$v_p = k_{pAA}[A\cdot][A] = (k_{pAA}/N_A)[A]_{eq}N\bar{Q} \tag{1}$$

where $[A]_{eq}$ is the equilibrium concentration of monomer A in the polymer particle, N is the number of particles, $\bar{Q}$ is the average number of radicals per particle, k_{pAA} is the propagation rate constant, and N_A is the Avogadro's constant.

For free radical copolymerization of monomers A and B the rate is given by the following expression

$$v_p = k_{pAA}[A\cdot][A] + k_{pAB}[A\cdot][B] + k_{pBA}[B\cdot][A] + k_{pBB}[B\cdot][B] \tag{2}$$

Here A· and B· represent growing radicals with terminal units A and B, k_{pAA}, k_{pAB}, k_{pBA}, and k_{pBB} are propagation rate constants.

From the steady-state assumption in free-radical copolymerization follows

$$k_{pAB}[A\cdot][B] = k_{pBA}[B\cdot][A] \tag{3}$$

Consequently

$$[B\cdot]/[A\cdot] = k_{pAA}r_B L/(k_{pBB}r_A) \tag{4}$$

and

$$[A\cdot][A] = v_p r_A/(k_{pAA}(r_A + 2L + r_B L^2) \tag{5}$$

where L is the ratio $[B]/[A]$ and r_A and r_B are the reactivity ratios (ratio k_{pii}/k_{pij}).

For emulsion copolymerization of monomers A and B the rate is expressed by the equation [7]

$$v_p = \frac{k_{pAA}k_{pBB}N\bar{Q}[M]_{eq}(r_A + 2L + r_B L^2)}{N_A(k_{pBB}r_A + k_{pAA}r_B L)(1 + L)} \tag{6}$$

where $[M]_{eq} = [A]_{eq} + [B]_{eq}$.

Consequently for emulsion homopolymerization

$$[A\cdot] = (N/N_A)\bar{Q} \tag{7}$$

and for copolymerization

$$[A\cdot] + [B\cdot] = (N/N_A)\bar{Q}_c \tag{8}$$

Let us consider an emulsion system where two monomers A and B are

copolymerized and the desorption of free radicals from polymer particles is taken into account. The *Nomura*'s model [4] predicting the radical desorption is extended for emulsion copolymerization. This model has the following steps:

1. Transfer of free radical activity to monomer within polymer particle

$$R_1 = k_{tr,A}[A]_{eq} \tag{9}$$

Consequently for comonomer system we can write

$$R_{1,c} = \frac{k_{tr,A}k_{tr,B}(r_A x_A^2 + 2x_A x_B + r_B x_B^2)[M]_{eq}}{(k_{tr,B}r_A x_A + k_{tr,A}r_B x_B)(1+L)} \tag{10}$$

where $k_{tr,A}$ and $k_{tr,B}$ are the transfer rate coefficients and x_A and x_B are the mole fractions of monomers A and B in the feed.

2. Diffusion of the resulting free radical to the particle surface. If this step is rate-determining, then

$$R_2 = 3zD_p k_{tr,A}/k_{pAA}2r_s^2 \tag{11}$$

and for the binary system we can write

$$R_{2,c} = \frac{3zD_p k_{tr,A}k_{tr,B}(k_{pBB}r_A x_A + k_{pAA}r_B x_B)}{2r_s^2 k_{pAA}k_{pBB}(k_{tr,B}r_A x_A + k_{tr,A}r_B x_B)} \tag{12}$$

where z is the degree of polymerization of the exiting radical, D_p is the diffusion coefficient of the free radical species in the particle, and r_s is the swollen particle radius.

3. Finally, if diffusion of free radicals away from the particle through the aqueous phase is rate-limiting, then

$$R_3 = 3zD_w k_{tr,A}/k_{pAA}qr_s^2 \tag{13}$$

For the binary system we propose

$$R_{3,c} = \frac{3zD_w k_{tr,A}k_{tr,B}(k_{pBB}r_A x_A + k_{pAA}r_B x_B)}{qr_s^2 k_{pAA}k_{pBB}(k_{tr,B}r_A x_A + k_{tr,A}r_B x_B)} \tag{14}$$

where D_w is the diffusion coefficient of the free radicals in the aqueous phase and q is the partition coefficient for the exiting radicals between the organic and aqueous phase. The value of q is calculated from the ratio $[M]_{eq}/[M]_{aq,sat}$ where $[M]_{aq,sat}$ is the saturated monomer concentration in the aqueous phase.

In the system where the desorption of free radicals is significant the average number of radicals per particle $\bar{Q}_f$ is given by the following equation [8]

$$\bar{Q}_f = 1/2(\sqrt{R_i^2/R_f^2 N^2 + 2R_i/R_f N} - R_i/R_f N) \tag{15}$$

where R_i is the rate of radical production, R_f is the average rate coefficient for the radical desorption from particles, and N is the total number of particles.

The parameter R_i is given by eqn (16)

$$R_i = 2fk_d [I] N_A = R_i' N_A \qquad (16)$$

where f stands for the initiator efficiency, k_d is the decomposition rate constant of initiator. [I] is the concentration of initiator and R_i' is the rate of initiation.

Experimental

Materials

Acrylonitrile (A) and butyl acrylate (B) were purified by conventional methods. Anal. grade ammonium persulfate was used as polymerization initiator. Dowfax 2A1 (sodium dodecylbenzenedisulfonate DW, molecular mass = 569) of polymerization grade was used as emulsifier. Water was distilled under pure nitrogen.

Procedure

Polymer emulsions were prepared by the batch technique as described earlier [9] under strict exclusion of oxygen. After vigorous stirring for 30 min in a thermostat at 70 °C, the polymerization was initiated by injection of an aqueous solution of the initiator. The polymerization was carried out for 2 h. The recipe in all runs comprised 140 g of water, about 97 g of monomer(s) (see later), and 0.772 g of ammonium persulfate. The emulsifier concentrations varied from (0.6 to 7.32) $\times$ 10^{-2} mol dm^{-3}.

The values of the equilibrium monomer concentration within polymer particles were determined by a "static swelling" method [7]. The particle sizes of latexes were determined by light scattering. All measurements were run at wavelength of 400 nm using a Specord UV VIS spectrophotometer, according to the method described in [10]. The number of polymer particles was determined from experimental data of latex particle radii and polymerization kinetic data according to the method described in [11—14].

Results and discussion

The values of the equilibrium monomer concentration, the propagating radical concentration, the rate of copolymerization, the average number of radicals per particle, and the number of latex particles are expressed as a function of the emulsifier concentration and the monomer feed composition in Tables 1 and 2.

Table 1

Kinetic parameters of the emulsion copolymerization of acrylonitrile (A) and butyl acrylate (B)
Initial monomer concentrations: [A] = 1.345 mol dm^{-3}, [B] = 2.24 mol dm^{-3}

$\dfrac{[DW] \cdot 10^2}{\text{mol dm}^{-3}}$	$\dfrac{[A]_{eq} \quad [B]_{eq}}{\text{mol dm}^{-3}}$ [a]	$\dfrac{[A\cdot] \quad [B\cdot]}{\text{mol dm}^{-3}}$ [b]	$\bar{Q}_c$ [c]	$\dfrac{N \cdot 10^{-18}}{1 \text{ dm}^{-3}}$ [d]	$\dfrac{v_p}{\text{mol dm}^{-3}\text{s}^{-1}}$ [e]
		$\times 10^7$			$\times 10^3$
7.32	2.1 3.4	5.5 17.3	2.0	0.69	35.3
2.88	2.1 3.4	2.7 8.5	1.9	0.35	17.0
1.18	2.0 3.4	2.1 6.6	3.0	0.17	13.3
0.63	2.0 3.3	1.4 4.4	2.3	0.15	8.7

a) The equilibrium monomer concentration within polymer particles; b) the radical concentration of propagating radicals within polymer particles; c) the average number of radicals per particle; d) the number of particles per 1 dm^3 of the aqueous phase; e) the rate of copolymerization of acrylonitrile and butyl acrylate in the interval 2, taken from [15].

Table 2

Kinetic parameters of the emulsion polymerization of butyl acrylate and copolymerization of acrylonitrile and butyl acrylate
[DW] = 7.32 × 10^{-2} mol dm^{-3}

Feed composition (mole fraction of butyl acrylate	$\dfrac{[A]_{eq} \quad [B]_{eq}}{\text{mol dm}^{-3}}$ [a]	$\dfrac{[A\cdot] \quad [B\cdot]}{\text{mol dm}^{-3}}$ [b]	$\bar{Q}_c$ [c]	$\dfrac{N \cdot 10^{-18}}{1 \text{ dm}^{-3}}$ [d]	$\dfrac{v_p}{\text{mol dm}^{-3}\text{s}^{-1}}$ [e]
		$\times 10^7$			$\times 10^3$
1.00	— 4.4	— 19.6	0.3	4.2	17.4
0.79	1.1 4.0	3.2 21.8	0.9	1.8	30.5
0.62	2.1 3.4	5.5 17.3	2.0	0.7	35.3
0.43	3.3 2.5	4.9 7.1	2.1	0.3	23.5
0.29	4.5 1.9	6.1 4.8	3.8	0.2	26.0

For a—e see the footnote to Table 1.

The value of [M]$_{eq}$ for acrylonitrile and butyl acrylate slightly increases with increasing emulsifier concentration. But it is more affected by the nature of monomer, *i.e.* the value of the equilibrium monomer concentration is directly related to the level of water solubility of the monomer as has been shown earlier [11—14]. As shown in [15], the value of [M]$_{aq, sat}$ for acrylonitrile, however, increases significantly with increasing emulsifier concentration.

Radical concentration is a function of the rate of polymerization, the mo-

nomer feed composition, and the homo- and the cross-propagation rate constants. It is estimated to increase with increasing emulsifier concentration and to reach a maximum with increasing butyl acrylate content in the feed. The concentrations of propagating macroradicals are estimated to be such that butyl acrylate ends mostly predominate in this series of experiments. This is to be expected from the relative reactivities of the acrylonitrile and butyl acrylate radicals and the monomer feed composition. The effect of the particle size is noticeable in the estimates of the average number of radicals per particle. The average number of radicals is a function of both the emulsifier concentration and the monomer feed composition. This is to be expected from the dependence of the particle size on the emulsifier concentration and the monomer feed composition, since the probability of coexistence of radicals increases with increasing particle size.

The effect of the additives on the kinetic parameters of emulsion polymerization is summarized in Table 3. The polymerization was carried out in the presence of radical scavengers: hydroquinone (QH_2) and benzoquinone (Q), which are highly soluble in water.

Table 3

Effect of hydroquinone (QH_2) and *p*-benzoquinone (Q) on the kinetic parameters of the emulsion polymerization and copolymerization of butyl acrylate (B) and acrylonitrile (A)
$[DW] = 7.32 \times 10^{-2} \, mol \, dm^{-3}$

Feed composition (mole fraction of butyl acrylate)	Additive	$[A \cdot]$ $[B \cdot]$ [a] $mol \, dm^{-3}$		$\bar{Q}_c$ [b]	$\dfrac{v_p}{mol \, dm^{-3} \, s^{-1}}$ [c]	$\dfrac{N \cdot 10^{-18}}{1 \, dm^{-3}}$ [d]
		$\times 10^7$			$\times 10^3$	
1.0	—	—	19.6	0.28	17.4	4.2
1.0	QH_2	—	0.28	0.004	0.25	4.61
1.0	Q	—	1.43	0.015	1.27	5.59
0.62	—	5.5	17.3	1.99	35.3	0.7
0.62	QH_2	0.35	1.1	0.13	2.25[e]	0.7
0.62	Q	0.34	1.1	0.12	2.2[e]	0.7
0.29	—	6.1	4.8	3.75	26.0	0.3
0.29	QH_2	0.33	0.27	0.05	1.4[f]	0.3
0.29	Q	0.96	0.75	0.15	4.1[f]	0.3

a) The radical concentration of propagating radicals within polymer particles; *b*) the average number of radicals per particle; *c*) the rate of polymerization and copolymerization in the interval 2; *d*) the number of particles (per 1 dm³ water); *e*) from Ref. [16]; *f*) from Ref. [17].

$[QH_2] = 1.74 \times 10^{-3} \, mol \, dm^{-3}$, $[Q] = 1.77 \times 10^{-3} \, mol \, dm^{-3}$.

As shown in Table 3, the rate of polymerization, propagating radical concentration, and the average number of radicals per particle are lower than those in the absence of the radical scavenger. These values show that most of radicals formed from persulfate in the aqueous phase are trapped by the scavenger, but some start the polymerization. After the latex particles are formed, the polymerization rate is governed by the entry rate of radicals and/or scavenger molecules. The polymerization in the presence of the scavenger shows a lower polymerization rate but unchanged molecular mass products [16, 17]. Accordingly, the lifetime of macroradicals within polymer particles should be the same for both systems (in the presence and in the absence of a radical scavenger).

The dependence of the rate of emulsion polymerization on the monomer feed composition is described by the curve with a maximum corresponding to a certain monomer feed composition (Tables 2 and 3). It is well known that the rate of emulsion polymerization increases with increasing concentration of polymer particles [6]. Here however the rate of polymerization does not run parallelly with the number of polymer particles. This indicates that also other factors influence the polymerization process. These include the reactivity of radicals, the nucleation history, the primary particle concentration, the stability of mature polymer particles, and the radical desorption as discussed later.

If we admit even an error $\pm 5\ \%$ in v_p and N values [15], Tables 1—3 show that the experimental inaccuracies cannot explain the variation of the average number of radicals with the emulsifier concentration and the monomer feed composition and therefore this explanation seems to be reasonable.

Tables 4 and 5 show the values of the rate coefficient for radical desorption from the particles and the average number of radicals per particle for both low

Table 4

Values of calculated kinetic parameters of emulsion copolymerization of acrylonitrile (A)
and butyl acrylate (B)
$[A] = 1.345\ \mathrm{mol\ dm^{-3}}$, $[B] = 2.24\ \mathrm{mol\ dm^{-3}}$

$\dfrac{[DW] \cdot 10^2}{\mathrm{mol\ dm^{-3}}}$	$\dfrac{R_{1,c}{}^a}{\mathrm{s^{-1}}}$	$\dfrac{R_{2,c}{}^b}{\mathrm{s^{-1}}}$	$\dfrac{R_{3,c}{}^c}{\mathrm{s^{-1}}}$	q^d	$\bar{Q}_f{}^e$	$R_{3,c}/R_{1,c}$	$\bar{Q}_c/\bar{Q}_f$
7.32	0.2	4.5	1.3	9.0	0.41	6.5	4.9
2.88	0.2	2.5	0.7	9.4	0.44	3.5	4.3
1.18	0.2	1.5	0.4	9.6	0.47	2.0	6.4
0.63	0.2	1.4	0.4	9.6	0.47	2.1	4.9

a—c) Rate coefficients for radical desorption; d) the ratio $[M]_{eq}/[M]_{aq,sat}$; e) the average number of free radicals per particle corrected on the radical desorption (for calculation $R_{1,c}$ values were used).

Table 5

Values of calculated kinetic parameters of emulsion polymerization and copolymerization of acrylonitrile (A) and butyl acrylate (B)
$[DW] = 7.32 \times 10^{-2} \, mol \, dm^{-3}$

Feed composition (mole fraction of butyl acrylate)	$\dfrac{R_{1,c}}{s^{-1}}$ [a]	$\dfrac{R_{2,c}}{s^{-1}}$ [b]	$\dfrac{R_{3,c}}{s^{-1}}$ [c]	q [d]	$\bar{Q}_f$ [e]	$R_{3,c}/R_{1,c}$	$\bar{Q}_c/\bar{Q}_f$
1.00	0.29	58.2	0.71	220	0.22	2.4	1.4
0.79	0.19	6.8	0.91	18.2	0.26	4.8	3.5
0.62	0.20	4.5	1.3	9.0	0.41	6.5	4.9
0.43	0.21	3.0	1.3	5.9	0.46	6.2	4.6
0.29	0.23	1.9	0.93	5.5	0.44	4.0	8.6

For *a—e* see the footnote to Table 4.

and high emulsifier concentrations and for different monomer feed compositions calculated on the basis of *Nomura*'s model [4]. For these estimations the following parameters were used: $k_{tr,A} = 0.065 \, dm^3 \, mol^{-1} \, s^{-1}$, $k_{tr,B} = 0.166 \, dm^3 \, mol^{-1} \, s^{-1}$ [18]; $z = 1$; $D_p = 1.3 \times 10^{-9} \, m^2 \, s$ [2] (at $\Phi_m = 0.6$); $D_w = 1.7 \times 10^{-9} \, m^2 \, s$ [2]; $f = 0.7$ [7], and k_d is estimated to be $7.0 \times 10^{-5} \, s^{-1}$ [19].

The rate coefficient for radical desorption shows a dependence on the monomer feed composition and the emulsifier concentration. The chain transfer is predicted to be the rate-limiting step for systems with acrylonitrile. In the system with butyl acrylate alone besides the chain transfer also the diffusion of free monomeric radicals away from the particle is the rate-limiting step most probably due to the much lower water solubility of butyl acrylate compared with that of acrylonitrile. Similar results were observed by desorption radical studies also in the systems with styrene [20] and methyl methacrylate [2].

In the range of low emulsifier concentrations also the transport of free radicals from particles seems to be the rate-limiting step. It is speculated that the desorption rate coefficients are affected by the change in diffusion characteristics of the reaction system concerning the thickness and density of the boundary particle surface layer of emulsifier. Adopting values for $[M]_{aq,sat}$ the degree of polymerization of butyl acrylate macromer which separates from the aqueous phase is 5 and for acrylonitrile/butyl acrylate comonomer system it is approximately 25 [17]. It is reasonable to expect that also these resulting oligomeric free radicals exit from polymer particles. This expectation leads to the conclusion that the rate coefficients $R_{2,c}$ and $R_{3,c}$ should be at least 5 or 10 times higher than those shown in Tables 4 and 5. Thus the chain transfer seems to be the rate-limiting step for the studied systems.

The radicals produced by the chain transfer to monomer which are located on the polymer particle surface or near this surface, will exit from latex particle easier than those generated and located within the polymer particle core. This approach seems to agree very well with the statement that the rate of desorption is inversely proportional to the particle radius [6, 21, 22].

Good agreement is observed between the average number of radicals $\bar{Q}_c$ (applying Smith—Ewart model) and $\bar{Q}_f$ for systems with butyl acrylate or its high content in the monomer feed. With rising the mole fraction of acrylonitrile in the monomer feed the ratio $\bar{Q}_c/\bar{Q}_f$ increases. Transfer coefficients for both monomers are approximately equal, they contribute to the ratio $\bar{Q}_c/\bar{Q}_f$ by the same portion. However, different water solubilities of butyl acrylate and acrylonitrile monomer and their oligomeric radicals are most probably responsible for the change in the ratio $\bar{Q}_c/\bar{Q}_f$ with changing monomer feed composition. Thus with increasing acrylonitrile concentration the concentration of monomeric or oligomeric radical soluble in water which is able to exit from the polymer particle into the aqueous phase increases.

The rate of copolymerization does not run with Q_c, Q_f or N but runs parallelly with the ratio $R_{3,c}/R_{1,c}$. This observation indicates that the diffusion of radicals through the particle/water interface into the aqueous phase plays an important role in the whole mechanism of polymerization. Thus the nature of particle surface dependent on the mechanism of particle growth (by particle coalescence or conversion of monomer within polymer particle) seems to influence the rate of radical desorption and the radical concentration within polymer particles.

The sorption and desorption processes proceed so quickly that the equilibrium distribution of radicals between the aqueous and the polymer particle phases is reached [23]. Exited radicals can take part in the initiation of polymerization or bimolecular termination in the aqueous phase or enter the monomer swollen emulsifier micelles or polymer-monomer particles [2, 3, 5]. Re--entered radicals can either initiate the growth of the macromolecular chain or terminate the growing polymer radicals.

Conclusion

This paper explains:

1. The Smith—Ewart kinetic model (case II) is applicable for the emulsion polymerization of butyl acrylate but it is not convenient for the emulsion copolymerization of butyl acrylate and acrylonitrile due to the radical desorption from polymer particles.

2. The chain transfer process is the rate-determining step in the desorption of radicals from the polymer-monomer particles.

3. The desorption of radicals plays an important role in the overall copolymerization process.

References

1. Litt, M., Patsiga, R., and Stannet, V., *J. Polym. Sci., Part A-1 8*, 3607 (1970).
2. Ballard, M. J., Napper, D. H., and Gilbert, R. G., *J. Polym. Sci., Polym. Chem. Ed. 22*, 3225 (1984).
3. Ballard, M. J., Napper, D. H., and Gilbert, R. G., *J. Polym. Sci., Polym. Chem. Ed. 19*, 939 (1981).
4. Nomura, M. and Harada, M., *J. Appl. Polym. Sci. 26*, 17 (1981).
5. Ballard, M. J., Gilbert, R. G., Napper, D. H., Pomery, P. J., and O'Donnel, J. H., *Macromolecules 17*, 504 (1984).
6. Smith, W. V. and Ewart, R. H., *J. Chem. Phys. 16*, 592 (1948).
7. Goldwasser, J. M. and Rudin, A., *J. Polym. Sci., Polym. Chem. Ed. 20*, 1993 (1982).
8. Nomura, M., Yamamoto, K., Horie, I., Fujita, K., and Harada, M., *J. Appl. Polym. Sci. 27*, 2483 (1982).
9. Capek, I., Bartoň, J., and Orolínová, E., *Chem. Zvesti 38*, 803 (1984).
10. Heller, W. and Tibibian, R. M., *J. Colloid Interface Sci. 12*, 25 (1957).
11. Gardon, J. L., *J. Polym. Sci., Part A-1 6*, 623 (1968).
12. Gardon, J. L., *J. Polym. Sci., Part A-1 6*, 643 (1968).
13. Gardon, J. L., *J. Polym. Sci., Part A-1 6*, 665 (1968).
14. Gardon, J. L., *J. Polym. Sci., Part A-1 6*, 2855 (1968).
15. Capek, I., Bartoň, J., and Orolínová, E., *Acta Polymerica 26*, 187 (1985).
16. Capek, I. and Bartoň, J., *Makromol. Chem. 186*, 1297 (1985).
17. Capek, I. and Bartoň, J., *Chem. Papers 40*, 45 (1986).
18. Capek, I., *Collect. Czechoslov. Chem. Commun. 51*, 2546 (1986).
19. Hakoila, E., *Ann. Univ. Turkuensis, Ser. A 66*, 7 (1963).
20. Gilbert, R. G. and Napper, D. H., *J. Macromol. Sci., Rev. Macromol. C 23*, 127 (1983).
21. Lukhovitsky, V. I., *Vysokomol. Soedin. 21A*, 319 (1979).
22. Nomura, M., Harada, M., Eguchi, W., and Nagata, S., in *Emulsion Polymerization.* (Piirma, J. and Gardon, J. L., Editors.) ACS Symposium Series, pp. 102—121. American Chemical Society, Washington, D.C., 1976.
23. Harriot, P., *J. Polym. Sci., Part A-1 9*, 1153 (1971).