(16) Roovers, J.; Bywater, S. *Macromolecules* **1972**, *5*, 384.
(17) Roovers, J. *Macromolecules* **1985**, *18*, 1359.
(18) Benoit, H.; Grubisic, Z.; Rempp, P.; Decker, D.; Zilliox, J. *J. Chim. Phys. Phys.-Chim. Biol.* **1966**, *63*, 1507.
(19) Wagner, H. L. *J. Phys. Chem. Ref. Data* **1985**, *14*, 1101.
(20) Szwarc, M. *Carbanions, Living Polymers and Electron Transfer Processes*; Interscience Publishers: New York, 1968.
(21) Day, J.; Cooney, J. D.; Wiles, D. M. *J. Appl. Polym. Sci.*, **1988**, *36*, 1097.
(22) Blundell, K. J.; Osborn, B. N. *Polymer* **1983**, *24*, 953.

Particle Formation and Catalyzed Agglomeration in Emulsion Polymerization

Herbert Schlueter

Research and Development, Dispersions Department, Hüls AG,
4370 Marl, Federal Republic of Germany.
Received April 13, 1989; Revised Manuscript Received August 14, 1989

ABSTRACT: Catalyzed agglomeration, restricted to the particle formation phase of emulsion polymerization, can be used to distinguish experimentally whether or not a homogeneous nucleation mechanism is operative in a given persulfate-initiated emulsion polymerization system. The agglomeration catalyst used had a mode of action disclosed in earlier work, which proves that a homogeneous and not the generally accepted micellar nucleation mechanism is effective in a persulfate-initiated polymerization system even for monomers of low water solubility, such as styrene and butadiene, and emulsifier concentrations > cmc. Using catalyzed agglomeration, particle size and the monodispersity coefficient as well as the particle formation time were investigated as a function of monovalent cation concentration, emulsifier concentration and polymerization temperature. All correlations found either were consistent with homogeneous nucleation or completely excluded micellar nucleation. This means that poor water solubility of monomers like styrene and butadiene can no longer be a criterion for micellar nucleation. Homogeneous primary particle formation followed by agglomeration, which may be more or less pronounced or—in a few cases—does not occur at all, is most applicable and seems to be the particle formation mechanism generally valid for persulfate-initiated emulsion polymerization.

Introduction

Emulsion polymerization is one of the most important processes for manufacturing polymers. However, many mechanistic aspects of emulsion polymerization remain unclear despite its industrial importance. This applies especially to the initial stage of emulsion polymerization, the particle formation phase. Many mechanisms have been proposed for particle formation in emulsion polymerization systems. The most important are micellar nucleation,[1-3] homogeneous nucleation,[4-8] and coagulative nucleation.[9-11] In this paper, an attempt will be made to use catalyzed agglomeration as a means of deciding experimentally whether or not a homogeneous nucleation is operative in a specific polymerization system using in particular styrene and butadiene as monomers.

According to the micellar nucleation mechanism, radicals generated in the aqueous phase enter monomer-swollen soap micelles and initiate polymerization to form monomer-swollen polymer particles. Only one of every 100–1000 micelles captures a radical and becomes a polymer particle: the others disband, giving off monomer and soap molecules to neighboring micelles that have captured a radical.

According to the homogeneous nucleation mechanism, the radicals generated in the aqueous phase add monomer molecules until the oligomer radicals have exceeded their solubility limit and precipitate. The precipitated oligomer radicals form spherical particles that adsorb emulsifier molecules and absorb monomer molecules, thus becoming primary particles. These primary particles may be stable or may be stabilized by agglomeration.

In view of the questions raised in this paper, it is advisable to particularly emphasize three characteristic differences between micellar and homogeneous nucleation:

(1) When initiation is in the micelles, the end of the particle formation phase is characterized by complete disappearance of the micelles. When initiation is in the aqueous phase, particle nucleation continues during the course of polymerization but is moderated by capture of precipitated oligomer radicals and by agglomeration of primary and secondary particles. Consequently, the rate of particle formation (dN/dt) is only initially the same as the rate of radical formation (R_i). Within a short period of time, a steady state is reached between initiation and capture of precipitating oligomer radicals (R_c) and agglomeration of primary and secondary particles (R_a):[5]

$$dN/dt = R_i - R_c - R_a$$

Therefore the number of particles remains unchanged if

$$R_c + R_a = R_i$$

(2) A fundamental difference between micellar and homogeneous nucleation is the different action of monomer droplets and soap micelles. For initiation in micelles, monomer droplets serve as reservoirs providing the micelles with monomers via the aqueous phase, whereas for initiation in the aqueous phase the micelles provide the emul-

sifier for stabilization of the polymer particles precipitating from the aqueous phase and possibly agglomerating.

(3) Micellar nucleation is generally considered to be the mechanism for those monomers that have a poor solubility in water, such as styrene, butadiene, and *n*-butyl acrylate. On the other hand, homogeneous nucleation is postulated as the mechanism for those monomers that are considerably more soluble in water, such as vinyl acetate, methyl acrylate, and acrylonitrile. For monomers with intermediate water solubility, such as ethyl acrylate, methyl methacrylate, and vinyl chloride, both mechanisms have been proposed in separate examples. Nonetheless, homogeneous nucleation has also been proposed for monomers of low water solubility, such as styrene.[4] Furthermore, there are some hints to homogeneous nucleation in order to explain some particularities observed in styrene/butyl acrylate polymerization.[12]

Uncertainties about the operative nucleation mechanisms remain, despite the new theory of "coagulative nucleation".[10] This theory has been derived from the positively skewed plot of particle volume distribution obtained in the early stage of the emulsion polymerization of styrene. Such a particle volume distribution agrees only with an increased production rate of new latex particles during the particle formation period and is inconsistent with both a one-step micellar or a one-step homogeneous nucleation mechanism. Consequently, a two-step "coagulative nucleation model" has been proposed. According to this model, in a first step "precursor particles" are formed either by micellar or by homogeneous nucleation and because of their insufficient stability they do not become "true" polymer particles until after agglomeration. It is argued that the precursor particles are so unstable chiefly because of their small size (<5 nm) and as a result agglomerate. Furthermore, it is emphasized that micellar nucleation cannot be excluded safely by the coagulation nucleation theory.

Coagulative nucleation, however, is also said to be applicable to emulsifier-free emulsion polymerization, in which a micellar nucleation mechanism must be excluded.[11]

Under these circumstances, it should be possible to distinguish between the two competing nucleation mechanisms by catalyzed agglomeration. This means attempting to accelerate the agglomeration postulated for coagulative nucleation specifically in the particle formation phase by means of agglomeration catalysts whose modes of action are sufficiently well-known and that, however, must possess the following properties:

(1) The catalysts must not be active when the precursor particles have formed in a micelle and, in the initial stage of polymerization, are still completely saturated with emulsifier molecules. This means that the catalyst does not work in the particle formation phase in the case of micellar nucleation (case 1).

(2) In the case of homogeneous nucleation, the catalysts must be active in the particle formation phase toward only the unstable precipitating precursor particles and induce no agglomerations of the more stabilized secondary particles, although these particles may be unsaturated with emulsifier. This means that a specific agglomeration activity, adjusted to the low stability of the precursor particles, is required (case 2).

In fact, catalysts with properties corresponding to case 1 have been described in the literature.[13-15] It is also known that the agglomeration activity of these catalysts can be adjusted at will.[16] Therefore, it should also be fairly easy to adjust the agglomeration activity as required by case 2.

Furthermore, the mode of action of these catalysts is based on sensitization of the polymer particles toward electrolytes. This means that the agglomerating action of electrolytes already present in the polymerization system is simply enhanced.[13]

Consequently, it is the primary goal of this paper to show how it has become possible with the aid of catalyzed agglomeration to establish the operative nucleation mechanism and thus to settle the fundamental question of the existence of a micellar or homogeneous nucleation mechanism. For these studies a polymerization system with monomers of low water solubility, styrene and butadiene, was chosen. This polymerization system is generally considered in the literature to have a micellar nucleation mechanism.

Experimental Details

Materials. Styrene and butadiene used had a percentage purity of >99.5%. Acrylic acid was 99.7% pure.

The emulsifier was a C_{14}–C_{17} sulfonate prepared by sulfochlorination (K30 from BAYER AG). The disulfonate fraction was 10%. The emulsifier contained 3.75% sodium chloride and 0.075% Na_2SO_4, which must be considered in the polymerization procedures.

Ammonium persulfate had a percentage purity of >99%.

The tetrasodium salt of ethylenediaminetetraacetic acid (EDTA) still contained about 13% di- and trisodium salts of EDTA. Sodium chloride, potassium chloride, and $(NH_4)_2SO_4$ were analytically pure products. *tert*-Dodecyl mercaptan had a percentage purity of >97%.

The agglomeration catalyst (PEO_{ox}) was prepared from a low molecular weight polyethylene glycol from Hüls AG by air oxidation on the basis of the patent specifications U.S. 3 330 795 and EP 0 330 865.[16]

Polymerization. Virtually all polymerizations were carried out in 40-L autoclaves in "batch operation" with the polymerization temperature during the particle formation period normally set at 50 °C. In a basic procedure, the following compounds were utilized (in parts): styrene (57.5), butadiene (40), acrylic acid (2.5), fully demineralized water (150), emulsifier K30 (0.5), EDTA (0.013), *tert*-dodecyl mercaptan (0.5), and ammonium persulfate (0.2). In three series of experiments, this basic procedure was modified as follows: (1) the concentration of ammonium, sodium, and potassium ions was varied by addition of different amounts of ammonium persulfate, ammonium sulfate, and sodium and potassium chloride. (2) The emulsifier concentration was varied. (3) The polymerization temperature during the particle nucleation period was altered. Further details can be found in Tables I–III.

Particle Size Determination. Samples were diluted with distilled water to give a concentration of between 0.01 and 0.05 g/cm^3 and were stained with OsO_4. The dispersions were sprayed onto Formvar-coated electron microscope grids and examined in a Philipps 200 electron microscope. In order to obtain representative sampling for particle size analysis, several grids were examined for each latex. For calibration, a micrograph of a diffraction grating was taken at the same microscope setting as that used to examine the latex particles. The particle size determinations were made by using a Carl Zeiss TGZ 3 particle size analyzer. For each sample, approximately 1000 particles were measured on enlargements of the electron micrographs. The data were analyzed in order to obtain the number- and volume-average diameters.

Theoretical Basis. The *particle number N* was calculated from the volume-average particle diameter d_v by using the formula

$$N = \frac{6KG}{\pi \rho d_v^3} \qquad (1)$$

where KG = polymer content in g/cm^3 and ρ = polymer density = 0.98 g/cm^3.

To determine the *stability factor W*, the following relation was derived from the Smoluchowski coagulation equation,[10] which had been extended by the formation rate g of the primary particles:

$$W = \frac{2.6k_BT}{\eta g}N^2 \tag{2}$$

where k_B = Boltzmann constant, T = absolute temperature, η = viscosity of aqueous medium, and g = formation rate of primary or precursor particles. Derivation of eq 2 is given in the Appendix.

The particle nucleation rate dN/dt as a function of time t is obtained by differentiation of the Smoluchowski coagulation equation extended by the particle formation term g

$$N = C \tanh\left(\frac{Bt}{2}\right) - \frac{g}{B}\,\frac{\sinh(Bt) + Bt}{\cosh(Bt) + 1} \tag{3}$$

with

$$B = 4\left(\frac{k_BTg}{6\eta W}\right)^{0.5} \quad \text{and} \quad C = \left(\frac{3Wg\eta}{2k_B\mathrm{T}}\right)^{0.5}$$

and by using the relation

$$BC = 2g$$

to give

$$\mathrm{d}N/\mathrm{d}t = g\left(\frac{1}{\cosh^2(B(t/2))^{-1}} + \frac{\sinh(Bt) + (Bt)\sinh(Bt)}{(\cosh(Bt) + 1)^2}\right) \tag{4}$$

The preceding equations are based on the assumption that secondary agglomerations do not occur after the particle formation period at higher polymerization conversions, as has already been postulated in the case of micellar nucleation according to the Smith–Ewart theory. As regards homogeneous nucleation, it is generally assumed that secondary particles generated in the course of the initial stage of polymerization act as nuclei that terminate the production of new particles when all primary particles formed thereafter are captured. To corroborate the absence of secondary agglomerations the monodispersity coefficient $K = d_n/d_v$ of the individual dispersions, with d_n being the number-average and d_v the volume-average particle diameter, was determined after all polymerizations. It is assumed that secondary agglomeration can be safely ruled out when the monodispersity coefficient is >0.95.

Results

Influence of Cation Concentration. The salts used to adjust the different cation concentrations are found in Table I. The sum of the cations was determined from the ammonium persulfate, ammonium sulfate, sodium chloride, and potassium chloride concentrations. It is especially important to note that the sodium ions allotted stoichiometrically to the emulsifier concentration are not included in this sum, as these ions are for the most part bound by micelles.[17] All salt concentrations are related to the volume of the aqueous phase. However, the concentration of the agglomeration catalyst is related to the weight of the monomers, styrene and butadiene.

Table I
Variation of Particle Diameter with Cation Concentration[a]

latex no.	ammonium persulfate concn, 10^3 mol dm^{-3}	$[NH_4^+] + [Na^+] + [K^+]$, 10^3 mol dm^{-3}	d_v (final), nm	K
		Noncatalyzed Reactions		
1	5.8	14.7	94	0.955
2	14.5	32.7	73	0.975
3	23.2	49.5	83	0.960
4	29	61.1	105	0.965
5	43.5	90.1	119	0.966
		Catalyzed Reactions		
6	5.8	14.7	99	0.96
7	8.7	20.5	108	0.975
8	11.6	26.5	111	0.985
9	14.5	32.1	138	0.985
10	5.8	32.1[b]	149	0.995
11	5.8	32.1[c]	145	0.976
12	14.5	43.8[d]	190	0.985
13	14.5	49.5[c]	230	0.990
14	23.2	49.5	230	0.976
15	29	61.1	283	0.993
16	23.2	72.1[e]	326	0.991
17	23.2	90.1[f]	334	0.983

[a] Emulsifier (C_{14}–C_{17} sulfonate) concentration = 9.025 mol × 10^{-3}; agglomeration catalyst (PEO_{ox}) = 40 ppm (ppm = parts per million/monomer). [b] Ammonium sulfate added, $[NH_4^+] = 17.4 \times 10^{-3}$ mol dm^{-3}. [c] Potassium chloride added, $[K^+] = 17.4 \times 10^{-3}$ mol dm^{-3}. [d] Sodium chloride added, $[Na^+] = 11.6 \times 10^{-3}$ mol dm^{-3}. [e] Ammonium sulfate added, $[NH_4^+] = 22.6 \times 10^{-3}$ mol dm^{-3}. [f] Ammonium sulfate added, $[NH_4^+] = 40.6 \times 10^{-3}$ mol dm^{-3}.

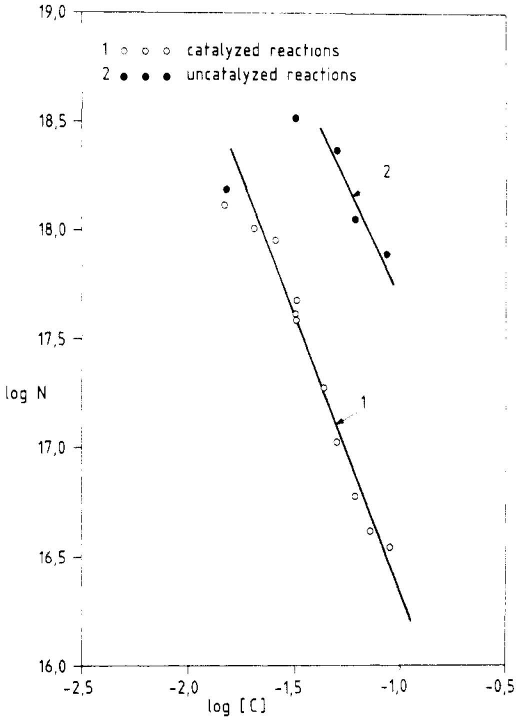

Figure 1. log particle number density (N) as a function of log cation concentration [C] computed from volume-average diameter d_v, eq 1, by using values given in Table I.

The data contained in Table I reveal the strong influence of cation concentration on the particle size in catalyzed reactions but a weak influence is also evident in the noncatalyzed reactions at higher concentrations. The values of the monodispersity coefficient K are lower in the noncatalyzed reactions, while in catalyzed reactions they level off at extremely high values for larger particle sizes. The corresponding particle number densities (N, dm^{-3}) were calculated from the particle diameters by using eq 1. Figure 1 shows the variation of particle number with cation concentration [C] for the catalyzed and noncatalyzed reactions and indicates that for both reactions a critical initial cation concentration is required to provoke an agglomeration effect. The declining linear portion of curve 1 shows a dependence that can be expressed by

$$\log N \sim -2.5 \log [\mathrm{C}]$$

To a first approximation, this dependence appears to also be valid for the noncatalyzed reaction corresponding to curve 2. Because of the uncontrolled course of agglomeration, reliable particle number values could no longer be determined for curve 2 at still higher cation concentrations.

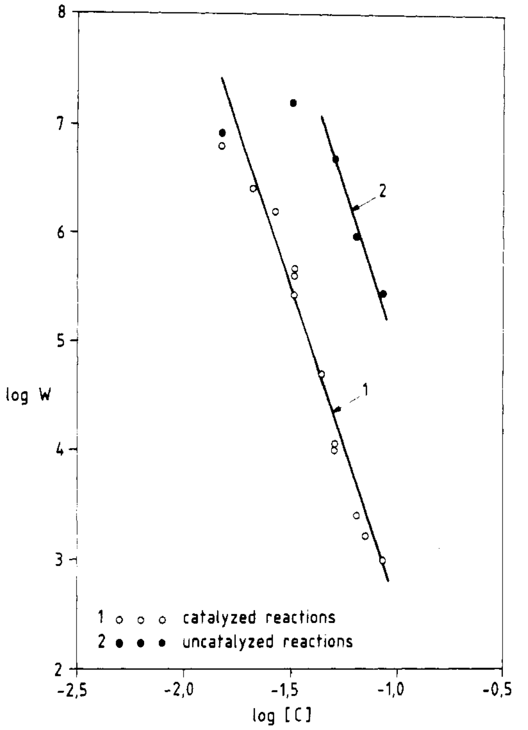

Figure 2. log stability ratio (W) as a function of log cation concentration [C] computed from particle number (N) and rate of production of primary particles (g), eq 2, by using values given in Table I.

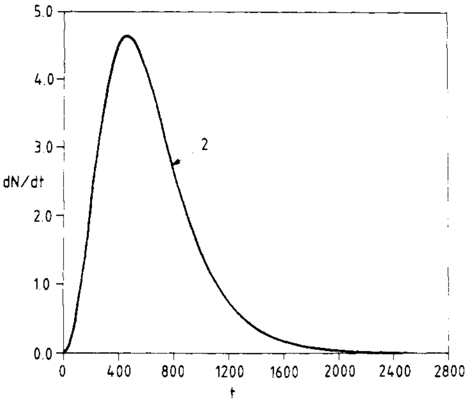

Figure 3. Particle formation rate dN/dt (particles/10^{-15} dm^3 s^{-1}) as a function of time t (s), computed from eq 4, by using parameters of latex 2 in Table I.

The stability factor W was calculated by using eq 2. The formation rate of primary particles g was estimated from the decomposition rate of 1×10^{-3} mol dm^{-3} of ammonium persulfate at 50 °C with $g \sim 10^{15}$ particles dm^{-3} s^{-1}.[10] The efficiency factor of persulfate was ~0.35 in this case. In Figure 2 the values calculated for W are plotted as in Figure 1 against the cation concentration [C] both for the catalyzed and for the noncatalyzed reactions. Curve 1 exhibits a dependence of

$$\log W \sim -6 \log [\mathrm{C}]$$

which again appears to be approximately valid for the non-catalyzed reactions. The distance between curves 1 and 2 is about 2.5 orders of magnitude. This means that the agglomeration rate of the primary particles is increased by a factor of 320 in the presence of the catalyst.

The particle formation rates as a function of time are calculated for some of the latices listed in Table I by using eq 4 and are plotted in Figures 3–5. Comparison of Figures 3 and 4, which are based on latex 2 or latex 16 of Table I, reveals a drastic difference between the polymerization carried out with and without agglomeration catalyst. Whereas in the first case without catalyzed agglomeration the particle formation period is not over until after about 1600 s, in a catalyzed agglomeration with a cation concentration of 72×10^{-3} mol dm^{-3} there are no new particles formed after only about 16 s. The duration of the particle formation period can be markedly influenced by the cation concentration and, in catalyzed reactions, it can even be controlled by relatively low cation concentrations in the aqueous phase. This is evident from Figure 5, in which the nucleation rates of a series of latices of Table I are plotted against the logarithm of time. The different levels of the curves in Figure 5 are caused by differing persulfate concentrations, which determine the formation rate of primary particles. Thus, curves 2, 9, 12, and 13 are based on an ammonium persulfate concentration of 14.5×10^{-3} mol dm^{-3} and curves 3, 14, and 16 on one of 23.2×10^{-3} mol dm^{-3}.

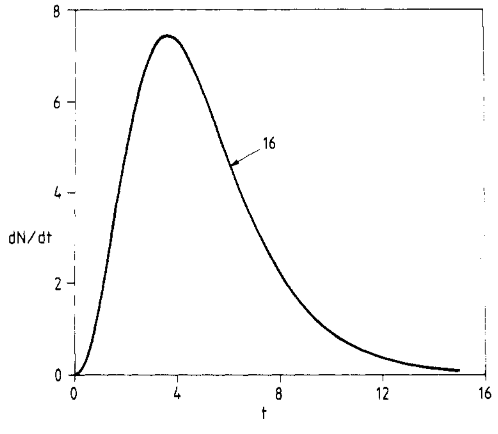

Figure 4. Particle formation rate dN/dt (particles/10^{-15} dm^3 s^{-1}) as a function of time t (s), computed from eq 4, by using parameters of latex 16 in Table I.

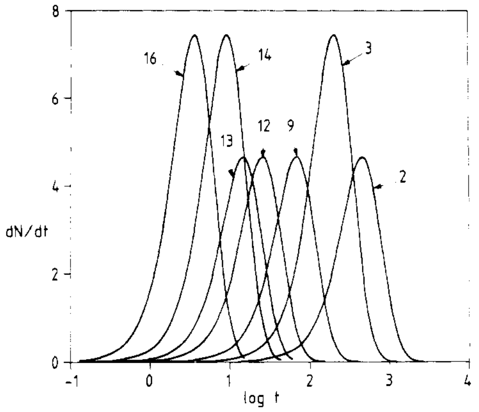

Figure 5. Particle formation rate dN/dt (particles/10^{-15} dm^3 s^{-1}) as a function of time t (s), computed from eq 4, by using parameters of latices 2, 3, 9, 12, 13, 14, and 16 in Table I.

Influence of Emulsifier Concentration. The same procedure was used to study the influence of emulsifier concentration as that used to study the influence of cation concentration. Preparative details can be found in Table II. The critical micelle concentration (cmc) of the emulsifier in pure water was determined as 1.5×10^{-3} mol dm^{-3}. With the influence of salts taken into account, all adjusted emulsifier concentrations are thus above the cmc. The data obtained show that the particle size decreases with increasing emulsifier concentration. The monodispersity coefficient K abruptly adapts to a lower value at the high emulsifier concentration. This is caused by a bimodal particle size distribution.

Table II
Variation of Particle Diameter with Emulsifier Concentration[a]

latex	C_{14}–C_{17} sulfonate concn, 10^3 mol dm^{-3}	d_v (final), nm	K
1	48.86	150	0.54[b]
2	36.1	145	0.970
3	18.05	150	0.988
4	9.025	190	0.991
5	6.32	208	0.998
6	3.61	276	0.990
7	1.62	280	0.995
8	0.90	337	0.988

[a] Ammoniumpersulfate concentration = 14.61 × 10^{-3} mol dm^{-3}; sodium chloride concentration = 11.96 × 10^{-3} mol dm^{-3}; agglomeration catalyst (PEO$_{ox}$) = 40 ppm (ppm = parts per million/monomer). [b] Bimodal particle distribution.

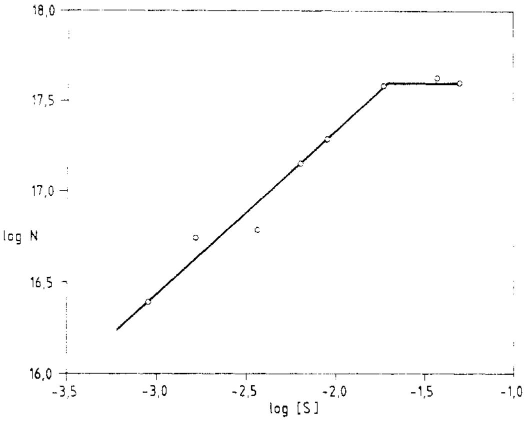

Figure 6. log particle number density (N) as a function of log emulsifier concentration [S] computed from volume-average diameter d_v, eq 1, by using values given in Table II.

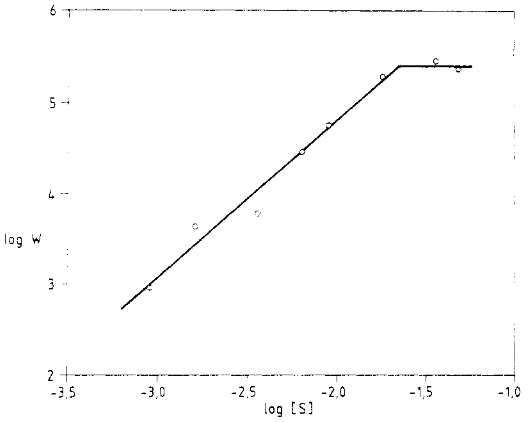

Figure 7. log stability ratio (W) as a function of log emulsifier concentration [S] computed from particle number (N) and rate of production of primary particles (g), eq 2.

In Figure 6, the particle number calculated by using eq 1 is plotted against the emulsifier concentration [S] on the double-logarithm scale. The slope of the rising straight line fits the relation

$$\log N \sim 0.9 \log [S]$$

The particle number is no longer dependent on the emulsifier concentration starting at 18.05 × 10^{-3} mol dm^{-3}. According to Figure 7, a similar curve is also obtained when log W is plotted against log [S]. The slope of the straight line fits the relation

$$\log W \sim 1.73 \log [S]$$

In Figure 8, the particle formation rate dN/dt is plotted against the logarithm of time. Here, as for the high cation concentrations, relatively short particle formation periods are obtained—however, at low emulsifier concentrations.

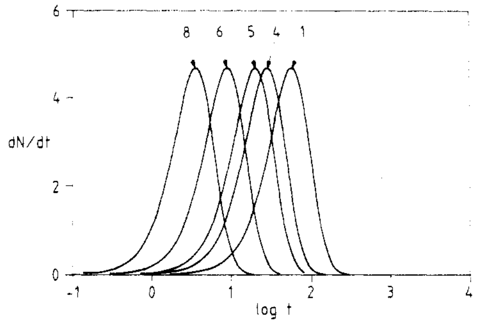

Figure 8. Particle formation rate dN/dt (particles/10^{-15} dm^3 s^{-1}) as a function of the log of time t (s) computed from eq 4, by using parameters of latices 1, 4, 5, 6, and 8 in Table II.

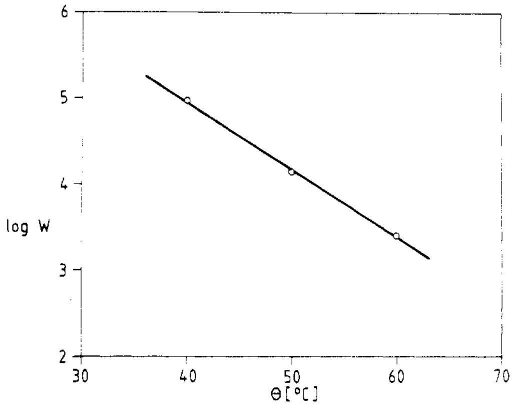

Figure 9. log stability ratio (W) as a function of temperature θ (°C) computed from particle number (N) and rate of production of primary particles (g), eq 2.

Table III
Variation of Particle Diameter with Temperature[a]

latex	ammonium persulfate concn, 10^3 mol dm^{-3}	$[NH_4^+]$ + $[Na^+]$ + $[K^+]$, 10^3 mol dm^{-3}	temp, °C	d_v (final), nm	K
1	23.2	49.5	40	176	0.98
2	23.2	49.5	50	227	0.98
3	23.2	49.5	60	251	0.99

[a] Cation concentration = 49.52 × 10^{-3} mol dm^{-3}; emulsifier concentration = 9.025 × 10^{-3} mol dm^{-3}; agglomeration catalyst (PEO$_{ox}$) = 40 ppm (ppm = parts per million/monomer).

Influence of the Polymerization Temperature. Preparative details and particle size data can be found in Table III. A pronounced influence of the polymerization temperature on particle size can be found in the temperature range from 40 to 60 °C. Larger particles are obtained with a higher polymerization temperature. This result conflicts with the usual findings for the influence of temperature on emulsion polymerization. In general, in emulsion polymerization, smaller particles are obtained with increasing temperature due to the more rapid decomposition of the polymerization activator. This has also been found for emulsifier-free polymerization.[18] The opposite effect of temperature found here is caused specifically by catalyzed agglomeration.

According to Figure 9, a strictly linear relation is obtained between the logarithm of the stability factor W and the polymerization temperature.

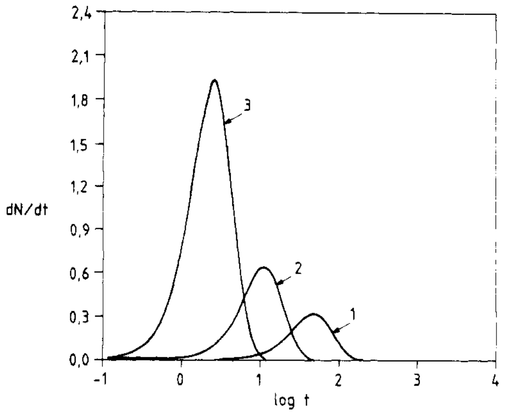

Figure 10. Particle formation rate dN/dt (particles/10^{-16} dm^3 s^{-1}) as a function of the log of time t (s) computed from eq 4, by using parameters of latices 1 (40 °C), 2 (50 °C), and 3 (60 °C) in Table III.

The influence of the polymerization temperature on the particle formation rate can be seen as a function of time in Figure 10, where the nucleation rate is plotted against the logarithm of time. Figure 10 shows that with increasing temperature the duration of particle formation shortens from about 100 to 10 s, with the height of the curves increasing considerably. This is caused by the increased formation rate g of the primary particles resulting from faster persulfate decomposition at higher temperatures. The formation rates g were calculated or if necessary extrapolated on the basis of rate constants of the persulfate decomposition at different temperatures, as taken from the literature. The efficiency factor of persulfate was assumed to be 0.3 in this case.

Discussion

The polymerizations described in detail in this paper were aimed primarily at gaining insight into the particle formation mechanism with the aid of catalyzed agglomeration. In doing so, the fundamental question of the presence of a micellar or a homogeneous nucleation mechanism in the polymerization system under study was to be settled.

The experimental results obtained clearly suggest that in the polymerization system studied, a homogeneous nucleation mechanism is operative, even with monomers of low solubility like styrene and butadiene. However, for these monomers the operation of a micellar nucleation mechanism is generally accepted in the literature. Why this is unlikely will be explained in detail.

First, it might be postulated that the agglomeration catalyst possesses the property of being inactive when the primary or precursor particles have formed in a micelle and are therefore enclosed by emulsifier molecules throughout the entire particle formation period. Proof of this is provided by individual results obtained in studies on the influence of cation concentration on final particle size.

The fact that (a) the catalyst molecules sensitize the polymer particles toward cations present in the aqueous phase and (b) the agglomeration rate changes with the sixth power of cation concentration, as revealed by the diagram of log W versus log [C] in Figure 2, clearly reveals that the agglomeration catalyst is highly active and that its mode of action is the same as that already demonstrated by agglomeration rate measurements after polymerization.[13]

Thus, if the mode of action of the catalyst can be considered to be the same for agglomeration after polymerization and in the nucleation phase, it must also be true that the catalyst molecules can only then be active when the emulsifier concentration in the aqueous phase is considerably below the cmc, and even below the critical emulsifier concentration needed for a complex formation between catalyst and emulsifier molecules,[19-21] as has been shown in earlier work.[15] The abrupt termination of the agglomeration reaction at a latex surface tension of 40–42 mN/m could be explained by such a complex formation between the catalyst (PEO_{ox}) and the soap molecules.[15] This means that at the start of polymerization the catalysts exist as emulsifier adducts in a latent state of reaction. In such a case, it is irrelevant that the primary particles are especially unstable due to their small size. The catalyst molecules can only become active when already in the first seconds of polymerization a large surface area has been formed by precipitation of "naked" primary particles. Then the catalyst/emulsifier adducts are disbanded and catalyst and emulsifier are adsorbed on the new polymer surface. During the reaction the catalyst is continuously replaced by the preferred adsorption of emulsifier as long as emulsifier is in excess, i.e., as long as micelles are present. Thus, it becomes obvious why agglomeration in the particle formation phase can also proceed according to the same mode of action as agglomeration following polymerization.[13,15] This explains why the agglomeration rate also changes with the sixth power of cation concentration. Further factors, such as rate of production of primary particles and rate of disbandment of catalyst/emulsifier adducts or of micelles, which must also be taken into account for the total course of agglomeration in the particle formation phase, can be considered to be nearly ineffective in this first series of experiments dealing with the dependence of agglomeration rate on cation concentration.

Second, it might be postulated that the agglomeration catalyst also possesses the property of being active only toward the unstable primary particles and, at higher polymerization conversions, induces no agglomeration of secondary particles although these particles may not be saturated with emulsifier. This is shown by the extremely high monodispersity coefficients found in Table I, which are obtained with catalyzed agglomeration. Thus, a micellar nucleation mechanism can be ruled out solely by the mode of action of the agglomeration catalyst in the particle formation phase.

However, further results to be discussed are either consistent with homogeneous nucleation or completely exclude micellar nucleation. Thus, in the second series of experiments the influence of the emulsifier on the agglomeration rate does not show the antagonistic effect already found for agglomeration after polymerization, which is acceleration of the agglomeration process as well as retardation or termination of it.[13,15] This is not surprising as the emulsifier molecules exist as micelles during agglomeration in the particle formation phase whereas they are adsorbed on the particle surface during agglomeration after polymerization.

The relation found, according to Figure 6

$$\log N \sim 0.9 \log [S]$$

corresponds to the findings that have usually been obtained for emulsion polymerizations. For example, an exponent of 0.72 was found for the emulsion polymerization of methylstyrene and of 1.0 for dimethylstyrene.[22] This comparison reveals that, in principle, the mode of action of the emulsifier is not influenced by catalyzed agglomeration. It is true that the exponents of 0.72 and 1.0 do not correspond to the value of 0.6 postulated for micellar nucleation from the Smith–Ewart theory. The prediction of this theory that

$$\log N \sim 0.6 \log [S]$$

was originally derived by assuming a micellar nucleation mechanism.[2,3] Later it was pointed out that the same exponent with respect to [S] is predicted also by a homogeneous nucleation mechanism.[4] According to the literature,[9] identical exponents should be predicted by virtually any mechanism when there is no agglomeration, and particle formation ceases when the total surface area can no longer be completely covered with emulsifier molecules. This, however, cannot explain the conformity obtained in the present investigations, as strong agglomeration occurs and the end of particle formation does not coincide with exhaustion of emulsifier.

In the present case the significantly higher exponent of 0.9 rather agrees with homogeneous nucleation than with micellar entry. This can be shown by analyzing this result mathematically with appropriate equations derived in a recent paper, although these equations deal with semicontinuous emulsion polymerization.[23]

Furthermore, the bimodal particle size distribution obtained at the high emulsifier concentration may be explained by the fact that at higher conversion agglomeration of primary and secondary particles is no longer possible due to the high surface coverage of the secondary particles that have incorporated too many sulfate groups from persulfate initiator decomposition and are highly covered with normal emulsifier molecules. As the surface tension of the latex is still sufficiently high, therefore it is not imaginable that emulsifier micelles play a role in the formation of new particles at higher conversion. Similar conclusions have also been drawn from studying particle formation in continuous emulsion polymerization of synthetic rubber latices.[24]

The dependence of log W on temperature is apparent in Figure 9. After transformation of this relationship into a true Arrhenius equation, a formal activation energy of 24 kcal mol^{-1} is obtained for the agglomeration rate in the particle formation period. However, an activation energy of 8 kcal mol^{-1} has since been determined for agglomeration after polymerization by using a polymerization system reported in an earlier work.[13] This means that the higher value of 24 kcal mol^{-1} is mainly determined by persulfate decomposition, which controls the production of primary particles. However, very different activation energies of 33.5 and 25 kcal mol^{-1} have been reported in the literature.[25] Hence, although there is a clear temperature dependence, which suggests a homogeneous nucleation mechanism, reliable activation energies of persulfate decomposition are required in order to safely discriminate between the two competing nucleation mechanisms.

Proof that there is no micellar nucleation is provided by the relatively short particle formation periods in connection with the high monodispersity coefficients K at higher cation concentrations, lower emulsifier concentrations, and higher polymerization temperatures obtained by eq 4 in all series of experiments. It may be taken as a rule that the higher the monodispersity coefficient, the shorter the particle formation period.[26]

According to Smith–Ewart, the equation

$$t_1 = 0.65\left(\frac{a_s[S]}{K^{2/3}g}\right)^{3/5} \tag{5}$$

with a_s = the surface area that a soap molecule covers, [S] = the emulsifier concentration, K = the volume growth rate of polymer particles, and g = formation rate of primary particles, is obtained for the nucleation time t_1 at which all emulsifier molecules are adsorbed on the latex particles and no new particles can be formed. When the particle formation time is calculated both from the Smith–Ewart relation and from the extended Smoluchowski coagulation equation (4), the order of magnitude of the duration of the particle formation period agrees only for the noncatalyzed reactions. Particle formation times of 10–20 s can only be explained by the fact that in such short time intervals so many stable secondary particles could be formed by agglomeration that they are capable, as nuclei, of subsequently capturing all primary particles forming thereafter. Whereas this is impossible for monomer-swollen primary particles that have formed in micelles and are still completely embedded by emulsifier molecules, it is possible for wholly or partly naked primary particles to agglomerate at an exceedingly high rate. It can be seen from the literature that agglomeration times of 10^{-3} s, are possible when the agglomeration reaction is nearly diffusion controlled.[13] Agglomeration in the particle formation phase also takes place in a matter of seconds at high cation concentrations, low emulsifier concentrations, and higher polymerization temperatures, as can be estimated to a first approximation from the computed stability factors W. Thus, these considerations very clearly show that a micellar nucleation is unlikely in the polymerization system used. The described procedure was applied to other persulfate-initiated systems on the basis of styrene/butadiene monomers. For instance the same correlations were obtained when the C_{14}–C_{17} sulfonate was replaced by potassium oleate and polymerization was carried out without acrylic acid, which may be considered as an in situ emulsifier generator to stabilize the particles during polymerization.

Thus, this work has shown how catalyzed agglomeration can be used to establish the homogeneous nucleation mechanism in a polymerization system with monomers of low water solubility and emulsifier concentrations > cmc. The experimental results suggest that homogeneous nucleation followed by a more or less pronounced agglomeration may be considered a generally valid particle formation mechanism in persulfate-initiated polymerization comprising emulsifier-containing and emulsifier-free polymerization systems.

The schematic representation in Figure 11 depicts this proposed mechanism in the light of the experimental findings. Assuming that the precipitating primary particles have a diameter of only 3 nm, in accordance with the size range of 2–5 nm given in ref 11 for the corresponding primary precursors, no agglomeration can be calculated in the case of latex A, considering the final particle size of 42 nm, despite the small size of the primary particle. This is only possible when the monomer/water ratio has been significantly increased as is shown by latex B. This result reveals that the monomer/water ratio is also an important factor for agglomeration in the particle formation period.

As there is no homoagglomeration of primary particles in the case of latex A and the Smith–Ewart theory provides no agglomeration, the duration of the particle formation period of this latex was calculated by using both the extended Smoluchowski equation (4) and the Smith–Ewart formula (5). It can be seen from Figure 12 that the Smith–Ewart time t_1 of 257 s coincides exactly with the time period at which the particle formation rate dN/dt reaches a maximum as predicted by eq 4. This suggests that in exceptional cases, i.e., only when no primary particles undergo homoagglomeration, the max-

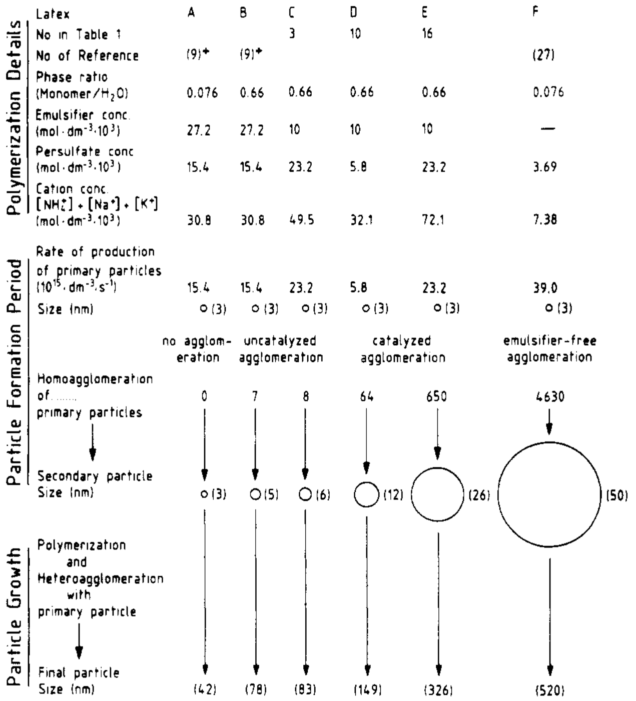

Figure 11. Schematic representation of particle formation and growth in persulfate-initiated emulsion polymerization comprising emulsifier-containing and emulsifier-free polymerization systems. †Polymerization was carried out under intense nitrogen gas flow.

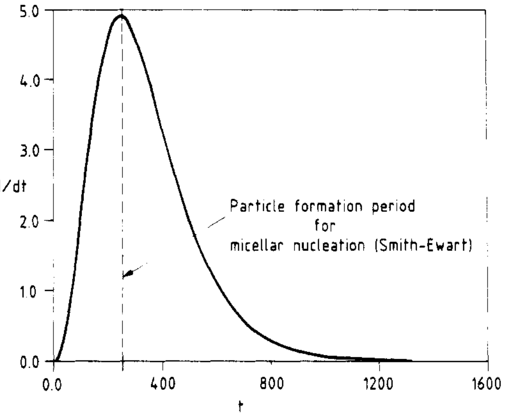

Figure 12. Particle formation rate dN/dt (particles/10^{-15} dm^3 s^{-1}) as a function of time t (s) computed from eq 4 by using parameters of latex A in Figure 11. Dashed line indicates time t_1 computed from the Smith–Ewart formula given in eq 5 with a_s = 0.6 nm^2 and K = 170 nm^3 s^{-1}.

ima of the Smoluchowski curves indicate the disappearance of emulsifier micelles. This feature, however, cannot prove a micellar nucleation mechanism but rather indicates that heteroagglomeration of primary and secondary particles becomes more and more the dominating process, according to the scheme in Figure 11. As heteroagglomeration becomes more pronounced with increasing size of the secondary particles, the scheme reveals and explains by the scaled secondary particle sizes the shifting of the maximum values of dN/dt to extremely short time periods as well as the great differences in final particle size between emulsifier-containing and emulsifier-free polymerization systems. Thus, catalyzed agglomeration fills the gap still existing between these two archetypal polymerization systems.

Acknowledgment. The collaboration of K. Walther (Hüls) in obtaining reliable polymerization data is gratefully acknowledged. I am indebted to J. Lohmar (Hüls AG) for particle size data determined by electron microscopy. I thank O. Schlueter (University of Kiel) for his assistance in carrying out computerized calculations and diagrams.

Appendix. Derivation of Equation 2

Equation 2 is derived by calculating N, the final particle number, as the particle number at infinite time from eq 3. (A derivation of (3) is found in ref 10, which also reasons the form of B and C.) Equation 3 gives

$$N = \lim_{t\to\infty} C \tanh\left(\frac{Bt}{2}\right) - \frac{g}{B}\,\frac{\sinh(Bt) + Bt}{\cosh(Bt) + 1}$$
$$= C - g/B$$

Using the relations

$$B = 4\left(\frac{k_B/Tg}{6\eta W}\right)^{1/2} \qquad C = \left(\frac{3Wg\eta}{2k_BT}\right)^{1/2}$$

it is easy to see that $g/B = C/2$. That gives

$$N = C/2$$
$$= \frac{1}{2}\left(\frac{3Wg\eta}{2k_BT}\right)^{1/2}$$

This may be solved for the stability ratio W to yield eq 2

$$W = \frac{2.6k_BT}{\eta g}N^2$$

References and Notes

(1) Harkins, W. D. *J. Am. Chem. Soc.* **1947**, *69*, 1428.
(2) Smith, W. V.; Ewart, R. H. *J. Chem. Phys.* **1948**, *16*, 592.
(3) Smith, W. V.; Ewart, R. H. *J. Am. Chem. Soc.* **1948**, *70*, 3695; **1949**, *71*, 4077.
(4) Roe, C. P. *Ind. Eng. Chem.* **1968**, *60*, 20.
(5) Fitch, R. M.; Tsai, C. H. In *Polymer Colloids*; Fitch, R. M., Ed.; Plenum Press: New York, 1971; p 73.
(6) Fitch, R. M. *Br. Polym. J.* **1973**, *5*, 467.
(7) Fitch, R. M.; Shib, L.-B. *Prog. Colloid Polym. Sci.* **1975**, *56*, 1.
(8) Hansen, F. K.; Ugelstad, J. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 1953.
(9) Lichti, G.; Gilbert, R. G.; Napper, D. H. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 269.
(10) Feeney, P. J.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1984**, *17*, 2520.
(11) Feeney, P. J.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1987**, *20*, 2922.
(12) Merkel, M. P. M.S. Thesis, Lehigh University, 1982.
(13) Schlueter, H. *Adv. Chem. Ser.* **1975**, *142*, 99.
(14) Schlueter, H. *Ind. Eng. Chem. Prod. Res. Dev.* **1977**, *16*, 173.
(15) Schlueter, H.; Schreier, G. *Prog. Colloid Polym. Sci.* **1980**, *67*, 107.
(16) Schlueter, H. U.S. 3 330 795, 1967; *Chem. Abstr.* **1965**, *63*, 16589. Schlueter, H.; Scholz, B. P.; Holtrup, W.; Walther, K. EP 0 330 865, 1989.
(17) Fromherz, P. *Nachr. Chem. Tech. Lab.* **1981**, *29*, 537.
(18) Goodwin, J. W.; Hearn, J.; Ho, C. C.; Ottewill, R. H. *Colloid Polym. Sci.* **1974**, *252*, 464.
(19) Jones, M. N. *J. Colloid Interface Sci.* **1967**, *23*, 36.
(20) Schwuger, M. J. *J. Colloid Interface Sci.* **1973**, *43*, 491.
(21) Cabane, B. J. *J. Phys. Chem.* **1977**, *81*, 1639.
(22) Gerrens, H.; Koehnlein, E. *Z. Elektrochem. Ber. Bunsenges. Physik. Chem.* **1960**, *64*, 1198.
(23) Novak, R. W. *Adv. Org. Coatings Sci. Technol. Ser.* **1988**, *10*, 54.
(24) Cecik, O. S.; Kljubin, W. W.; Sacharowa, N. A. *Kautschuk i Resina* **1988**, *2*, 34.
(25) Kolthoff, I. M.; Miller, I. K. *J. Am. Chem. Soc.* **1951**, *73*, 3055. Bartholome, E.; Gerrens, H.; Herbeck, R.; Weith, H. W. *Z. Elektrochem.* **1956**, *60*, 334.
(26) La Mer, V. K.; Dinegar, H. *J. Am. Chem. Soc.* **1950**, *72*, 4847.
(27) Goodal, A. R.; Wilkinson, M. C.; Hearn, J. *J. Polym. Sci.* **1977**, *15*, 2193.

Registry No. (Acrylic acid)(butadiene)(styrene) (copolymer), 25085-39-6.