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The Preparation of Sterically Stabilized Polymer Dispersions

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Summary: The emulsion polymerizations of styrene (St) and butyl acrylate (BA) stabilized by nonionic polyoxyethylene type emulsifiers did not show the long stationary rate interval. This was discussed in terms of two opposing effects: 1) the decreased monomer concentration at the reaction loci due to the depletion of monomer droplets or depressed monomer droplet degradation and 2) the increased number of polymer particles with increasing conversion. The continuous particle nucleation is attributed to the continuous release of emulsifier from the emulsifier saturated monomer droplets and/or the presence of monomer swollen micelles (microdroplets). The limited particle flocculation operative at lower emulsifier concentrations increases the nonstationary-state polymerization. The particle agglomeration is accompanied by the increased reaction order x (N_p vs. $[E]^x$) above 0.6. The increased uniformity of monomer emulsion stabilized by Tween 20 by homogenization of monomer emulsion increased the final conversion and the polymerization rate as well. The polymerization rate vs. conversion curve of the homogenized emulsion characterized with broader stationary rate interval reminds the four rate intervals system typical for miniemulsion. The accumulation of polymer and nonionic emulsifier within the monomer phase preserves the monomer droplets up to high conversion. The decreased monomer droplet degradation rises the monomer-starved condition or the depressed transport of both monomer and emulsifier to the reaction loci.

Introduction

The accumulation of hydrophobic polymer in the monomer phase or the sonification of monomer emulsion containing a small amount of polymer increases the colloidal stability of monomer (droplets) emulsion. The depressed transfer of monomer from the stable monomer droplets to the aqueous phase and predominate location of emulsifier at the droplet surface decrease the amount of monomer and emulsifier in the aqueous phase for the micellar particle nucleation. The presence of predissolved polystyrene (hydrophobe) (ca. 0.5wt %) in the monomer phase increased the stability of (homogenized) monomer droplets (reduced monomer droplet degradation or Ostwald ripening) 1) and the extend of monomer droplet nucleation 2). The monomer droplet nucleation is a new polymerization technique which allows preparation of submicron latex particles within the range 100 nm < particle radius < 500 nm. This process involves generation of a large population of submicron monomer

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droplets in water (termed the miniemulsion) by intensive shear force with the aid of adequate emulsifier and coemulsifier (hydrophobe). The stable monomer droplets have an extremely large surface area and, therefore, they can compete effectively with the monomer-swollen micelles for oligomeric radicals generated in water. Monomer droplets may thus become the predominant loci for particle nucleation and polymerization.

The initial Ostwald ripening rate $((D_m^3)/dt/(nm^3/min))_i$ for the dodecyl methacrylate (DMA) miniemulsion stabilized by sodium dodecyl sulfate (SDS) was depressed when NP-40 (nonylphenol polyethoxylate with an average of 40 ethylene oxide units per molecule) was added 3). Furthermore, the monomer droplet saturated with NP-40 and polymer preserved the unnucleated monomer droplets up to a very high conversion in the emulsion polymerization of styrene stabilized by NP-40 alone and by the mixture of emulsifiers (NP40 and SDS) 4,5). The stationary-rate interval was found to increase with increasing fraction of nonionic emulsifier within the emulsifier (NP40 + SDS) mixture. The preserved monomer droplets at high conversion (up to ca. 95%) in polymerizations with SDS alone 6,7), mixtured SDS/NP40 emulsifiers 5) and NP 40 alone 4) are not consistent with the classical emulsion polymerization. The prolonged pre-emulsification interval was connected with the formulation of more stable and smaller monomer droplets due to accumulation of polymer (as a result of thermal polymerization) and emulsifier in the monomer phase. It was concluded that the thermal polymerization did not influence the kinetics of the styrene emulsion polymerization at temperature range 50 – 80 °C or its effect was negligible 6). The further experiments and discussion led to the conclusion that the accumulation of PSt within the monomer phase preserved monomer droplets up to high conversion 4,5,7). This is connected with the depressed transfer of monomer and emulsifier to the reaction loci. Under such conditions, the polymerisation can proceed under the monomer-starved condition or diffusion controlled regime. The formation of monodisperse polymer particles formed in the emulsion polymerisation stabilized by non-ionic emulsifier is connected with the diffusion controlled polymerisation 8,9). The low weight ratio of monomer to polymer (ca. 0.2) at ca. 30 – 40% conversion results from the polymerization proceeding under the monomer-starved condition 10).

Nonionic emulsifiers (Tweens and Tritons, [emulsifier] ≤ CMC) were capable of accelerating Ostwald ripening (OR) by facilitating the transport of oil molecules between monomer droplets 11). At the high emulsifier concentration ([emulsifier] >> CMC), however, the OR rate was decreased and the droplet size was independent of ageing time. That is, Tween 20 and 40 and Tritons are capable of accelerating ripening at relatively low concentrations, but they retard it at high concentration. Thus, the first aim of the present work is to follow the emulsion polymerization at high nonionic concentration and so to follow the effect of increased stability of monomer droplets on the polymerization behaviour.

The major thrust of this work is to study the kinetics of emulsion polymerization of butyl acrylate and styrene stabilized by relatively hydrophilic nonionic emulsifiers (Tween 20 (HLB = 16.7) and NP40 (HLB = 17.8)). The hydrophilic non-ionic emulsifier is expected to concentrate more in the aqueous phase and in the interfacial layer as well. The nonionic emulsifier partitions between the monomer and water phases. By using the high shear rate increases the droplet surface area and the amount of emulsifier located at the interfacial layer. The depressed oil solubility of emulsifier can be achieved by the accumulation of polymer within the monomer phase (polymer is incompatible with emusifier). These are supposed to increase the initial amount of nonionic emulsifier available for nucleation and stabilization. Furthermore, the increased stability (uniformity) of monomer droplets simulates the diffusion-controlled emulsion polymerization. Kinetics and colloidal parameters of the emulsion polymerization of butyl acrylate and styrene stabilized by non-ionic emulsifiers (NP 40 and Tween 20) are followed as a function of reaction conditions.

Experimental Part

Materials. Commercially available butyl acrylate (BA) and styrene (St) (Fluka) were purified by distillation under reduced pressure. Extra pure ammonium peroxodisulfate (APS, Fluka) was used as supplied. The emulsifiers used was the reagent-grade Tween 20 (Tw 20, non-ionic emulsifier, polyoxyethylene sorbitan monolaurate, provided by Serva in the form of a 97% aqueous solution, HLB = 16.7), NP40 (nonylphenol polyethoxylate with an average of 40 ethylene oxide units per molecule, HLB = 17.8) and sodium dodecyl sulfate (SDS) (Fluka). Doubly distilled water was used as a polymerization medium.

Recipe and Procedures. Batch emulsion polymerizations of BA and St were carried out at 60 °C with the recipe comprising 100 g water and 40 g monomer. The coarse as well as homogenized monomer emulsions (the homogenizer Ultra Turrax, IKA Works, USA) were used. The amounts of initiator (APS) and emulsifier (NP40 or Tw 20) varied as shown later.

The monomer conversion was determined by both the dilatometric and gravimetric methods. The particle size was determined by the light scattering method. The polymerization technique, the preparation of polymer latex for size measurements, the estimation of particle number and particle size distribution were the same as described earlier 12-15).

The coarse emulsions were prepared by dissolving emulsifier (Tw 20 or SDS) and monomer (BA or St) in water and mixed with a mechanical agitator at 400 rpm for 20 min at room temperature. The resultant coarse emulsion was homogenized by the homogenizer Ultra Turrax (IKA Works, USA) for 5 min. The average monomer droplet size of diluted homogenized ((mini)emulsion) emulsion was followed by the dynamic light scattering method as a function of ageing time. The colloidal stability of the (non-diluted) fine emulsion ((mini)emulsion) product was monitored by placing about 100 ml sample in a glass vial at 25 °C. The position of the creaming line from the bottom of the sample and the time necessary for a visible monomer phase on the top of sample to appear were then recorded.

Results and Discussion

The shelf-life

The shelf-life and the time necessary for appearance of a visible monomer phase on the top of the sample (SDS/BA/water emulsion) for the homogenized SDS/BA/water emulsion were much shorter than those for the homogenized Tween 20(Tw 20)/BA/water ((mini)emulsion) emulsion (Table 1). A visible BA phase on the top of Tw 20/BA/water sample did not appear even after three months. The diluted BA (mini)emulsions, however, underwent the monomer droplet degradation:

D_{drop}(nm)/time(min): 500/1, 600/1.5, 700/2, 700/2, 850/2.5, 900/3, 1000/4, 1050/5, 1050/6, 1000/7, 1000/8, 1000/9, 950/10

Table 1. Colloidal parameters of homogenized monomer emulsion ((mini)emulsion).a)

Run	Monomer	Emulsifier	Shelf-life	
			b)	c)
1	St	SDS	1-2 min	
2	BA	SDS	9 hr	
3	St	Tw 20	10 hr	20 s
4	BA	Tw 20	> 2 months	no separation

a) 100 g water, 40 g monomer, [Tw 20] = 1 x 10^{-3} mol.dm^{-3}; [SDS] = 10 x 10^{-3} mol.dm^{-1}; rpm = 25 000, 25 °C; b) 25 °C, c) 60 °C

The dilution is accompanied by the fast transport of ingredients from the oil phase to the interface and then to the aqueous phase and, subsequently, the external phase will be saturated with emulsifier 16).

The shelf-life for was shorter for the homogenized Tw 20/St/water emulsion 17) than that for the homogenized Tw 20/BA/water emulsion ((mini)emulsion) (Table 1). The hydrophobic St was expected to produce more stable monomer emulsion than polar BA. The results show that the reverse is true. A visible monomer phase on the top of sample (capillary) did not appear in the (mini)emulsion polymerization of BA at 60 – 80 °C. The reverse is true for the (mini)emulsion polymerization of St. Thus, the (mini)emulsion containing polar BA is stable while that containing apolar St is instable. The clouding temperature of the monomer (1.3 g)/Tw 20 (0.8 mol.dm^{-3})/water (100 g) solution was much lower for St containing solution (CP = 42 °C) than for BA containing one (CP = 62 °C). The droplet flocculation is much more pronounced in the St containing systems. The interaction between Tw 20 and monomer within the microdroplet is more pronounced with BA (salting-in effect).

Under the condition, [Tw 20] >> CMC, the droplet size was nearly independent of ageing time 18). The non-ionic emulsifier (Tw 20) is assumed to take part in a number of possible processes. First, association of Tw 20 can form colloids other than the spherical micelles at relatively high emulsifier concentration and these transport oil differently. Secondly, the nonionic emulsifiers can form multilayers around the monomer droplets, which retard the movement of oil molecules from the droplets to the surrounding aqueous phase. Third, the nonionic emulsifier can act as hydrophobe especially at high temperature. Forth, the high solubility of nonionic emulsifier in the oil phase changes the orientation of the emulsifier molecule at the interface and increases the specific surface area. Fifth, BA acts as a good coemulsifier at high emulsifier concentration 19,20) while styrene is surface-inactive.

Table 2 shows that the water/BA/Tw 20 solution after ceased shaking (ca. 30 min at 400 rpm) equilibrated to a two-phase system (at 20 – 30 °C). The upper milky phase corresponds to w/o emulsion and the lower one to the aqueous micellar solution. At temperatures 40 and 50 °C, the three-phase system appears 21). The upper phase is transparent (oil phase), medium is milky and lower one is blue coloured typical for microemulsion, At 70 – 90 °C, the lower aqueous phase (microemulsion) transforms to the milky emulsion. The volume of lower aqueous phase is constant and independent of temperature. The three-phase monomer/Tw 20/water system is transformed by a slight homogenisation (400 rpm) to milky one and so used for the polymerisation (60 °C). The initial monomer emulsion is supposed to contain the monomer swollen micelles (microdroplets) and large monomer droplets. On the contrary, the lower aqueous phase of the water/Tw 20/St solution transforms microemulsion above 60 °C.

Table 2. Phase-behavior of water/BA/Tw 20 and water/St/Tw 20 solutions. [a)]

Temp. (°C)	BA			St		
	Lower	Medium Phase	Upper	Lower	Medium Phase	Upper
20	T (8)	-	M (4)	One SM phase (13)		
30	T (8)	-	M (4)			
40	SBC (8)	M (3.5)	T (0.5)	M (6.5)	-	M (6.5)
50	BC (8)	M (3)	T (1)	M (6.5)	-	SlM (7.5)
60	SlM (8)	SM (2.5)	T (1.5)	T F(5.5)	-	SlM (7.5)
70	M (8)	SM (1.5)	T (2.5)	T (5.5)	-	BC (7.5)
80	M (8)	SM (0.5)	T (3.5)	T (5.0)	M (0.5)	BC (7.5)
90	M (8)	SM (0.5)	T (3.5)	T (4)	M (1.5)	BC (7.5)

a) 100 g water, 40 g monomer, 2 g Tw 20; T –transparent, M – milky, SlM – slightly milky (low turbidity), SM – strongly milky (high turbidity), SBC - slightly blue coloured (slightly turbid), BC – blue coloured. T – transparent with the foam on walls. The value in bracket means the volume (in arb. units).

Kinetic parameters

The conversion-time data for the emulsion polymerization of styrene (St) initiated by ammonium peroxodisulfate (APS) at different emulsifier concentrations are shown in Fig. 1. The emulsifier concentrations were much above the CMC of NP40 (2.9 x 10^{-4} mol/dm^{-3} at 25 °C) [22)]. The conversion time curves are concave without any linear portion. Furthermore, the limiting conversion appears nearly in all runs. Variations of the rate of polymerization with NP40 concentration and conversion are illustrated in Fig. 2. The three rate intervals (with a distinct Interval 2) typical for the emulsion polymerization do not appear. On the contrary, the profiles of non-stationary rate intervals appear [23,24)]. First the rate of polymerization (R_p) abruptly increases to the maximum ($R_{p,max}$) and then continuously decreases up to the final conversion.

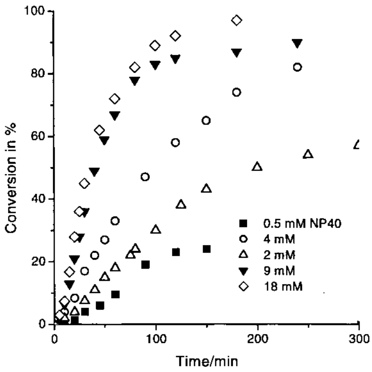

Fig. 1. Variation of monomer conversion in the emulsion polymerization of St with the reaction time and NP40 concentration. Recipe: 100 g water, 17.6 g St, 0.025 g $NaHCO_3$, [APS] = 1.4 x 10^{-3} $mol.dm^{-3}$, 60 °C.

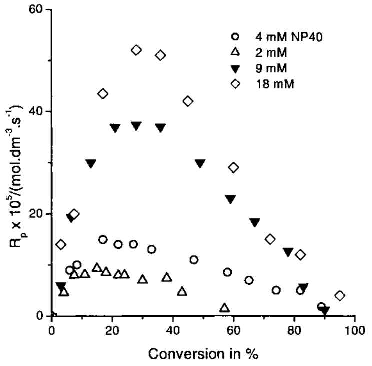

Fig. 2. Variation of the rate of polymerization in the emulsion polymerization of St with conversion and NP40 concentration. Other conditions see in the legend to Fig. 1.

According to the micellar model, the reaction order x from the relationship $R_p \propto [\text{Emulsifier}]^x$ is 0.6 [25)]. The estimated reaction order x = 0.84 (data take from Fig. 2) shows that $R_{p,max}$ rises stronger than the model prediction. The increased stability of polymer particles (decreased limited particle flocculation) with increasing NP 40 concentration is responsible for the increased rate of polymerisation. The formation of larger particles or particle agglomerates typical for the runs with low emulsifier concentration decreases the polymerisation rate. The thick close packed interfacial layer typical for the large amount of emulsifier provides the stable polymer particles and fast polymerization. Furthermore, the exit/entry kinetic model of the emulsion polymerization of styrene stabilized by poly(oxyethylene)- nonylphenol type emulsifier gave the entry and exit rate coefficients an order of magnitude smaller than those for electrostatic - stabilized particles of the same size

[26,27]. The longer residence time of radicals within the "hairy" layer particles could increase the propagation (pseudo-living polymerization) step.

The stationary-rate interval (containing the rate shoulder at ca. 60-70 %) conversion appeared in the emulsion polymerisation of styrene with prolonged pre-emulsification interval (Fig. 3). The dependence reminds the four-rate intervals curve typical for the miniemulsion polymerisation of styrene [28]. The first maximal rate (at ca. 20% conversion) was attributed to the formation and growth of polymer particles and the second maximal rate (at ca. 60-70% conversion) to the gel effect. The two maximal rates were also observed in the emulsion polymerization of styrene stabilized by NP40 with the prolonged pre-emulsification period (ca 2h) at 70 °C [4]. The preserved monomer droplets (increased stability of monomer droplets) with a prolonged emulsification period increased the width of stationary-rate interval and the final conversion. The presence of stable monomer droplets was connected with the decreased weight ratio of monomer to polymer in the growing polymer particles and the diffusion controlled polymerisation [10]. The depressed transfer of monomer from monomer droplets to the reaction loci can be connected with the increased polymer fraction in the monomer/polymer particles and the gel effect at ca. 60-70%.

The conversion-time data for the emulsion polymerization of BA initiated by APS at different Tw 20 concentrations are shown in Fig. 4. The emulsifier concentrations were much above the CMC of Tw 20 (8×10^{-5} mol.dm^{-3}). The conversion curves are concave without any linear portions and the final conversion are much below 100%. The limiting conversion observed is nearly independent of Tw 20 concentration. The electrosteric (or electrostatic) stabilization is more pronounced at low emulsifier concentration while the steric one at high emulsifier concentration. The surface charged oligomeric radicals derived from APS form the electrical double layer around the particle and so take part in the (electrostatic or electrosteric) particle stabilization (at low emulsifier concentration). At high emulsifier concentration the role of charged groups is depressed and the charged ions are dispersed within the thick interfacial layer. The limiting conversion is attributed to the consumption of initiator and/or immobilization of monomer and initiator within the (non)micellar aggregates. The slight consumption of APS at 60 °C [29], however, excludes the initiator consumption as a possible explanation for the strong decrease of polymerization at high conversion. Table 3 shows that the particle agglomeration should be responsible for the limited conversion or the slow polymerization at high conversion. The immobilization of monomer, emulsifier and initiator within the particle agglomerates depresses the polymer growth. Furthermore, the low monomer concentration at high conversion depresses the aqueous phase polymerization and the formation of surface active radicals able to enter the polymer particles.

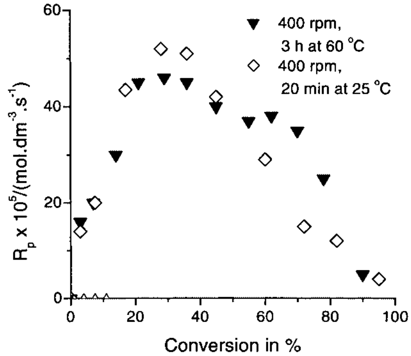

Fig. 3. Variation of the rate of polymerization in the emulsion polymerization of St with the degree of homogenization and conversion. Recipe: 100 g water, 17.6 g St, 0.025 g $NaHCO_3$, [NP40] = 1.8 x 10^{-2} mol.dm^{-3}, [APS] = 1.4 x 10^{-3} mol.dm^{-3}, 60 °C.

Variations of the rate of emulsion polymerization with Tw 20 concentration and conversion are illustrated in Fig. 5. The three rate intervals (with a distinct Interval 2) typical for the emulsion polymerization did not appear. On the contrary, the profiles of non-stationary rate intervals, typical for the microemulsion, miniemulsion or precipitated polymerization appeared [23,24]. The reaction order x = 0.88 (Fig. 5) shows that $R_{p,max}$ rises stronger than the model prediction. The deviation from model is caused by the limited particle flocculation at low emulsifier concentration (see the colloidal parameters).

Table 3. Variation of kinetic and colloidal parameters of emulsion and (mini)emulsion polymerization of BA with Tween 20 concentration.[a)]

[Tw 20] x10^2 (mol.dm^{-3})		$R_{p,max}$ x 10^4 (mol.dm^{-3}.s^{-1})		D (nm)		N_p x 10^{-16} /dm^3		Con.fin (%)		Coagulum (wt.%)	
Initiator		1)	2)	1)	2)	1)	2)	1)	2)	1)	2)
APS	0.49	3.0	15	500	330	0.2	1.7	58	86	30	Traces
APS	0.98	4.4	-	300	-	1.5	-	59		25	-
APS	1.96	10.5	18	170	225	7.8	5.4	63	88	10	0

a) Recipe: 100 g water, 40 g BA, 0.023 g $NaHCO_3$, 60 °C, [APS] = 1 x 10^{-3} mol.dm^{-3};
b) Total coagulation, 1) 400 rpm, 20 min, 2) 25 000 rpm, 10 min.

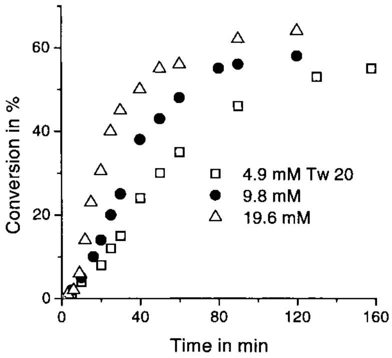

Fig. 4. Variation of monomer conversion in the emulsion polymerization of BA initiated by APS with the reaction time and Tween 20 (Tw 20) concentration. Recipe: 100 g water, 40 g BA, 0.025 g $NaHCO_3$, [APS] = 1 x 10^{-3} $mol.dm^{-3}$., 60 °C.

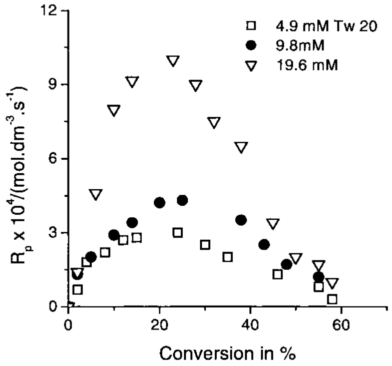

Fig. 5. Variation of the rate of emulsion polymerization of BA initiated by APS with conversion and Tween 20 concentration. Other conditions see in the legend to Fig. 4.

Variations of the rate of emulsion and (mini)emulsion polymerization with Tw 20 concentration and conversion are illustrated in Fig. 6 and Table 3. The direct result of homogenization of monomer emulsion is the increased final conversion and depressed coagulation (Table 3). Interval 2 was overlapped with the maximal rate at low conversion. The profiles of non-stationary rate intervals are more pronounced [23,24)]. The homogenization of BA/Tw 20 aqueous solution increased both the colloidal stability of polymer latex and the rate of polymerization (Table 3). Fig. 6 shows that the rate of polymerization (R_p) abruptly increased with conversion to the first maximum ($R_{p,max1}$) and then decreased with conversion and leveled off or reached the second maximal rate ($R_{p,max2}$). The first maximal rate (at ca. 10% conversion) can be attributed to the increased formation of polymer particles, the polymerization proceeding under monomer-saturated conditions and the presence of peroxide content in Tw 20 (the accumulation of peroxide groups in Tw 20 as a result of interaction between APS derived radicals or oxygen with Tw 20). The rate of blank emulsion polymerization (without APS) of BA is ca. by one order in magnitude lower that that initiated with APS. The degradable monomer droplets (the homogenized upper monomer phase, see Table 2) saturate the reaction loci with monomer at low conversion. The depletion of degradable monomer droplets decreased the monomer concentration at the reaction loci and so the rate of polymerisation. The diffusion controlled regime is assumed to be operative after the depletion of degradable monomer droplets. The present of monomer-saturated micelles (microdroplets) keeps the constant rate up to ca. 50% conversion. In the terms of the four-rate interval approach (miniemulsion) the second maximal rate can be attributed to the gel effect $^{28)}$. In the miniemulsion polymerisation of styrene the first rate maximum was located at ca. 20% conversion and the second one at ca. 60% conversion. The two maximal rates were also observed in the emulsion polymerization of styrene stabilized by NP40 with the prolonged pre-emulsifier period $^{4)}$. The polymerization proceeded under the monomer-starved condition even though the monomer droplets were preserved up to ca. 95% conversion. The (mini)emulsion polymerization of BA deviates from the classical miniemulsion polymerization or the polymerization with prolonged pre-emulsification period in the location of maximal rates, that is, the first maximal rate is located at ca. 10% conversion and the second one (a rate shoulder or the constant rate) at ca. 40% conversion. The reaction order x = 0.57 ($R_{p,max,1}$ vs. [Tw 20]^x, data taken from Fig. 6) is in a good agreement with the micelle model (x = 0.6). The trend of second maximal rates (the constant rate), however, deviates from the micellar model. The slight dependence of $R_{p,max2}$ on [Tw 20] (the reaction order x = 0.17) could result from the depressed transfer of both monomer and emulsifier from the monomer droplets to the reaction loci (diffusion controlled regime) (Table 4). The effect of gel effect on the

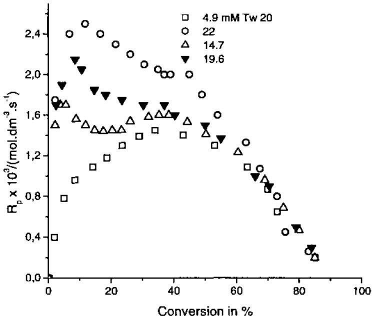

Fig. 6. Variation of the rate of polymerization with conversion and Tween 20 concentration in the (mini)emulsion polymerization of BA initiated by APS. Recipe: 100 g water, 40 g BA, 0.025 g $NaHCO_3$, [APS] = 1 x 10^{-3} mol.dm^{-3}, 60 °C.

polymerization process is not ruled out. The onset of gel effect in the bulk polymerization of alkyl (meth)acrylate appears at ca. 30% conversion 30). The gel effect is known to depress the variation of the polymerisation rate with increasing concentration of reactant.

Table 4. Variation of kinetic and colloidal parameters of (mini)emulsion polymerization of BA with Tw 20 concentration.[a]

$[Tw\ 20] \times 10^2$ (mol.dm^{-3})	$R_{p,max} \times 10^3$ (mol.dm^{-3}.s^{-1})		D (nm)		$N_p \times 10^{16}$ /dm^3	Con.$_{fin}$ (%)
	1)	2)	3)	4)	3)	
0.49	1.0	1.5	330	450 ± 50	1.7	86
1.47	1.7	1.6	320	430 ± 50	1.8	87
1.96	2.1	1.8	225	400 ± 50	5.4	88
2.2	2.5	2.0	210	380 ± 50	6.4	86

a) 100 g water, 40 g BA (= 3.1 mol.dm^{-3}), 60 °C, [APS] = 1 x 10^{-3} mol.dm^{-3}, 1) $R_{p,max1}$, 2) $R_{p,max2}$, 3) Final size and number of polymer particles, 4) Initial size of monomer droplets – extrapolated to zero aging time.

Colloidal parameters.

Variation of the average hydrodynamic particle size in the emulsion polymerisation of St stabilized by NP40 on conversion is described by a curve with a minimum at ca. 20 % conversion (Fig. 7). After the start of polymerization, the large particles appeared. As a polymerization proceeded the strong decrease in the average hydrodynamic particle size was observed. The abrupt decrease in the average particle size results from the continuous particle nucleation. Furthermore, the large highly-monomer swollen particles disappeared already at 20 % conversion. The dialysis of the initial polymer latex samples (at low conversion) strongly decreased the particle size from D ≈ 500 nm to D ≈ 100 nm. The large highly-

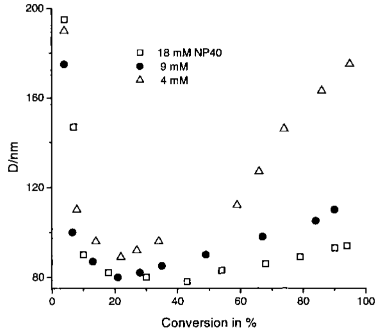

Fig. 7. Variation of the average hydrodynamic particle diameter (D) in the emulsion polymerization of St with NP40 concentration and conversion. Other conditions see in the legend to Fig. 1.

monomer swollen particles shrank during the polymerization. The particle size again increased above ca. 20% conversion and the increase wass inversely proportional to the emulsifier concentration. The strong increase in the particle size with conversion for the run with [Tw 20] = 4 mM can be attributed to the limited flocculation of less stable polymer particles.

The dependence of the particle number vs. conversion strongly varies with the emulsifier concentration (Fig. 8). At 18 mM of NP40, the number of polymer particles (N_p) increased nearly up to final conversion. This can be attributed to the continuous release of emulsifier from the monomer droplets and/or the presence of monomer-swollen micelles (microdroplets) during the whole polymerization. The microdroplets (slightly turbid lower aqueous phase, Table 2) are supposed to take part in the particle nucleation up to high conversion. The decreased particle concentration beyond ca. 40% or 70% with 4 mM or 9 mM emulsifier results from the limited particle flocculation (the lack of free emulsifier initiates the particle agglomeration). The high oil solubility of NP40 decreases the amount of emulsifier available for particle stabilization and the micellar fraction is much smaller than that initially charged into the system. The degree of particle flocculation is supposed to be closely related to the dependence of N_p on [Emulsifier]. The values of the reaction order x ($\log N_p \propto \log [\text{Emulsifier}]^x$) 0.61 and 1.3 estimated at 20-30% conversion (without particle agglomeration) and final conversion (with limited particle flocculation in the runs with a small amount of emulsifier) result from the different particle stability (data taken from Fig. 8). The reaction order $x = 0.61$ estimated before the onset of the particle agglomeration agrees very well the micellar model. On the contrary, the reaction order $x = 1.3$ estimated from the particle number data within the limited particle agglomeration range deviates from the micellar model. The reaction order x can be taken as a measure of particle agglomeration. For example, the limited agglomeration of polymer particles stabilized by SDS/NP40 mixed emulsifiers was connected with the reaction order $x = 1.6$ 31). The increased reaction order was estimated when the amount of NP40 was greater than 60 wt%, and the steric stabilization effect provided by NP40 was not sufficient to prevent latex particles from flocculation. The large reaction order $x = 2.66$ estimated in the emulsion polymerisation of styrene stabilized by non-ionic emulsifier emulphogene BC-84C was also accompanied with the limited particle flocculation 9).

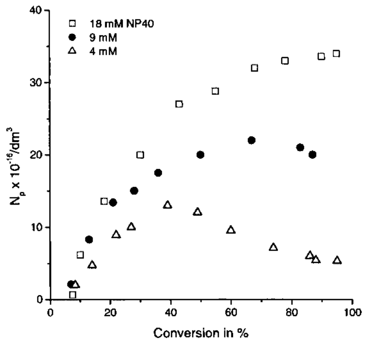

Fig. 8. Variation of the particle number (N_p) in the emulsion polymerization of St with NP40 concentration and conversion. Other conditions see in the legend to Fig. 1.

The colloidal stability of polymer particle can be related to the conformation of PEO chains at the particle surface. The conformation of PEO chains of nonionic emulsifier at high coverage (emulsifier concentration) is extended, making a packing monolayer, impeding EO-surface interactions. At low coverage (low emulsifier concentration), when the flexibility of the EO chains is high, these contacts may occur [32]. A direct consequence of the increased emulsifier concentration will be the change in the emulsifier layer configuration, which passes from extended to flat. The particle flocculation via the extended surface PEO chains (bridging flocculation mechanism) is more pronounced at flat emulsifier layer configuration [33].

The increased pre-emulsification interval was accompanied with the increased PSt particle size and levelling off the particle number at conversion ca. 50 % (Figs. 9 and 10). The increased uniformity (stability) of monomer droplets by the accumulation of small amount of

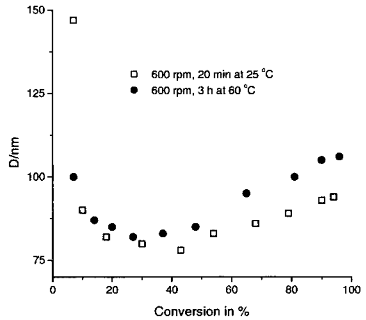

Fig. 9. Variation of the average hydrodynamic particle diameter (D) in the emulsion polymerization of St with degree of homogenisation and conversion. Other conditions see in the legend to Fig. 3.

PSt in the monomer phase caused by the thermal polymerisation increased the particle size (decreased the particle number) [5,10]. This differs from the classical emulsion polymerisation where the number of polymer particles increased up to the final conversion. The increased consumption of free emulsifier decreased the amount of emulsifier available for particle nucleation. The similar behaviour was observed in the emulsion polymerisation of styrene with NP40 alone or NP40/SDS mixed emulsifiers where the particle number increased up to ca 40% conversion and then levelled off[4,5].

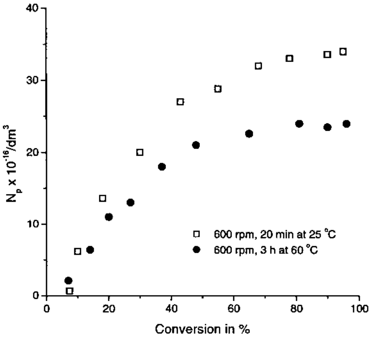

Fig. 10. Variation of the particle number (N_P) in the emulsion polymerization of St with the degree of homogenization and conversion. Other conditions see in the legend to Fig. 3.

The dependence of the average hydrodynamic particle size vs. conversion in the emulsion polymerisation of BA stabilized by Tw 20 is described by the curve with minimum at ca. 10% conversion (Fig. 11). The large polymer particles were formed after the start of polymerisation. The average particle size strongly decreased with conversion, reached the minimum at ca. 10% conversion and then again increased. The strong increase in the particle size beyond the particle size minimum is ascribed to the particle flocculation that is inversely proportional to the emulsifier concentration. At 19.6 mM of Tw 20, N_p increased up to the

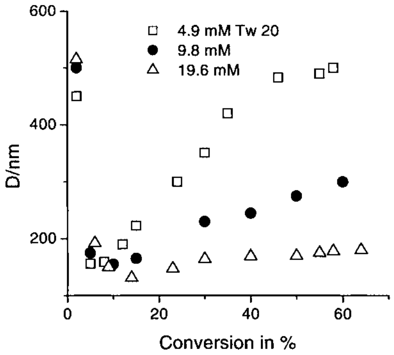

Fig. 11. Variation of the average particle diameter (D) in the emulsion polymerization of BA with Tw 20 concentration and conversion. Other conditions see in the legend to Fig. 4.

final conversion and the increase was much more pronounced at low conversion (Fig. 12). The initial strong increase in the particle number paralleled with the degradation of emulsifier-saturated monomer droplets. At 4.9 and 9.8 mM of Tw 20, the dependence of the particle number vs. conversion was described by a curve with a maximum at ca. 7% and 15% conversion, respectively. The decreased particle rate formation (or the increased particle flocculation) results from the lack of free emulsifier. The similar results were obtained in the emulsion polymerisation of styrene stabilized by NP40 (Fig. 8).

The phase behavior data (Table 2) indicate that there are two sources of emulsifier available for the particle nucleation and stabilization: 1) the large emulsifier saturated monomer droplets (formed by homogenization of upper monomer phase) and 2) the monomer-saturated micelles (microdroplets, the lower microemulsion phase).

The colloidal stability of Tw 20/BA emulsion, however, strongly increased with homogenization (Table 3). The hydrodynamic diameter of polymer particles in the (mini)emulsion polymerisation of BA continuously increased with conversion and the number of particles increased up to ca. 40% conversion and then levelled off (Table 5). This behavior is similar to that observed in the emulsion polymerisation with prolonged pre-emulsification period (Fig. 10) [4,5] and differs from the classical emulsion polymerisation where the number of polymer particles increased up to the final conversion (Fig. 12). The increased consumption of free emulsifier leads to the particle nucleation up to ca. 40% conversion. The depletion of degradable monomer droplets decreases the critical amount of emulsifier necessary for the particle nucleation and the released emulsifier is preferentially adsorbed by

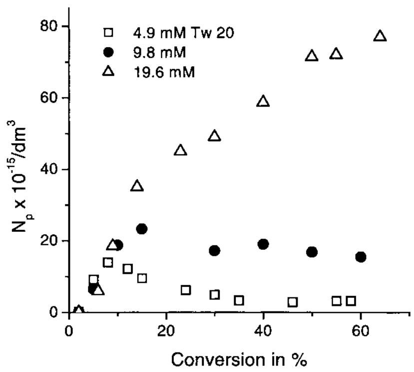

Fig. 12. Variation of the particle number (N_p) in the emulsion polymerization of BA with Tw 20 concentration and conversion. Other conditions see in the legend to Fig. 4.

the growing particles. The final number of polymer particles ca. 5 x 10^{16}/dm^3 (Fig. 12, 14.7 mM of Tw 20) for the CE polymerisation of BA is larger than $N_{p,mini}$ = 1.8 x 10^{16}/dm^3 for the (mini)emulsion polymerisation of BA (Table 5). In the latter, the increased fraction of buried emulsifier within the polymer particles formed by the nucleation of emulsifier-saturated monomer droplets could decrease the amount of emulsifier for particle nucleation and stabilization.

Table 5. Colloidal parameter of (mini)emulsion polymerisation of BA. [a)]

Conv. (%)	D (nm)	N_p x 10^{-16} /dm^3	a) Recipe: 100 g water, 40 g BA, 0.025 g $NaHCO_3$, [APS] = 1 x 10^{-3} mol.dm^{-3},
8	190	0.8	60 °C, [Tw 20] = 14.7 x 10^{-3} mol.dm^{-3}.
21	220	1.4	
40	250	1.8	
50	270	1.75	
69	300	1.8	
85	320	1.8	

St (mini)emulsions (homogenized water/Tw 20/St solution) as well as polymer latexes were unstable when the reaction mixture contained a large amount of styrene (100 g water and 40 g St). However, the emulsion polymerisation carried out under reaction conditions summarized in Table 6 (a smaller amount of St) produced stable polymer latexes [17)]. The slightly homogenized monomer emulsion (400 rpm, 25 °C, stirring time = 20 min) was unstable and separated into two phases after ceased stirring: upper monomer phase and lower

Table 6. Colloidal and kinetic parameter of emulsion polymerisation of styrene. [a)]

Conv. (%)	D (nm)	N_p.10^{-16} /dm^3	$R_{p,max}$ x 10^4 (mol.dm^{-3}.s^{-1})	a) Recipe: 150 g water, 15g St, 0.025 g $NaHCO_3$, [APS] = 1 x 10^{-3} mol.dm^{-3},
1	480			60 °C, [Tw 20] = 40 x 10^3 mol.dm^{-3}.
3	340			
8	220	0.02	1.0	
18	160	0.6		
24	100	4	6.8	
34	70	20	8.7	
50	60	50	4.0	
80	55	80	0.5	
96	55	100		

o/w milky emulsion. When the St/Tw 20 aqueous solution was heated to 60 °C (ceased stirring), the system also equilibrated to the two phases. The blue coloured lower phase reminds microemulsion. This indicates that the emulsion polymerization of St at 60 °C (Table 6) proceeds in the presence of large unstable monomer droplets and stable microdroplets. Table 6 shows that the large particle appear after the start of polymerisation. Then the average particle size strongly decreased and the initial milky reaction mixture was continuously transformed to semitransparent one. The strong initial increase in turbidity was also observed in the microemulsion polymerisations 23,34,35). The formation of large monomer/polymer (highly monomer-swollen) particles was attributed to the heterocoagulation of unstable polymer particles and monomer droplets 36,37). This was reflected by an increased fluorescence emission intensity ratio (monomer to excimer) and the presence of blue dye in the polymer particles formed at the beginning of polymerization 17,37). The large polymer particles, however, were not observed by TEM. The initially formed large particles are highly monomer-swollen polymer particles which serve as a monomer reservoir and so saturate the reaction loci and microdroplets as well with monomer and emulsifier 17,36,37). The degradation of large monomer droplets and highly monomer-swollen particles and the presence of microdroplets are accompanied with an abrupt increase in the initial rates of polymerisation and particle nucleation.

The number of polymer particles continuously increased with conversion and the increase was more pronounced at low conversion (Table 6). In the microemulsion polymerization N_p increased with a constant rate up to the final conversion 23,35). In the miniemulsion polymerization N_p increased up to ca. 40 - 50% conversion 24). The continuous nucleation is supposed to result from the continuous release of non-ionic emulsifier from the monomer droplets and the present of monomer-swollen micelles (microdroplets). The depletion of large monomer droplets (ca. at 20-30% conversion) led to the transformation of the milky system to the semitransparent. The depletion of large unstable monomer droplets (resulted from homogenized upper styrene phase, Table 2) decreased the amount of free emulsifier in the aqueous phase paralleled with the lowered particle nucleation rate.

Conclusion

The emulsion polymerizations of styrene (St) and butyl acrylate (BA) stabilized by nonionic emulsifiers (Tween 20 and NP40) deviate from the classical micellar model, that is, the three rate intervals typical for the emulsion polymerization did not appear. This is discussed in terms of two opposing events; 1) the decreased monomer concentration at the reaction loci after the depletion of free monomer droplets or decreased degradation of monomer droplets and 2) the continuous particle nucleation up to high conversion. The continuous particle nucleation up to high conversion is attributed to the release of emulsifier from the shrinking monomer droplets and the presence of monomer-swollen micelles (microdroplets) as well. The participation of microdroplets in the particle nucleation results from the phase behavior of monomer/Tw 20/water solutions. The large monomer droplets (homogenized upper monomer phase of the monomer/Tw 20/water solution) serve as a reservoir of monomer and emulsifier. Microdroplets (lower phase) are supposed to take part in the particle nucleation (the large surface area). The reaction order x close to 0.6 (N_p vs. $[E]^x$) indicates the formation of stable polymer latexes. The limited particle agglomeration at lower emulsifier concentration increases the reaction order x above 0.6. The homogenization of monomer emulsion increased the polymerization rate, the final conversion, the length of particle nucleation and the uniformity of polymer latexes.

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