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A Contribution to the Semicontinuous Emulsion Polymerization

III. Particle Formation and Particle Size

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SUMMARY:

Semicontinuous emulsion copolymerization of butyl methacrylate and butyl acrylate with a monomer emulsion feed has been investigated. The distribution of a constant amount of anionic emulsifier between the initial reactor charge and the emulsion of monomers was varied. The surface tension during the feeding of the monomer emulsion as well as the size distribution and average particle size in the final latices were measured. It was found, that the distribution of emulsifier affected the mechanism of the particle growth and the final particle size. At a high content of emulsifier in the initial reactor charge a large number of small particles appeared, which underwent extensive limited flocculation during the later stages of polymerization. The extent of the flocculation was controlled by the overall amount of emulsifier. In case of a very low content of emulsifier in the initial reactor charge no flocculation occured and even a nucleation of new particles took place towards the end of the monomer emulsion feeding.

ZUSAMMENFASSUNG:

Es wurde die semikontinuierliche Copolymerisation von Butylmethacrylat/Butylacrylat in Emulsion bei allmählichem Zufluß einer Monomer-Emulsion untersucht. Die Verteilung einer konstanten Menge des anionischen Emulgators zwischen dem Anfangsansatz im Reaktor und der zulaufenden Monomeremulsion wurde variiert. Die Oberflächenspannung während der Zugabe der Monomeremulsion sowie die Größenverteilung und die Durchschnittsgröße der Partikel in den hergestellten Latices wurden gemessen. Es wurde gefunden, daß die Verteilung des Emulgators den Mechanismus des Partikelwachstums und die Endgröße der Partikel beeinflußt. Bei hohem Gehalt an Emulgator im Ausgangsansatz des Reaktors bildeten sich viele kleine Partikel, die in späteren Polymerisationsphasen stark, aber im Umfang beschränkt, agglomerierten. Der Bereich der Agglomeration wurde durch die Gesamtmenge des Emulgators bestimmt. Im Falle eines sehr kleinen Gehalts an Emulgator im Ausgangsansatz kam es zu keiner Agglomeration, und es wurde sogar die Entstehung neuer Partikel am Ende der allmählichen Zugabe der Monomeremulsion beobachtet.

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Introduction

In previous papers[1,2] the effect of polymerization conditions on the semicontinuous emulsion copolymerization of butyl methacrylate (BMA) and butyl acrylate (BA) was studied and the utilization of the steady state copolymerization in the reactivity ratios calculation were described. This paper deals with the possibility of regulating the particle sizes in the final latex.

Butyl methacrylate and butyl acrylate are water-insoluble monomers. Thus, according to the Harkins-Smith-Ewart theory[3,4] the micellar nucleation of particles is expected. In the case of a batch polymerization, the early stage of the polymerization determines the final number of particles. In this interval the emulsifier is present in the micellar form and a nucleation of new particles proceeds. The surface of a growing particle remains saturated with emulsifier and the area per molecule of emulsifier is the same on the micelle and particle surfaces. The micellar emulsifier is either adsorbed on the growing polymer particles, or it becomes nonmicellar when a micelle absorbs a radical to become a particle. When all emulsifier is adsorbed on the particles, the micelles disappear and the particle nucleation stops. At the initial concentrations normally employed in the preparation of approximately 50 per cent polymer dispersions this occurs usually after between 10 and 20 per cent of the total monomer have been converted into the polymer. The disappearance of the micellar emulsifier causes an increase of the surface tension.

If N_t is the number of particles per cm^3 of water at a time t, the constant S is the surface area (in cm^2) of emulsifier molecules present in a cm^3 of water and A_t is the total surface of all particles in a cm^3 of water at the time t, the nucleation velocity may be expressed[5] as $dN_t/dt \sim 1 - A_t/S$. It is evident, that the particle nucleation proceeds only if $A_t < S$.

In case of the semicontinuous emulsion polymerization with a monomer feed, when all the emulsifier is charged into the reactor, the value of S is constant and the particles form during the preparation of the seed latex[6]. In this interval of polymerization $A_t > S$ is usually reached and no new particles appear during the monomer feeding. When the polymerization is run without the seed latex formation, a great number of small particles is produced in its early stage, which flocculate[7] during the following polymerization.

When monomers are fed in the form of a water emulsion, a different situation arises. In such a case the emulsifier is fed into the reactor simultaneously with the monomers and, consequently, the value of S is not constant.

2

Gerrens[6] found, that the particle nucleation during the feeding of monomer emulsion is affected by the preperiod as well as by the feeding rate.

In this paper particle size and particle formation in a special case of semicontinuous emulsion polymerization with a monomer emulsion feed was studied. A part of water and emulsifier were charged into the reactor and the monomers were fed into the reactor in the form of a water emulsion without preperiod, i.e. without the preparation of seed latex. The effects of the total amount of emulsifier and its distribution between the reactor charge and the emulsion were observed.

Experimental

The polymerizations were run under alkaline conditions in a nitrogen atmosphere, in the presence of an anionic emulsifier Etoxon EPA and the persulfate/metabisulfite initiating system. The equipment described in a previous paper[1] was used. 200 g water, 4 g sodium metabisulfite, 5 g ammonia and a portion of the total amount of emulsifier were charged into the polymerization reactor. After reaching 70 °C, a monomer emulsion containing 800 g monomers, 500 g water, 4 g ammonium persulfate, 25 g ammonia and the remaining portion of emulsifier was added at a constant rate during about 2 hrs. The weight ratio BMA/BA/acrylic acid was 79/19/2.

Butyl methacrylate from VCHZ Synthesia Kolín was stabilised by 15 ppm of monomethyl ether of hydroquinone, butyl acrylate and acrylic acid from BASF were used as supplied. Etoxon EPA (sodium alkylpolyoxyethylene sulfate) supplied by Spolek pro chemickou a hutní výrobu Ústí nad Labem, ammonium persulfate p.a., sodium metabisulfite p.a., ammonia 25% p.a. supplied by Lachema Brno and demineralised water were used.

Surface tension was evaluated by the stalagmometric method and the relative polymerization rate was calculated from the temperature changes in a thermally insulated reactor during the initial period of polymerization[1,8]. Particle sizes of the final latices were measured by electron microscopy.

Results and Discussion

In the polymerization method investigated, the polymerization rate (R_p) at the early stages is strongly affected by the amount of surfactant in the initial reactor charge as is shown in Fig. 1. For the two monomers used $R_p \sim N$ is valid. Consequently it may be stated that the number of particles formed at the beginning is proportional to the amount of emulsifier charged into the reactor. Hence, at a constant amount of emulsifier, the initial number of particles will be determined by the distribution ratio of emulsifier between the initial reactor charge and the monomer emulsion feed. This ratio will be characterized by R/E.
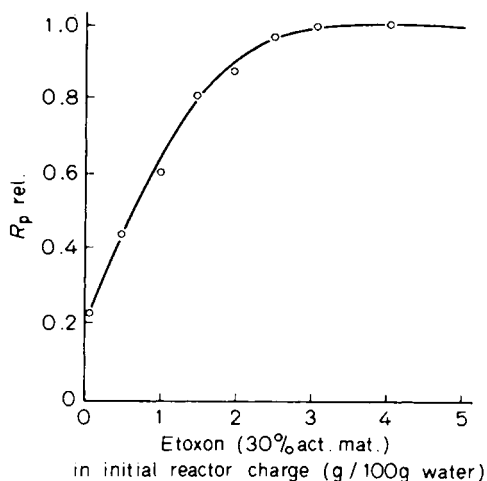
Fig. 1. Relative polymerization rate in relation to the content of emulsifier in the initial reactor charge. Emulsifier Etoxon EPA (100 % active matter) in monomer emulsion feed: 1 wt.-% related to monomers.

Surface Tension During the Feeding of the Monomer Emulsion

The surface tension of the polymerizing system during the feeding of the monomer emulsion was measured in experiments, where 1 wt.-% of surfactant (with regard to monomers) was used. With various R/E ratios, the surface tension changed as shown in Fig. 2*. If a high amount of emulsifier is present in the initial reactor charge, e.g. R/E = 75/25, 50/50 or 25/75, the initial surface tension value is about 30 dyn/cm. This value corresponds to the presence of micellàr emulsifier**. Soon after the feeding of the monomer emulsion has started, the surface tension increases and remains in the region of 47—50 dyn/cm. This development of the surface tension illustrates, that a constant saturation of the particles surface is kept during the later stages of polymerization.

Another limiting case was found at the ratio R/E = 0/100. In this case, the surface tension decreases from values over 60 dyn/cm to a value close

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* The found values of the surface tension were slightly increased at higher solid content, apparently due to the film formation on the drop surface.

** The critical micellar concentration of Etoxon EPA at 70°C was 1.85 g/1000 ml as found by conductivity measurements.
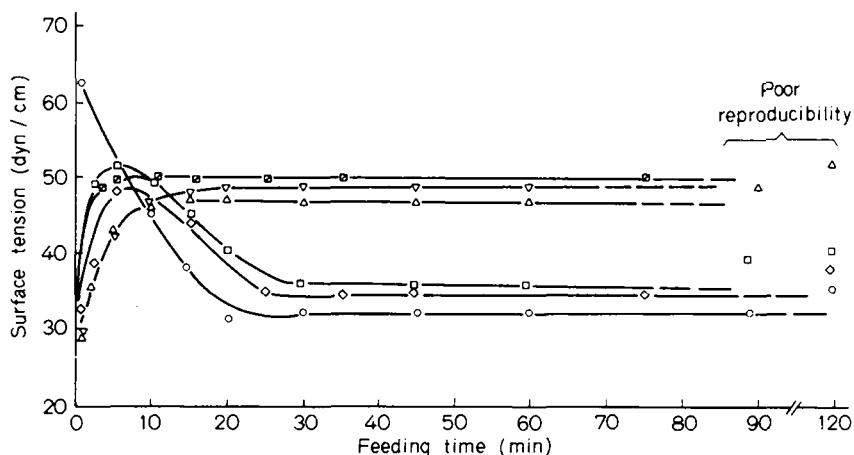
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Fig. 2. Change of surface tension during the feeding of monomer emulsion in relation
to the distribution of emulsifier between the initial reactor charge and monomer
emulsion. R/E ratios: ○ 0/100, ◇ 1/99, □ 5/95, ▨ 25/75, ▽ 50/50, △ 75/25.
Total amount of emulsifier: 1 wt.-% related to monomers.

to 30 dyn/cm. The low surface tension during the polymerization indicates
the presence of emulsifier in the micellar form. Thus, the nucleation of new
particles may be expected.

Between the two above mentioned limiting cases R/E ratios exist at which
the emulsifier concentration in the initial reactor charge is close to critical
mizell concentration (CMC), e. g. ratios R/E = 1/99 or 5/95. At such a distribu-
tion the surface tension sharply increases at the beginning, but decreases
later again. It is possible to suppose, that the number of particles formed
at the beginning of the polymerization is not too large and the relatively
high amount of emulsifier fed into the reactor facilitates the surface saturation
of the growing particles. It may be expected, that no apparent flocculation
occurs at those distributions. The nucleation of new particles at later stages,
however, cannot be excluded.

Particle Size

The dependence of the final particle sizes on the R/E ratios is shown
in Fig. 3. The particle sizes 0.22 ± 0.02 μm were found for R/E over 15/85
independently of the absolute value of R/E distribution ratio. This indicates,

5

that a large number of primary particles subsequently undergo an extensive limited flocculation. Electrostatic repulsive forces are assumed to be essential in the stabilization of primary particles. Flocculation, then, will occur until a critical surface potential is formed which effectively prevents further flocculation[9]. Consequently, the flocculation of particles is controlled by an immediate concentration of emulsifier present. It occurs at a stage, where the total surface area of the particles becomes so small, that the amount of emulsifier present just provides the required stability. Similar results have been obtained in vinyl acetate and VV 911* copolymerization[10].

The particle flocculation is a random process. It is evident from the identical particle size distributions of latices prepared in the region R/E above 15/85. The average particle sizes at those emulsifier distributions are largely independent of polymerization conditions. For example at R/E = 25/75 and feeding times from 60 to 132 min invariably $\bar{d} = 0.23 \pm 0.02\,\mu m$ were found. The same average particle diameters were obtained for R/E = 25/75, feeding time approximately 120 min and polymerization temperatures from 50 to 80 °C.
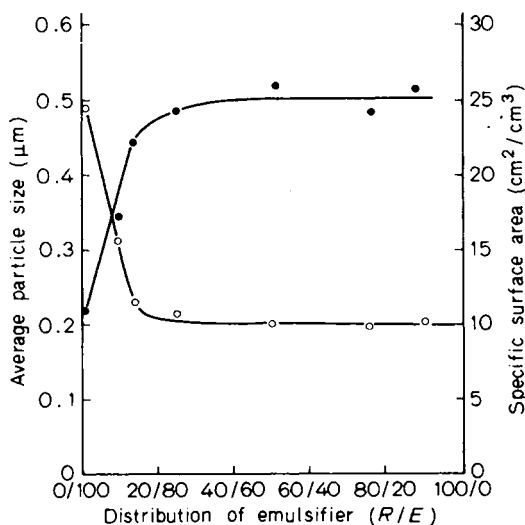

Fig. 3.   Average particle size ○ and specific surface area ● in relation to the distribution of emulsifier between the initial reactor charge and monomer emulsion. Total amount of emulsifier: 1 wt.-% related to monomers.

* Shell registered trade mark, vinyl esters of branched carboxylic acids (Versatic) containing 9–11 carbon atoms.

Larger particle sizes were found for R/E distributions lower than 15/85. This corresponds to the change in the surface tension. In this region of R/E distributions a poorer reproducibility was found, as results from the distribution curves of particle sizes in Fig. 4. For example, the average diameters from 0.33 to 0.45 μm were found at R/E = 9/91. This indicates a high sensibility of the system to the polymerization conditions. Especially, small variations in the induction period will affect the number of primary particles, because the emulsifier is added simultaneously with the monomers.
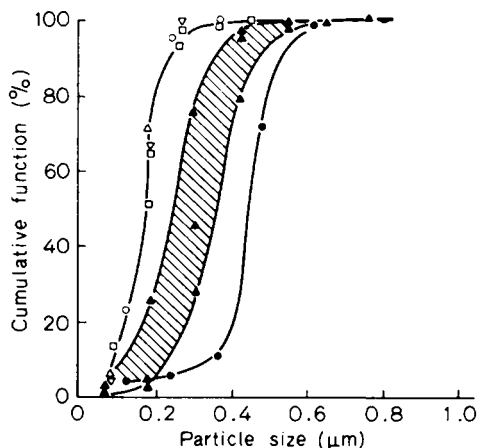

Fig. 4. Cumulative particle size distributions in relation to the distribution of emulsifier between the initial reactor charge and monomer emulsion. R/E ratios: ● 0/100, ▲ 9/91, ○ 25/75, △ 50/50, □ 75/25, ▽ 87.5/12.5. Total amount of emulsifier: 1 wt.-% related to monomers.

In the experiment with R/E = 0/100 new particles were formed towards the end of the monomer emulsion feeding as shown by the double-peaked particle size distribution in Fig. 5. This phenomena is in good agreement with the surface tension course and with the fact, that the total surface of particles increases roughly with a two-thirds power of the monomer feed[11]. Thus, if the amount of emulsifier is sufficient to cover the particle surface in the early polymerization stages, the sufficient saturation of the particle surface as well as the presence of micellar emulsifier may be assumed even towards the end of the monomer emulsion feeding.

The effect of the total amount of emulsifier was studied at R/E = 25/75, i.e. within the region corresponding to the controlled flocculation (Fig. 6).
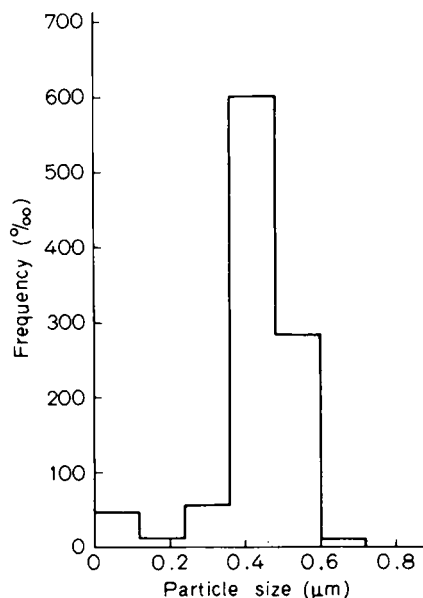
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Fig. 5.   Particle size histogram of latex prepared at distribution ratio $R/E = 0/100$. Total amount of emulsifier: 1 wt.-% related to monomers.
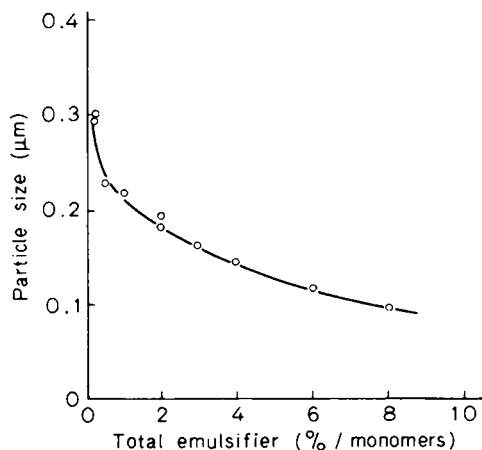

Fig. 6.   Average particle size in relation to the total amount of emulsifier. Distribution ratio $R/E = 25/75$.

The relationship found testifies, that the extent of flocculation depends on the total amount of emulsifier, which determines the limiting interfacial surface of the colloidal system.

Conclusions

The distribution of the emulsifier between the initial reactor charge and the monomer emulsion affects the final particle size as well as the mechanism of the particle growth. At R/E distribution ratios higher than 15/85, a large number of particles forms which flocculate during the following polymerization. The extent of the flocculation is limited by the total amount of emulsifier present. In the region of R/E distributions corresponding to the controlled flocculation, the final particle size is practically independent of the polymerization conditions. At lower R/E distributions no flocculation occurs and larger particles result. When the content of emulsifier in the initial reactor charge is very low, nucleation of new particles occurs towards the end of the monomer emulsion feeding.

In technical emulsion polymerization it is often desirable to alter the polymerization rate or particle size without altering the overall recipe. It was shown in this paper how this can be achieved by the variation of the emulsifier distribution in semicontinuous polymerization with a monomer emulsion feed. Within the region of controlled flocculation the polymerization rate is high, an immediate conversion over 90% may be easily reached[2] and the final particle sizes are reproducibly controlled by the total amount of emulsifier. The mechanical stability of those latices, however, is very poor because of the unsufficient saturation of the particle surfaces by the emulsifier. As the colloid system lies practically at the limit of flocculation, a secondary stabilization has to be applied.

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