The suspension copolymerisation of butyl methacrylate with methacrylic acid in the presence of a copolymer of 2-acrylamido-2-methylpropane sulphonic acid of different composition

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SUMMARY
An investigation was made of the influence of the composition of a copolymer of 2-acrylamido-2-methylpropane sulphonic acid with methyl methacrylate (MMA) on the suspension copolymerisation of butyl methacrylate (BMA) with methacrylic acid (MAA) and the particle size distribution of the polymer formed. With increase in the content of methyl methacrylate units in the studied polymeric dispersing agent, an increase was observed in the degree of dispersion of the BMA–MAA suspension copolymer, accompanied with an increase in the content of highly dispersed fraction. Possible reasons for the observed results are discussed.

The suspension method of polymerisation is widely used in industry for producing homopolymers of vinyl chloride, styrene, and methyl methacrylate, and also their copolymers of different composition [1]. Among its advantages are effective reaction heat removal by using water as the dispersion medium and the formation of polymers with a narrower molecular weight distribution by comparison with the block method. The polymer suspension formed contains polymer particles of 5-1000 µm size, which, in contrast to those obtained by the emulsion method, are readily isolated and washed [2].

The development of suspension polymerisation processes always presents a number of problems associated with ensuring the stability of the polymerising emulsion and with preventing the occurrence of secondary processes leading to the formation of a highly dispersed particle fraction. An important role in solving these problems is played by the choice of polymeric dispersing agent. In Kuryzhova and Kulikova [3], the basic possibility is shown of using copolymers of 2-acrylamido-2-methylpropane sulphonic acid (AMPSA) for the stabilisation of polymer-monomer particles during the suspension copolymerisation of methyl methacrylate with methacrylic acid in a watersalt medium. Earlier [4] we showed that, in the presence of a copolymer of 2-acrylamido-2-methylpropane sulphonic acid with methyl methacrylate (MMA), in the process of suspension copolymerisation of butyl methacrylate with methacrylic acid, more stable polymer suspensions are formed by comparison with suspensions obtained in the presence of polyvinyl alcohol and hydrolysed polyacrylonitrile. The absence in the literature of information concerning the influence of the composition of the polymeric dispersing agent on the stability of polymer suspensions makes it impossible to decide on one.

The aim of this work was to study the influence of the structure of the polymeric dispersing agent AMPSA on the stability of the reaction system during the copolymerisation of butyl methacrylate (BMA) with methacrylic acid (MAA).
EXPERIMENTAL

BMA-MAA copolymers were obtained by suspension polymerisation in water in the presence of the initiator benzoyl peroxide (BP) and a polymeric dispersing agent – copolymer AMPSA-MMA or polyvinyl alcohol (PVA) of different composition. The BMA-MAA copolymers were synthesised in an Ecoclave chemical reactor (Büchi Glus Uster, Switzerland) consisting of a glass, flat-bottomed vessel of 1.4 L volume with a sleeve and bottom discharge and systems for automatic maintenance of the temperature and rate of mixing of the reaction mass. The BMA:MAA mass ratio amounted to 95.5:4.5, the concentration of benzoyl peroxide to 1.6 wt%, and the content of AMPSA-MMA copolymer to 0.2 wt%. The water modulus was 1:3. Calculated quantities of water with polymeric dispersing agent were charged into the glass reactor, mixing at 500 rpm was actuated, and heating was begun. At 40°C, an already prepared monomer mixture with an initiator was introduced into the reactor at 40°C, and heating was continued to 80°C. After 20-30 min, after the temperature of the reaction mass had reached 80°C, an arbitrary 2-8°C rise in temperature was observed by an exothermic reaction. On completion of exothermy and reduction in temperature in the reactor to 80°C, the reaction mass was held for 3 h and then cooled to 30°C. The copolymer was separated out by filtration through a nylon-6 filter, washed with distilled water, dried at 40°C to a moisture content of less than 0.2 wt%, and passed through a 3000 µm sieve.

The following materials were used in the study: monomers – BMA (Degussa, Germany) and MAA (TU 2431-027-55856863-2003); polymeric dispersing agents – AMPSA-MMA copolymers obtained by solution polymerisation of 2-acryloamido-2-methylpropane sulphonic acid (grade 2404; Lubrizol, USA) with methyl methacrylate in dimethylformamide by the procedure described by Lisovtsev [5] and PVAIs of grades 20/4 and 20/12, synthesised in the laboratory, and 16/1 and 18/1 (GOST 10779-78); initiator – BP (TU 2417-32-524701-75) without additional purification; distilled water.

The interphase tension at the boundary of the aqueous solution of polymeric dispersing agent with BMA was determined by the stalagmometric method using a DVT-50 tensiometer (Tirit, Germany) at a temperature of 25°C.

The size of the associates of macromolecules was determined by photon correlation spectroscopy.

The stabilising action of the AMPSA-MMA copolymer was assessed from the degree of dispersion of the BMA-MAA copolymer obtained in its presence, using differential curves of particle size distribution. For this, the particle size distribution of the copolymer was determined on sieves with a cell diameter of 3000, 1500, 1000, 630, 400, 315, 250, and 200 µm.

The content of highly dispersed fraction was assessed by the gravimetric method. For this, ~20 g of mother liquor obtained after filtration of the suspension of copolymer BMA–MAA through a paper filter was dried at a temperature of 100-110°C to constant weight. The content of highly dispersed fraction of the polymer was calculated by means of the formula:

\[ \alpha = \frac{m_{\text{dry}}}{m_{\text{mother}}} \times 100\% - C_{\text{AMPSA–MMA}} \]

where \( m_{\text{dry}} \) is the mass of residue obtained after drying of the mother liquor sample to constant weight (g), \( m_{\text{mother}} \) is the mass of the mother liquor sample (g), and \( C_{\text{AMPSA–MMA}} \) is the mass concentration of the AMPSA-MMA copolymer in the aqueous phase (0.07 %).

The solubility of butyl methacrylate in water and in aqueous solutions of a copolymer of 2-acrylamido-2-methylpropanesulphonic acid with methyl methacrylate was determined from the refraction of the aqueous phase of the monomer-saturated emulsion [14] on a BHA-22 refractometer. The colloidal solubility of butyl methacrylate in associates of macromolecules of the dispersing agent was calculated from the difference between the values of its solubility in aqueous solutions of the polymeric dispersing agent and in water.

RESULTS AND DISCUSSION

Figure 1 gives differential curves of the particle size distribution of a BMA-MAA suspension copolymer obtained in the presence of a stabiliser – copolymer AMPSA-MMA.

It can be seen that change in the content of methyl methacrylate units in the AMPSA-MMA copolymer from 50 to 25 wt% leads to a reduction in the mass content of particles of about 300 µm size. The absence of methyl methacrylate units in the polymeric dispersing agent displaces the maximum of the curve towards particles sizes of about 600 µm. Thus, reduction in the content...
of lipophilic units in the macromolecules of the AMPSA-MMA copolymer leads to a reduction in the degree of dispersion of the suspension particles.

Differential curves of the particle size distribution of the polymer obtained in the presence of PVAl are given in Figure 2. It was shown that reduction in the amount of acetate units from 12 to 4 wt% in this case also leads to displacement of the maximum of the differential curve of the particle size distribution of the BMA-MAA copolymer from 300 to 600 μm.

Similar results were obtained by Andor [6] in a study of the influence of the content of methyl methacrylate units in an MAA-MMA copolymer on its stabilising action in the suspension polymerisation of methyl methacrylate. Displacement of the maximum of the curve of the particle size distribution towards a reduction in diameters with increase in the proportion of lipophilic groups in the polymeric dispersing agent was found. The obtained results were attributed to the increase in the adsorption capacity of the dispersing agent and to the increase in the thickness of the adsorption layers formed by it on the surface of the particles.

Figures 3 and 4 give isotherms of the interphase tension at the boundary of BMA with aqueous solutions of the investigated dispersing agents. It can be seen that increase in the amount of lipophilic units in copolymers AMPSA-MMA and PVAl leads to a reduction in interphase tension, which indicates an increase in their surface-active properties.

Increase in the thickness of adsorption layers on the surface of monomer drops with increase in the content of methyl methacrylate units in the copolymer was attributed to the emergence of intermolecular hydrophobic interactions between the ester groups of the macromolecules, leading to the formation of supermolecular formations. Investigation of associates of macromolecules, which are formed in aqueous solutions of PVAl, showed that their size is not dependent on the content of acetate groups in the polymer. The size of associates of macromolecules of copolymer AMPSA-MMA decreases with increase in the amount of MMA units in the copolymer. Thus, reduction in the size of the polymer particles with increase in the content of hydrophobic groups in PVAl and copolymer AMPSA-MMA seems not to be due to increase in the thickness of the adsorption layer formed by them.

It is known that the suspension polymerisation of methyl methacrylate [7, 8] is often accompanied with the secondary formation of a highly dispersed fraction of polymer particles from coils of associates of macromolecules of the dispersing agent or microdrops of the monomer. This process is undesirable, as it leads to a reduced yield and to deterioration in the properties of the suspension polymer. It was suggested that change in the hydrophilic-lipophilic balance of the dispersing agent by changing the content of lipophilic groups will make it possible to lower the content of highly dispersed particle fraction.

Tables 1 and 2 give the results of investigating the influence of the composition of the AMPSA-MMA copolymer and also the degree of acetylation of PVAl on the content of highly dispersed particle fraction.
It can be seen that the introduction of MMA units in a quantity of up to 50 wt% into the AMPSA copolymer leads to an increase in the content of highly dispersed fraction of the polymer from 1.1 to 5.6 wt%, while an increase in the degree of acetylation of PVAl from 4 to 10 wt% hardly affects its formation.

As follows from data given in Figure 5, with increase in the amount of MMA units in the AMPSA-MMA copolymer there is an increase in the colloidal solubility of BMA in associates of macromolecules of the dispersing agent. The variation in the colloidal solubility of BMA in coils of macromolecules of PVAl of different composition is negligible (Figure 6). This gives grounds for assuming that one of the reasons for the increase in the number of particles formed from associates of macromolecules of the dispersing agent may be the increase in the amount of lipophilic groups in the AMPSA-MMA copolymer.

**CONCLUSIONS**

1. Increase in the content of lipophilic units in the AMPSA-MMA copolymer increases its surface-active properties, leading to an increase in the degree of dispersion of the BMA-MAA suspension copolymer. Change in the content of methyl methacrylate units from 25 to 50 wt% leads to an increase in the mass content of particles of 300 µm size. The absence of methyl methacrylate units in the polymer displaces the maximum of the curve into the region of a 600 µm particle size.

2. With increase in the amount of MMA units in the AMPSA-MMA copolymer to 50 wt%, during the suspension copolymerisation of BMA with MAA there is an increase in the content of highly dispersed particle fraction in the polymer suspension. One of the reasons for the observed relationship may be an increase in the colloidal solubility of the monomers in aqueous solutions of the tested polymeric dispersing agents.

**REFERENCES**


