The course of seeded emulsion polymerization of methyl methacrylate (MMA) initiated by water-soluble initiator ammonium peroxodisulfate (APS) in the presence of poly(butyl acrylate) seed particles (PBA) depends on the MMA—PBA mass ratio ($w_r$) and the presence or absence of potassium nitrosodisulfonate (Fremy's salt, FS) in the system. In the presence of FS an inhibition period for both "low" (0.637 and 0.675) and "high" (3.25) $w_r$(MMA—PBA) was observed. Retardation of polymerization rate after inhibition period only for "high" $w_r$(MMA—PBA) was found. In conditions of Stage 2 ($w_r = 3.250$) of seeded emulsion polymerization the rate of seeded emulsion polymerization of MMA initiated by APS is lower than the rate found for Stage 3 ($w_r = 0.675$). Polymer particle size for a given conversion of monomer depends on the value of $w_r$(MMA—PBA). Under conditions of Stage 2 of seeded emulsion polymerization the presence of FS lowers slightly the polymer particle size.

The results confirmed that the water-phase events of free radicals are of primary importance for core/shell polymer particle formation and generation of a new crop of structurally homogeneous poly(methyl methacrylate) particles.

A useful method for achieving a compositionally heterogeneous core/shell structure of the polymer particles is that of the seed latex. A monomer polymerizes in the presence of a polymer dispersion prepared in advance (i.e. two-stage emulsion polymerization). Staged emulsion polymerization produces latices which exhibit a variety of properties dependent on their particle morphology. The understanding of the factors which control the formation of the polymer particles is extremely important for the design of structured latex products and for the understanding of the mechanism of emulsion polymerization [1]. Two-stage emulsion polymerization offers an interesting possibility for the preparation of interpenetrating polymer networks [2—6]. The preparation of graft copolymers by two-stage emulsion process was also described. The use of poly(butyl acrylate) as seed latex in the seeded emulsion polymerization of styrene [7, 8], acrylamide [9], and methyl methacrylate [10] has been published recently.

In the previous paper [10] the principle of partitioned polymerization [11] was applied for the seeded emulsion polymerization of methyl methacrylate in the presence and/or absence of oil-soluble free-radical inhibitor 2,2,6,6-tetramethyl-4-octadecanoyloxy-piperidinyl-1-oxyl (STMPO). It was reported [10] that the kinetics of seeded emulsion polymerization of methyl methacrylate and the mechanism of polymer particle formation depended on the methyl methacrylate/poly(butyl acrylate) particle mass ratio and on the presence or absence of oil-soluble inhibitor. It was shown that the oil-soluble inhibitor STMPO did not inhibit the seeded emulsion polymerization of methyl methacrylate. For systems modelling the Stage 2 of emulsion polymerization (monomer droplets are available) the presence of oil-soluble inhibitor STMPO leads to only slight retardation of polymerization rate beyond conversion of ca. 20 % (in comparison to polymerization rate determined for system not containing oil-soluble inhibitor). The presence of STMPO facilitated however, the formation of a new crop of poly(methyl methacrylate) particles.

The shape of conversion curve of the system modelling the Stage 3 of emulsion polymerization (no monomer droplets are present in the system) manifested clearly retardation of polymerization in comparison to the conversion curve found for system without oil inhibitor STMPO. Formation of a new crop of poly(methyl methacrylate) particles was not observed and only particles of the core/shell structure were formed.

Further information on the oil- and water-phase reactions which influence the formation of core/shell polymer particles vs. formation of structurally homogeneous poly(methyl methacrylate) particles should
be given by the seeded emulsion polymerization of methyl methacrylate initiated by water-soluble initiator in the presence and/or absence of water-soluble free-radical inhibitor as well as the seeded emulsion polymerization of methyl methacrylate initiated by oil-soluble initiator in the presence and/or absence of water-soluble inhibitor. In this paper the method of partitioned polymerization [11] was applied to the former system, i.e., for discussion of experimental results obtained for methyl methacrylate seeded emulsion polymerization initiated by water-soluble initiator ammonium peroxodisulfate in the presence and/or absence of water-soluble free-radical inhibitor potassium nitrosodisulfonate (Fremy’s salt). The results of the study of the seeded emulsion polymerization of methyl methacrylate initiated by oil-soluble initiator dibenzyl peroxide in the presence and/or absence of Fremy’s salt will be reported in the next paper [12].

EXPERIMENTAL

Butyl acrylate (BA) (technical; Chemical Works Sokolov, Sokolov, The Czech Republic) and methyl methacrylate (MMA) (technical; Chemical Works, Žilina, The Slovak Republic) were freed of inhibitor as described in [10]. Ammonium peroxodisulfate (APS) (purum; Lachema, Prague, The Czech Republic) was recrystallized from distilled water and ethanol. Sodium dodecyl sulfate (SDS) (for tenside research; Merck and Schuchardt, Hohenbrunn/München, FRG) and potassium nitrosodisulfonate \( \text{(SO}_3\text{K)}_2\text{NO}_2 \) (FS, Fremy’s salt; Aldrich, Milwaukee, USA) were used without further purification. Distilled water was deprived of oxygen by heating to the boiling point and cooling under stream of nitrogen.

Poly(butyl acrylate) latex was prepared by batch emulsion polymerization as previously reported [10]. Emulsion polymerization of methyl methacrylate in the presence of seed poly(butyl acrylate) latex proceeded according to the general procedure described in [10]. Recipes are given in Table 1.

Table 1. Recipes for Emulsion Polymerization of Methyl Methacrylate in the Presence of Seed Poly(butyl Acrylate) Latex

<table>
<thead>
<tr>
<th>Run</th>
<th>( m(\text{PBA}) ) g</th>
<th>( m(\text{MMA}) ) g</th>
<th>( m(\text{Water}) ) g</th>
<th>( m(\text{APS}) ) mg</th>
<th>( m(\text{FS}) ) mg</th>
<th>( m(\text{SDS}) ) mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>77.3</td>
<td>9.6</td>
<td>20</td>
<td>2.88</td>
<td>0.54</td>
<td>73.1</td>
</tr>
<tr>
<td>2</td>
<td>77.3</td>
<td>9.6</td>
<td>20</td>
<td>2.88</td>
<td>0.54</td>
<td>73.1</td>
</tr>
<tr>
<td>3</td>
<td>51.9</td>
<td>9.6</td>
<td>20</td>
<td>2.88</td>
<td>0.54</td>
<td>57.6</td>
</tr>
<tr>
<td>4</td>
<td>51.9</td>
<td>9.6</td>
<td>20</td>
<td>2.88</td>
<td>0.54</td>
<td>57.6</td>
</tr>
<tr>
<td>5</td>
<td>51.9</td>
<td>9.6</td>
<td>20</td>
<td>2.88</td>
<td>0.54</td>
<td>57.6</td>
</tr>
<tr>
<td>6</td>
<td>20.7</td>
<td>18.4</td>
<td>40</td>
<td>4.5</td>
<td>4.5</td>
<td>115.3</td>
</tr>
<tr>
<td>7</td>
<td>20.7</td>
<td>18.4</td>
<td>40</td>
<td>4.5</td>
<td>4.5</td>
<td>115.3</td>
</tr>
<tr>
<td>8</td>
<td>20.7</td>
<td>18.4</td>
<td>40</td>
<td>4.5</td>
<td>1.1</td>
<td>115.3</td>
</tr>
</tbody>
</table>

a) Mass of poly(butyl acrylate) latex.

At the determination of polymer particle size a Particle Sizer Model BI-90 of Brookhaven Instrument Corporation was used. All measurements were performed at 25 °C.

RESULTS

The kinetics of seeded emulsion polymerization of methyl methacrylate depends strongly on the value of \( w_r(\text{MMA—PBA}) \) and the presence and/or absence of Fremy’s salt (Figs. 1 and 2, Table 2). Thus, for example, for “low” values of \( w_r(\text{MMA—PBA}) \) (0.637 and 0.675) the polymerization time necessary for reaching the conversion of 50 % is shorter (35 min) than that (105 min) for “high” \( w_r(\text{MMA—PBA}) \) (3.25).

A significant retardation of polymerization rate after inhibition period was found only for “high” \( w_r(\text{MMA—PBA}) \). Fremy’s salt inhibits the seeded emulsion polymerization of methyl methacrylate irrespective of the value of \( w_r(\text{MMA—PBA}) \). Inhibition period is, however, shorter for “high” value of \( w_r(\text{MMA—PBA}) \).

The change of polymer particle diameter with polymerization time is illustrated in Fig. 3. Only small increase of polymer particle diameter was observed.

Fig. 1. Conversion vs. time (t) curves for methyl methacrylate polymerization initiated by ammonium peroxodisulfate in the presence of poly(butyl acrylate) seed particles at 60 °C. ○ Run 1, △ run 2, □ run 3, ▲ run 4, ■ run 5. For further details see Table 1.
for "low" \( w_r \) (MMA—PBA) value (from 183 nm to 204 nm). The increase of polymer particle diameter is more significant for "high" values of \( w_r \) (MMA—PBA) (from 183 nm to 255 nm). The presence and/or absence of FS in the system has practically no effect on the polymer particle diameter providing the recipe yielding "low" value of \( w_r \) (MMA—PBA) was used (cf. Fig. 3, runs 2 and 4 and Table 2). For systems with "high" values of \( w_r \) (MMA—PBA) the presence of FS seems to decrease slightly the polymer particle diameter at a given conversion of MMA (cf. Fig. 3, run 6 vs. run 8 and Table 2).

REFERENCES

Inverse Microemulsion Polymerization of Acrylamide in the Presence of Bi-Unsaturated Vinyl Monomers

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The effect of divinylbenzene and N,N-methylenebisacrylamide on the polymerization of acrylamide in inverse microemulsion was studied. Studying the polymerization kinetics, polymer particle sizes, degree of swellability measurements, and the chemical composition of the products we have found that in the presence of bi-unsaturated vinyl monomers the character of conversion curve as well as crosslinking and particle sizes of the products have been changed. The interpretation of the obtained results is based on previously proposed mechanism of the initiation of free radical polymerization and formation and growth of polymer particles in inverse microemulsion.

Crosslinking of water-soluble vinyl monomers by bifunctional monomers in water has been studied in detail [1—4]. In these systems, deviations from the ideality have been observed. The gels prepared in this way have been considerably inhomogeneous and they contained domains of different degrees of crosslinking [3]. For the explanation of this phenomenon, several factors should be considered, e.g., various reactivity of double bonds in monomers [4], decreased reactivity of double bonds in polymers in comparison to that of their monomers, and the primary (inside of one molecule) and the secondary (between several molecules) cyclization [2]. A combination of all the above-mentioned factors could lead to a very high copolymerization rate, and at the same time, also to the appearance of macroscopic as well as microscopic inhomogeneities in the network of the gel obtained [1].

In the present work, we tried to utilize the possibilities provided by the usage of heterogeneous systems. One of them is also the copolymerization of comonomers of various water solubility. Therefore, the copolymerization of acrylamide with divinylbenzene and N,N-methylenebisacrylamide in inverse microemulsion has been studied from the viewpoint of the processes kinetics and of the basic characteristics of the products formed.

EXPERIMENTAL

Monomers acrylamide (AAM), pure (Fluka, Buchs, Switzerland) and N,N-methylenebisacrylamide (MBAAm), ultra pure (Polyscience, USA) have been used without further purification. Divinylbenzene (DVB) (Merck, Germany) has been deprived of in-