

Partitioned Polymerization

VII.* Seeded Emulsion Polymerization of Methyl Methacrylate in the Presence and/or Absence of Frey's Salt

J. BARTOŇ and V. JURANIČOVÁ

*Polymer Institute, Slovak Academy of Sciences,
SK-842 36 Bratislava*

Received 26 October 1993

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 (Frey'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

*For Part VI see Bartoň, J., *Macromol. Chem., Rapid Commun.* 12, 675 (1991).

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 ($(\text{SO}_3\text{K})_2\text{NO}^*$ (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

Run	$m(\text{PBA})^a$ g	$m(\text{MMA})$ g	$m(\text{Water})$ g	$m(\text{APS})$ mg	$m(\text{FS})$ mg	$m(\text{SDS})$ mg
1	77.3	9.6	—	2.88	—	73.1
2	51.9	9.6	20	2.88	—	57.6
3	51.9	9.6	20	2.88	—	57.6
4	51.9	9.6	20	2.88	0.54	57.6
5	51.9	9.6	20	2.88	0.54	57.6
6	20.7	18.4	40	4.5	—	115.3
7	20.7	18.4	40	4.5	—	115.3
8	20.7	18.4	40	4.5	1.1	115.3

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" $w_r(\text{MMA—PBA})$ value. No retardation was, however, found for "low" $w_r(\text{MMA—PBA})$. 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

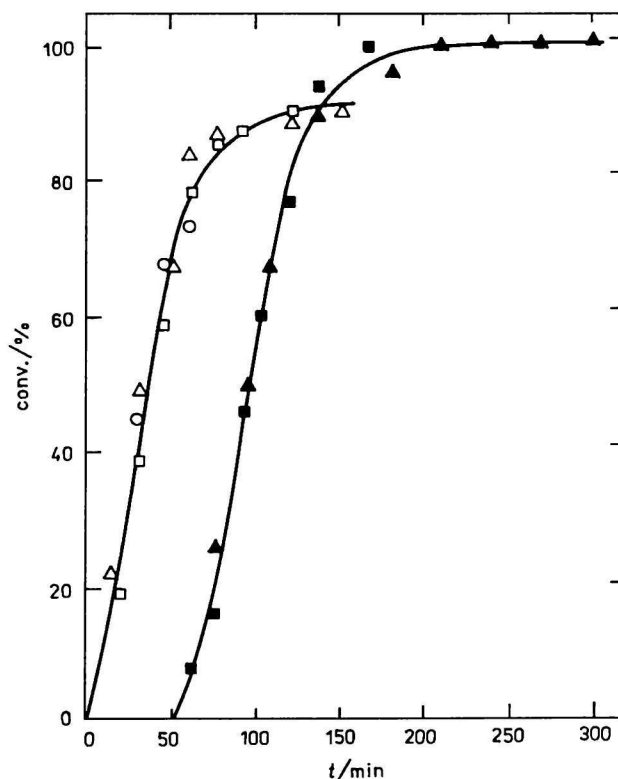


Fig. 1. Conversion vs. time (*t*) curves for methyl methacrylate polymerization initiated by ammonium peroxodisulfate in the presence of poly(butyl acrylate) seed particles at 60 °C. ○ Run 1, △ run 2, □ run 3, ▲ run 4, ■ run 5. For further details see Table 1.

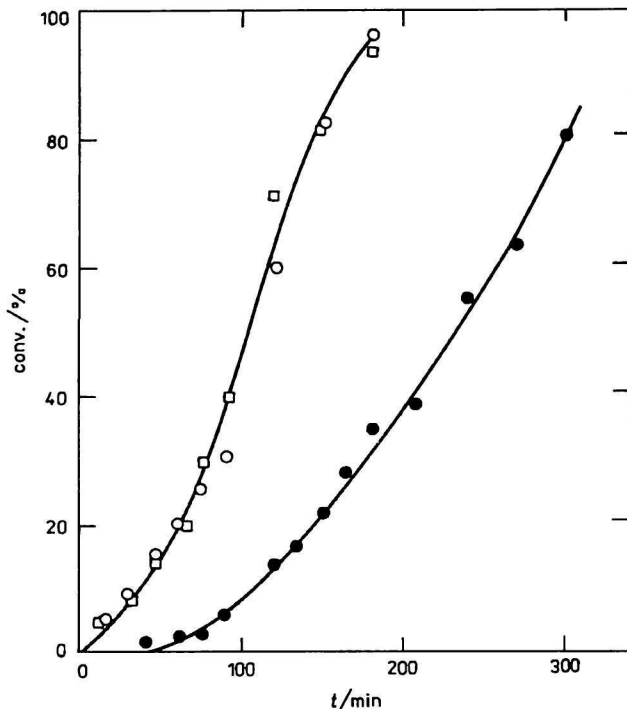


Fig. 2. Conversion vs. time (t) curves for methyl methacrylate polymerization initiated by ammonium peroxodisulfate in the presence of poly(butyl acrylate) seed particles at 60 °C. ○ Run 6, □ run 7, ● run 8. For further details see Table 1.

Table 2. Characteristic of Seeded Emulsion Polymerization of Methyl Methacrylate in the Presence of Poly(Butyl Acrylate) Latex at 60 °C^a

Run	$w_r(\text{MMA—PBA})^b$	τ_{inh}^c min	$t(50\%)^d$ min	d/nm (conv./%) ^e
1	0.637	0	35	
2	0.675	0	35	204 (91)
3	0.675	0	35	204 (98)
4	0.675	55	95	
5	0.675	55	95	
6	3.25	0	105	256 (96)
7	3.25	0	105	
8	3.25	35	230	240 (80)

a) For further details see Table 1; b) mass ratio of MMA and PBA polymer of poly(butyl acrylate) latex; c) inhibition period; d) time needed for conversion 50 %; e) polymer particle diameter d obtained for conversion.

for “low” $w_r(\text{MMA—PBA})$ value (from 183 nm to 204 nm). The increase of polymer particle diameter is more significant for “high” values of $w_r(\text{MMA—PBA})$ (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 $w_r(\text{MMA—PBA})$ was used (cf. Fig. 3, runs 2 and 4 and Table 2). For systems with “high” values of $w_r(\text{MMA—PBA})$ 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).

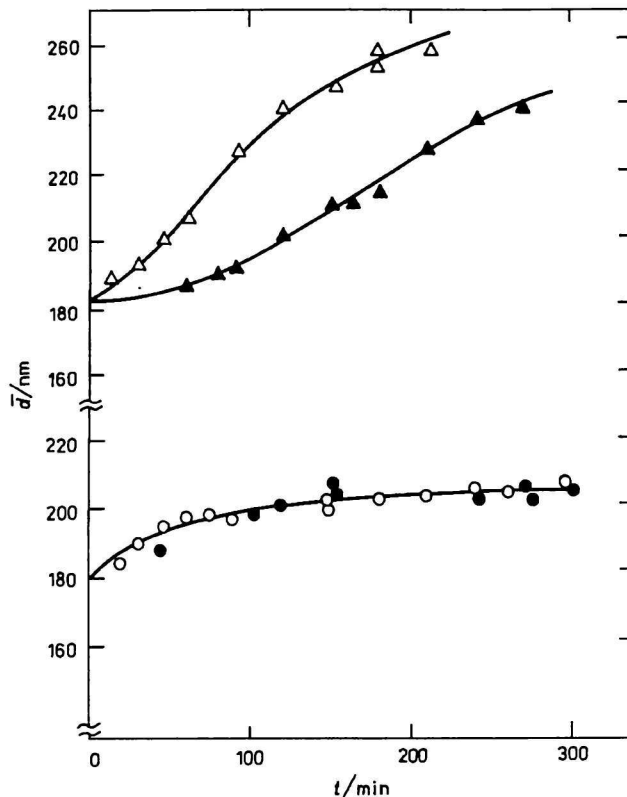


Fig. 3. Polymer particle diameter (\bar{d}) vs. time (t) of seeded emulsion polymerization of methyl methacrylate. ○ Run 2, ● run 4, △ run 6, ▲ run 8. For further details see Table 1.

DISCUSSION

System characterized by “low” value of $w_r(\text{MMA—PBA})$ is the model of Stage 3 of emulsion polymerization [13, 14]. Monomer is present in polymer seed particles and up to its solubility limit also molecularly dispersed in the continuous water phase. No monomer droplets are present in the system. For water-soluble initiator APS the presence of FS in the polymerization system leads to inhibition of radical reactions in water phase and as a result distinct inhibition period of polymerization was therefore observed (Fig. 1). The rate of MMA seeded emulsion polymerization after inhibition period is practically the same as the rate of MMA seeded emulsion polymerization in the absence of FS in the system. It is interesting to note that for “low” value of $w_r(\text{MMA—PBA})$ and for system containing FS the levelling off of the conversion curve is observed at higher conversion (95 %) in comparison to the conversion (approx. 85 %), observed for system not containing FS. Similar effect was observed in emulsion polymerization of styrene in the presence of oil-soluble inhibitor 4-*tert*-butyl catechol [15]. The reason for this peculiar behaviour is the formation of smaller polymer particles than those obtained in the absence of inhibitor. This implies that a large number of parti-

cles have been generated and that this increased number of polymer particles has been more than sufficient to overcome the reduced polymerization rate per particle due to reduction of average number of radicals in particle. The reduction of the average number of radicals in particle was a result of termination reactions of radicals with 4-*tert*-butyl catechol. When using oil-soluble inhibitor STMPO [10] no inhibition of polymerization rate but only strong retardation of the MMA seeded emulsion polymerization was observed. The reasons for the retardation of MMA seeded emulsion polymerization rate were discussed previously [10]. Oligomeric radicals of MMA formed in water phase due to the reaction of MMA with radicals which stem from the APS decomposition in water phase enter the poly(butyl acrylate) particles swelled by MMA and start the propagation reaction in polymer particle. As a competitive reaction to the propagation reaction of oligomer radical in polymer particle is the termination reaction with oil-soluble inhibitor in monomer-swelled polymer particle. The mutual proportion of both competitive reactions of oligomer radicals determines the extent of propagation and termination reactions in polymer particle. Such a mechanism of initiation of polymerization is, of course, excluded if instead of oil-soluble inhibitor a water-soluble inhibitor like FS is present in the system. Thus the experiments with seeded emulsion polymerization of MMA in the presence of FS support the opinion expressed in [10] on the locus of initiation of MMA polymerization in seeded emulsion polymerization system, which is a water phase.

System characterized by "high" value of $w_r(\text{MMA—PBA})$ is the model of Stages 1 and 2 of emulsion polymerization [13, 14]. Here monomer is present also in the form of monomer droplets and in micelles of emulsifier. If APS was used as initiator the presence of FS in the water phase leads to an inhibition of polymerization (*cf.* also Ref. [16]). The inhibition period is, however, shorter than that for "low" $w_r(\text{MMA—PBA})$. This is a consequence of higher concentration of MMA in water phase for the system with "high" $w_r(\text{MMA—PBA})$. The fraction of radicals which escape the termination reaction with FS increases with increasing concentration of MMA in water phase. The situation can arise that in spite of the presence of FS in the system, some of oligomer radicals succeed to enter polymer particle and to start the polymerization process in polymer particle. The relatively high concentration of monomer MMA in water phase (solubility limit 150 mmol dm^{-3}) (Ref. [1], p. 140) in comparison to Frey's salt (0.1 mmol dm^{-3}) increases the probability of addition reaction of initiator radicals on monomer molecules dissolved in water phase and further propagation of monomer radicals. The probability of this reaction is likely to

be comparable to the probability of termination reactions of primary or oligomer radicals with relatively stable free radical, Frey's salt. The oligomer radicals besides being captured by polymer particles and starting the propagation in monomer-swelled polymer particles can also propagate with monomer in the water phase. After reaching their limit of solubility in water phase, oligomer radicals and/or oligomer molecules precipitate and form primary oligomer particles which are swelled by monomer from monomer droplets (remember that the Stage 2 of emulsion polymerization is operative) and thus finally a new crop of polymer particles is formed.

Contrary to the system characterized by "low" value of $w_r(\text{MMA—PBA})$ the polymerization rates either in the presence or absence of FS are clearly lower for the "high" value of $w_r(\text{MMA—PBA})$ (*cf.* Figs. 1 and 2). This is the consequence of the two loci of propagation reactions, *i.e.* in seed polymer particles and in polymer particles of a new crop. The resulting polymerization rate is thus a function of the number of polymerizing sites of both kinds. The different polymerization rate in seed polymer particles and polymer particles belonging to the new crop of polymer particles can be explained by several ways. It might be a different monomer concentration in different loci of propagation, the microviscosity of propagation locus, affecting the extent of gel effect, the differences in the rates for exit and entry of radicals from and into seed polymer particle and/or polymer particle of a new crop, *etc.* At present it is not possible to distinguish the impact of the individual mentioned factors on the polymerization rate.

The change of polymer particle diameter during seeded emulsion polymerization of methyl methacrylate initiated by ammonium peroxydisulfate in the presence and/or absence of oil-soluble inhibitor STMPO was thoroughly discussed in the previous paper [10]. The change of the polymer particle diameter with conversion observed for systems characterized by the presence and/or absence of FS follows the same pattern only for systems with "low" $w_r(\text{MMA—PBA})$. For "high" $w_r(\text{MMA—PBA})$ the presence of FS seems to lower slightly the polymer particle diameter in comparison to the system not containing FS. The latter fact can be explained by the existence of two kinds of structurally different polymer particles (PMMA particles and PBA—PMMA core/shell particles) in the system.

REFERENCES

1. Bartoň, J. and Capek, I., *Radical Polymerization in Disperse Systems*, Chapter 6. Horwood/Veda, Publishing House of the Slovak Academy of Sciences, Chichester and Bratislava, 1993.

2. Sperling, L. H., *Interpenetrating Polymer Networks and Related Materials*. Plenum Press, New York, 1991.
3. Sheu, H. R., El-Aasser, M. S., and Vanderhoff, J. W., *J. Polym. Sci., Part A, Polym. Chem.* **28**, 629 (1990).
4. Capek, I., *Chem. Papers* **45**, 481 (1991).
5. Capek, I., *Acta Polym.* **42**, 273 (1991).
6. Somani, R. H. and Shaw, M. T., *Macromolecules* **14**, 1549 (1981).
7. Min, T. I., Klein, A., El-Aasser, M. S., and Vanderhoff, J. W., *J. Polym. Sci., Polym. Chem. Ed.* **21**, 2845 (1983).
8. Gasperowicz, A., Kolendowicz, M., and Skowronski, T., *Polymer* **23**, 839 (1982).
9. Bartoň, J., Vašková, V., and Juraničová, V., *Makromol. Chem.* **187**, 257 (1986).
10. Bartoň, J., Hloušková, Z., and Juraničová, V., *Makromol. Chem.* **193**, 167 (1992).
11. Bartoň, J., Juraničová, V., and Hloušková, Z., *Makromol. Chem.* **189**, 501 (1988).
12. Bartoň, J. and Juraničová, V., to be published.
13. Smith, W. V. and Ewart, R. H., *J. Chem. Phys.* **16**, 592 (1948).
14. Smith, W. V. and Ewart, R. H., *J. Am. Chem. Soc.* **70**, 3695 (1948).
15. Huo, B. P., Campbell, J. D., Penlidis, A., MacGregor, J. F., and Hamielec, A. E., *J. Appl. Polym. Sci.* **35**, 2009 (1987).
16. Bartoň, J. and Juraničová, V., *Makromol. Chem., Rapid Commun.* **12**, 669 (1991).

Translated by J. Bartoň

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

V. VAŠKOVÁ, M. STILLHAMMEROVÁ, and J. BARTOŇ

*Polymer Institute, Slovak Academy of Sciences,
SK-842 36 Bratislava*

Received 8 December 1993

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-