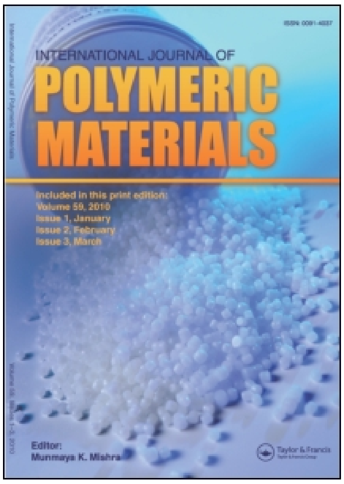

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Emulsion Copolymerization of Butyl Acrylate with Watersoluble Monomers in the Absence of Emulsifier

N. V. Kozhevnikov[a]; M. D. Goldfein[a]; A. V. Trubnikov[a]
[a] Saratov State University, Saratov, Russia

To cite this Article Kozhevnikov, N. V. , Goldfein, M. D. and Trubnikov, A. V.(2000) 'Emulsion Copolymerization of Butyl Acrylate with Watersoluble Monomers in the Absence of Emulsifier', International Journal of Polymeric Materials, 46: 1, 95 — 105

To link to this Article: DOI: 10.1080/00914030008054844

URL: http://dx.doi.org/10.1080/00914030008054844

Intern. J. Polymeric Mater., 2000, Vol. 46, pp. 95–105
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

Emulsion Copolymerization of Butyl Acrylate with Watersoluble Monomers in the Absence of Emulsifier

N. V. KOZHEVNIKOV, M. D. GOLDFEIN and A. V. TRUBNIKOV

Saratov State University, Astrakhanskaya St. 83, Saratov, 410601 Russia

(Received 8 June 1998)

Paper has connection with emulsion copolymerization of butyl acrylate with water soluble monomers in the absence of emulsifier. It was measure of kinetics of this reaction for different conditions and mechanism of this reaction is discussed.

Keywords: Emulsion copolymerization; butyl acrylate; emulsifier; comonomers; methacrylic acid; acrylonitrile

INTRODUCTION

It is known that latexes can be formed during emulsion polymerization without an emulsifier [1]. Such polymer emulsions consist of particles with "pure" surface and obtain some specific properties [2]. However, emulsion synthesis is complicated by the necessity of achieving of emulsion colloidal stability, which is achieved during the common emulsion polymerization by adding of emulsifier. When the latter is absent, the particles in very diluted systems (with starting monomers' concentration lower than their water solubility) can be stabilized by the ionized groups on the surface of macromolecules, which appears during the initiation of polymerization by ion-radicals formed from persulfate initiators. For more concentrated latexes such stabilization is not sufficient. It can be increased when hydrophobic monomers are copolymerized with ionizing or hydrophilic comonomers [2]. In the present work methacrylic acid (MAA) and acrylonitrile (AN) are used as such comonomers.

RESULTS AND DISCUSSION

Monomers were purified according to the standard procedure involving distillation at decreased pressure in an atmosphere of inert gas and condensation in vacuum. Twice distilled water was used as dispersion medium. Polymerization was initiated by ammonium persulfate (APS), purified by crystallization. The total monomer concentration was 20%. The concentration of comonomers was changed by corresponding changes of butyl acrylate (BA) concentration. Reaction kinetics was studied by dilatometric method. Polymerization was carried out in an oxygen-free system in helium atmosphere. The monomers and aqueous solution of initiator were deaerated by repeated freezing, vacuumization and defrosting of evaporated vessel. The mixing of solutions was carried out in the reaction vessel of dilatometer directly before beginning of the reaction. The formed emulsions were analyzed by turbidity spectrum method.

Our investigations showed that it is possible to synthesize polymer emulsions when copolymerization is carried out without an emulsifier, but only in specially selected conditions and often with low stability. Instability of the emulsions manifested itself in the formation of coagulum in the process of synthesis and also in the appearance of sediment or “clarified” layer in the upper part of the emulsion on storage. “Clarified” layer in this work means the upper layer of emulsion with lowered concentration of polymer-monomer particles (PMP). The formation of the sediment occurred during first twenty four hours of storage; afterwards its quantity did not change. The clarified layer, on the contrary, appeared only in few days and afterwards its volume gradually increased.

These phenomena seem to be caused by the presence of too large particles in the emulsion and their insufficient stabilization. The appearance of the sediment while emulsion still exists in the remained volume points to the existence of particles of various dimensions. The largest of them form the sediment, and the smallest remain in the emulsion. The considerable variety of the dimensions of latex particles is possible when their formation stage is quite long. This effect is not observed when emulsifier is present, because in this case the rate of the formation of PMP is high and after that they grow with equal probability. This latter process leads to the formation of particles with similar dimensions. The appearance of the clarified layer without formation of the sediment points to the fact that sometimes in the polymerization without an emulsifier large particles with similar dimensions can be obtained. These particles gradually precipitate due to insufficient stabilization and form two layers with raised and lowered content of latex particles.

It is shown that synthesis conditions (temperature, initiator concentration, composition and concentration of monomers) strongly influence polymerization kinetics and emulsion properties. The absence of emulsifier leads to the changing of kinetic curves comparing with classic emulsion polymerization: it is observed that polymerization rate grows for a longer time and the achieved degree of conversion during this growth is greater. When the dependence of polymerization rate W upon reaction conditions was analyzed, we took into consideration the maximum value of the rate, which was achieved when the degree of conversion became equal to a certain value x_{max}.

The formation of emulsion became more probable with increasing reaction temperature. For example, when [APS] = $4\,10^{-2}$ mole/l, the emulsion appears when the temperature is not below 70°C. Otherwise during the reaction polymer precipitates. When the temperature increases, the reaction rate and the number of latex particles also increase while the dimensions of particles and the amount of coagulum decrease. Therefore, the emulsion stability improves and the amount of sediment during storage decreases. Effective activation energy in the absence of emulsifier (96 KJ/mole) is greater than in presence of emulsifier – Neonol AF9-12C (78 KJ/mole) [3]. The increase of reaction temperature, on the one hand, promotes the formation of radicals (due to the acceleration of initiator decomposition), which leads to more frequent penetration of charged oligomer radicals $^\bullet RSO_4^-$ into PMP's. This increases particle charge, improves their stability, and decreases the dimensions of the particles. On the other hand, the temperature increase leads to an increase of the number of oligomer radicals in the water phase. Therefore, the probability of their bimolecular termination with the formation of associations of watersoluble surface-active oligomers also increases. These oligomers possess micelle-forming properties and promote nucleation [2]. The chain growth rate increases simultaneously, which leads to the growth of probability of oligomer reaching the critical chain length n_{cl}, when they became insoluble and form PMP. As a result, the temperature influence on the polymerization rate is larger than in the presence of emulsifier, and the effective activation energy increases.

When the initiator concentration increases, the considerable growth of polymerization rate is observed. The number of latex particles in the emulsion N in the beginning increases too, but when initiator concentration became large, N begins to decrease. On the contrary, the mean radius of particles $\bar{r}^{\circ}$ in the beginning decreases rapidly, and after that slowly increases. The conversion degree corresponding to the maximum rate increases with the increase of initiator concentration (Fig. 1). The emulsion quality also changes: the coagulum amount increases along with the amount of sediment; the clarified layer

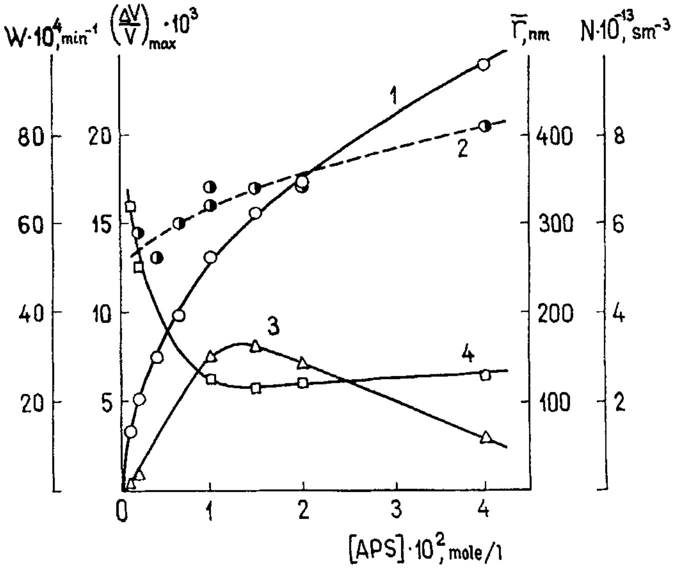

FIGURE 1 Rate of emulsion copolymerization of BA with AN (4%) and MAA (14%) without emulsifier (1), degree of conversion corresponding to the maximum rate value (2), number of latex particles in emulsion (3) and their mean radius (4) *versus* concentration of initiator, 85°C.

decreases on storage. When APS concentrations are relatively small, the clarified layer is formed, but there appears no sediment and coagulum; when APS concentrations are large, there exists coagulum and sediment, but no clarified layer.

When initiation rate is low, the amount of radicals in water phase is small, because their interaction is improbable. As a result at the initial stage of polymerization the majority of radicals grows to critical dimensions and forms PMP's according to homogeneous nucleation mechanism. As the quantity of latex particles grows, they start to capture a considerable part of emerging radicals and the formation of new PMP's ceases. The "old" particles continue to grow, and after the end of the polymerization they reach considerable dimensions. When initiator concentration increases (and, therefore, the amount of radicals in water phase increases too), the probability of bimolecular termination grows, which leads to the formation and accumulation of short watersoluble oligomeric surface-active compounds (SAC), playing the part of emulsifier. These oligomers form micelles, which after some time turn into PMP's. Thus, when APS concentration is high, the formation of one latex particle large amount of initial radicals is consumed. When homogeneous nucleation mechanism is taking place at low concentration of APS, PMP is formed in the beginning of the reaction from each of the initial radicals. Because of that, with the growth of [APS] the number of latex particles begins also to grow, but when the termination of radicals in water phase became substantial, the number of latex particles starts to decrease. In our experiments (85°C) this effect is observed when $[\mathrm{APS}] > (1-1.5)\,10^{-2}$ mole/l. The transition from one mechanism of PMP formation to another must influence the parameters of reaction kinetics, in particular, the kinetic order towards initiator n_i. Indeed, we found the "fracture" on the curve of logarithmic dependence of polymerization rate upon initiator concentration in the point corresponding to $[\mathrm{APS}] = 10^{-2}$ mole/l (Fig. 2). The n_i value is changing from 0.59 ($[\mathrm{APS}] < 10^{-2}$ mole/l) to 0.38 ($[\mathrm{APS}] > 10^{-2}$ mole/l).

When the initiation rates are high, the effectiveness of oligomer radicals in the process of latex particle formation decreases and the stage of nucleation is prolonged. This effect moves the time of reaching the maximum polymerization rate to the greater degree of conversion. There exist "old" large PMP's and "young" small PMP's in emulsion.

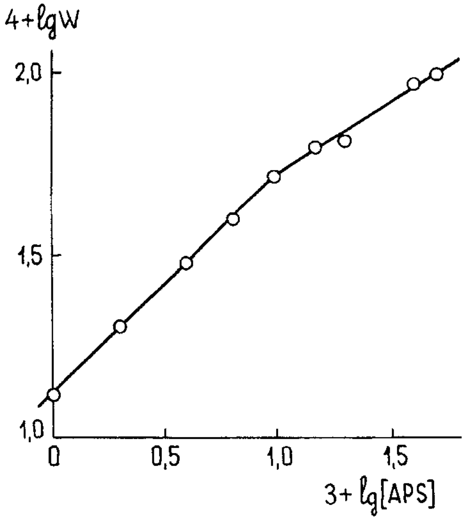

FIGURE 2 Rate of emulsion copolymerization of BA with AN (4%) and MAA (14%) without emulsifier as a function of initiator concentration, 85°C.

Increasing of dimensional heterogeneity of particles promotes the formation of coagulum and sediment on emulsion storage. On the other hand, when [APS] increases, the dimensions of PMP's decreases and charged oligomer radicals $^\bullet RSO_4^-$ penetrate PMP's more often with the effect of increasing the particle charge. This enhances PMP stabilization the and reduces the clarified layer.

The different character of dependence of polymerization rate and latex particles number upon initiator concentration (Fig. 1) points to the possibility of the simultaneous presence of several radicals in PMP when initiation rate is high.

The reaction temperature influence the dependence of x_{max} upon [APS]. For example, when $t = 70°C$, the [APS] growth at first leads to the decreasing of x_{max} (in contrast to $t = 85°C$), and after that to the increasing of x_{max}. When temperature is low and [APS]s are relatively small, the latex particles are formed mainly by homogeneous mechanism with low rate. When the initiator concentration starts to grow, at first the acceleration of nucleation by homogeneous mechanism takes place with decreasing of x_{max}, and after that, – the transition to "micelle" mechanism, leads to decreasing of nucleation rate and increasing of $x_{\max}$. The decrease of $x_{\max}$ when initiation rates are very low, as it seems, takes place also when $t = 85°C$.

The suppression of homogeneous nucleation and strengthening of the role of micelle mechanism of latex particles formation was observed ([4]) when initiation rate of emulsion polymerization in the presence of emulsifier was increased. It was proved by the growth of kinetics order towards emulsifier with the increasing [APS].

Latexes formed during emulsion polymerization without emulsifier contain considerably smaller number of large particles than in the presence of emulsifier Neonol [3]. The polymerization rates without emulsifier when initiation rate was relatively low ([APS] = $0.4 \cdot 10^{-2}$ mole/l, 70°C, or [APS] = $4 \cdot 10^{-2}$mole/l, 40°C) turned out to be several times less than in the presence of emulsifier.

Apparently, the equality of polymerization rates when particles numbers are different is caused by the fact that in the large particles several radicals simultaneously can grow when initiation rate in high, because the probability of such phenomenon grows with the increase of particle dimensions and radical generation rate.

Comonomer (methacrylic acid (MAA) and acrylonitrile (AN)) concentration influence the polymerization without emulsifier. Increasing of [MAA] in monomer systems BA-MAA and BA-AN(4%)-MAA leads to the growth of polymerization rate and, to an even greater degree, to of the number of latex particles in emulsion (Fig. 3). (In the presence of emulsifier both characteristics decrease [3]). Besides, the amounts of the sediment and coagulum decrease along with the rate of precipitation of latex particles and clarified layer formation on emulsion storage. Simultaneously, this increases the degree of conversion corresponding to the maximum value of the reaction rate (Fig. 3).

It was noted in [3], that in the presence of MAA the probability of bimolecular termination of oligomer radicals in water phase grows. This fact is caused by increasing of MAA concentration in water and by proceeding of copolymerization in water solutions with priority of MAA molecules participation [5]. As a result the water solubility of oligomer radicals improves, n_{cl} increases and the transition of radicals from water phase to PMP became hampered as a result of the decrease of their oil solubility. Simultaneously, the rate of oligomer radicals growth decreases because of the chain propagation in weakly acid solutions (pH6) is low [6]. All these effects increase the living time of

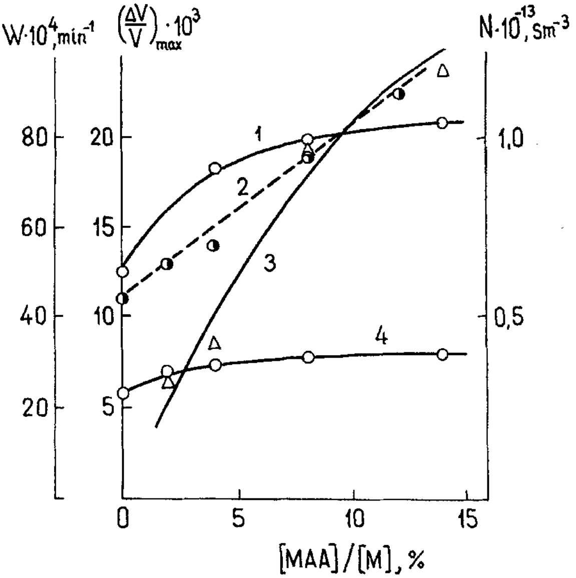

FIGURE 3 Rate of emulsion copolymerization of BA with AN (4%) and MAA without emulsifier (4), degree of conversion corresponding to the maximum rate value (2), rate of copolymerization of bicomponent system BA with MAA (1) and number of latex particles in formed by this reaction emulsion (3) *versus* concentration of MAA. [APS] $10^2 = 1.5$ (1,3) and 4 mole/l (2,4) $t = 70°C$ (2,4) and 85°C (1,3).

oligomer radicals in water phase and the contribution of bimolecular termination and "micelle" mechanism of PMP formation in the polymerization without emulsifier. As a result, the rate of the nucleation decreases. In addition, the presence of ionized monomer promotes the modification of particle surface, and improves the better stability of particles. Thus, the influence of MAA upon kinetics of a process without an emulsifier is opposite to such influence in the case of emulsion polymerization with an emulsifier [3]. Meanwhile the character of MAA influence on separate elementary reactions remains unchanged, but the part played by these reactions in polymerization process is changed.

Increasing of the probability of oligomer radicals termination in water phase under MAA influence in the presence of emulsifier leads to a decrease of N and W and growth of $\bar{r}$ [3]. Without an emulsifier the number of particles depends less on the existence of bimolecular termination (which lowers the PMP's formation rate and increases

x_{max}), than on the efficiency of particle stabilization. If all PMPs are formed by homogeneous nucleation mechanism, then particles are stabilized only through the existence of ionizing hydrophilic groups on their surface. The increase of the bimolecular termination leads to the formation of water-soluble surface-active oligomer, which can play the part of emulsifier, solvate the growing particles, preventing their flocculation, and increasing, thus, the number of the particles and polymerization rate. The observed decrease of coagulum, sediment amount and clarified layer on emulsion storage is explained by reinforcement of PMP stabilization and by the decrease of their dimensions.

AN also increases emulsion stability. Nevertheless, increasing of its concentration in the system BA-MAA (14%)-AN lowers the rate of polymerization without emulsifier, although the number of latex particles grows (Fig. 4). When emulsifier is present, AN decreases both the rate and the number of particles [3]. Increasing of N, as in the case of MAA, is connected with improving of latex particle stabilization. In the present case it is caused by copolymerization with hydrophilic monomer having polar —CN groups. AN increases the number of latex particles in emulsion to a smaller degree than MAA. For example, when BA is copolymerized with AN(14%) without emulsifier, the emulsion is formed, 1 cm^3 of which contains $0.2\,10^{-13}$ particles with mean radius 270 nm ([APS] = $1.5\,10^{-2}$ mole/l, 85°C); when BA is copolymerized with the same amount of MAA – $N = 1.2\,10^{13}$, $\bar{r} = 160$ nm.

It was noted earlier that MAA increases the dimensions of latex particles formed in the presence of emulsifier, but decreases them when emulsifier is absent. This effect in the BA-MAA system in shown in Figure 5. When third comonomer AN is included in the system, $\bar{r}$ continues to diminish, which lowers the probability of existence of several radicals in the particles. Furthermore, MAA and AN can influence the effective constant of propagation reaction in PMP. As a result the rate of polymerization without emulsifier decreases, in spite of growth of N (in the case of AN), or increases, but not so quickly as N (in the case of MAA).

We succeeded in obtaining stable emulsions (during polymerization without emulsifier), in which no sediment or clarified layer is formed during storage, only when temperature was high (80 – 85°C), interval

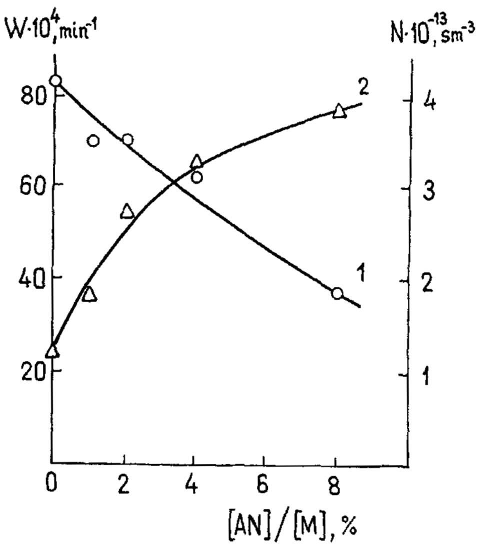

FIGURE 4 Rate of emulsion copolymerization of BA with MAA (14%) and AN without emulsifier (1) and number of latex particles in emulsion (2) as a function of AN concentration. [APS] = 1.5 10^{-2} mole/l, 85°C.

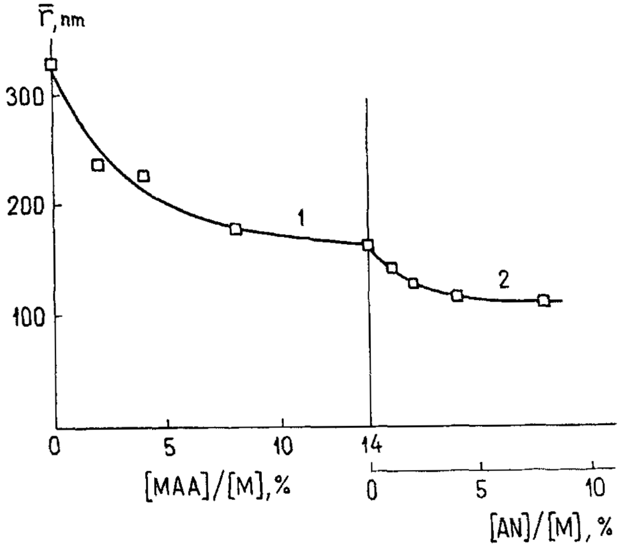

FIGURE 5 Dimensions of latex particles in emulsions formed while copolymerization without emulsifier of BA with MAA *versus* MAA concentration (1) and while copolymerization of BA with MAA (14%) and AN – *versus* AN concentration (2). [APS] = 1.5 10^{-2} mole/l, 85°C.

of APS concentrations was narrow ((1 – 2) 10^{-2} mole/l) and AN and MAA were present in the system simultaneously. When [APS] was < 10^{-2} mole/l, there was no clarified layer formation after a few days; when [APS] was > 2 10^{-2} mole/l, there was no clarified layer, but the sediment was formed. In the presence of only one of mentioned comonomers in the interval of concentrations 0 – 14% clarified layer was formed, but its volume and rate of formation decreased along with increases of comonomer concentration. When BA was copolymerized with MAA (14%) ([APS] = 1.5 10^{-2} mole/l, 85°C), clarified layer appeared after 10 days of emulsion storage at room temperature.

In the case of partial change of BA to third comonomer – AN this period of time increased and when [AN] was equal to 1%, clarified layer appeared after 15 days; when AN was equal to 2% – after 25 days. When AN concentration was equal to 4% or more, emulsion stayes stable through the entire period of observation (3 months).

References

[1] Eliseeva, V. I., Ivanchev, S. S., Kuchanov, S. I. and Lebedev, A. V. (1976). *Emulsion Polymerization and its Application in Industry*, Moscow.

[2] Eliseeva, V. I. and Aslamasova, T. P. (1991). *Uspekhi Khimii*, **60**(2), 398.

[3] Kozhevnikov, N. V., Zyubin, B. A., Simontsev, D. V., Simontsev, V. I., Bulkin, Yu. I., Goryunova, N. N. and Belova, T. P. (1995). *Vysokomolekulyarnye Soedineniya, A*, **37**(5).

[4] Kozhevnikov, N. V., Goldfein, M. D., Zyubin, B. A. and Trubnikov, A. V. (1991). *Vysokomolekulyarnye Soedineniya, A*, **33**(6), 1272.

[5] Nazarova, I. V. and Eliseeva, V. I. (1967). *Zhurnal Vsesoyuzn. Khim. Obschestva*, **12**(4), 587.

[6] Kabanov, V. A., Kurilova, A. I. and Topchiev, D. A. (1973). *Vysokomolekulyarnye Soedineniya, B*, **15**(9), 712.