Microemulsion Polymerization of Butyl Acrylate Initiated by γ Rays

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SYNOPSIS

Radiation polymerization of butyl acrylate was carried out in a microemulsion stabilized with sodium 12-butinoyloxy-9-octadecenate (SBOA). The stable and reddish latex with high polymer content and low emulsifier content was successfully produced in this way. It was found that, for most cases, the polymerization rate shows three intervals: the increasing period, the plateau period, and the decreasing period. The length of the nucleation period becomes longer at a higher dose rate (D) and lower emulsifier content (E). The plateau region of polymerization rate is lengthened with the increase of monomer and emulsifier content and shortened with the increase of dose rate. It was shown that monomer content, emulsifier content, and dose rate have great effects on R_p (the polymerization rate in the plateau region, or the maximum polymerization rate during polymerization) and M_n (the molecular weight of the polymer). $R_p \propto [M]^{0.93} D^{1.27} [E]^{-1.07;} M_n \propto [M]^{0.65} D^{0.28} [E]^{-1.66}$. The polymerization mechanism is discussed based on these results. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Microemulsion polymerization has been investigated quite extensively since the first report[1] in 1980. Many researchers attained the spherical and monodisperse latex particles by the polymerization of styrene (St), methyl methacrylate (MMA), and butyl acrylate (BA) in an oil/water microemulsion with sodium dodecyl sulfate (SDS) as the emulsifier and pentanol as the coemulsifier.[2-9] It was found that there are great differences between the microemulsion polymerization and conventional emulsion polymerization. At first, due to the small size and great number of microdroplets in microemulsion, microdroplets became the principal locus of nucleation in microemulsion polymerization. The nucleation process continued to a very high conversion. Furthermore, most radicals produced in the aqueous phase were captured by microdroplets instead of being captured by polymer particles. The result is that there are only a few polymer chains in each polymer particle while there are hundreds or even thousands of polymer chains in the polymer particles produced by conventional emulsion polymerization. Moreover, for most microemulsion systems, there were only two intervals observed for the polymerization rate. This may be attributed to the much lower monomer content in the microemulsion. Recently it was reported that the constant polymerization rate appeared at a low initiator concentration or low temperature when St was polymerized in a microemulsion with alkyl chain cationic surfactants, such as dodecyl trimethylammonium bromide (DTAB), as emulsifier.[10-13]

Up to now, in the microemulsion used for polymerization, the ratio of monomer to emulsifier was less than 1.0 and the concentration of emulsifier was usually larger than 10 wt %. Therefore, much has to be done before the industrialization of microemulsion polymerization. Especially the monomer content in the polymerization system should be greatly increased and the emulsifier content should be lowered. It was found that sodium 12-butinoyloxy-9-octadecenate (SBOA) was an efficient emulsifier for BA microemulsion.[14] In this study BA was polymerized in microemulsions stabilized with SBOA, in which the monomer to emulsifier ratio was about 2.5 and BA content about 30 wt %. The

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polymerization kinetics and mechanism of BA microemulsion at such conditions were discussed.

EXPERIMENTAL

Materials

BA from Dongfang Chemical Factory was distilled at 10 mmHg to remove inhibitor and stored at $-10°C$. 12-Butinoyloxy-9-octadecenoic acid (BOA) was synthesized at 130°C by direct esterification of butanoic acid with 12-oxy-9-octadecenoic acid (OOA) with H_2SO_4 as catalyst. BOA was further neutralized with NaOH to yield SBOA.

Preparation of Monomer Microemulsion

BA was added into the aqueous solution of SBOA in a capped ampoule. The contents of the ampoule were agitated slowly at room temperature with a magnetic stirrer for about 10 min to form a translucent monomer microemulsion. The monomer microemulsion was also produced by following routine. At first the mixture of BA and BOA was added to the pure water; then the aqueous solution of NaOH was added dropwise while stirring. In this study the second routine was adapted, because it needed less time to acquire balance.

Polymerization

Before polymerization, the microemulsion was degassed twice with a water pump for about 10 min. After that, it was fed directly into the dilatometer. Then the dilatometer was irradiated with a γ ray while the temperature of the system was accurately controlled with a regulator. The microemulsion remained stable and reddish after polymerization. The dilatometer used in this experiment was specially designed for radiation polymerization,[15] in which the change of the mercury (Hg) height in the capillary was linearly converted to the change of the volt across the electrical bridge. In this way, the polymer conversion was recorded as a function of time and the polymerization rate was derived by differentiation.

Molecular Weight Determination

The polymerized microemulsion lattices were precipitated in a large quantity of methanol. The polymer was dissolved in acetone and then reprecipitated with water to remove the emulsifier completely. After that the polymer was dried under vacuum. The molecular weight was measured with Ubbelohde capillary viscometer[16]: $[\eta] = 6.85 \times 10^{-3}[M_n]^{0.75}$ (mL/g).

RESULTS AND DISCUSSION

Effect of BA Concentration

Microemulsion polymerization rates at different contents of BA are depicted in Figure 1. The overall polymerization rate increased with the increase of monomer concentration. The plateau of polymerization rate, which was scarcely observed in the microemulsion polymerization, emerged at high monomer content (>20%). In interval I, the generating rate of polymer particles was bigger than the dying rate, so the number of living polymer particles increased with the conversion; it caused a further increase of the polymerization rate. With the accumulation of the living polymer particles, the dying rate also rose. When the dying rate rose to the generating rate, the number of living particles was kept constant and interval II appeared. With further polymerization, the monomer content was reduced to such a low level that it could not keep the monomer concentration in the living particles constant. Consequently, the polymerization rate started to diminish and the interval II ended.

It was shown in Figure 1 that the length of interval I seemed to be independent of monomer concentration and the plateau (interval II) became longer with the increase of monomer concentration. When the BA concentration was lower than 20 wt
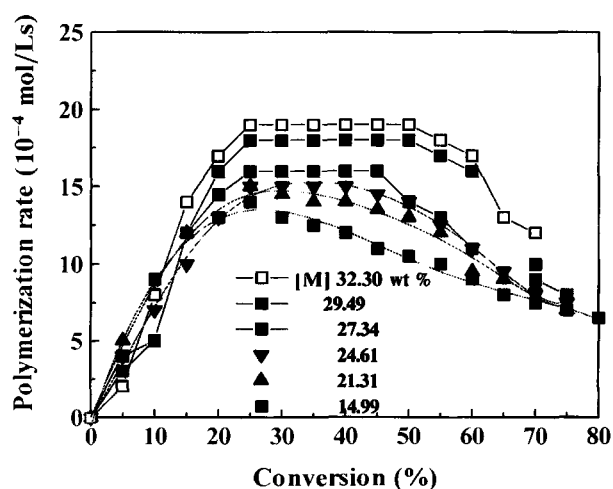
Figure 1 The rate of microemulsion polymerization vs. conversion at different monomer contents $[E]$, 10.1 wt %; pH, 7.5; dose rate, 46.42 Gy/min; T, 311 K.
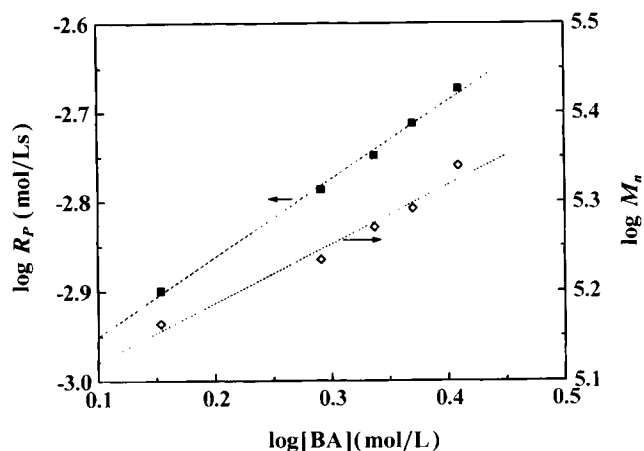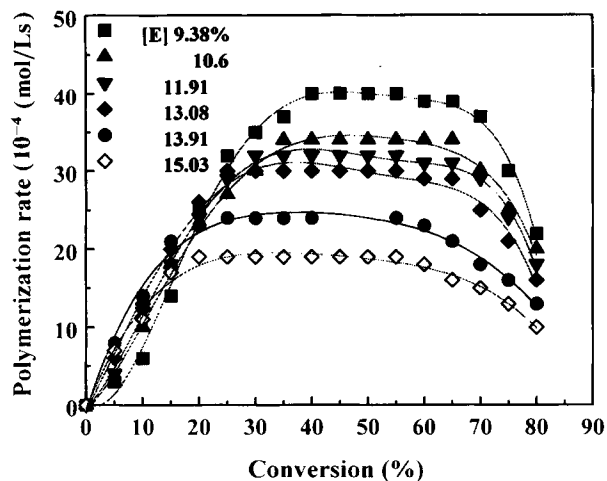
Figure 2 The effect of monomer concentration on R_p and M_n with the same conditions listed in Figure 1.

Figure 3 The rate of polymerization vs. conversion at different emulsifier contents. $[M]$, 30 wt %; pH, 7.5; dose rate, 46.42 Gy/min; T, 311 K.

%, the plateau disappeared completely. This suggested that the number of the living polymer particles remained unchanged with the variation of the monomer content. Figure 2 showed that R_p (the polymerization rate of the plateau, or the maximum polymerization rate at the end of interval I) was 0.93 with respect to BA concentration, and M_n (polymer molecular weight) was 0.65. All the above facts suggested that the increases of R_p and M_n were mainly attributed to the higher concentration of monomer at the polymerization loci.

Effect of Emulsifier

With the increase of emulsifier concentration $[E]$ from 10 to 15 wt %, the polymer conversion at which the polymerization rate plateau appears was lowered from 40 to 15% and the length of plateau was prolonged (Fig. 3). The dependences of R_p and M_n on emulsifier concentration were -1.07 and -1.66 power, respectively (Fig. 4).

It was thought that many factors contributed to the observed results. First, the emulsifier content in this system is still very high and surpasses the amount needed to form a monomolecular layer around the microemulsion droplets. Increasing emulsifier concentration leads to a thicker or a more rigid emulsifier layer. As a result, it retards the entry of radicals generated by γ ray in the aqueous phase, and the generating rate of living particles is reduced. Consequently, the number of living particles in interval II diminishes and the content of monomer at the end of interval I gets higher. Therefore, R_p decreases and the plateau of polymerization rate is lengthened.

Second, although the ratio of emulsifier to monomer compared with other microemulsion systems is low, the hydrocarbon tails may still make up an appreciable fraction of the droplet volume. So the true core solubilized monomer is suppressed with the increase of emulsifier concentration. Thus, the reduction of the polymerization rate and polymer weight may be partly ascribed to the decrease of the monomer concentration in the vicinity of the reaction loci.
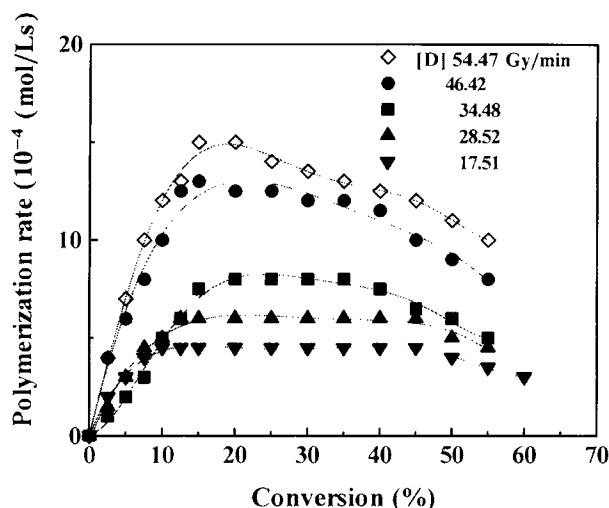
Finally, the transferring of growing polymer chains to emulsifier may also be important, and it might contribute to the decrease of R_p and M_n.

The equation of the molecular weight of the polymer produced may be expressed as the following:

$$1/X_n = R_i/R_p + C_m + C_e*[E]/[M], \qquad (1)$$
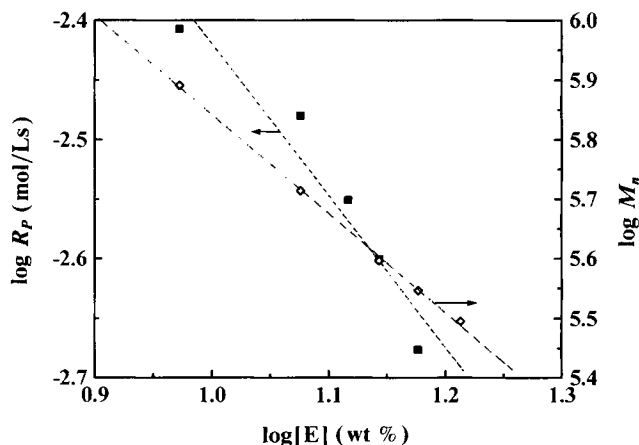
Figure 4 The effect of emulsifier content on R_p and M_n with the same conditions listed in Figure 3.

Figure 5 The rate of polymerization vs. conversion at different dose rates. $[E]$, 10.8 wt %; $[M]$, 26.0 wt %; water, 63.2 wt %; pH, 7.5; T, 308 K.

where R_i is the generating rate of radicals (mol/L s), R_p is the polymerization rate (mol/Ls), C_m is the chain transfer constant for monomer, C_e is the chain transfer constant for emulsifier, $[E]$ is the concentration of emulsifier, and $[M]$ is the monomer concentration. When $[E]$ is 13.08 wt %, $[BA]$ is 15 wt %, and dose rate (D) is 46.42 Gy/min $(R_i = 2.78 \times 10^{-7}$ mol/Ls$)$,[17] the actual R_p and M_n were 2.68 $\times 10^{-3}$ mol/Ls and 5.01 $\times 10^5$, respectively. Although the direct data of BA is difficult to find, the data of ethyl acrylate was found[16]: C_e of ethyl acrylate (EA) radicals to methyl oleate is 3.66 $\times 10^{-4}$; the C_m of EA is 3.22 $\times 10^{-5}$. As an approximation, these values were used for BA. Then the following values were derived: $R_i/R_p = 10.3 \times 10^{-5}$; $C_m = 3 \times 10^{-5}$; $C_e*[E]/[M] = 5.7 \times 10^{-5}$; the theoretical X_n is about 5.2 $\times 10^3$ and is in good agreement with the actual value of X_n measured (3.9 $\times 10^3$).

The above simple estimation suggests that the chain transfer to emulsifier only plays a minor role, for the third term is almost equal to the second term and less than the first term in eq. (1).

In summary, the decrease of R_p and M_n are mainly ascribed to the thick monomolecular layer around the living polymer particles and the large fraction of the hydrocarbon tails in the particles.
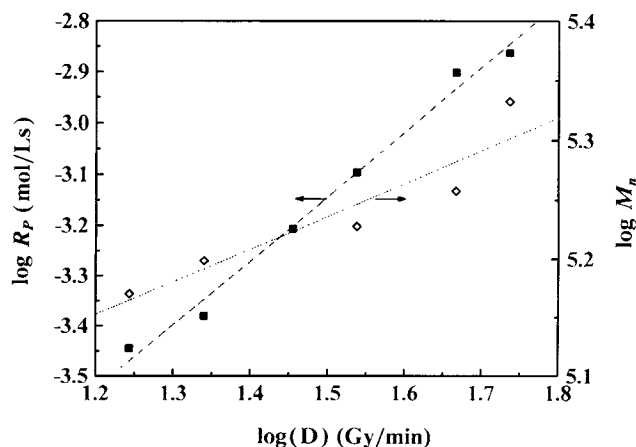
Effect of Dose Rate

The effect of dose rate on the polymerization is shown in Figure 5. As expected, when the dose rate is raised from 17.51 to 34.48 Gy/min, the generating rate of living polymer particles increases due to a larger radical flux. So the length of interval I be-

comes longer, and the number of living particles at balance in interval II increases. Meanwhile, the increase of dose rate leaves a smaller fraction of uninitiated monomer microdroplets at the end of interval I; as a result the length of interval II becomes shorter naturally. If the dose rate is raised further, then before the dying rate of living polymer particles equals the generating rate; the monomer left is already so low that the system cannot keep the monomer content in the living particles constant. Therefore, the polymerization rate starts to decrease before the balance between the dying rate and the generating rate is built up. This causes interval II to disappear, and the apparent length of interval I even decreases at a dose rate up to 50 Gy/min.

The dependence of R_p and M_n on dose rate was found to be 1.27 and 0.28 powers, respectively, as depicted in Figure 6. It was not expected that M_n increased with the increase of dose rate. It may be caused by two competitive factors with opposite effects. On the one hand, M_n should decrease and R_p increase with the increase of dose rate normally, which means that $R_p \propto D^{0.4} M_n \propto D^{-0.6}$ if they conform to the Smith–Ewart theory for conventional emulsion polymerization. On the other hand, the emulsifier layer around the polymerization loci became thinner for the number of loci increase at the higher dose rate, and the thinner emulsifier would cause R_p and M_n to increase according to the effect of the emulsifier discussed above. In fact, the powers for both R_p and M_n are about 0.9 higher than that expected from Smith–Ewart theory.

Effect of Temperature

As expected, the effect of temperature on radiation microemulsion polymerization is less obvious than

Figure 6 The effect of dose rate on R_p and M_n with the same conditions as shown in Figure 5.
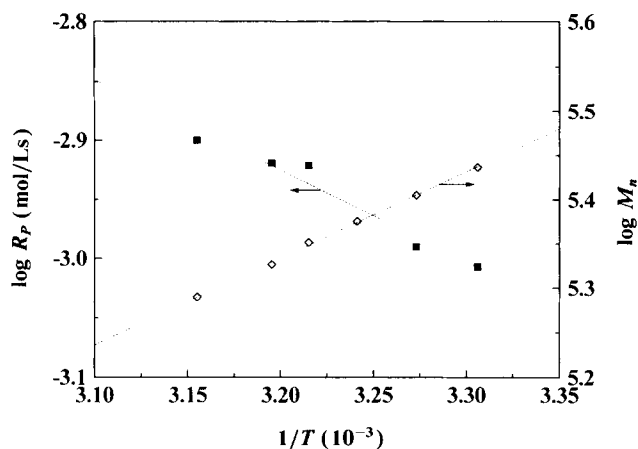
Figure 7 The Arrhenius plots of log R_p and log M_n vs. $1/T$. [E], 10.8 wt %; [M], 26.0 wt %; dose rate, 46.4 Gy/min; pH, 7.5.

that on polymerization initiated by chemical initiators, because the activation energy of radical generation by radiation is much less. The Arrhenius plots of log R_p and log M_n versus $1/T$ are shown in Figure 7. The overall activation energies (E_a) of R_p and M_n are 14.0 and -7.8 kJ/mol, respectively.

CONCLUSIONS

In this study the microemulsion composed of BA, SBOA, and water was irradiated with γ rays to produce a stable, reddish microlatex at high monomer concentration (about 30%). The constant polymerization period (interval II), which was seldom observed in other microemulsion systems with low monomer content, appeared in most cases. It was found that interval I ends at a lower dose rate and higher emulsifier content. The length of interval II mainly depends on the number of living polymer particles and the monomer content left at the end interval I. After all, much has to be done to understand the mechanism of microemulsion polymerization at high monomer content.

REFERENCES

1. J. O. Stoffer and T. Bone, *J. Polym. Sci. Part A: Polym. Chem.*, **18**, 2641 (1980).
2. H. Tang, P. I. Johnson, and E. Gulari, *Polymer*, **25**, 1357 (1984).
3. S. Holdcroft and E. L. Guiliet, *J. Polym. Sci. Part A: Polym. Chem.*, **18**, 1823 (1990).
4. P. L. Johnson and E. Gulari, *J. Polym. Sci. Part A: Polym. Chem.*, **22**, 3967 (1984).
5. J. S. Guo, M. S. El-Aasser, and J. W. Vanderhoff, *J. Polym. Sci. Part A: Polym. Chem.*, **27**, 691 (1989).
6. J. S. Guo, E. D. Sudol, J. W. Vanderhoff, and M. S. El-Aasser, *J. Polym. Sci. Part A: Polym. Chem.*, **30**, 691 (1992).
7. J. S. Guo, E. D. Sudol, J. W. Vanderhoff, and M. S. El-Aasser, *J. Polym. Sci. Part A: Polym. Chem.*, **30**, 703 (1992).
8. I. Capek, *Makromol. Chem.*, **191**, 2549 (1990).
9. I. Capek and P. Potisk, *J. Polym. Sci. Part A: Polym. Chem.*, **33**, 1675 (1995).
10. M. Antoniett, W. Bremser, D. Muschenborn, C. Rosenauer, B. Schupp, and M. Schmidt, *Macromolecules*, **24**, 6636 (1991).
11. J. E. Puig, V. H. Perez-Luna, M. Perez-Gonzalez, E. R. Macias, R. E. Rodriquez, and E. W. Kaler, *Colloid Polym. Sci.*, **271**, 114 (1993).
12. L. M. Gan, C. H. Chew, and I. Lee, *Makromol. Chem.*, **193**, 1249 (1992).
13. L. M. Gan, C. H. Chew, K. C. Lee, and S. C. Ng, *Polymer*, **34**, 3064 (1993).
14. X. Xu, B. Fei, Z. Zhang, and M. Zhang, *J. Polym. Sci. Part A: Polym. Chem.*, **34**, 1657 (1996).
15. Z. Zhang, P. Jiang, and M. Zhang, *J. Radiat. Res. Radiat. Process*, **8**(2), 100 (1990).
16. J. Brandrup and E. H. Immergnt, Eds. *Polymer Handbook*, 3rd ed., Wiley, New York, 1989.
17. G. V. Buxton, in *Radiation Chemistry: Principles and Application*, Farhataziz and M. A. J. Rodgers, Eds., VCH, New York, 1987, Chap. 10.