Microemulsion Polymerization of Methyl Methacrylate Initiated with γ Ray

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ABSTRACT: Polymerization of methyl methacrylate was studied in an oil and water microemulsion stabilized with styrene 12-butinoyloxy-9-octadecenoic acid. During the polymerization the size change of the monomer-swollen particles with conversion was measured with photon correlation spectroscopy, and the hydrodynamic diameter of the final polymer latex was about 50 nm. The polymerization kinetics in this microemulsion were also investigated. The apparent plateau of the polymerization rate was observed at a low dose rate and high emulsifier content. The mechanism leading to this plateau was discussed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2621–2626, 1999

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INTRODUCTION

Oil and water microemulsion polymerization of styrene has been extensively investigated up to now.[1–4] However, there were only several articles that reported the microemulsion polymerization of a polar monomer, such as methyl methacrylate (MMA)[5–8] or butyl acrylate.[9,10] It is known that emulsion polymerization of polar monomers differs substantially from that of sparingly water-soluble monomers. At first the increased solubility of a polar monomer in water may lead to homogeneous nucleation. Then the polar monomer may act as a coemulsifier and change the properties of the interfacial layer. Investigation of the microemulsion polymerization of polar monomers is very important to shed more light on the mechanism of microemulsion polymerization. In this study polymerizations of MMA in a microemulsion stabilized with styrene 12-butinoyloxy-9-octadecenoic acid (SBOA) were initiated with a γ ray, because a γ ray permits experiments over a wider range of temperatures than any chemical initiator and it is easier to control. The polymerization kinetics and colloidal properties are reported and discussed.

EXPERIMENTAL

Materials

MMA was distilled and stored at −10°C. BOA was synthesized following the process described in Xu et al.[11]

Preparation and Polymerization of Microemulsion

At first the mixture of MMA and BOA was added to the distilled water. Then the aqueous solution of NaOH was dropped into the mixture with stir-

Figure 1 The diameter (D_p) and its distribution of swollen particles as a function of polymer conversion while the microemulsion was initiated with a γ ray at 306 K. The microemulsion composition is 17 wt % MMA, 12 wt % SBOA, and 71 wt % H_2O; the dose rate is 32.5 Gy/min.

ring until the turbulent mixture suddenly turned clear.

The process of radiation microemulsion polymerization of MMA was the same as that described in Xu et al.[11]

Molecular Weight Determination

The polymerized microemulsions were precipitated in a large quantity of methanol. The polymer was dissolved in acetone and then reprecipitated with methanol to completely remove the emulsifier. Then the polymer was dried under a vacuum. The mean molecular weight of the polymer (M_v) was measured with an Ubbelohde capillary viscometer in acetone solution at 25°C: $[\eta] = 5.5 \times 10^{-2} M_v^{0.73}$ (mL/g).[12]

Particle Size Determination

The particle sizes D_p (hydrodynamic diameter) of the microemulsion latex and its distribution were determined by photon correlation spectroscopy using a Brookhaven BI-200SM instrument at 25°C. The latex was diluted 200 times to minimize particle–particle interactions without removing dust.

RESULTS

Growth of Poly(MMA) PMMA Particles

Figure 1 and Table I show information about the growth of PMMA particles. In Table I the estimated total number of monomer-swollen polymer particles (N_p) was based on the assumption that all of the monomer was located in the polymer particles after dilution at 100–200 times. The D_p at about 6% conversion was the biggest among all samples. This coincides with the fact that the transparent microemulsion became translucent just after the polymerization started, and then the transparency increased slowly with conversion. It is also in good agreement with the predication based on the thermodynamic model proposed by Guo and colleagues for styrene microemulsion.[4]

MMA as a polar monomer is moderately soluble in water. Therefore, in the microemulsion of MMA the micelle entry and homogeneous nucleation can both proceed. According to Bleger et al.,[8] at the early stage of polymerization the homogeneous nucleation dominates. Once the primary polymer particles are formed, the monomer

Table I Variation of Physical Values with Polymerization Conversion in Microemulsion Polymerization of Methyl Methacrylate

Conversion (%)	D_p[a] (nm)	Poly.[b]	N_p[c] (10^{18}/L)	M_v[d] (10^5)	n_p[e]
5.6	179	0.275	0.09	6.82	91
13.4	55.9	0.202	2.00	8.15	8.0
33.8	38.5	0.091	7.50	7.92	5.5
59.4	39.4	0.069	6.22	8.28	11.2
100	50.7	0.145	3.05	7.86	40.5

[a] Hydrodynamic diameter of monomer-swollen polymer particles.
[b] Polydispersity of monomer-swollen polymer particles.
[c] Total number of monomer-swollen polymer particles in the microemulsion.
[d] Molecular weight of the polymer at different conversions.
[e] Average number of polymer chains per polymer particles.

Figure 2   Affect of dose rate on polymerization of microemulsion containing 20 wt % MMA and 12 wt % SBOA at 318 K.

rapidly transports to these fine particles. This leads to the drastic increase of particles at low conversion.

At about 13% conversion, small particles appear (Fig. 1) and the large monomer-swollen particles shrink by transporting the monomer to small particles. Therefore, the particle distribution broadens. At about 30% conversion, the large particles disappear and the small particles continue to grow; therefore, the distribution narrows.

Table I shows that N_p continues to increase up to above 30% conversion. Meanwhile, the size of the smallest particles in the system above 13% conversion continues to increase (Fig. 1). It was obvious that the growth of the smallest size could not be attributed to the coagulation of polymer particles. Otherwise, the total N_p should have decreased from 13 to 33% conversion.

We assumed that the nucleation mechanism changed from homogeneous nucleation to microdroplet nucleation at middle conversion.

MMA acted as a cosurfactant and changed the prosperity of the emulsifier layer because of its high polarity. When the conversion is high enough, the MMA concentration in the aqueous phase and the emulsifier layer will both decrease and the effect of MMA will certainly be reduced. Then the stability of the small micelles (microdroplets) is also reduced, and the size of them will increase with conversion. Meanwhile, the MMA concentration in the aqueous phase is also reduced with the increase of conversion and the probability of homogeneity is minimized. Therefore, at a higher conversion micellar nucleation predominates. Because the sizes of micelles (microdroplets) increase with conversion, the size of newly formed growing polymer particles increased with conversion.

The N_p decreases above 50% conversion, because of the coagulation of polymer particles. We came to this conclusion by comparing the number of polymer chains per particle (n_p) at the middle and high conversion shown in Table I.

Polymerization Kinetics

Effect of Dose Rate

The affects of dose rate on microemulsion polymerization of MMA are shown in Figures 2 and 3. As expected, the polymerization rate increases with the dose rate and the molecular weight of PMMA decreases simultaneously: R_p [D]$^{0.93}$, $M_v \propto$ [D]$^{-0.31}$. These two powers are close to that reported for polymerization of styrene in a similar microemulsion.[13]

Note that there is an apparent plateau of the polymerization rate at a low dose rate. This fact was also observed in the polymerization of an MMA microemulsion stabilized with a cationic emulsifier[5] and in polymerization of a styrene microemulsion stabilized with an anionic emulsifier.[13] In order to understand the mechanism leading to the plateau, the dose rate was changed when the polymerization came into the plateau region (at about 20% conversion). Figure 4 shows that if the dose rate is decreased, the polymerization rate decreases and if the dose rate is increased, the polymerization rate increases.

As pointed in Xu et al.,[13] in microemulsion polymerization, when polymerization comes into the constant polymerization region, the balance between the generating rate and terminating rate of growing particles is established. In the plateau it is the number of growing polymer particles being kept constant, rather than the number of total polymer particles. Because the stable num-

Figure 3   Affect of dose rate on polymerization rate and molecular weight of the polymer.

Figure 4 Affect of changing dose rate during polymerization at 306 K. The microemulsion is composed of 20 wt % MMA and 12 wt % SBOA.

Figure 5 Affect of monomer content on polymerization of microemulsion containing 12 wt % SBOA at 316 K. The dose rate is 46.4 Gy/min.

ber of growing particles was in proportion to the generating rate that was linear to the dose rate, it was easy to understand that the R_p almost linearly increased with the increase of dose rate. At a low dose rate the stable number of growing polymer particles would be lowered. The diffusion of monomer to growing particles would be fast enough to keep the monomer concentration in growing particles constant up to higher conversion. Therefore, the plateau of polymerization rate is more apparent at a low dose rate.

When the polymerization reached the plateau, if the dose rate was increased, the generating rate of active particles was sure to increase and the system built a new balance and the total number of growing polymer particles increased. This would further cause the increase of polymerization rate and vice versa. This result is shown in Figure 4.

Effect of Monomer Concentration

Polymerization curves at different MMA contents are depicted in Figure 5. The overall polymerization rate increased with the increase of monomer concentration. There is no apparent plateau of the polymerization rate. The polymerization rates increase up to about 30% conversion and then decrease. This may be caused by the high dose rate adapted for the experiment. As shown in Figure 6, $R_p \propto [\text{MMA}]^{0.31}$, $M_v \propto [\text{MMA}]^{0.77}$. The power of the polymerization rate to the monomer concentration is much lower than expected. For styrene polymerization in a similar microemulsion,[13] this power was reported to be 1.25.

As pointed out by Potisk et al.,[10] in the microemulsion polymerization of polar monomers initiated with water-soluble initiators, the polymer-

ization loci are the emulsifier layer. Due to the high polarity of the monomer, MMA acted as a cosurfactant. On the one hand, the monomer concentration in the polymerization loci (emulsifier layer) was determined by the interface characteristic. Therefore, it was only slightly increased with the total monomer content in the system. On the other hand, homogeneous nucleation played an important role in the microemulsion polymerization at the early stage of polymerization. The higher the monomer content in the polymerization system, the more important the homogeneous nucleation. Bleger et al.[8] pointed out that the nucleation rate through homogeneous nucleation is much slower. Both of the above two factors led to the much lower power of R_p to monomer content.

For styrene microemulsion polymerization, because of the low polarity of the monomer, microdroplet nucleation predominated for the whole polymerization process and the polymerization

Figure 6 Affect of monomer content on polymerization rate and molecular weight of the polymer.

loci were considered to be the core of the polymer particles swollen with monomer. Therefore, the power of R_p to monomer content was close to 1.

Effect of Emulsifier Concentration

Polymerization at different emulsifier concentrations [SBOA] is shown in Figure 7. The overall polymerization rate and polymer molecular weight decrease with the increase of SBOA: $R_p \propto$ [SBOA]$^{-1.19}$, $M_v \propto$ [SBOA]$^{-1.05}$ (Fig. 8). These powers are also quite different from that in styrene microemulsion polymerization.[13]

As discussed above, in MMA microemulsion polymerization, at the early stage of polymerization, the homogeneous nucleation predominates. The main role of the emulsifier is to stabilize the formed particles, and it should have no obvious effect on the nucleation process. The polymerization rate should not change with the increase of emulsifier content for this reason. On the other hand, because the polymerization loci are the emulsifier layer, the monomer concentration in the emulsifier layer is suppressed with the increase of emulsifier concentration. This causes the polymerization rate and the molecular weight of PMMA to both decrease.

For styrene microemulsion polymerization the polymerization loci were believed to be the core of polymer particles swollen with monomer. Therefore, the dilution effect of the emulsifier on the monomer concentration at the polymerization loci was much less and the increase of emulsifier content almost did not affect the polymerization rate.

Taking into account that the polymerization rate is depressed with increasing emulsifier content, the diffusion of the monomer from inactive particles would be fast enough to keep the mono-

Figure 8   Affect of emulsifier content on polymerization rate and molecular weight of the polymer.

mer content in growing particles constant over a wider conversion. Therefore, as shown in Figure 7, the obvious plateaus of the polymerization rate are observed at high emulsifier content.

CONCLUSIONS

There are obvious differences between the microemulsion polymerization behavior of polar monomer MMA and nonpolar monomer styrene.[11]

In MMA microemulsion polymerization, the homogeneous nucleation predominates at the early stage of polymerization. With the increase of conversion, the microdroplet nucleation becomes more and more important and it dominates at high conversion. In addition, MMA may act as a cosurfactant and the monomer content in the emulsifier layer is very high. This causes the emulsifier layer to become the main polymerization loci and makes the polymerization kinetics become quite different from that of the nonpolar monomer.

Figure 7   Affect of emulsifier content on polymerization of microemulsion containing 20 wt % MMA at 312 K. The dose rate is 34.5 Gy/min.

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