Polym. Bull. (2011) 66:599–608
DOI 10.1007/s00289-010-0295-9

ORIGINAL PAPER

High monomer content batch microemulsion polymerization of butyl acrylate and acrylonitrile initiated with gamma ray

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Received: 11 November 2009 / Revised: 9 March 2010 / Accepted: 14 May 2010 /

Abstract Gamma ray-induced polymerization of butyl acrylate (BA) and acrylonitrile (AN) was carried out at room temperature in a microemulsion with high monomer content stabilized by a mixture of sodium of 12-acryloxy-9-octadecenoic acid (AOA) and sodium dodecyl sulfate (SDS) at a weight ratio of 4. Special Y-shaped structure of AOA promotes the efficiency of monomer solubilization and gamma ray radiation contributes to the stability of microemulsion during the polymerization process. Microlatexes were characterized by dynamic light scattering (DLS) and scanning electron microscopy (SEM). Results showed that microlatex particles with a narrow size distribution were obtained. The effects of monomer composition, dose rate, monomer concentration, and surfactant concentration on the microlatexes are discussed.

Keywords Microemulsion polymerization · Gamma ray radiation · High monomer content · Butyl acrylate · Acrylonitrile

Introduction

Microemulsions are transparent liquid systems consisting of at least ternary mixtures of oil, water, and surfactant. Sometimes a cosurfactant is needed for the formation of a thermodynamically stable microemulsion. Because of their well-defined nature,

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microemulsions have been used as potential media for polymerization to prepare well-defined polymeric microlatexes in the size range 10–100 nm which are not easily obtained from other systems [1]. The polymerized microlatexes in view of their immense potential in industrial and pharmaceutical applications are expected to be environmentally friendly, nontoxic, and biodegradable.

Microemulsion polymerization has been quite actively studied since the first reports [2]. However, two main drawbacks limit its broad applications: (1) a high surfactant-to-monomer ratio, usually larger than 1, and (2) a low monomer concentration with respect to water (low polymer content of the final latexes), usually less than 10 wt%. Consequently, efforts have been undertaken to obtain microlatexes containing higher polymer contents with lower surfactant dosage, which can be subdivided into two different approaches. The first way is to search more effective surfactant systems that are able to solubilize the larger amount of monomer or to improve the polymer content in the conventional microemulsion polymerization. One of surfactant systems is to use special Y-shaped surfactants such as sodium salts of 12-butinoyloxy-9-octadecenate (SBOA) [3] or 12-hexinoyloxy-9-octadecenate (SHOA) [4] which allow the formulation of microemulsions with the higher content of butyl acrylate and/or styrene, compared to non-branched surfactants such as cetyltrimethylammonium bromide. The use of comonomers which also act as cosurfactants in surfactant system is another alternative to improve polymer content, but this method cannot decrease the amounts of surfactant [5–8]. The other approach is through some special methods to increase the amount of polymer produced for a given amount of surfactant. It involves various semi-continuous microemulsion polymerization techniques. Gan et al. [9] successfully designed a new system termed Winsor I-like system, i.e., a pure monomer phase is placed on the top of a ternary o/w microemulsion, to polymerize styrene up to 15 wt% using only about 1 wt% surfactant. The author also polymerized methyl methacrylate in Winsor I-like system and produced a relatively high weight ratio (8:1) of polymer to surfactant [10]. Xu et al. [11, 12] firstly demonstrated the seeded microemulsion polymerization of butyl acrylate and styrene with gamma ray. Ming et al. [13–15] prepared microlatexes from styrene, methyl methacrylate, and butyl acrylate using modified microemulsion polymerization which is to directly add monomer dropwise to a pre-polymerized microemulsion. He et al. [16, 17] synthesized polymer nanoparticles by adding monomer in a differential manner into a preheated mixture containing a designed amount of initiator, surfactant, and deionized water.

The present article is concerned with microemulsion polymerization of butyl acrylate and acrylonitrile. Understanding the copolymerization behavior in microemulsion was the main subject of many reports [18–20]. In our study, we aimed at the preparation of stable, transparent butyl acrylate–acrylonitrile copolymer microlatexes by batch microemulsion polymerization with high monomer content. A polymerizable anionic surfactant, sodium of 12-acryloxy-9-octadecenoic acid (AOA) with a special Y-shaped structure, instead of the usual aliphatic alcohols combined with SDS was used to form a microemulsion with higher monomer content. The advantage of this approach is that the polymerizable surfactant with a higher emulsifying efficiency can be incorporated in the final polymer to improve the polymer content in the microlatex. Microlatexes particles with a narrow size distribution were obtained via gamma ray-induced batch microemulsion polymerization at room temperature.

Experimental

Materials

A Y-shaped AOA was used as received from USTC ChuangXing Co., LTD. (China). Sodium hydroxide (NaOH), sodium dodecyl sulfate (SDS), butyl acrylate (BA), and acrylonitrile (AN) were used as received from Shanghai Chemical Reagent Co. (China). BA and AN monomers were purified by distillation under reduced pressure before use. Deionized (DI) water was used for all experiments.

Preparation and polymerization of microemulsion

At first, AOA and SDS were added in the deionized water. Then the aqueous solution of NaOH (1 M) was dropped into the mixture to adjust the pH value to 8.0 and obtain a clear solution. A transparent monomer microemulsion was formed by adding mixture of BA and AN into the clear solution with agitating slowly at room temperature by a magnetic stirrer.

Before polymerization, nitrogen with high purity was bubbled slowly through the microemulsion at room temperature for about 15 min to get rid of oxygen. After that, the samples were irradiated in the field of ^{60}Co γ-ray source at ambient temperature. The dose rate was detected by Fricke ($FeSO_4$) dosimeter. To achieve complete conversion, each sample was subjected to a radiation dose of about 16 KGy.

Characterization methods

To obtain microemulsions with maximum monomer content, aqueous solutions of surfactant system with different concentrations were prepared. The single phase regions of the microemulsions were determined visually from their transparency by titrating monomer into the aqueous surfactant solution in screw-capped glass tubes.

The size and size distribution of polymer microlatexes were measured by dynamic light scattering (DLS) carried out on a Malvern Zetasizer Nano ZS90 with a He–Ne laser (633 nm) and 90° collecting optics. Before measuring, the latex was diluted to 100–150 times to minimize the interaction between the particles. The data were analyzed by Malvern Dispersion Technology Software 4.20. The number of particles per milliliter of water was computed from the following relationship:

$$N_{\mathrm{p}} = \frac{6M_{\mathrm{mw}}x}{\pi\rho_{\mathrm{p}}{D_{\mathrm{p}}}^3}$$

where M_{mw} is the initial monomer-to-water ratio (g/mL), x is the fractional conversion, ρ_p is the density of microlatex particles, and D_p (cm) is the average diameter of the particles.

The particles' sizes of microlatexes were also estimated from scanning electron microscope (SEM) on a JEOL JSM-6700 field-emission scanning electron microanalyzer.

The copolymers resulted from microemulsion polymerization were isolated by the solvent precipitation method using methanol as a precipitating solvent, washed several times with water to ensure complete removal of surfactant, and dried under vacuum until a constant weight was obtained. The infrared spectrum (IR) was recorded with VECTOR22 FT-IR. A Shimadzu DSC-60 differential scanning calorimeter (DSC) was used to measure the glass transition temperature (T_g) of the copolymers. The scan was performed at a heating rate of 10 °C/min under argon atmosphere.

Results and discussion

Formation and polymerization of high monomer content microemulsion

The microemulsion stabilized by SDS often needed the alcohol as cosurfactant and resulted in very lower polymer content microlatexes with a large amount of surfactant or cosurfactant. In our previous works, a high efficient surfactant system has been developed, in which a special Y-type polymerizable surfactant, sodium of AOA, instead of the usual aliphatic alcohols was combined with SDS to form microemulsions of butyl acrylate [21] or methyl methacrylate [22] with higher monomer content. In this article, we attempted to use the high efficient surfactant system to perform microemulsion copolymerization of butyl acrylate and acrylonitrile with high monomer content. To improve polymer content in the resulted microlatexes, we chose the mixture of AOA and SDS with a weight ratio ~4 as surfactant system to form microemulsions.

Microemulsions of BA and AN with different weight ratio were formed using the mixture of AOA and SDS with a weight ratio ~4 as surfactant system. Table 1 shows the characteristics of the microemulsions with maximum monomer content

Table 1 Characteristics of microlatexes produced by microemulsion polymerization of BA and AN at different weight ratio with maximum monomer content under gamma ray at a dose rate of 88.7 Gy/min

Run	BA/AN (w/w)	Monomer (wt%)	Surfactant (wt%)	Appearance		D_p (nm)	PSD
				Before polymerization	After polymerization		
1	4	32.2	6.8	Transparent, fluid	Bluish, transparent	56.8	0.027
2	2	34.6	6.5	Transparent, fluid	Bluish, transparent	62.9	0.027
3	1	37.0	6.3	Transparent, fluid	Bluish, transparent	54.5	0.032
4	0.5	37.5	6.3	Transparent, fluid	Bluish, transparent	59.6	0.037

before or after polymerization. It was found that the surfactant system of AOA and SDS with weight ratio ~4 was effective for producing microemulsions with high monomer content. The maximum solubilized monomer content in microemulsion increases when the weight ratio of BA to AN decreases from 4 to 0.5. In this study, γ-ray radiation was used to initiate the microemulsion polymerization. In comparison with the thermal decomposition of chemical initiators, radiation-induced polymerization can be controlled more easily because of the homogeneously penetrating through the sample and the independence of temperature. Also, no additional component is introduced in the system which might influence the phase behavior [23]. After polymerization, all microemulsions became stable, bluish-transparent microlatexes. From the Table 1, we can also see that all the resulted microlatexes have a narrow size distribution. The possible reason is that the used polymerizable surfactant AOA has an advantage over nonpolymerizable cosurfactants since the templating effect of the amphiphilic interface may be better preserved during polymerization [24].

The particle size was further confirmed by SEM. One of the resulting images (Run 3) is shown in Fig. 1. The number average diameter of the particles (Run 3) is about 52 nm in Fig. 1, which corresponds well to the result as measured by dynamic light scattering method. The particle size distribution is also rather narrow from the Fig. 1.

Effect of monomer composition on the microlatexes

In order to investigate the effect of monomer composition on the resulted microlatexes, we fixed the concentration of monomer and surfactant but just changed the weight ratio of BA to AN in microemulsion. The detailed formulations are listed in the Table 2. It was found that formed microemulsions of BA and AN

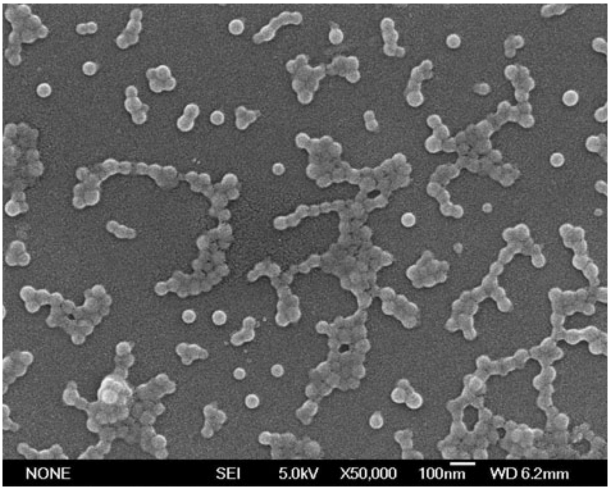

Fig. 1 SEM images of Run 3 (Table 1) microlatex particles

Table 2 Effect of monomer composition on the characteristics of microlatexes produced by microemulsion polymerization under gamma ray at a dose rate of 88.7 Gy/min

Run	BA/AN (w/w)	Monomer (wt%)	Surfactant (wt%)	Appearance		D_p (nm)	PSD
				Before polymerization	After polymerization		
5	4	31.0	6.9	Transparent, fluid	Bluish, transparent	53.3	0.064
6	2	31.0	6.9	Transparent, fluid	Bluish, transparent	53.6	0.049
7	1	31.0	6.9	Transparent, fluid	Bluish, transparent	49.7	0.041
8	0.5	31.0	6.9	Transparent, fluid	Bluish, transparent	50.1	0.040

with different weight ratio kept transparent before or after polymerization and the particle size of resulted microlatexes did not change evidently with the variation of weight ratio of BA to AN. All the microlatexes have a narrow size distribution.

The IR spectra of the microlatexes are shown in Fig. 2. The stretching vibrations due to the nitrile group of AN appear at 2,241 cm^{-1}, and the stretching vibrations due to the carbonyl group of BA appear near 1,731 cm^{-1}. The glass transition temperatures of the copolymers were determined from DSC. The determined values of the glass transition temperature lie between those of pure poly(butyl acrylate) (−56 °C) and polyacrylonitrile (105 °C). The variation of glass transition temperature of the copolymers with composition is shown in Fig. 3. It is found that T_g value increases with the increase of the weight fraction of acrylonitrile in the feed. The DSC scan was performed from −105 to 150 °C to rule out the possibility of any homopolymer formation. The presence of such a single value for the T_g may suggest that a random copolymer is formed in conformity with the reactivity ratio values and the general observations [25].

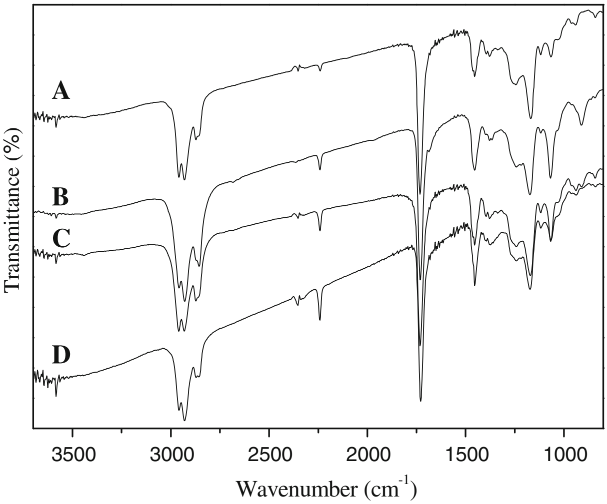

Fig. 2 IR spectra of butyl acrylate–acrylonitrile copolymers with different weight ratio of butyl acrylate to acrylonitrile: (*a*) 4, (*b*) 2, (*c*) 1, (*d*) 0.5

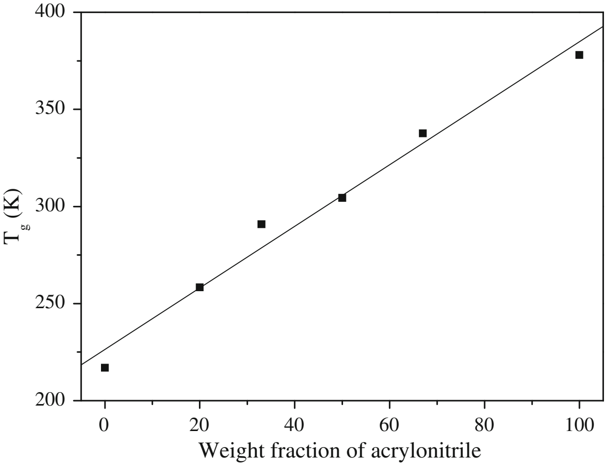

Fig. 3 Variation of the glass transition temperature of butyl acrylate–acrylonitrile copolymers with composition

Effect of dose rate on the particle size

In the radiation-induced microemulsion polymerization process, radiation dose rate corresponds to the concentration of initiator. In order to investigate the effect of dose rate on the particle size of resulted microlatexes, we carried out microemulsion polymerization of BA and AN at a weight ratio of 1 at different dose rate. The effect of dose rate on particle size and particle number is shown in Fig. 4. It is found that the particle size decreased from 52.1 to 43.7 nm when the dose rate increased from 15.2 to 88.7 Gy/min. Because the parent microemulsion is the same, the number of the initial monomer-swollen micelles should be about the same. At larger dose rate the free radical flux is larger, which helps more monomer-swollen micelles become

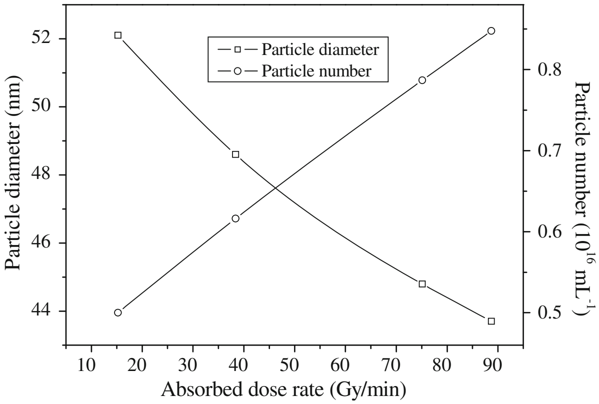

Fig. 4 Effect of dose rate on the particle diameter and number (Monomer concentration: 25.0 wt%; total surfactant concentration: 7.5 wt%; dose: 16 kGy)

particles by capturing radical during polymerization process for a certain microemulsion system. Finally, a larger dose rate corresponds to a larger number of particles with a smaller average diameter in the resulted microlatex.

Effect of solubilized monomer content on the particle size

Figure 5 shows the effect of solubilized monomer content in microemulsion of BA and AN at a weight ratio of 1 on particle size and particle number. The particle size increases from 26.4 to 54.5 nm when the solublized monomer content increases from 15 to 37 wt%. When the surfactant concentration in water keeps constant, while the content of solubilized monomer increases, the size of monomer-swollen micelles increases and probability of collision among the formed particles becomes higher, which results in a smaller number of particles and hence the size of particles becomes larger.

Effect of surfactant concentration on the particle size

Surfactant concentration is a key factor for the microemulsion polymerization. In order to investigate the effect of surfactant concentration on particles size and particle number, we conducted microemulsion polymerization with different surfactant concentrations at a fixed monomer content with BA and AN at a weight ratio of 1. The results are showed in Fig. 6. It is found that particles size decreases with the increase of surfactant concentration. The number of monomer-swollen micelles increases with increasing surfactant concentration, and the sizes of the micelles may decrease slightly because of a decreasing amount of monomer per micelle at a fixed monomer concentration, which enhance the probability of radical capture by the monomer-swollen micelles. Finally, a larger number of particles are formed with the increase of surfactant concentration, as the result smaller particle sizes are obtained in the resulted microlatex.

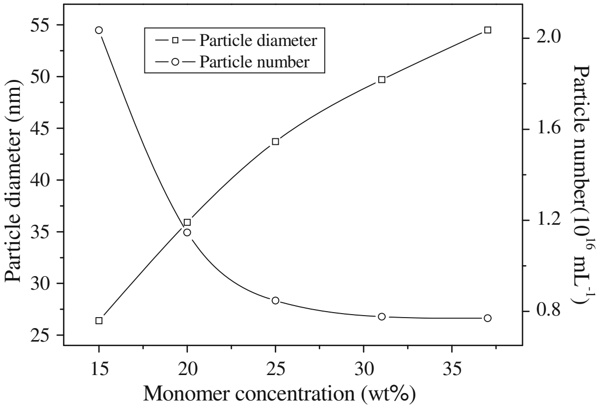

Fig. 5 Effect of solubilized monomer content on the particle diameter and number. (Weight ratio of total surfactant to water: 10/90; dose rate: 88.7 Gy/min; dose: 16 kGy)

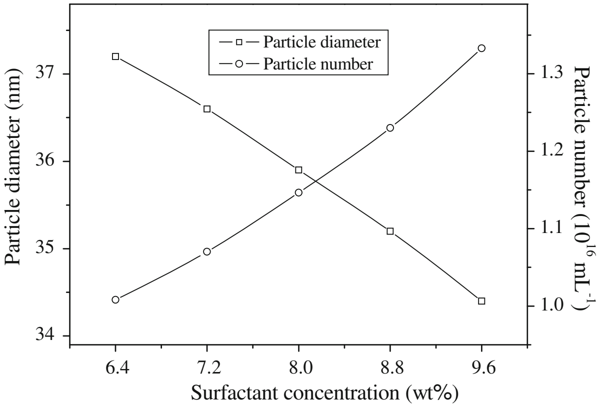

Fig. 6 Effect of surfactant concentration on the particle diameter and number (Monomer content: 20 wt%; dose rate: 88.7 Gy/min; dose: 16 kGy)

Conclusion

Stable transparent poly(butyl acrylate-co-acrylonitrile) microlatexes can be obtained from microemulsions composed of monomer with different composition, a mixture of AOA and SDS at a weight ratio of 4, and water at higher monomer content with a lower SDS amount. The use of special Y-type AOA and gamma ray radiation is believed to play an important role in batch microemulsion polymerization. IR and DSC results show the formation of random copolymers of BA and AN. Microlatex particles have a narrow size distribution from the DLS and SEM results. The particle size of microlatex increases from 26.4 to 54.5 nm when the solublized monomer content increases from 15 to 37 wt%. Particle size decreases with the increase of dose rate and surfactant concentration.

Acknowledgments Support of the Program of Ma'anshan Scientific and Technological Bureau (2008-11), the Research Fund for the Returned Overseas Talents of Anhui Province (2006Z041), Development Program of China (863 program, 2009AA03Z529) and the Program for New Century Excellent Talents in University of China (NCET-06-0556) is gratefully acknowledged.

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