

# Formation of Microporous Polymeric Materials by Microemulsion Radiation Polymerization of Butyl Acrylate

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**ABSTRACT:** A microemulsion system composed of butyl acrylate (BA) and water with a mixture of sodium 12-acryloxy-9-octadecenate (SAO) and octylphenoxypoly(ethoxyethanol) as an emulsifier was initiated by  $\gamma$ -ray radiation at room temperature to polymerize and produce microporous polymeric materials. The morphology and swelling characteristics of the resulting polymeric materials were studied. It was found that they strongly depended on the composition (water content, crosslinker content, emulsifier content) of the precursor microemulsions. In addition, the swelling properties of the polymer so prepared were found to be sensitive to the pH of the swelling medium. The change in swelling behaviors of the polymeric materials is discussed in terms of the polyelectrolyte effect exhibited by the polymerized anionic emulsifier SAO. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1989–1993, 2000

**Key words:** bicontinuous microemulsion polymerization; microporous polymer; morphology; swelling; polymerizable emulsifier

## INTRODUCTION

The microstructure of a microemulsion depends on the composition of the system, for example, water in oil (w/o) droplets at lower water content, oil in water (o/w) droplets at higher water content, and a bicontinuous structure at intermediate water content. The polymerizations in w/o and o/w microemulsions have been extensively investigated and they have also been successfully used for preparing nanoparticles of polymers, as well as inorganic compounds.<sup>1–3</sup> However, interest in polymerization of a monomer-containing bicontinuous microemulsion has been relatively limited.

Porous polymeric membranes can be produced by phase inversion from polymer solutions<sup>4</sup> and

polymerization of concentrated emulsions.<sup>5</sup> Much work has been based on these two methods. It is known that the precise control of the pore size of a membrane is not easy because even a slight fluctuation of the processing conditions might lead to a broad distribution of pore size. Published work in the polymerization of bicontinuous microemulsions indicates that this method is a potential route for preparing porous polymeric materials.<sup>6–9</sup>

The polymeric materials so formed may find potential applications in separation technology.<sup>10,11</sup> Further, this technique could have significant technological importance because it utilizes the microstructure existing in bicontinuous microemulsions to form the membranes in a one-step organic solvent-free process starting from monomer(s).<sup>12</sup>

In order to alleviate the occurrence of phase separation during the course of polymerization, a fast polymerization rate and low polymerization temperature are required, although they are not

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very critical. Both conditions can be fulfilled by using a suitable initiation mechanism such as  $\gamma$ -ray initiation. In our work sodium 12-acryloxy-9-octadecenate (SAO) is used as a polymerizable anionic emulsifier, and its introduction is expected to have some important effects on the properties of polymers (e.g., swelling behaviors).

The factors that affect the morphology and swelling behaviors of porous polymeric materials thus prepared were investigated.

## EXPERIMENTAL

### Materials

Butyl acrylate (BA) from Dongfang Chemical Factory was distilled at 10 mmHg to remove inhibitor and stored at  $-10^{\circ}\text{C}$ . Pentaerythritol tetramethacrylate (TMPTA), sodium 12-acryloxy-9-octadecenate (SAO), and octylphenoxypoly(ethoxyethanol) (OP-10) were used as received from Shanghai Chemical Reagent Co. (China). NaOH and HCl were analytically pure.

### Preparation of Monomer Microemulsion

The monomer microemulsion was produced as follows. The monomer, emulsifiers, and distilled water were first mixed together; the crosslinker TMPTA was also added into some samples. Then the aqueous solution of NaOH was added dropwise with stirring until the system suddenly turned clear. The SOA to OP-10 ratio was maintained at 3/2. The pH values for all the microemulsion samples were 7.0–9.0.

### Polymerization

After bubbling with nitrogen gas for 30 min, each sample was sealed and then polymerized in the field of a  $2.59 \times 10^{15}$  Bq  $^{60}\text{Co}$   $\gamma$ -ray source. The radiation polymerization was carried out for 10 h at room temperature. The polymerized sample was cut into small pieces and washed with methanol and water to remove unpolymerized monomer and emulsifier, then dried in a vacuum oven to a constant weight. The temperature was always kept below  $50^{\circ}\text{C}$  during the purification and drying process to ensure that the conformation of the sample was not changed.

### SEM

The surface morphology of the polymeric materials was examined under a Hitachi II-800 scan-

ning electron microscope with an accelerating voltage of 25 kV. The samples were first frozen in liquid nitrogen and then fractured mechanically.

### Swelling Measurement

The samples were swelled at room temperature in distilled water or aqueous solutions having various pH values controlled by NaOH or HCl. They were periodically removed from the swelling medium, blotted lightly to remove excess surface water, and weighed. The extent of swelling was evaluated as the percentage of the increase in weight of the polymer samples due to absorption of the swelling agent relative to the weight of the dried polymer sample prior to swelling.

## RESULTS AND DISCUSSION

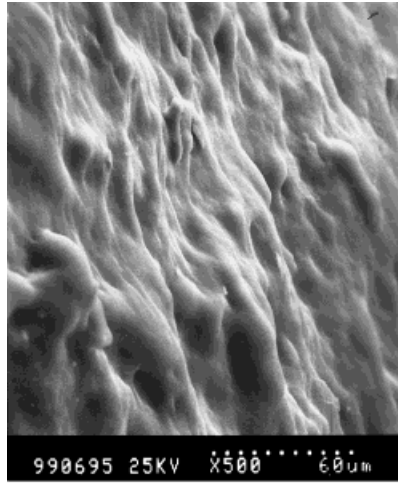
### Effect of Water Content

The effect of water content in the precursor microemulsion on the morphology of polymeric materials formed after polymerization is illustrated in Figure 1. It shows that the porosity of the polymer increased with the increase of water content. The open-cell pores emerged [Fig. 1(c)]. Similar results were also observed in other systems as reported in the literature.<sup>12,13</sup> Polymerization of bicontinuous microemulsions leads to formation of an open-cell structure. The pores or voids in the polymer are believed to be water-filled spaces between the incompletely coalesced aggregates.

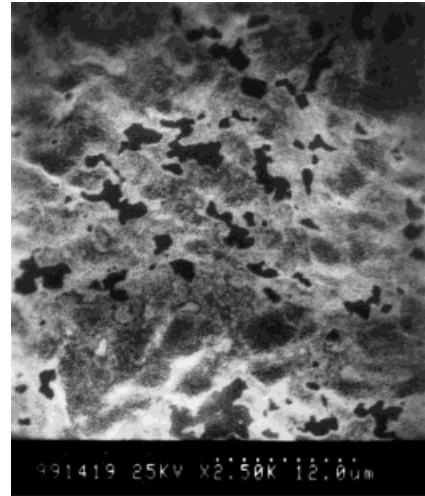
The sizes of the pores as observed in Figure 1(c) are about 1–7  $\mu\text{m}$ . These pore sizes are considerably larger than the size of microstructures expected in the precursor microemulsion. This may be due to the occurrence of phase separation during polymerization.

### Effect of Crosslinker Content

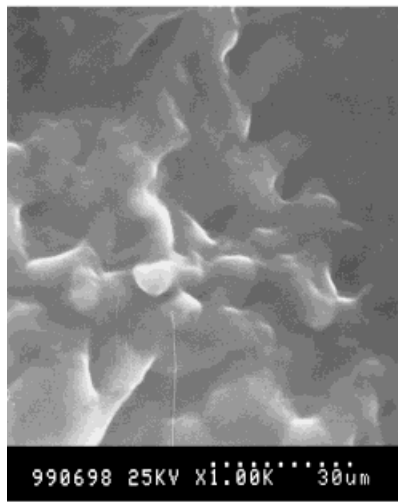
When the crosslinker was added to the microemulsion with the same precursor composition as that of the polymer sample shown in Figure 1(b), the change in morphology of the polymer was remarkable (Fig. 2). With the increase of crosslinker content from 0 to 4 wt % based on the weight of BA, the pore size decreased while the number of pores increased. It was clearly shown that the extent of swelling of the polymer sharply decreased after the addition of crosslinker into the precursor microemulsion (Fig. 3).



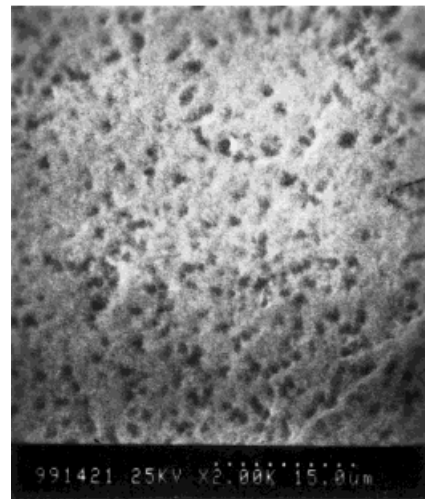
(a)



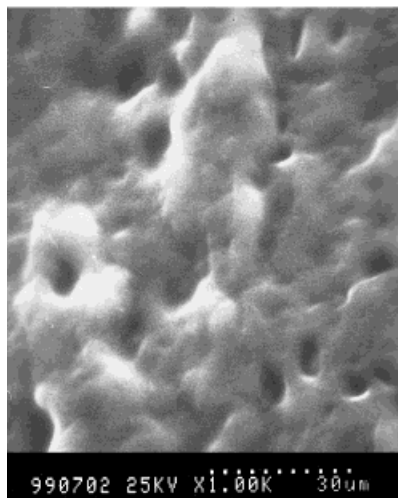
(a)



(b)



(b)

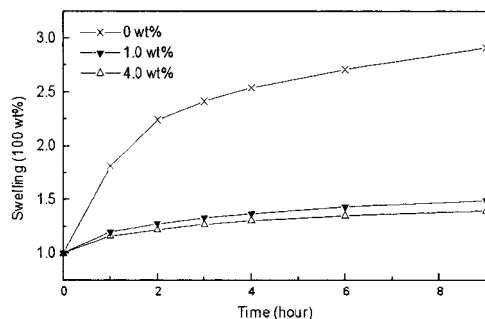


(c)

**Figure 2** SEM micrographs of the polymer samples obtained by polymerizing microemulsions containing crosslinker TMPTA contents (wt %) of (a) 1.0 and (b) 4.0 based on the weight of BA.

The distribution of the pore size was found to be narrower, for instance, at about 0.5–1.5  $\mu\text{m}$  in Figure 2(b). A smooth surface was also observed after the addition of crosslinker, and the smoother surface appeared at higher crosslinker content. These results may be attributed to the

**Figure 1** SEM micrographs of the polymer samples obtained by polymerizing microemulsions having the same BA : SAO : OP-10 weight ratio of 10 : 3 : 2 and water contents (wt %) of (a) 17.7, (b) 25.6, and (c) 32.2.

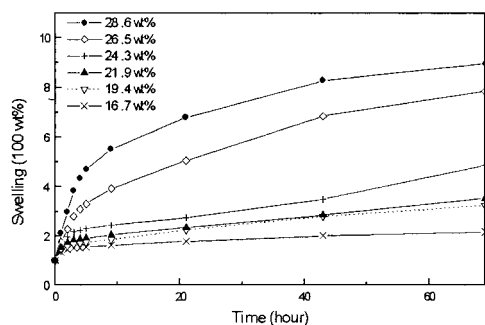


**Figure 3** The results of swelling measurements for the polymer samples from precursor microemulsions having the same BA : SAO : OP-10 : H<sub>2</sub>O weight ratio of 10 : 3 : 2 : 5 and various crosslinker (TMPTA) contents.

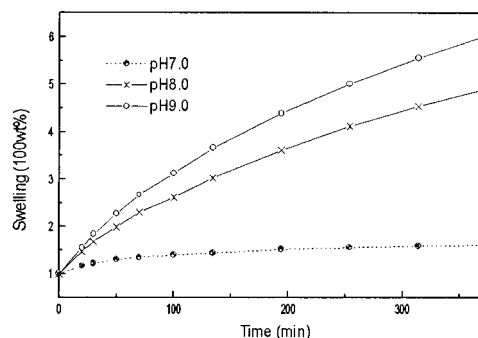
alleviation of the occurrence of phase separation during the polymerization of crosslinker-containing microemulsion. It is believed that the oil-water interfaces of the bicontinuous microemulsions are flexible and fluctuating and they can easily undergo deformations. It was reported that the bicontinuous structure was difficult to preserve during polymerization.<sup>14,15</sup> In our work the crosslinker was added to help shorten the gelation time and minimize the rearrangement of the microstructures of the microemulsion during polymerization. Also, the addition of crosslinker helped increase the mechanical strength of the polymeric materials.

#### Effect of Emulsifier Content

The swelling of the porous polymer was studied in distilled water as a function of the emulsifier content of the precursor microemulsion (Fig. 4). As



**Figure 4** The results of swelling measurements for the polymer samples from precursor microemulsions with various contents of a combined emulsifier (SAO and OP-10). The weight ratio of BA to H<sub>2</sub>O was fixed at 2/1.



**Figure 5** The results of swelling measurements for the polymer samples were obtained from precursor microemulsions having the same BA : SAO : OP-10 : H<sub>2</sub>O weight ratio of 10 : 3 : 2 : 5 and a pH range of 7.0–9.0.

the emulsifier concentration increased, the extent of swelling of the polymer was found to increase. It was more obvious for emulsifier content above 24.3 wt %.

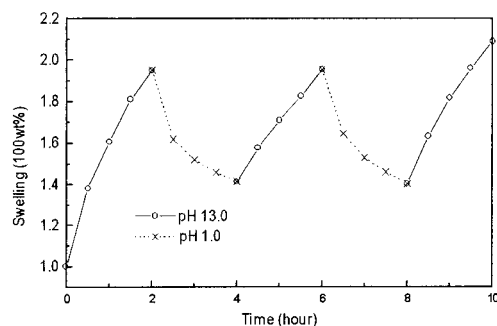
This can be explained by the polyelectrolyte effect exhibited by polymerized SAO, which has been widely investigated.<sup>16</sup> The carboxyl groups of SAO incorporated into the polymer matrix become ionized in water. Then the ionization causes mutual repulsion between the ionized groups, thus helping the polymeric network to swell in water. As more SAO was incorporated into the polymer matrix, the polyelectrolyte effect was more obvious.

This kind of polyelectrolyte effect exhibited by SAO is also consistent with the results shown in Figure 5. With the increase of the pH of the precursor microemulsion from 7.0 to 9.0, the extent of swelling of the polymer obviously increases. This is not strange because the carboxyl groups of polymerizable SAO are partly ionized in the precursor basic microemulsion.

#### Effect of pH of Swelling Medium

It was found that the swelling behaviors of the polymer materials were sensitive to the pH of the swelling medium (Fig. 6). When the swelling medium was alternated between the basic 0.1M NaOH aqueous solution and the acidic 0.1M HCl aqueous solution, the polymer sample swelled and shrank, respectively. This may be due to the fact that the unionized carboxyl groups of polymerized SAO were ionized in basic aqueous solution and the resulting mutual repulsion between the ionized groups caused the polymer to swell. However, in acid aqueous solution the ionized





**Figure 6** The effect of the pH of the swelling medium on the swelling behavior of the polymer from a precursor microemulsion having the same BA : SAO : OP-10 : H<sub>2</sub>O weight ratio of 10 : 3 : 2 : 5.

carboxyl groups were neutralized by HCl and the created mutual repulsion between the ionized groups disappeared, causing the the polymer network to shrink and lose some part of the water that had been absorbed in the basic aqueous solution. This result is also consistent with our earlier discussion about the polyelectrolyte effect in distilled water.

## CONCLUSIONS

Microporous polymerized materials were successfully prepared by radiation polymerization of a microemulsion of BA. The SEM observations indicated that the morphology of the porous structure in the polymer could be easily varied by variation of the compositions (water content, crosslinker content) of the precursor microemulsion. The porosity of the polymer increased with the water content increase. After the addition of the crosslinker TMPTA, the pore size of the polymer decreased while the number of pores increased. Also, the addition of crosslinker caused the narrower pore size distribution and the smoother surface.

The swelling behaviors of the final polymeric materials were significantly affected by the introduction of the polymerizable anionic emulsifier SAO. The swelling characteristics of the polymer increased with increases of the emulsifier content, the pH values of the precursor microemulsion, and the pH of the swelling medium.

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