

# Microcellular Polymeric Materials from Microemulsions: Control of Microstructure and Morphology

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## SYNOPSIS

The effect of a crosslinking agent on the formation of porous solids by polymerizing microemulsions formulated with monomers was investigated. Phenomenological studies were carried out to evaluate the possibility of controlling the morphology of the porous polymeric materials by using precursor microemulsions having a distinct microstructure. A microemulsion system, containing methyl methacrylate (MMA), acrylic acid (AA), the crosslinking agent ethyleneglycol dimethacrylate (EGDMA), water, and sodium dodecylsulfate (SDS) as surfactant, was studied. An identical surfactant-free system, formed using the same monomers, crosslinking agent, and water, but without surfactant, was also studied. Microemulsion samples from both these systems, having a water in oil droplet microstructure and also samples exhibiting bicontinuous microstructural characteristics, were used as precursor systems for polymerization. The morphology of the polymeric solids obtained was examined using scanning electron microscopy and thermogravimetric analysis. The results of this study indicate the possibility of forming porous polymeric solids having specifically tailored morphology and microstructure by the polymerization of monomer containing microemulsions. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

The formation of porous polymeric solids by polymerizing monomers dispersed in microemulsions is an area of current research interest.<sup>1-6</sup> Microemulsions exhibit thermodynamic stability and have an ordered microstructure.<sup>16-18</sup> In the present study, Winsor-IV microemulsion systems have been examined. These are macroscopically monophasic, transparent, isotropic systems, which are ordered at a microstructural level.<sup>19-20</sup> The microstructure is dependent on the composition of the system and consists of water droplets dispersed in oil at low water contents, which changes to droplets of oil dispersed in water at high water contents. At intermediate water contents, a microstructure, which is bicontinuous in oil and water, exists.<sup>8,16-20</sup>

The formation of microemulsions and the characterization of the microstructure for the system

made up of MMA, AA, EGDMA, and water had been investigated in our earlier study.<sup>8</sup> The characterization of the microemulsion microstructure in that study had confirmed the existence of droplet and bicontinuous microstructures for various compositions of the phase behavior diagram. It was also demonstrated that the microstructure and properties of this system were closely related to the surfactant-based system made up of MMA, AA, EGDMA, water, and SDS.<sup>8</sup> A preliminary investigation of the polymerization of these microemulsions had indicated the feasibility of obtaining porous solid materials.

The focus of the present study was to investigate the influence of the microstructure of the precursor microemulsion on the microcellular porous structure and morphology of the polymeric solid obtained. The process of gelation of the microemulsion on polymerization was studied with the purpose of optimizing the polymerization conditions to obtain the desired morphology of the polymer. The optimum concentration of crosslinking agent to aid the gelation process was also determined. This research

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used single phase microemulsion systems having a W/O-droplet microstructure and also microemulsion systems having a bicontinuous microstructure as precursors for polymerization. The objective of this study was to retain the major microstructural characteristics of the precursor microemulsion in the polymeric solid. Our results indicate that porous polymeric materials can be synthesized from microemulsions with considerable control over the microcellular porous structure and morphology.

## EXPERIMENTAL

### Materials

The monomers MMA, AA, and crosslinking agent EGDMA used in the study were obtained from Aldrich and had purity greater than 99%. The surfactant SDS, of 98% purity, was obtained from Aldrich. The water used for formulating microemulsions was doubly distilled. The microemulsion samples were prepared by pipetting the required amount of the various components into glass sample tubes. The sample tubes were hand shaken and equilibrated in a water bath at  $25 \pm 0.1^\circ\text{C}$  for 48 h before making measurements.

### Microemulsion Characterization

The details pertaining to the microemulsion preparation and characterization procedures were described in the earlier study.<sup>8</sup> The microstructure of the microemulsion was investigated using conductivity measurements, viscosity measurements, quasielastic light scattering (QELS), and static light scattering (SLS) studies.

### Polymerization Procedure

Photopolymerization of the microemulsion was carried out using 2,2-dimethoxy-2-phenyl-acetophenone (DMPA) as the initiator. DMPA used was of 99% purity and was obtained from Aldrich. The amount of initiator used was 0.02 g for 10 g of microemulsion and the microemulsion samples were purged with dry nitrogen gas at a flowrate of 0.56 L/h at 1 atm for 15 min prior to polymerization. The photopolymerization was carried out in a reaction cell,<sup>8</sup> using a 450 W ultraviolet source at a temperature of  $25 \pm 0.1^\circ\text{C}$  for a duration of 1 h.

### Gelation Measurements

Gelation studies were performed by rheological measurements, which were carried out using a

Brookfield digital viscometer mounted on the reaction cell. The change in viscosity of the reacting microemulsion system was monitored by recording the torque necessary to overcome the viscous resistance to the rotation of the viscometer spindle. The measurements were carried out at a speed of 0.3 rpm of the spindle, which corresponded to a shear rate of 0.39/s.

### Morphology Observation

Samples for scanning electron microscopy studies were made by drying the polymer formed at  $55^\circ\text{C}$  and preparing samples using the freeze fracture technique. The polymer samples were coated using a Polaron E5400 coating machine and a ISI SX 40 scanning electron microscope (SEM) was used to study the polymer morphology.

### Pore Continuity

The continuity of the pore structure of the polymer was studied by thermogravimetric analysis. The distinction between open cell porous structures and closed cell porous structures in the polymer was made, based on the pronounced difference in the shape of the drying rate curve for the two pore structures.<sup>9-12</sup> A Dupont Instruments TGA 2950 thermogravimetric analyzer was used for the study. The polymer obtained from the polymerization cell, which contained water, was dried in a stream of dry nitrogen gas at a temperature of  $70^\circ\text{C}$  for 300 min. The drying rate curve at  $70^\circ\text{C}$  for the polymer sample was constructed using the data on the loss in weight of sample, which was recorded as a function of time by the thermogravimetric analyzer using the Dupont thermal analyst system, TGA 5.1 program. The shape of the drying rate curve for open cell porous structures differs from that for closed cell porous structures since the transport processes occurring during drying are dependent on the geometry of the pores.<sup>9,10</sup> In closed cell porous structures, the drying rate in the falling rate period of the drying rate curve decreases exponentially until the equilibrium moisture content is reached. This is because the drying process in closed cell structures is diffusion limited, resulting in an exponential decrease in drying rate with decreasing moisture content. In contrast, open cell porous structures exhibit a linear decrease in drying rate in the falling rate portion of the curve up to the stage when insufficient water is left to maintain a continuous film across the pores.<sup>9,10</sup> This behavior is the result of the drying process in open cell porous materials, being domi-

nated by transport of moisture from the interior of the solid to its surface by capillary forces generated in the pores.

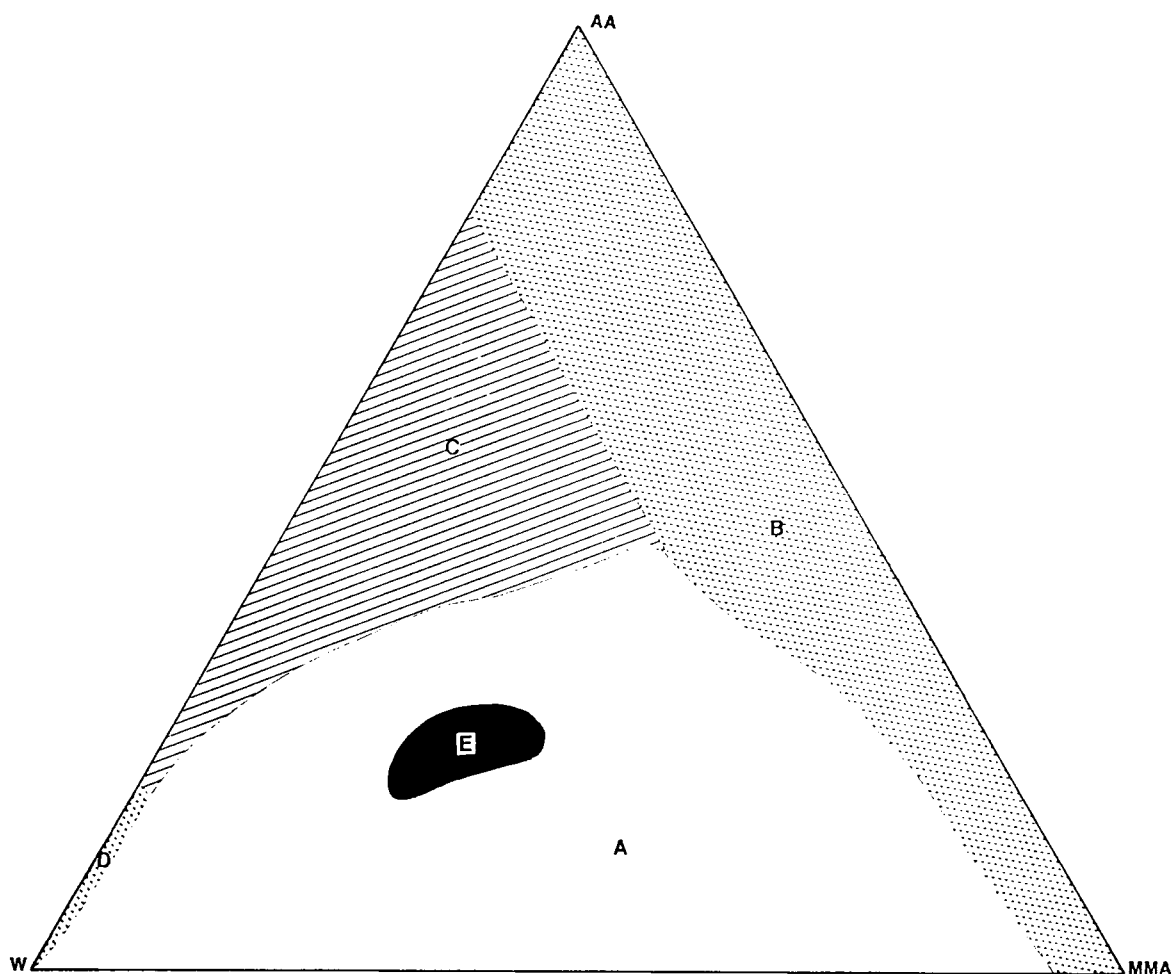
The results of the drying rate analysis, using the TGA, were used in conjunction with the results of morphological studies, using the SEM, to evaluate the characteristics of the pore structure in the polymeric solids formed by the polymerization of microemulsions.

## RESULTS

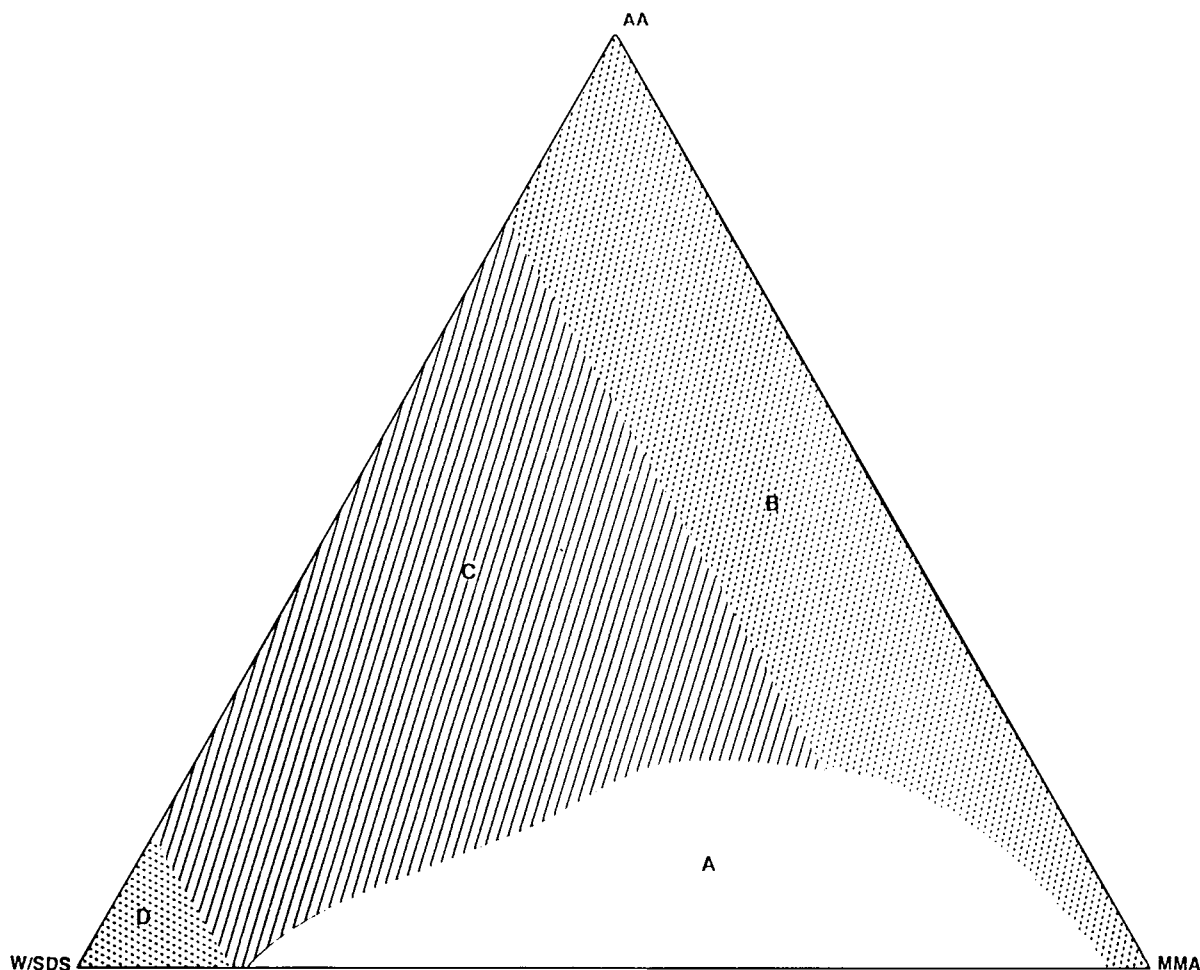
The phase behavior diagrams for the surfactant-free and surfactant-based systems described in our earlier study<sup>8</sup> were used as a guide in the formulation

of microemulsion samples for the present study. The phase behavior diagrams have been reproduced in Figures 1 and 2 to provide information on the various microstructures that exist. Our earlier investigations, pertaining to the characterization of these microemulsion systems,<sup>8</sup> had indicated the microemulsions with water contents less than 20% as having a droplet microstructure of water in oil (W/O) which changed over to a bicontinuous microstructure for water contents in the 20–80% range.

In the present study, the relationship between the microstructure of the precursor microemulsion and the morphology of the polymeric solid obtained after polymerization was examined by polymerizing various microemulsion samples having a constant ratio of MMA to AA, but having different water



**Figure 1** Ternary phase diagram for the system, Methyl methacrylate (MMA), Acrylic acid (AA), Water (W), and Ethyleneglycol dimethacrylate (EGDMA) at  $25 \pm 0.1^\circ\text{C}$  and 1 atm. Compositions are on wt % basis and EGDMA content is 4% of the combined weight of MMA and AA. Domain A: 2-phase region, Domain B: W/O Winsor-IV, Domain C: Bicontinuous Winsor-IV, Domain D: O/W Winsor-IV Domain E: Unstable 3-phase region.



**Figure 2** Ternary phase diagram for the system, Methyl methacrylate (MMA), Acrylic acid (AA), 20 wt % solution of Sodium dodecylsulfate in water (W/SDS) and Ethyleneglycol dimethacrylate (EGDMA) at  $25 \pm 0.1^\circ\text{C}$  and 1 atm. Compositions are on wt % basis, EGDMA content is 4% of the combined weight of MMA and AA. Domain A: 2-phase region, Domain B: W/O Winsor-IV, Domain C: Bicontinuous Winsor-IV, Domain D: O/W Winsor-IV.

contents. This choice of microemulsion systems for polymerization provided precursor systems with a droplet structure of W/O for water contents below 20% and a bicontinuous structure for water contents between 20–80%.

The precursor microemulsion in its liquid state is thermodynamically stable, with the existence of a stable microstructure formed by using suitable amphiphilic surface active agents. However, on polymerizing these systems, there are significant changes in the electrostatic and steric interactions, which were originally present between the various components of the system. Hence the original thermodynamic stability of the system is disturbed. This results in phase separation effects, which are widely

reported in the polymerization of microemulsion systems.<sup>1,6,7</sup> In order to rigidify the microemulsions by polymerization and to preserve their distinct microstructure, the tendency of the reacting system to phase separate must be controlled.

Phase separation occurs by a rearrangement of the originally stable microemulsion microstructure. To preserve the microstructure of the microemulsion, this rearrangement would have to be minimized. The technique used in this study to minimize rearrangement was to conduct the polymerization process at a rapid rate. This minimized the time available for the reacting system to undergo rearrangement of its microstructure. A kinetic limitation was thus imposed on the phase separation process

and its occurrence was minimized. The underlying assumption was that rearrangement of the microemulsion microstructure could be minimized if the transition from the low viscosity, highly fluid microemulsion state to the rigid polymeric state could be achieved very quickly.

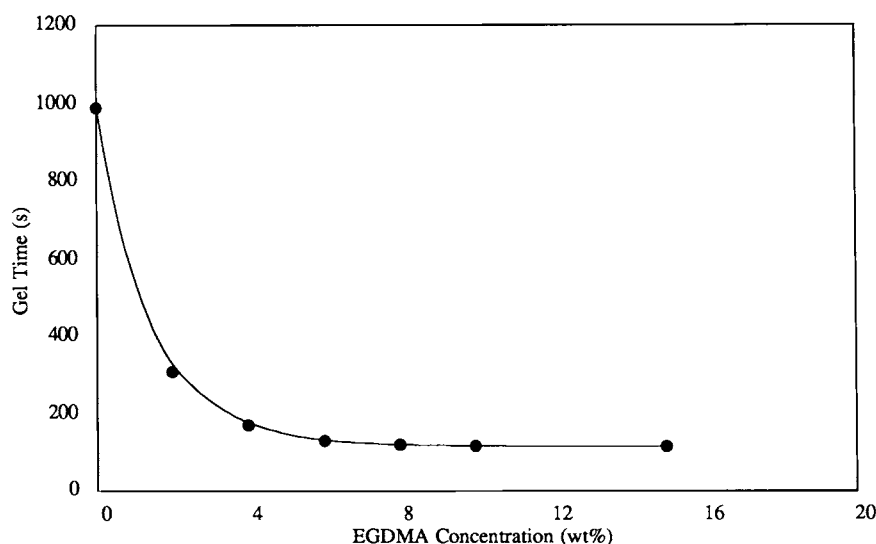
### Evaluation of the Gelation Characteristics of the Microemulsion on Polymerization

In order to investigate this possibility, a study of the gelation characteristics of the microemulsion system using the crosslinking agent EGDMA was carried out. The crosslinking agent was added to the precursor microemulsion in order to accelerate the gelation process and also to impart greater structural stability to the polymeric solid formed. This strategy was adopted, as in our earlier work<sup>6</sup> on the polymerization of bicontinuous monomer containing microemulsions and not containing a crosslinking agent, and had involved a relatively long time for gelation. Further, the polymer obtained had exhibited substantial phase separation effects.

The present study of the gelation characteristics was performed by recording the time taken for the precursor microemulsion to gel on polymerization as a function of increasing EGDMA concentration from 0% to 15% by weight of monomer content of the microemulsion. The gel point of the system was indicated by a drastic rise in the viscosity of the reacting system, resulting in an increase in the torque on the viscometer spindle, which was beyond

the measurable range of the viscometer. The physical state of the reacting system changed from a viscous liquid to a gel at this point. The results of the reaction time to achieve gel point as a function of crosslinking agent concentration is shown in Figure 3. The microemulsion system used for this study contained 15% by weight of MMA, 45% by weight of AA, and 40% by weight of water, with EGDMA content varying from 0% to 15% by weight of monomer content.

The results shown in Figure 3 indicate that the time for gelation decreases sharply as the concentration of the crosslinking agent is increased. The optimum concentration of the crosslinking agent is around 4% by weight of monomer content. Further increases in crosslinking agent concentration does not cause a significant decrease in the time for gelation. It was observed that microemulsions with EGDMA concentrations below 10% by weight of monomer content yielded clear transparent polymeric solids. On increasing EGDMA concentrations above 10% of the monomer weight, the polymer obtained became increasingly translucent and for EGDMA concentrations above 15% of monomer weight, the polymer obtained was an opaque white solid. This is indicative of an increase in the dimensions of the pores in the polymeric solid as the EGDMA content is increased, thereby resulting in an opaque solid at high EGDMA content. Based on these results, the concentration of EGDMA in all the precursor microemulsions used in this study was maintained at 4% in order to accelerate the process of gelation and to minimize phase separation effects.



**Figure 3** Photopolymerization time for microemulsion to attain gel point as a function of EGDMA concentration at  $25 \pm 0.1^\circ\text{C}$ .

### Morphology of the Porous Polymeric Materials

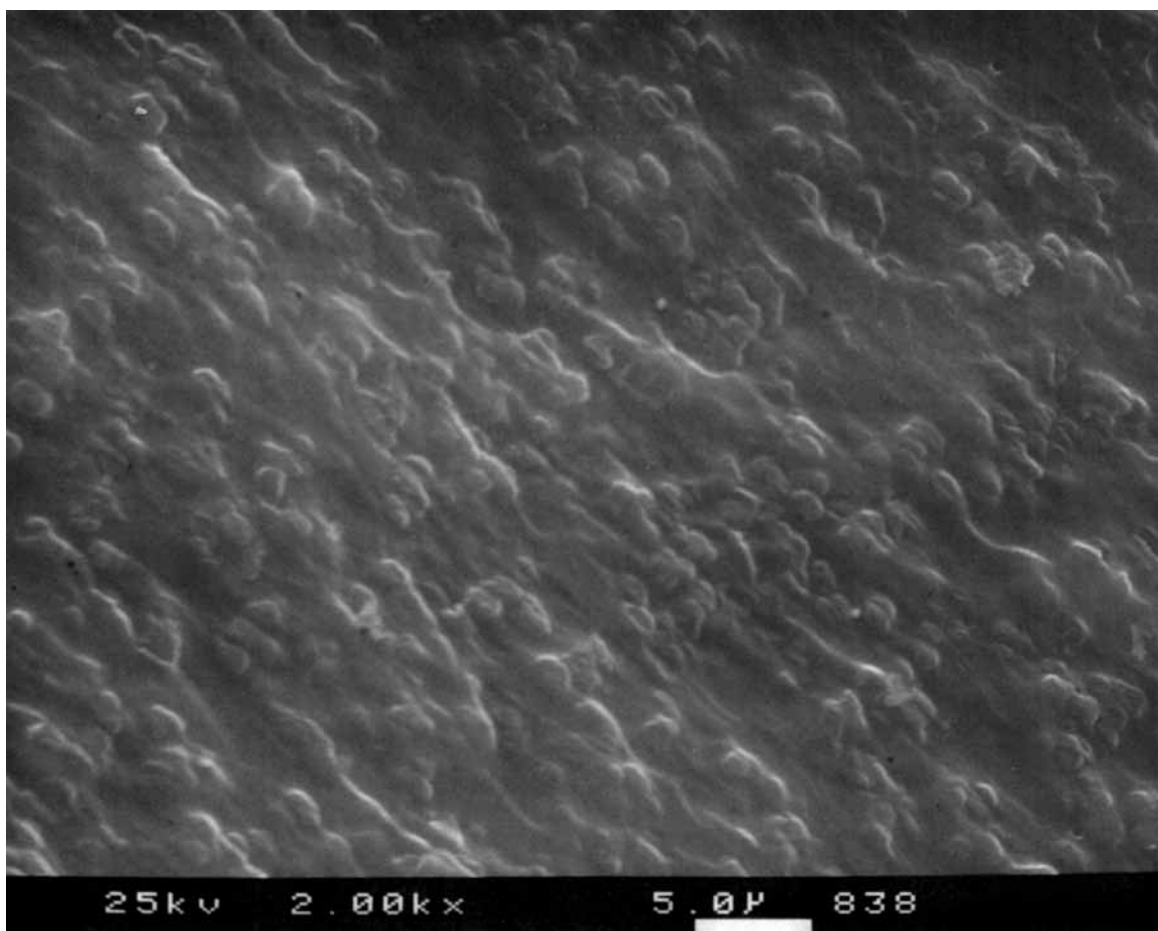
Scanning electron microscopy was used to study the morphology of the polymeric materials synthesized. A set of microemulsion samples of the surfactant-free system, all with an AA:MMA ratio of 4 : 1, containing EGDMA (4% of monomer content) and water content ranging from 10% to 55%, were polymerized. Characterization studies of these microemulsions<sup>8</sup> had indicated a W/O droplet structure for microemulsions at water concentrations below 20% and a bicontinuous microstructure in the 20–55% water content range.

The scanning electron micrograph for a polymer obtained by polymerizing a precursor microemulsion of the surfactant-free system containing 10% water is shown in Figure 4. The precursor microemulsion had a W/O droplet structure and yielded a polymeric material having a closed cell structure on polymer-

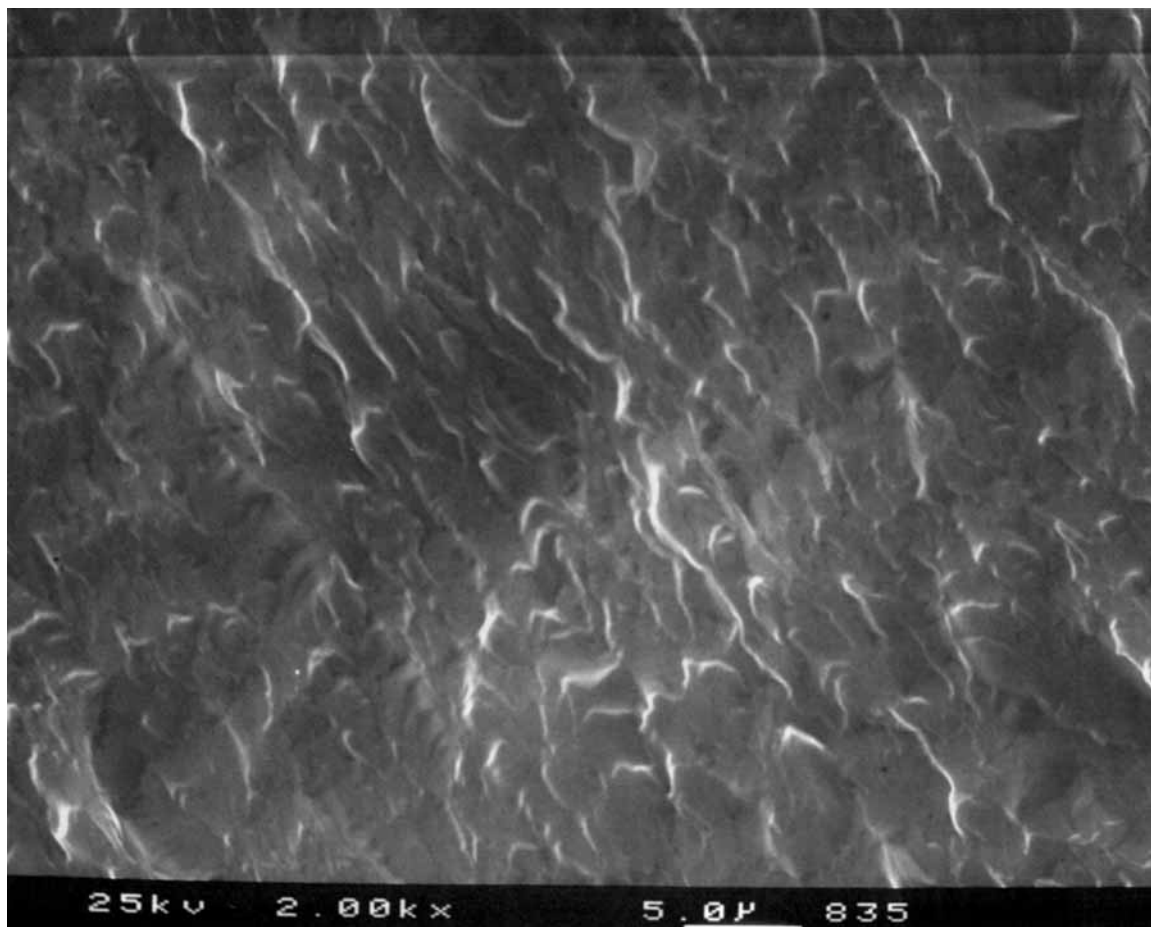
ization. The SEM micrograph shows the polymer morphology to be made up of disjoint cellular structures. This is typical of closed cell porous polymeric material. The water droplets of the microemulsion become trapped in the polymer matrix after polymerization, yielding a closed cell porous structure.

The morphology of the polymer, obtained on polymerizing microemulsions of the surfactant-free system containing 20% water, is shown in Figure 5. The scanning electron micrograph shows the onset of the formation of a connected porous network in the polymer. The disjoint cellular structure in Figure 4 is replaced by the connected porous structure in Figure 5. This corresponds to the transition from droplet to bicontinuous microstructure in the microemulsion system, described by Figure 1.

On polymerizing the precursor microemulsion of the surfactant-free system containing 30% water, the morphology of the polymer indicates an open



**Figure 4** SEM micrograph of the morphology of the polymer obtained by polymerizing a microemulsion sample of composition MMA: 18%, AA: 72%, water: 10%, and EGDMA: 4% of combined weight of MMA and AA.



**Figure 5** SEM micrograph of the morphology of the polymer obtained by polymerizing a microemulsion sample of composition MMA: 16%, AA: 64%, water: 20%, and EGDMA: 4% of combined weight of MMA and AA.

cell porous structure, as seen in the SEM micrograph of Figure 6. The characterization study of the precursor microemulsion had indicated the presence of a bicontinuous microstructure. Hence, the major microstructural features of the precursor microemulsion appear to have been retained after polymerization.

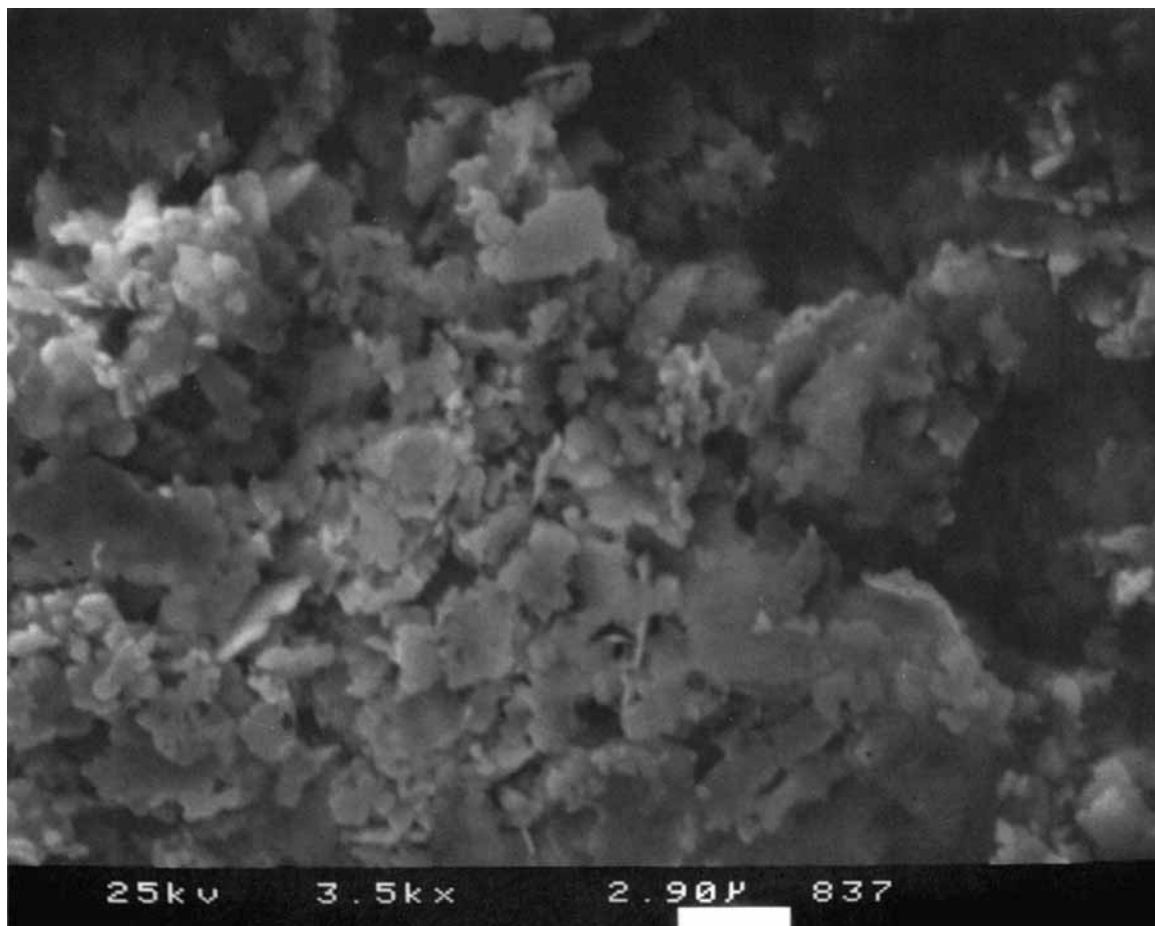
The dimensions of the open cell porous structure increased with increasing water content of the precursor microemulsion, although the polymer morphology remains similar. The scanning electron micrograph, shown in Figure 7 for polymer synthesized from precursor microemulsion containing 55% water, indicates the pore sizes to be in the 2–4  $\mu\text{m}$  range. In contrast, the pore sizes are 1–2  $\mu\text{m}$  in Figure 6 for polymer obtained from precursor microemulsion of 30% water content.

The morphology of the polymer, obtained by polymerizing microemulsion samples from the surfactant-based system, is similar to that of polymer from

the surfactant-free system at equivalent water contents. Figure 8 shows the morphology of the polymer formed using the microemulsion from the surfactant-based system. The microemulsion was made with AA:MMA ratio of 1:1.25, containing EGDMA to the extent of 4% of the monomer content and 55% by weight of SDS solution in water (20 wt % SDS). The open cell porous structure of the polymer is similar to that obtained using the surfactant-free system. However, the pores of the polymer are better defined in the case of polymer obtained using the surfactant-based system (Fig. 8) when compared to the polymer obtained from the surfactant-free system (Fig. 5, 6, and 7).

#### Determination of Continuity of Pore Structure by Thermogravimetric Analysis

The results shown by SEM micrographs are indicative of the polymer morphology at the surface of



**Figure 6** SEM micrograph of the morphology of the polymer obtained by polymerizing a microemulsion sample of composition MMA: 14%, AA: 56%, water: 30% and EGDMA: 4% of combined weight of MMA and AA.

freeze fracture for the polymer specimen. Additional information pertaining to the continuity of the pore structure is required for classifying the polymeric material as having an open or closed cell structure. An open-cell polymeric material would be characterized by an interconnected porous structure extending throughout the polymeric material. In the case of closed cell porous polymeric materials, the pores would be distributed as discrete pockets throughout the solid.

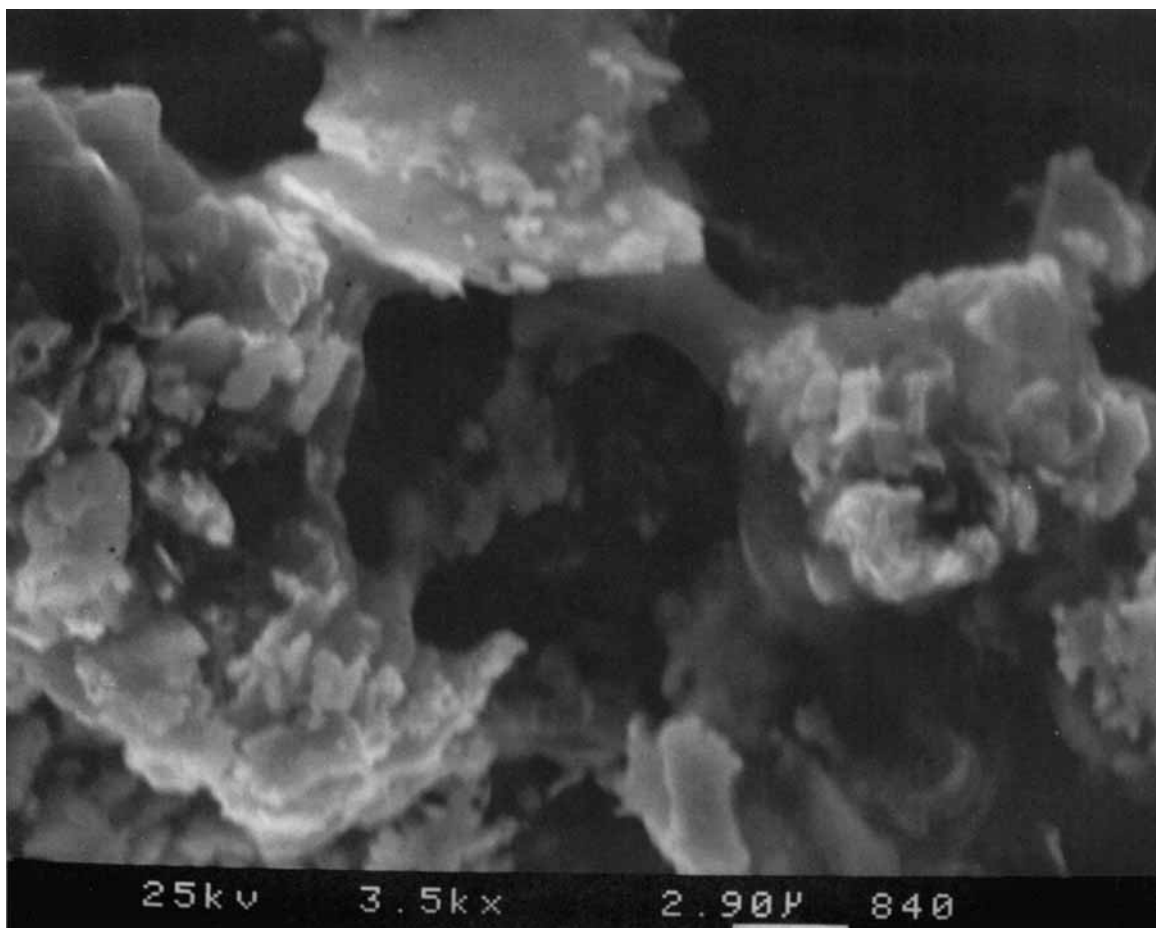
Investigation of the continuity of the pore structure in the porous polymeric materials that were synthesized was done by thermogravimetric analysis using the experimental techniques and data analysis procedures described earlier. The drying rate curves were obtained using thermogravimetric analysis for polymeric solids of composition, identical to that studied by scanning electron microscopy. This study was made for polymeric samples obtained from mi-

croemulsions of the surfactant-free system and also the surfactant-based system.

The drying rate curves for a polymer formed using microemulsions from the surfactant-free system, containing 10% water, is shown in Figure 9 (the morphology of this polymer sample is shown in Fig. 3). The shape of this drying rate curve shows an exponentially decreasing trend, which agrees with the results from published literature for closed cell materials.<sup>9,10</sup> The shape of the drying rate curves for polymer samples, synthesized from microemulsions containing water contents less than 18%, were all similar to that of Figure 9. This drying rate behavior was obtained for both the surfactant-free and surfactant-based systems.

The polymer sample formed using microemulsion from the surfactant-free system, containing 20% water, yielded a drying rate curve, which is shown in Figure 10 (the morphology of this polymer sample





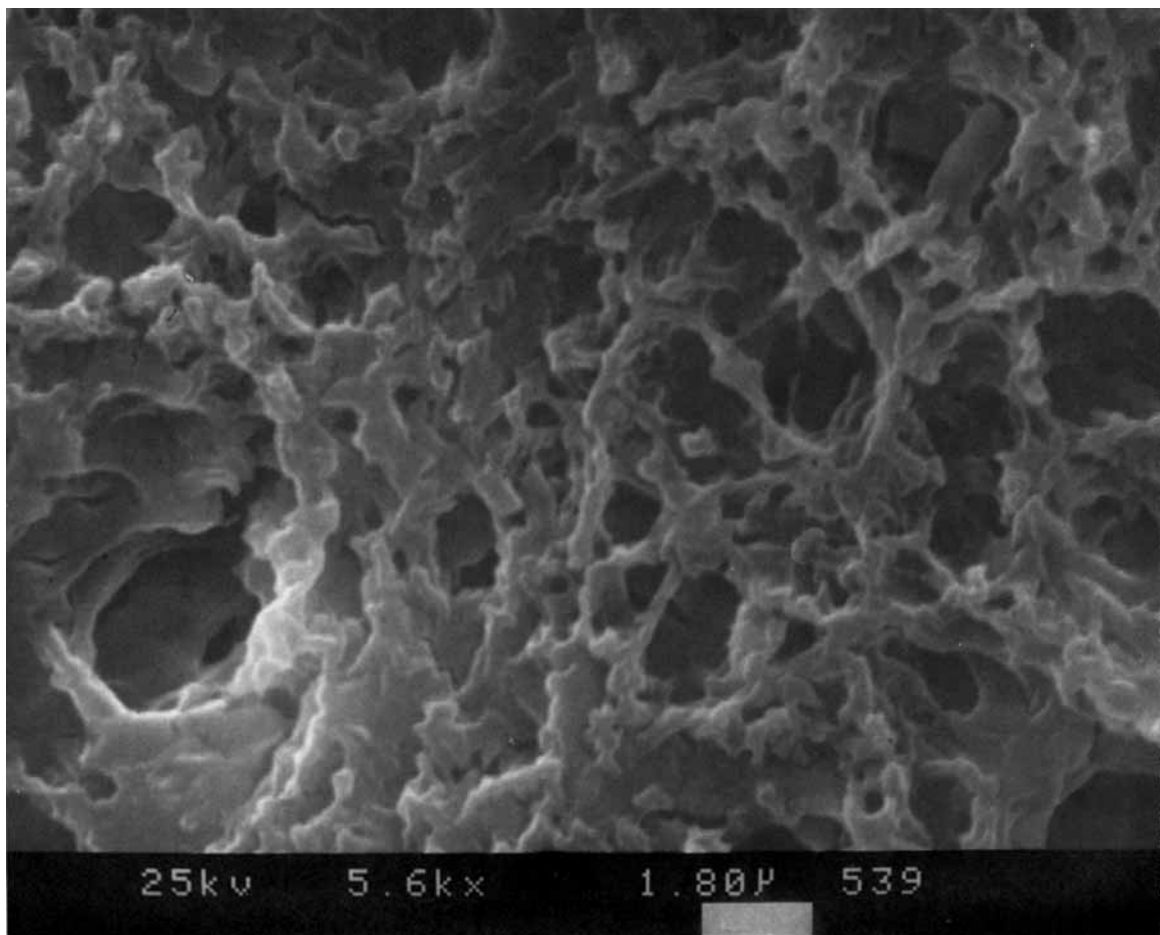
**Figure 7** SEM micrograph of the morphology of the polymer obtained by polymerizing a microemulsion sample of composition MMA: 9%, AA: 36%, water: 55%, and EGDMA: 4% of combined weight of MMA and AA.

is shown in Fig. 4). The drying rate curve in Figure 10 indicates the presence of a linear falling rate period. This drying rate behavior is typical of open cell porous solids.<sup>9,10</sup> Similar results were obtained for polymer samples formed using microemulsions of water content in the range of 20–70%. It was observed that the section of the drying rate curve, corresponding to the first linear falling rate period, increases with increasing water content of the precursor microemulsion. This is evident from Figure 11, which shows the drying rate curve for the polymer formed from a microemulsion of the surfactant-free system containing 55% water. The shape of the drying rate curve in Figure 11 is representative of the drying rate curves for polymer samples formed from microemulsions containing water in the 30–70% range. The drying rate curves for polymer samples formed from microemulsion samples of the surfactant-based system were similar to the drying rate

curves for polymer samples obtained from the surfactant-free system for equivalent water contents.

## DISCUSSION

The incorporation of the crosslinking agent EGDMA in the precursor microemulsion has been found to be of assistance in accelerating the process of gelation. The EGDMA concentration of 4% by weight of monomer content has been found to be most effective for this application. At this concentration of crosslinking agent, the gel point was reached after 120 sec of polymerization for microemulsions containing 15% by weight of MMA, 45% by weight of AA, and 40% by weight of water. The kinetic limitation, which was imposed on the phase separation process, had a favorable effect in retaining the major microstructural features of the mi-



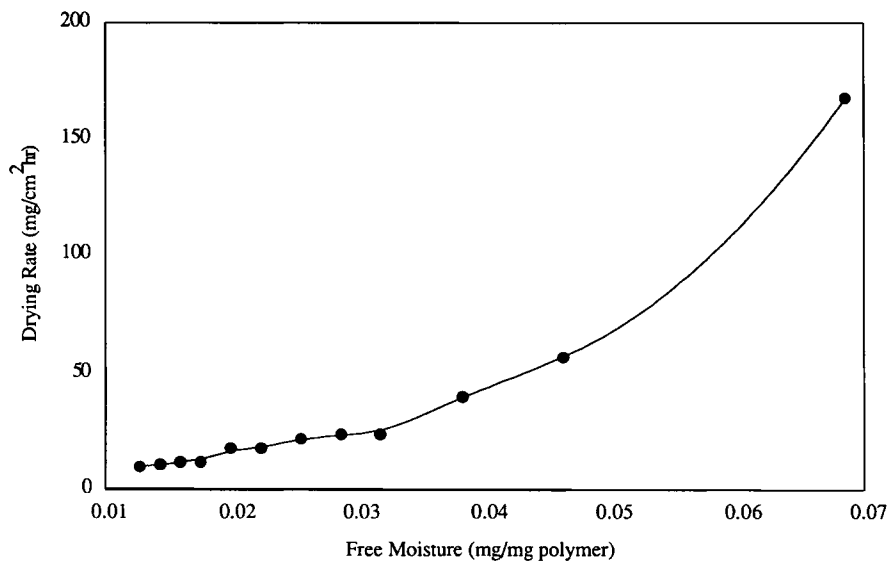
**Figure 8** SEM micrograph of the morphology of the polymer obtained by polymerizing a microemulsion sample of composition MMA: 25%, AA: 20%, SDS-water solution: 55%, and EGDMA: 8% of the combined weight of MMA and AA.

croemulsion after polymerization. This is observed from the results of scanning electron microscopy and thermogravimetric analysis. The increase in pore diameter on increasing EGDMA content of the precursor microemulsion, above 10% by weight of monomer, can be attributed to an increase in phase separation effects. This could possibly be due to the more hydrophobic nature of EGDMA as compared with MMA.

The SEM micrographs indicate that a monomer containing microemulsions having a W/O droplet structure yield a polymer having a closed cell structure on polymerization, whereas the polymerization of microemulsions having a bicontinuous structure results in a polymer having an interconnected porous structure. These results are indicative to a considerable degree of the retainment of the microemulsion microstructure on polymerization. However, the dimensions of the porous structure obtained are con-

siderably larger than dimensions characteristic of microemulsions. This can be attributed to the existence of phase separation effects during polymerization as well as effects due to drying. The retainment of the gross microstructural features of the precursor microemulsion on polymerization indicates the effectiveness of the crosslinking agent in minimizing phase separation effects. An examination of the micrographs of polymer samples formed from bicontinuous microemulsions shows the dimensions of the pores to increase from 1–2  $\mu\text{m}$  at 30% water content and to 2–4  $\mu\text{m}$  at 55% water content.

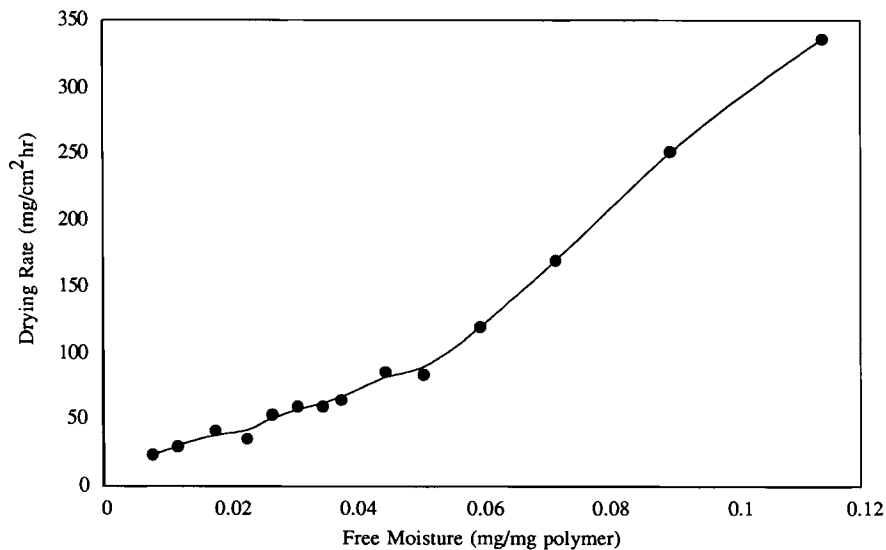
The SEM micrograph of the porous microstructure, obtained by polymerizing microemulsion samples from the surfactant-based system, (Fig. 8) shows the porous microstructure to be more ordered in appearance than that of the polymer from the surfactant-free system (Figs. 6 and 7). This could



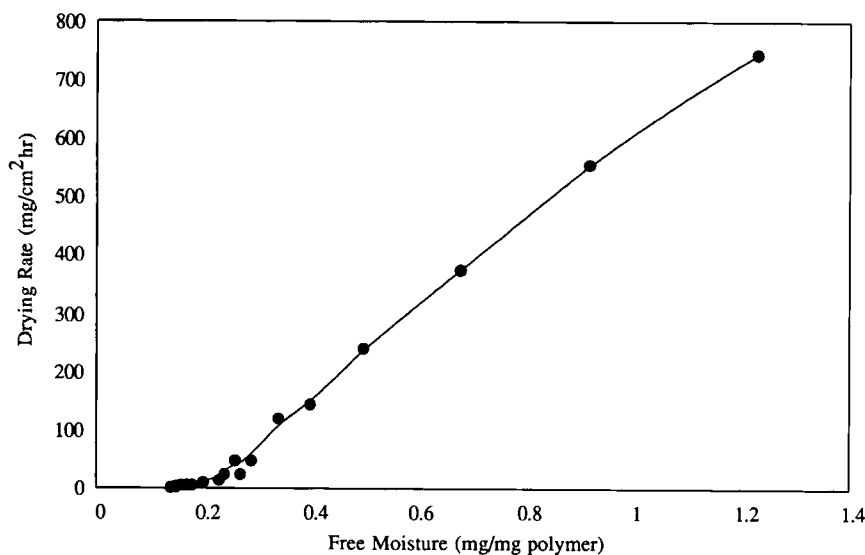
**Figure 9** Drying rate curve for porous polymer formed from microemulsion of composition MMA: 18%, AA: 72%, water: 10%, and EGDMA: 4% of combined weight of MMA and AA.

be attributed to the presence of the surfactant SDS in the surfactant-based system. This, in turn, could possibly result in greater stability of the microemulsion microstructure during the course of polymerization. However, the morphology of the polymer obtained from microemulsions of the surfactant-free system is comparable to that from the surfactant-based system.

The study of the polymer formed from microemulsions using SEM has shown the morphology to exhibit gross features, which resemble results published in literature of the study of microemulsion microstructure using freeze fracture transmission electron microscopy (FFTEM).<sup>13</sup> The FFTEM micrographs of microemulsions having a droplet structure showed features that were similar to those of



**Figure 10** Drying rate curve for porous polymer formed from microemulsion of composition MMA: 16%, AA: 64%, water: 20% and EGDMA: 4% of combined weight of MMA and AA.



**Figure 11** Drying rate curve for porous polymer formed from microemulsion of composition MMA: 9%, AA: 36%, water: 55%, and EGDMA: 4% of combined weight of MMA and AA.

Figure 4, at the transition from droplet to bicontinuous microstructure the FFTEM micrograph was similar to Figure 5, and for bicontinuous microemulsions, features in the FFTEM micrographs resembled Figures 6, 7, and 8. The dimensions of the two-phase domains shown in the FFTEM micrographs were, however, significantly smaller than the dimensions observed in the SEM micrographs of the present study. This is indicative of the phase separation effects that occur during the polymerization of the microemulsions. The results from this study are also similar to the results reported on the formation of microcellular polymeric materials by the polymerization of lyotropic liquid crystals containing monomers,<sup>14,15</sup> thereby retaining the highly ordered structure of the lyotropic liquid crystals.

The study of pore connectivity using thermogravimetric analysis provided results that are consistent with the results of polymer morphology obtained from SEM studies. The morphology of a polymer formed using microemulsions containing less than 20% water was observed to be a disjointed cellular structure from SEM studies. TGA studies confirmed that these polymer samples as possessed a closed cell porous structure. Similarly, the interconnected porous morphology, indicated by SEM for a polymer formed from microemulsions containing water in the 20–70% range, was shown by TGA studies to be made up of an open cell porous structure.

The TGA studies were conducted for polymeric solids obtained from microemulsions having water contents in the range of 10% to 70% by weight. The results of these studies do not indicate a sharp transition from a closed cell to an open cell porous structure of the polymeric solid with increasing water content of the precursor microemulsion. Instead, this transition is seen to be gradual, with an increase in the length of the linear falling rate period of the drying rate curve with increasing water content of the precursor microemulsion. The onset of this transition is seen to occur at a water content of 20% in the precursor microemulsion.

A possible interpretation of this behavior could be the existence of both closed and open cell porous structures in the polymeric solids pertaining to the microemulsions of transition compositions. At water contents below 15% in the precursor microemulsions, the pore structure is largely closed cell and at water contents above 30%, the solid has a predominantly open cell structure.

The formation of a combination of closed and open cell structures in the polymeric solids could be attributed to phase separation effects occurring during polymerization and the change in microstructure of the microemulsion with changing water content. In microemulsions corresponding to the transition compositions, the volume fraction of the water phase is around 20% and the thickness of the water phase in the bicontinuous structure would be small. Con-

sequently, with the occurrence of phase separation during polymerization, certain portions of the bi-continuous monomer containing oil phases could coalesce, due to the small distance of separation, and could trap some water, forming a closed cell. Based on the results obtained, it can be inferred that the proportion of pore volume occupied by closed cells decreases as the water content of the precursor microemulsions is increased. This is due to the reduced possibility of coalescence of the monomer containing oil phases by phase separation, due to the larger length scale of the water phase separating them.

## CONCLUSIONS

The results of morphological studies using SEM, in conjunction with the results of TGA studies, provide a detailed description of the porous structure. The microemulsions having a W/O droplet structure yield closed cell porous polymeric solids, having a morphology characterized by a disjointed cellular structure, whereas the polymerization of microemulsions having a high water content and a bicontinuous structure results in a polymer having an interconnected porous structure. At intermediate water contents of the precursor microemulsions, a combination of open and closed cell porous structures exists, with the proportion of each type dependent on the water content of the particular precursor microemulsion. These results are indicative to a considerable degree of the retainment of the microemulsion microstructure on polymerization. However, the length scale of the porous structure obtained (1–4  $\mu\text{m}$ ) is considerably larger than the length scale characteristic of microemulsions (less than 0.1  $\mu\text{m}$ ), due to phase separation effects during polymerization. The incorporation of the crosslinking agent EGDMA has been effective in reducing the occurrence of phase separation, although phase separation effects could not be altogether avoided. This is observed from the closer resemblance of the polymer morphology to the original microstructure of the microemulsion when compared to the results of studies conducted without using a crosslinking agent.<sup>6,7</sup>

## REFERENCES

1. J. O. Stoffer and T. Bone, *J. Dispersion Sci. Tech.*, **1**, 4, 393 (1980).
2. F. M. Menger, T. Tsuno, and G. S. Hammond, *J. Am. Chem. Soc.*, **112**, 1263 (1990).
3. S. Qutubuddin, E. Haque, W. J. Benton, and E. J. Fendler, In *Polym. Assoc. Structures: Microemulsions and Liquid Crystals*, M. A. El-Nokaly, Ed., ACS Symp. Series **384**, 64 (1989).
4. C. H. Chew and L. M. Gan, *J. Polym. Sci. Poly. Chem. Ed.*, **23**, 2225 (1985).
5. J. O. Stoffer and T. Bone, *J. Dispersion Sci. Tech.*, **1**, 1, 37 (1980).
6. M. Sasthav and H. M. Cheung, *Langmuir*, **7**, 1378 (1991).
7. E. Haque and S. Qutubuddin, *J. Polym. Sci. Part C Polym. Lett.*, **26**, 429 (1988).
8. W. R. Palani Raj, M. Sasthav, and H. M. Cheung, *Langmuir*, **7**, 2586 (1991).
9. J. M. Coulson and J. F. Richardson, In *Chemical Engineering*, Ed. II, Vol. II, Pergamon, New York, 1968, p. 620.
10. W. L. McCabe, J. C. Smith, and P. Harriott, In *Unit Operations of Chemical Engineering*, ed. IV, McGraw-Hill, New York, 1985, p. 716.
11. T. K. Sherwood, *Ind. Eng. Chem.*, **21**, 12 (1929).
12. R. W. Corben and D. M. Newitt, *Trans. Inst. Chem. Eng.*, **33**, 52 (1955).
13. J. F. Bodet, J. R. Bellare, H. T. Davis, L. E. Scriven, and W. G. Miller, *J. Phys. Chem.*, **92**, 1898 (1988).
14. D. M. Anderson and P. Strom, In *Polym. Assoc. Structures: Microemulsions and Liquid Crystals*, M. A. El-Nokaly, Ed., ACS Symp. Series **384**, 204 (1989).
15. S. E. Friberg, and J. Fang, *J. Colloid Interface Sci.*, **118**, 2, 543 (1987).
16. P. A. Winsor, *Trans. Faraday Soc.*, **44**, 376 (1948).
17. M. Clause, J. Heil, J. Peyrelasse, and C. Boned, *J. Colloid Interface Sci.*, **87**, 584 (1982).
18. G. Warr, R. Sen, and D. F. Evans, *J. Phys. Chem.*, **92**, 774 (1988).
19. S. J. Chen, D. F. Evans, and B. W. Ninham, *J. Phys. Chem.*, **88**, 1631 (1984).
20. A. Loic, J. P. Cotton, R. Ober, and C. Taupin, In *Microemulsion Systems*, H. L. Rosano and M. Clause, Eds., Marcel Dekker, New York, 1987, pp. 225.

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