Porous Polymeric Materials from Cationic Microemulsions

T. D. Li[a]; C. H. Chew[a]; S. C. Ng[a]; L. M. Gan[a]; W. K. Teo[b]; J. Y. Gu[c]; G. Y. Zhang[c]

[a] Department of Chemistry, National University of Singapore, Singapore [b] Department of Chemical Engineering, National University of Singapore, Singapore [c] Research Institute of Daily Chemical Industry, Taiyuan, People's Republic of China

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POROUS POLYMERIC MATERIALS FROM CATIONIC MICROEMULSIONS

T. D. LI, C. H. CHEW, S. C. NG, and L. M. GAN*

Department of Chemistry

W. K. TEO

Department of Chemical Engineering

National University of Singapore
10 Kent Ridge Crescent, Singapore 0511

J. Y. GU and G. Y. ZHANG

Research Institute of Daily Chemical Industry
Taiyuan 030001, People's Republic of China

ABSTRACT

A polymerizable cationic surfactant of acryloyloxyundecyl trimethylammonium bromide was synthesized and polymerized with methyl methacrylate and a crosslinker, ethylene glycol dimethacrylate, in microemulsions. Transparent porous materials were obtained by photoinitiated polymerization of a series of the bicontinuous microemulsions. Scanning electron micrographs of the polymerized samples show that porous microstructure polymers ranging from 0.10 to 0.20 μm were formed from precursor microemulsions containing 15 to 40% water. The microstructure is believed to be an open cell type as revealed from the drying rate curves by thermogravemetric analysis.

INTRODUCTION

Polymerization of water-soluble and oil-soluble monomers in microemulsions has attracted considerable interest recently [1, 2]. Microemulsions are thermodynamically stable, transparent isotropic liquids consisting of water and oil phases stabilized by surfactants and/or a combination of surfactants and cosurfactants. Three types of microemulsions are known: oil-in-water (o/w), water-in-oil (w/o), and bicontinuous microemulsions [3, 4]. For the latter system, organic and aqueous phases coexist in interconnected domains stabilized by surfactant molecules.

Porous polymeric materials have been produced by polymerization of methyl methacrylate (MMA) or styrene in w/o microemulsions [5, 6] and in bicontinuous microemulsions [7–12]. The results [13] reveal that bicontinuous microemulsions yield polymers with open-cell structures whereas microemulsions with less than 20% water (w/o microemulsion) form closed-cell structures. It seems possible to control the microcellular structures of polymers [10] by using a polymerizable anionic surfactant of potassium undecenoate (PUD). However, PUD cannot readily be polymerized to high molecular weights because it is very prone to allylic chain transfer reactions.

We have synthesized several readily polymerizable anionic surfactants [14–16], such as sodium acrylamidoundecanoate (NaAAU), sodium acrylamidostearate (NaAAS), and sodium 11-(N-ethyl acrylamido)undecanoate (Na11-EAAU). The use of Na11-EAAU in w/o microemulsions containing MMA produced transparent polymeric materials with microstructures [17]. However, it was not so successful for microemulsion systems using either NaAAS or NaAAU [14, 18, 19].

It has been reported [20] recently that transparent polymeric materials with microstructures can also be produced from bicontinuous microemulsions using polymerizable cationic surfactants. In this paper, the synthesis of a polymerizable cationic surfactant of acryloyloxyundecyl trimethylammonium bromide (AUMAB, $CH_2=CHCOOCH_2(CH_2)_9CH_2N^+(CH_3)_3Br^-$) and its copolymerization with MMA in bicontinuous microemulsions are described.

EXPERIMENTAL

Materials

Trimethylamine (anhydrous), 11-bromoundecanol, 11-aminoundecanoic acid (all from Fluka), acryloyl chloride, and 2,2-dimethyl-2-phenyl acetophenone (DMPA) (both from Aldrich) were used as supplied. Methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA) from Merck were purified by vacuum distillation. Dry tetrahydrofuran (THF) and superdry ethanol were used and stored over molecular sieves of 3Å. All solvents used were distilled and stored over molecular sieves of 3Å. Water was purified by a Milli Q water purification system.

Synthesis of Monomer

The monomer acryloyloxyundecyl trimethylammonium bromide (AUMAB) has the following structure:
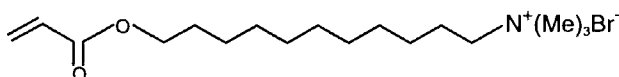
was prepared by either one of the following two methods.

Method A

11-N,N-Dimethylaminoundecanol (DAUO). N,N-Dimethylundecanoic acid (DMUA) was prepared by the interaction of 11-aminoundecanoic acid with 90% formic acid and 37% aqueous formaldehyde as described by Ralston et al. [21]. DAUA was first esterified with ethanol/HCl and then reduced with LiAlH$_4$ in THF under N$_2$ atmosphere. A pale yellow liquid, obtained after the usual work-up procedure, was vacuum distilled to afford a colorless viscous liquid (DAUO), yield 81%, mp 24–26°C.

^{1}H NMR: (CDCl$_3$), δ: 3.06t (2H, $-$CH$_2$O$-$), 2.49s (1H, $-$OH), 2.24m (2H,$-$CH$_2$N), 2.21s (6H, $-$N(CH$_3$)$_2$), 1.55m (2H, $-$CH$_2$$-C-$O), 1.45m (2H, $-$CH$_2$$-C-$N), 1.34–1.22m (14H, $-$(CH$_2$)$_7$$-$).

11-N,N-Dimethylaminoundecylacrylate (DMAUA). Acryloyl chloride (9.5 mL) in THF (20 mL) was added to a solution of DAUO (23.3 mmol) in THF (20 mL) at 0°C and was stirred at room temperature under N$_2$ atmosphere for 2 hours. A yellow residue was obtained after THF was removed under reduced pressure. After neutralizing with saturated NaHCO$_3$ solution, extracting with ether, and work-up as usual, it yielded a light orange liquid. The crude product was vacuum distilled to afford a pale yellow liquid (DMAUA, bp $\approx$ 100°C/0.1 mmHg) with 69% yield.

^{1}H NMR: (CDCl$_3$), δ: 6.39d (1H, *trans* CH$_2$=C), 6.12d (1H, C=CH$-$), 5.81d (1H, *cis* CH$_2$=C), 4.15t (2H, $-$COOCH$_2$), 2.24t (2H, $-$CH$_2$$-$N), 2.21s (6H, $-$N(CH$_3$)$_2$), 1.66m (2H, $-$O$-$C$-$CH$_2$), 1.45m (2H, $-$CH$_2$$-C-N-$), 1.37–1.25m (14H, $-$(CH$_2$)$_7$$-$).

Acryloyloxyundecyltrimethylammonium Iodide (AUMAI). DMAUA (7.4 mL) was refluxed with CH$_3$I (0.5 mL) in dry acetone (20 mL) overnight in the presence of a small amount of hydroquinone. After removal of solvents, the pale yellow residue was recrystallized from acetone to afford a white crystalline solid of the desired monomer. Yield 79%, mp 123–124.5°C.

^{1}H NMR: (CDCl$_3$), δ: 6.39d (1H, *trans* CH$_2$=C), 6.12d (1H, C=CH$-$), 5.82d (1H, *cis* CH$_2$=C$-$), 4.15t (2H, $-$COOCH$_2$), 3.61m (2H, $-$CH$_2$N$-$), 3.47s (9H, $-$N(CH$_3$)$_3$), 1.76m (2H, $-$OC$-$CH$_2$$-$), 1.67m (2H, $-$CH$_2$$-C-N-$), 1.43–1.25m (14H, $-$(CH$_2$)$_7$$-$).

The AUMAI can easily be converted into the bromide (AUMAB) or chloride (AUMAC) by using an ion-exchange resin (Dowex 1 × 2-100). AUMAB, mp 155–156°C. AUMAC, mp 181–182.5°C.

Method B

Bromoundecylacrylate (BUA). Bromoundecanol (0.32 mol) and 320 mL THF were mixed in a flask at 0°C under N$_2$, followed by the addition of 80 mL acryloyl chloride. The reaction system was bubbled with N$_2$ at room temperature for 2 hours and then left overnight. The unreacted acryloyl chloride and solvent were removed by a rotary evaporator. The yellowish residue was dissolved in ether and washed with saturated sodium hydrogen carbonate solution until the aqueous layer was basic. After evaporation of the ether, a viscous yellowish liquid of BUA was obtained. The yield was 90%.

Acryloyloxyundecyl trimethylammonium bromide (AUMAB).   AUMAB (yield, 75%) was obtained by reacting BUA with trimethylamine gas in diethyl ether at 0°C as described by Michas et al. [22]. The ^{1}H-NMR spectrum of the product was identical to that of AUMAB obtained by Method A.

^{1}H-NMR: (CDCl$_3$), δ: 6.39d (1H, *trans* CH$_2$=C), 6.12d (1H, C=CH−), 5.82d (1H, *cis* CH$_2$=C−), 4.13t (2H, −COOCH$_2$), 3.32m (2H, −CH$_2$N−), 3.08s (9H, −N(CH$_3$)$_3$), 1.62m (2H, −COOCCH$_2$), 1.28m (14H, −(CH$_2$)$_7$−).

Microemulsion Phase Diagram

The single-phase region of the microemulsion system was determined visually by titrating a specific amount of MMA and AUMAB with water in a screw-capped tube at room temperature (about 30°C). Each titration was thoroughly mixed using a vortex mixer. The clear–turbid boundaries were established from systematic titrations. The resulting transparent microemulsion region is represented by the shaded area in Fig. 1.

Conductivity and Surface Tension

Electrical conductivity of microemulsion samples were measured using an Omega CM-155 conductivity meter with a cell constant of 1.209 cm^{-1} at 30 ± 0.1°C and 1 atm. The surface tensions were determined using a torsion balance tension meter (White Electric Instrument Co.).
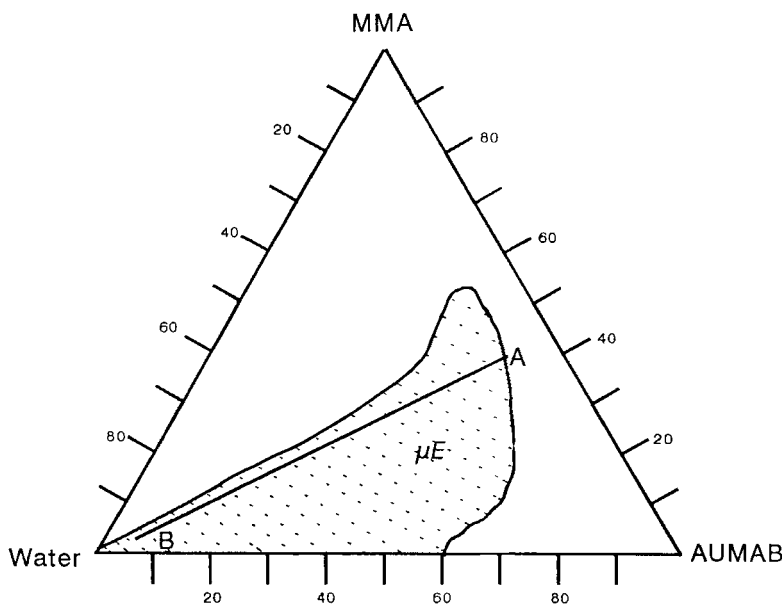

FIG. 1.   Ternary phase diagram for MMA/AUMAB/water system at 30°C. Compositions are on weight basis.

Microemulsion Polymerization

Each microemulsion sample was placed in an ampule and purged with nitrogen before it was sealed. The sealed ampule was sonicated for about 1 minute in order to expel any possible tiny bubbles from the microemulsion phase. The polymerization was performed in a Rayonet Photochemical reactor chamber operating at a wavelength of 253.7 nm for 1 hour at about 35°C.

Morphology Observation

A S-4100 scanning electron microscope (SEM) was used to study the polymer morphology. Samples for SEM were first cut as small pieces from different sections, frozen in liquid nitrogen, and fractured immediately. The fractured samples were vacuum dried for 24 hours at room temperature and coated with gold using a JEOL ion sputter JEC-1100 coating machine.

Drying Rate of Water Desorption

The drying rate of water desorption from the solid polymer was monitored using a Dupont Instruments TGA2100 thermogravimetric analyzer. The polymer was dried in a stream of dry nitrogen gas isothermally at 70°C for 5 hours; then the temperature was increased to 100°C in the rate of 2°C/min for 1 hour. The loss in weight of the sample was recorded as a function of time throughout the experiment, and the sample dimensions were measured again after drying. The drying rate for the polymer sample based on the average of the initial and final surface areas was plotted against the free moisture content of the sample to yield a drying-rate curve.

Leaching of Polymer Solids

The final crosslinked polymer solids were first dried and then extracted with toluene followed by hot water at 60°C for 48 hours. From these successive treatments of drying and extracting, the loss of free water and unreacted monomers or their homopolymers from the polymer solids can be estimated.

RESULTS AND DISCUSSION

Phase Behavior of Microemulsion

Figure 1 shows a ternary microemulsion system of H_2O/AUMAB/MMA. A large single phase emanates from the water-rich region and extends toward the MMA and AUMAB apexes.

Several microemulsions along Line AB of Fig. 1 were characterized by electrical conductivity and surface tension measurements. The weight ratio of MMA to AUMAB was fixed at 1:1.2 along Line AB, and only the water content was varied. When the water content exceeded 9%, its conductivity increased abruptly, reaching a maximum of $3.0 \ S \cdot cm^{-1}$ at about 45% water as shown in Fig. 2. Beyond this, decreasing conductivity was observed on increasing water content. The variation of electrical conductivity of microemulsions as a function of water content is due to
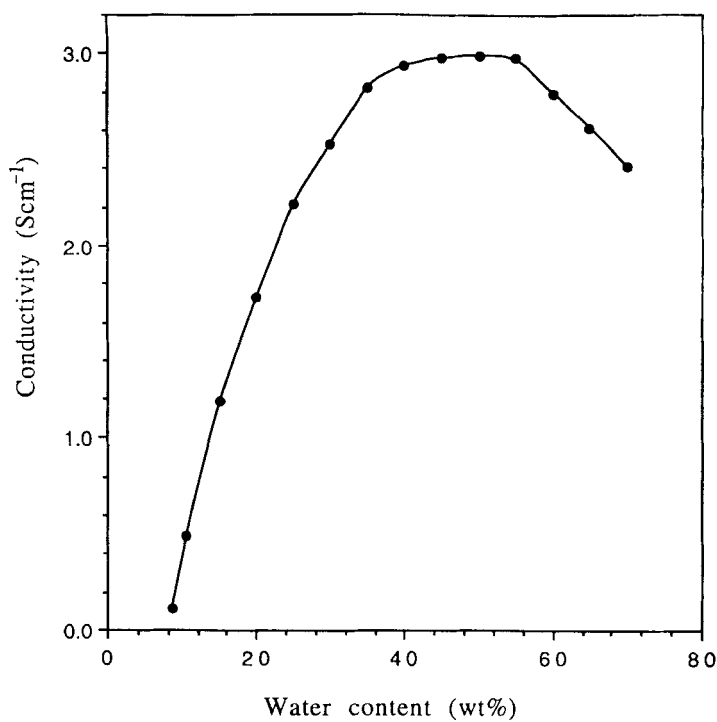
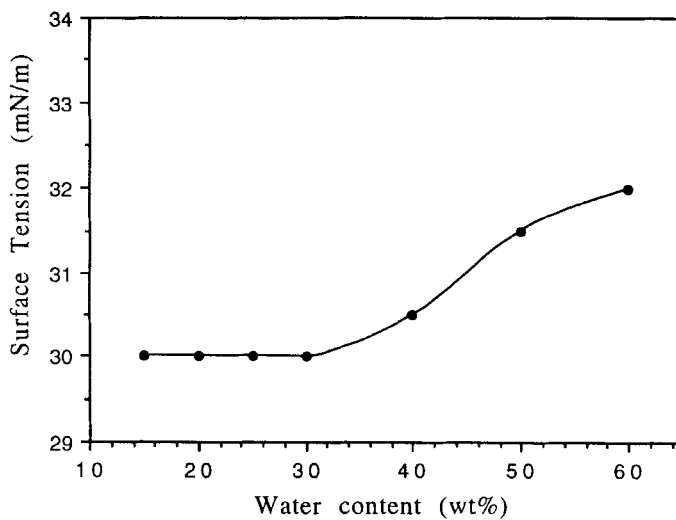FIG. 2.   Conductivity of microemulsion as a function of the water content along Line AB in Fig. 1.

FIG. 3.   Surface tension of microemulsion as a function of the water content along Line AB in Fig. 1.

the continuous change of the microemulsion structure from water-in-oil droplets at a low water content through a bicontinuous structure to oil-in-water droplets at a higher water content. Such a transformation of microstructures in a microemulsion system is well known [23–25]. According to the conductivity, a bicontinuous microemulsion may exist along Line AB with a water content ranging from about 15 to 50 wt%.

The surmise on the bicontinuous microemulsion may also be supported by the surface tension measurements as shown in Fig. 3. The surface tension is almost constant in the region along Line AB containing about 15 to 40 wt% water, indicating no major change of microstructure for bicontinuous microemulsions in that range. However, an increase in surface tension can be observed at high water contents, implying the change from a bicontinuous phase to an oil-in-water microemulsion.

Polymerization of Bicontinuous Microemulsions

A series of bicontinuous microemulsions in a fixed weight ratio of MMA to AUMAB (1:1.2) but with various water contents (15 to 50%) as shown in Table 1 were polymerized. The photoinitiated polymerization proceeded rather rapidly. The system became viscous after 10 minutes of polymerization and progressively formed a transparent gel within 20 minutes. The final transparent polymer solids were obtained without any apparent phase separation. A phase separation as exhibited by the appearance of turbidity is commonly observed from this type of microemulsion polymerization [5, 10]. In order to minimize the modification of microstructures of precursor microemulsions during polymerization, a fast rate of cross-polymerization between MMA, EGDMA, and AUMAB seems to be very important. Several initiators were tested. Photoinitiator DMPA was the most suitable one for producing transparent polymers. Moreover, the use of crosslinker EGDMA was limited to 1–2% based on the total weight of MMA and AUMAB. The resulting polymer was

TABLE 1.   Compositions of Microemulsions and Weight Loss of Polymers after Treatment[a]

	Compositions of microemulsion			Successive weight loss, %		
No.	H₂O	MMA	AUMAB	Sample drying	Toluene extracting	Water extracting
B-1	14.8	37.95	46.08	13.37	0.56	0.44
B-2	19.7	35.39	43.26	17.99	0.64	0.52
B-3	29.61	31.29	37.94	27.52	0.73	0.62
B-4	39.74	26.71	32.60	42.90	0.83	0.71
B-5	49.55	22.29	27.25	47.62	0.95	0.82

[a]1–2 wt% of crosslinker EGDMA was added to each microemulsion based on the total weight of MMA and AUMAB. In addition, 0.3 wt% of photoinitiator DMPA was used based on the total weight of each microemulsion.
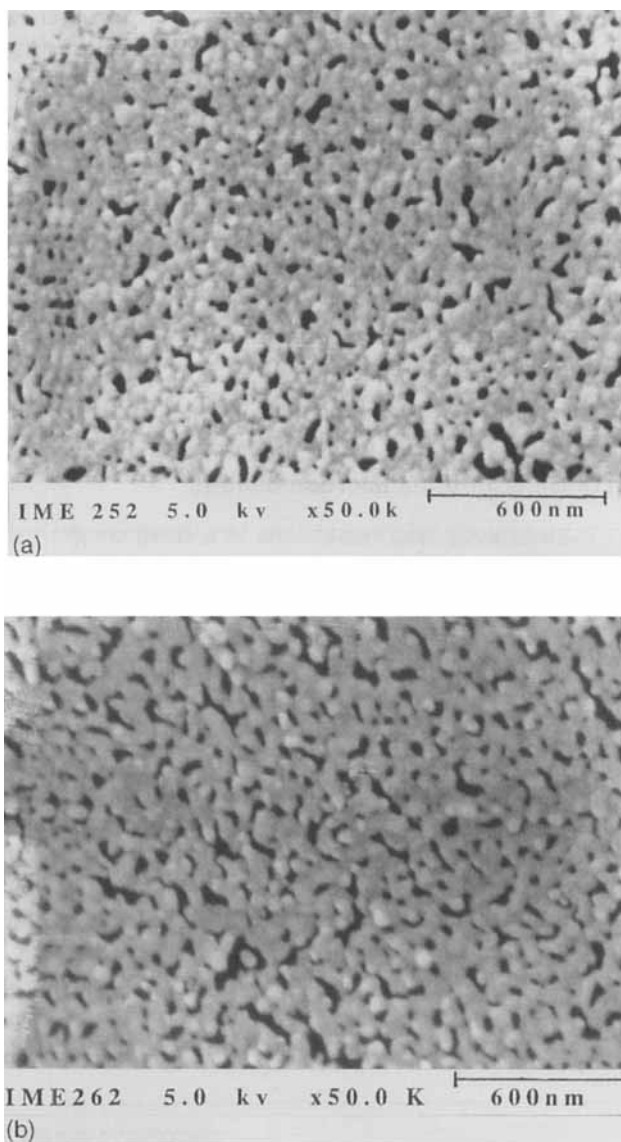
FIG. 4.   SEM micrographs of the fractured surface of samples. (a) B-1 (15% water). (b) B-3 (30% water).

turbid with a higher EGDMA content. Since MMA, EGDMA, and AUTMAB include a similar reactive functional group ($CH_2=CRCO-$), they might have terpolymerized to form a crosslinked polymer matrix with microstructures.

Table 1 shows the weight loss of the transparent polymer solids after several successive treatments. The first weight loss step from drying the sample at 70°C for 12 hours was close to the water content in the precursor microemulsions. The dried
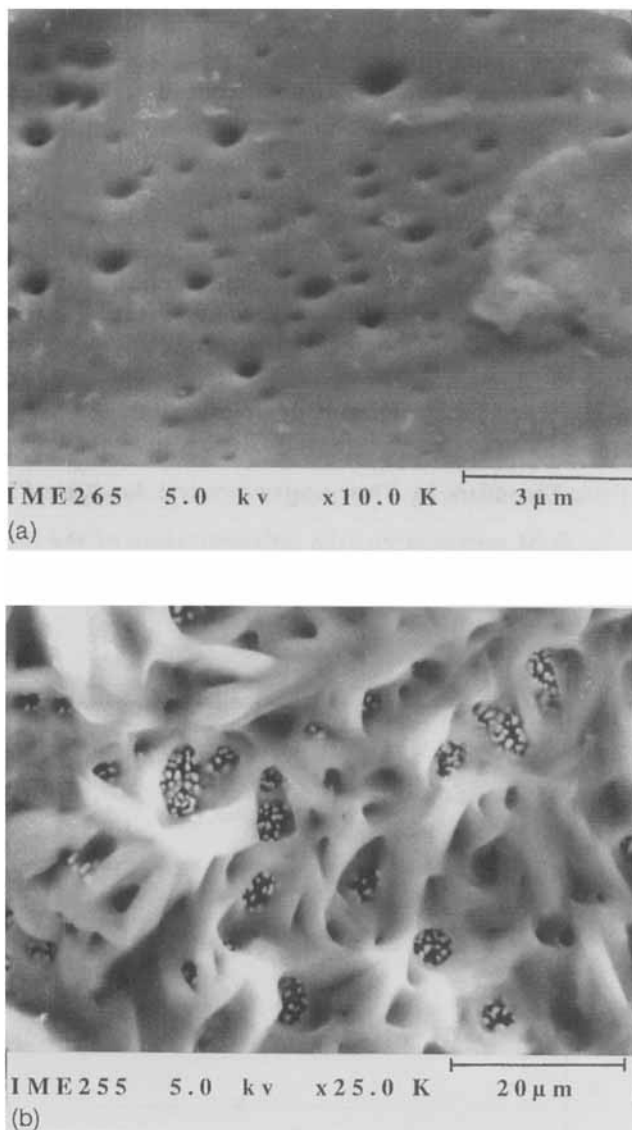
FIG. 5. SEM micrographs of sample B-5 (50% water). (a) The normal surface. (b) The fractured surface.

samples were subsequently subjected to extraction by toluene, which would remove the unreacted MMA or its homopolymer. After which, the toluene-treated polymer was further extracted with hot water in order to remove unreacted AUMAB or its homopolymer. The results show that the unreacted MMA and AUMAB for all the samples were less than 2% based on the total weight of the monomers. This indicates that the transparent polymers obtained were highly crosslinked.

Microporous Structures

Some SEM micrographs of transparent polymer solids with different water contents are shown in Figs. 4 and 5. The polymer with 15% water (Sample B-1) exhibits some porous structures which become more interconnected at 30% water (Sample B-3) as can be seen in Fig. 4. When the water content in the precursor microemulsions is changed from 15 to 40%, the pore size of these microstructures increases from 0.10 to 0.20 μm. However, micron-size porous structures were obtained from the precursor microemulsion with 50% water (Sample B-5) as shown in Fig. 5. Spherical pores are observed for the sample surface (Fig. 5a), but its fractured surface is made up of irregular pores (Fig. 5b). It is not possible at present to correlate the bicontinuous structures existed in precursor microemulsions to the pore structures of the final polymer solids. It is possible that the bicontinuous structures might have been changed during polymerization.

Continuity of Pore Structure by Thermogravimetric Analysis (TGA)

As shown by SEM micrographs, the polymerization of the bicontinuous microemulsions listed in Table 1 produced transparent polymers with some microstruc-
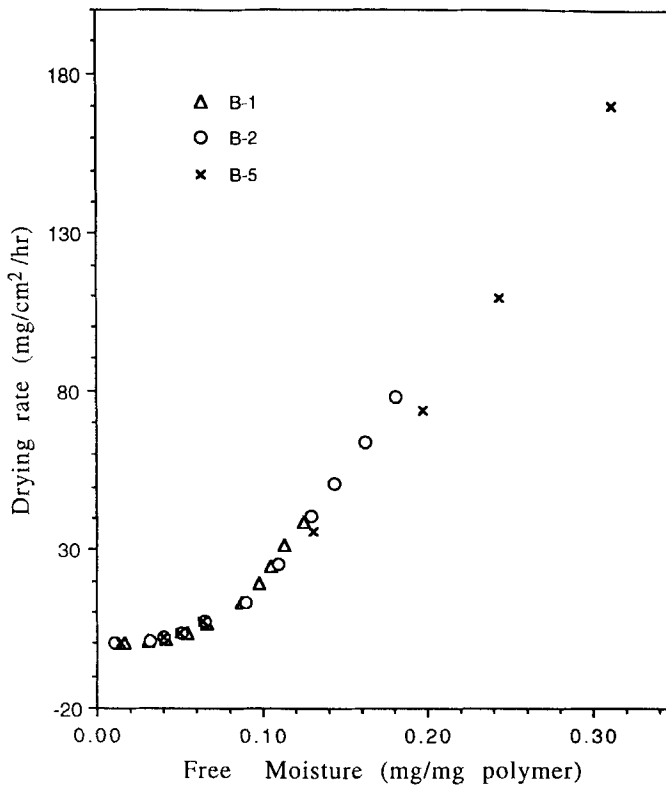

FIG. 6.   Drying-rate curves for porous polymers of Samples B-1, B-2, and B-5.

tures. Additional information pertaining to the continuity of the pore structures can be derived from thermogravimetric analysis. The drying rate curves for all samples listed in Table 1 show a linear falling rate period which is characteristic of open-cell porous materials [26, 27]. The linear falling rate period for three samples increased with the water content of the precursor microemulsion. Moreover, all three samples followed the same drying-rate curve (Fig. 6), indicating that they possess similar open-cell-type structures.

CONCLUSION

An extremely large ternary microemulsion region can be formed using a polymerizable cationic surfactant (AUMAB), MMA, and water. Bicontinuous microemulsions are believed to exist in a system containing 15 to 50% water. Bicontinuous microemulsions would produce transparent polymeric materials with open-cell-type structures.

ACKNOWLEDGMENT

REFERENCES

[1] F. Candau, in *Encyclopedia of Polymer Science and Engineering*, Vol. 9 (H. F. Mark, N. M. Bikales, C. G. Overberger, and G. Menges, Eds.), Wiley, New York, 1987, p. 718.

[2] F. Candau, in *Polymerization in Organized Media* (C. M. Paleos, Ed.), Gordon and Breach, 1992, Chap. 4.

[3] L. E. Scriver, *Nature, 263*, 123 (1976).

[4] Y. Talmon and S. Prager, *J. Chem. Phys., 69*, 2984 (1978).

[5] J. O. Stoffer and T. Bone, *J. Dispersion Sci. Technol., 1*, 393 (1980).

[6] F. M. Menger, T. Tsuno, and G. S. Hammond, *J. Am. Chem. Soc., 112*, 1263 (1990).

[7] S. Qutubuddin, E. Haque, S. J. Benton, and E. J. Fendler, in *Polymer Association Structures: Microemulsions and Liquid Crystals* (ACS Symp. Ser. 384, M. A. El-Nokaly, Ed.), 1989, p. 64.

[8] M. Sasthav and H. M. Cheung, *Langmuir, 7*, 1378 (1991).

[9] W. R. Palani Raj, M. Sasthav and H. M. Cheung, *Ibid., 7*, 2586 (1991).

[10] W. R. Palani Raj, M. Sasthav, and H. M. Cheung, *Ibid., 8*, 1931 (1992).

[11] W. R. Palani Raj, M. Sasthav, and H. M. Cheung, *J. Appl. Polym. Sci., 47*, 499 (1993).

[12] W. R. Palani Raj, M. Sasthav, and H. M. Cheung, *Polymer, 34*(15), 3305 (1993).

[13] M. Sasthav, W. R. Palani Raj, and H. M. Cheung, *J. Colloid Interface Sci., 152*, 376 (1992).

[14] C. H. Chew and L. M. Gan, *J. Polym. Sci., Polym. Chem. Ed., 23*, 2225 (1985).

[15] K. W. Yeoh, C. H. Chew, L. M. Gan, L. L. Koh, and H. H. Teo, *J. Macromol. Sci. – Chem., A26*, 663 (1989).

[16] K. W. Yoeh, C. H. Chew, L. M. Gan, and L. L. Koh, *Ibid., A27*, 63 (1990).

[17] L. M. Gan, C. H. Chew, and T. H. Chieng, Paper Presented at Macromolecular Symposia: Polymex-3, Cancun, Mexico, November 1993.

[18] L. M. Gan and C. H. Chew, *J. Dispersion Sci. Technol., 4*, 29 (1983).

[19] L. M. Gan and C. H. Chew, *Ibid., 5*, 179 (1984).

[20] A. Price, US Patent 5,151,217 (1992).

[21] A. W. Ralston, D. N. Eggenberger, and P. L. Du Brow, *J. Am. Chem. Soc., 70*, 977 (1948).

[22] J. Michas, C. M. Paleos, and P. Dais, *Liq. Cryst., 5*(6), 1737 (1989).

[23] M. Clausse, A. Zradba, and L. Nicholas-Morgantini, in *Microemulsion System* (H. L. Rossano and M. Clausse, Eds.), Dekker, New York, 1987, p. 387.

[24] S. J. Chen, D. F. Evans, and B. W. Ninham, *J. Phys. Chem., 88*, 1631 (1984).

[25] J. Geoges and J. W. Chen, *Colloid Polym. Sci., 264*, 896 (1986).

[26] J. M. Coulson and J. F. Richardson, in *Chemical Engineering*, Vol. 2, 2nd ed., Pergamon Press, New York, 1968, p. 620.

[27] W. L. McCabe, J. S. Smith, and P. Harriot, in *Unit Operation of Chemical Engineering*, 4th ed., McGraw-Hill, New York, 1985, p. 716.