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Morphology of microporous polymeric materials by polymerization of methyl methacrylate and 2-hydroxyethyl methacrylate in microemulsions

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A microemulsion system consisting of methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA) and a crosslinking agent, ethylene glycol dimethacrylate, in water using sodium dodecyl sulfate as a surface-active agent was investigated. A study on the phase behaviour of the system was conducted to determine the type of microstructures that may be present. Polymerization was carried out at room temperature using dibenzyl ketone as a photoinitiator. The morphology (microstructure) of the resulting polymeric materials was found to depend strongly on the composition (water content, surfactant content, and MMA to HEMA ratio) of the precursor microemulsions.

(Keywords: microporous polymers; morphology; microemulsion polymerization)

INTRODUCTION

Microemulsions are thermodynamically stable, transparent, isotropic liquids consisting of water and oil phases stabilized by a surfactant or a combination of surfactant and cosurfactant. Short-chain alcohols are usually used as cosurfactant. The microstructure of a microemulsion depends on the composition of the system, e.g. water-in-oil (w/o) droplets at low water content, oil-in-water (o/w) droplets at high water content, and a bicontinuous structure at intermediate water content. The microstructures of w/o and o/w microemulsions have been widely studied and they have been successfully used for preparing nanoparticles of polymers as well as inorganic compounds by polymerizing the microemulsions[1–4]. Since it was first suggested by Scriven[5], the bicontinuous structure of microemulsions has also been extensively investigated using electron photomicrographs, viscosity, conductivity and n.m.r. measurements[6–10]. In spite of this, little work has been done on the polymerization of bicontinuous microemulsions. Only recently an increase in interest has emerged in studying the formation of porous polymeric solids by polymerization of monomer-containing microemulsions with bicontinuous structures[11–17].

This paper describes the factors that affect the morphology of porous polymeric materials prepared by polymerization of precursor microemulsions ranging from w/o droplets to bicontinuous structures.

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EXPERIMENTAL

Materials

Methyl methacrylate (MMA) from BDH, 2-hydroxyethyl methacrylate (HEMA) and ethylene glycol dimethacrylate (EGDMA) from Merck were purified under reduced pressure before use. Dibenzyl ketone (DBK) of purity greater than 98% and sodium dodecyl sulfate (SDS) of purity greater than 99% were used as received from TCI and Fluka respectively. Deionized and doubly distilled water of electrical conductivity approximately 1.0 μS cm^{-1} was used.

Phase diagram of microemulsion

A stock solution containing 20 wt% SDS in water was prepared. The single-phase region of the microemulsion was determined visually by titrating a specific amount of MMA, HEMA and EGDMA with the stock solution in a screw-capped tube at 30°C. EGDMA added was 4 wt% based on the total weight of monomers used. The transparent microemulsion region was established from the clear–turbid boundaries based on systematic titrations.

Conductivity and viscosity measurements

Both conductivity and viscosity measurements for the microemulsion samples were conducted at room temperature after the samples had been equilibrated for 48 h. An Omega CM-155 conductivity meter with a cell constant of 1.0291 cm^{-1} was used for conductivity

Table 1 Microemulsion compositions used for polymerization[a]

Microemulsion system	Compositions (wt%)				Appearance of the system[b]	
	MMA	HEMA	SDS	Water	BP	AP
H4	57	38	1	4	C	C
H8	54	36	2	8	C	C
H12	51	34	3	12	C	C
H16	48	32	4	16	C	WY
H24	42	28	6	24	C	O
H32	36	24	8	32	C	O
H40	30	20	10	40	C	O
S14	36	24	14	26	C	O
MH55	30	30	8	32	C	O
MH37	18	42	8	32	C	WY
MH19	6	54	8	32	C	WY

[a]Weight ratio of MMA:HEMA was fixed at 3/2 for systems H4, H8, H12, H16, H24, H32, H40 and S14, while that for systems MH55, MH37 and MH19 varied from 5/5 to 3/7 and 1/9 respectively. EGDMA added was 4 wt% based on the total weight of MMA and HEMA, and photoinitiator DBK added was 0.3 wt% based on the total weight of each microemulsion sample

[b]BP = before polymerization; AP = after polymerization; C = clear; WY = white yellowish; O = opaque

measurement. The viscosity was measured using a Cannon (USA) Calibrated Ubbelohde Dilution Viscometer (Size-100).

Microemulsion polymerization

The photoinitiator, DBK, was used for initiating the microemulsion polymerization and the amount added was 0.3 wt% based on the total weight of each microemulsion sample. The samples were flushed with nitrogen gas in ampoules before being sealed. They were then placed in a Rayonet Photochemical reactor chamber operated at a wavelength of 235.7 nm for 2 h at 35.0 ± 0.5°C. The changes in the appearance of the microemulsion samples were also observed throughout the course of polymerization. A particular microemulsion sample, H32 of composition shown in *Table 1*, was selected to study polymer conversion. A series of ampoules containing sample H32 were polymerized for different times. At the end of each period of time, the sample was precipitated or washed in a large quantity of methanol and hexane and was then leached with hot water at 50°C for 48 h in order to remove all unpolymerized monomers and surfactant. The absence of sulfur, which indicates complete removal of surfactant in the polymer matrix, was confirmed by elemental analysis. The final polymer conversion was determined based on the total amount of monomers used in the precursor system.

Morphology observation

A JEOL JSM-T220A scanning electron microscope (SEM) operating at an accelerating voltage of 20 kV was used for examining the polymer morphology. Samples were first frozen in liquid nitrogen and then fractured mechanically. The fractured samples were vacuum dried for 24 h at room temperature before being coated with gold using a JEOL ion-sputter JFC-1100 coating machine.

RESULTS AND DISCUSSION

Phase behaviour of microemulsions

The phase diagram for the system consisting of water/MMA/HEMA/SDS and 4 wt% EGDMA based on the total weight of MMA and HEMA is shown in *Figure 1*. A large single-phase transparent microemulsion region, which comprises regions A, B and C, and a two-phase region D were obtained. Rough demarcation within the transparent microemulsion region was deduced from the results of conductivity and viscosity measurements on the microemulsions. It is believed that region A represents w/o microemulsions, region B o/w microemulsions and region C bicontinuous microemulsions.

Figure 2 shows the variations of conductivity and viscosity of the system as a function of the amount of SDS stock solution along the line L of *Figure 1* with the weight ratio of MMA to HEMA maintained at 60:40. The stock solution contains 20 wt% SDS in water. The

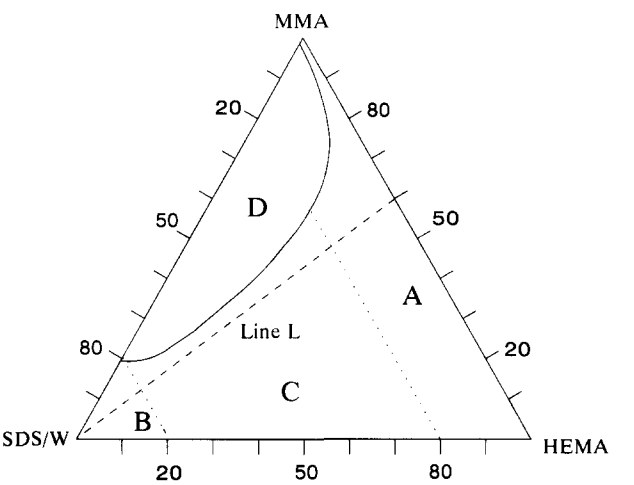

Figure 1 The phase diagram of the system water(W)/MMA/HEMA/SDS and 4 wt% EGDMA based on the total weight of MMA and HEMA. SDS used was 20 wt% in water. Domains: A, w/o microemulsion; B, o/w microemulsion; C, bicontinuous microemulsion; and D, two-phase region

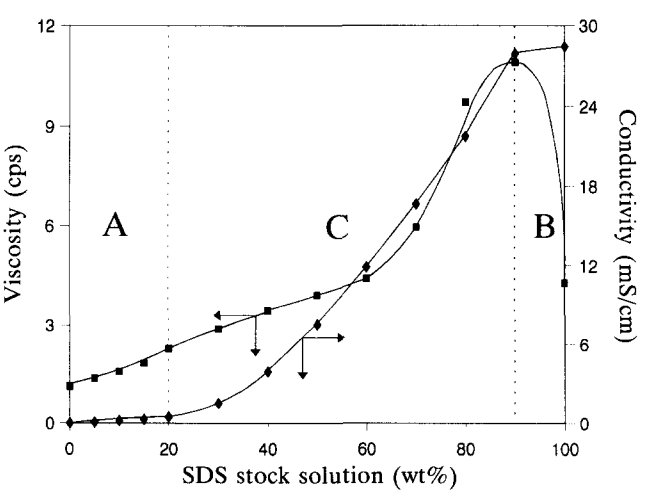

Figure 2 The variations of conductivity and viscosity of microemulsions as a function of the amount of SDS stock solution. The weight ratio of MMA to HEMA was maintained at 60/40. The stock solution contains 20 wt% SDS in water

small increase in conductivity with increasing SDS stock solution at water content below 20 wt% indicates the formation of w/o droplet microstructure in region A. A substantial increase in conductivity can be seen as the water content is increased from about 20 to 80 wt% in region C. This is attributed to the presence of bicontinuous structures in which both water and oil domains are interconnected with each other forming conducting channels. At higher water content, as indicated by region B, the system changes into an o/w microemulsion with the conductivity approaching the maximum and remaining almost constant in value.

A continuous increase in viscosity is observed in the microemulsions on increasing the water content up to about 80 wt%. This is because the number of droplets or channels increases on increasing the water content, which in turn increases the interactions between them. There is a drop in viscosity on increasing the water content beyond 80 wt%, showing the transition from bicontinuous structure to o/w droplet structure. Both conductivity and viscosity results show similar trends to those reported in the literature[18–21].

Polymerized microemulsion systems

It is known that MMA, HEMA and EGDMA are very reactive and they can be readily copolymerized to form a crosslinked terpolymer. Based on the phase diagram of *Figure 1*, one can perform terpolymerization of MMA, HEMA and EGDMA in various microemulsions with increasing water content from region A (w/o microemulsions), through region C (bicontinuous microemulsions) to region B (o/w microemulsions). Transparent solid materials could only be obtained from polymerization of w/o microemulsions with less than 20 wt% water in region A. Opaque polymeric materials with mechanical strength still strong enough to be self-supporting were produced from polymerization of bicontinuous microemulsions with water content less than 70 wt% in region C. At higher water contents, the materials produced were soft and opaque after polymerization. When the water content was increased above 80% in region B, polymerization of the o/w microemulsions could produce turbid, translucent or transparent latexes depending on the compositions of the microemulsions.

In this paper, we intend to discuss only the preparation of solid polymeric materials based on compositions from region A and region C up to 40% water content. The detailed compositions are listed in *Table 1*. The changes in appearance during the course of photoinitiated polymerization for those microemulsions containing more than 20 wt% but less than 70 wt% water can be briefly described as follows:

clear microemulsion (initially)
→ bluish yellow transparent microemulsion (2 min, 0.6%)
→ turbid emulsion (5 min, 1.2%)
→ turbid gel (10 min, 4.8%)
→ opaque polymeric materials (30 min, 66.5%)
→ final opaque polymeric solid (2 h, >97%)

The time of polymerization and its respective polymer conversion indicated inside the brackets were used on the microemulsion sample H32 chosen for the polymer conversion study. Polymerization took place rapidly and gelation started within 10 min at ca. 5% polymer conversion. These changes indicate that the initial structure of the microemulsion is not preserved during polymerization and it is substantiated by the final microstructure of the polymeric solids obtained, which consists of coagulated spherical or globular particles as revealed by electron microscopy. This seems inevitable because these microemulsions are of low viscosity and their microstructures are continuously rearranging due to the formation of very large macromolecules in the aqueous or oil domains of the medium during polymerization. This behaviour has also been observed in the polymerization of isotropic bicontinuous microemulsions in other systems as reported in the literature[22,23]. The change in the appearance of the microemulsion samples from initial clear microemulsions to opaque solids during polymerization was due to the continuous increase in the polymer particle size. The detailed mechanism of the formation of this kind of porous polymeric material is currently under investigation.

Polymerization of all the compositions studied took place homogeneously with no apparent phase separation on a macroscopic scale. Fast polymerization rate and low polymerization temperature are needed though not very critical in order to alleviate the occurrence of phase separation during the course of polymerization. Both conditions are fulfilled by using a suitable photoinitiator such as DBK.

Morphology of polymeric materials

The effect of water content in the precursor microemulsions on the morphology of polymeric materials produced after polymerization is illustrated by the SEM micrographs in *Figure 3*. The micrographs show the fracture surfaces of polymeric materials containing 8%, 16%, 24% and 40% water based on the compositions as listed in *Table 1*. MMA to HEMA ratio was maintained at 3/2. Rather smooth fracture surfaces were observed for the polymeric materials containing less than 5 wt% water. This may be due to the fact that the water added to the system was strongly bonded to the hydrophilic SO_4^- and OH groups situated on SDS and HEMA respectively. It is also consistent with the conductivity result, which shows hardly any increase in value for the microemulsion samples containing less than 5 wt% water. For the sample with 8 wt% water, the fracture surface was no longer smooth but had no particular recognizable structure. At 16 wt% water, the polymeric material exhibits porous structure with pores seen to be of the closed-cell type and not interconnected. The microstructure became very distinctive for samples containing more than 20 wt% water. For instance, *Figure 3c* shows the globular microstructure with the dimension of micrometres. They stacked onto each other and the voids (pores) formed resembled the packing of a chromatographic column using fine particle materials. It is believed that these pores were interconnected and were water-filled spaces generated between the incompletely coalesced spherical aggregates. These results clearly show the formation of closed-cell structure at water content below 20 wt% and open-cell (interconnected) structure at water content greater than 20 wt%. Our previous work and those reported by others also show similar

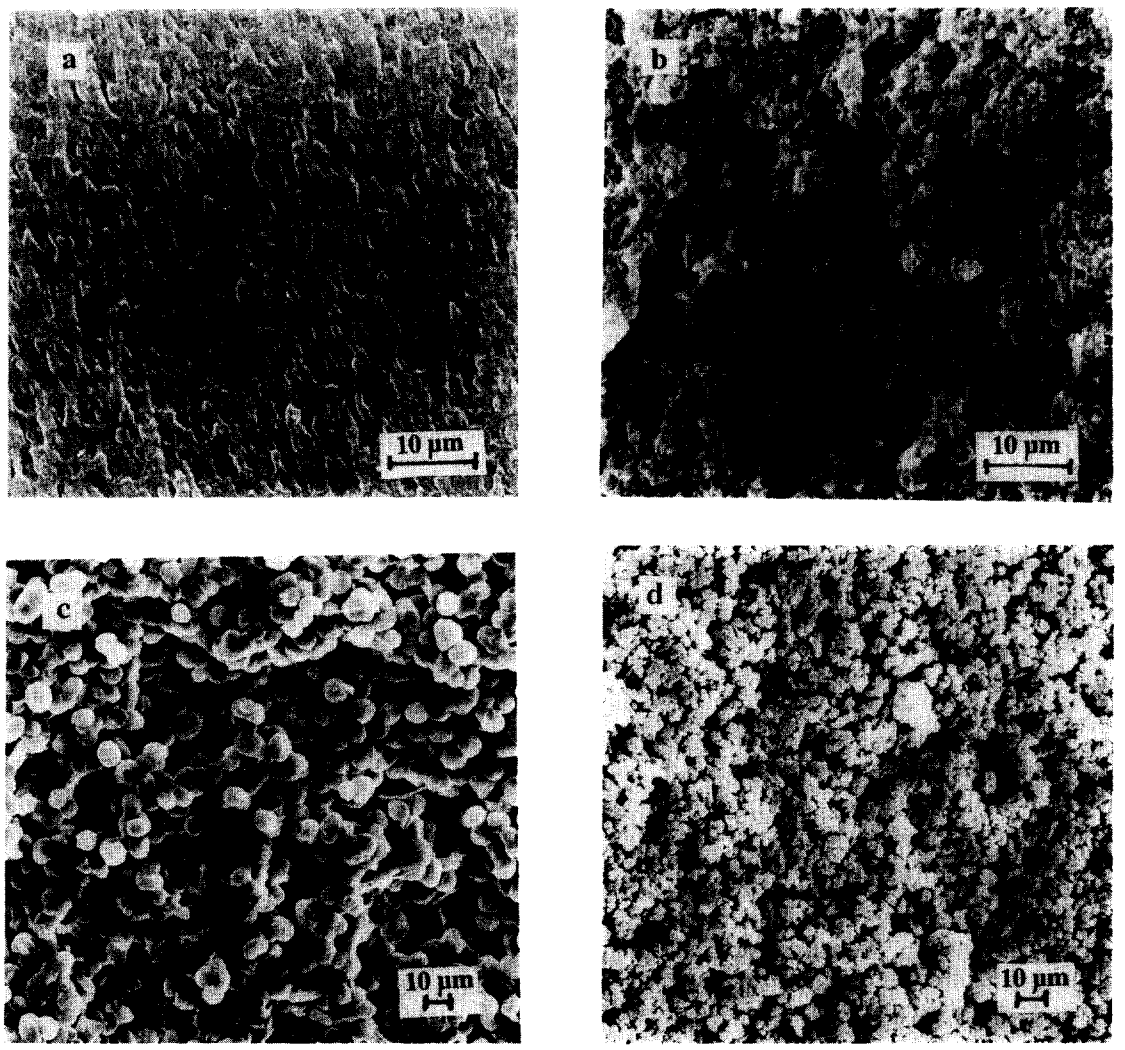

Figure 3 SEM micrographs of the morphology of the polymeric solids formed from precursor microemulsions containing different water contents: (a) 8%, (b) 16%, (c) 24% and (d) 40%

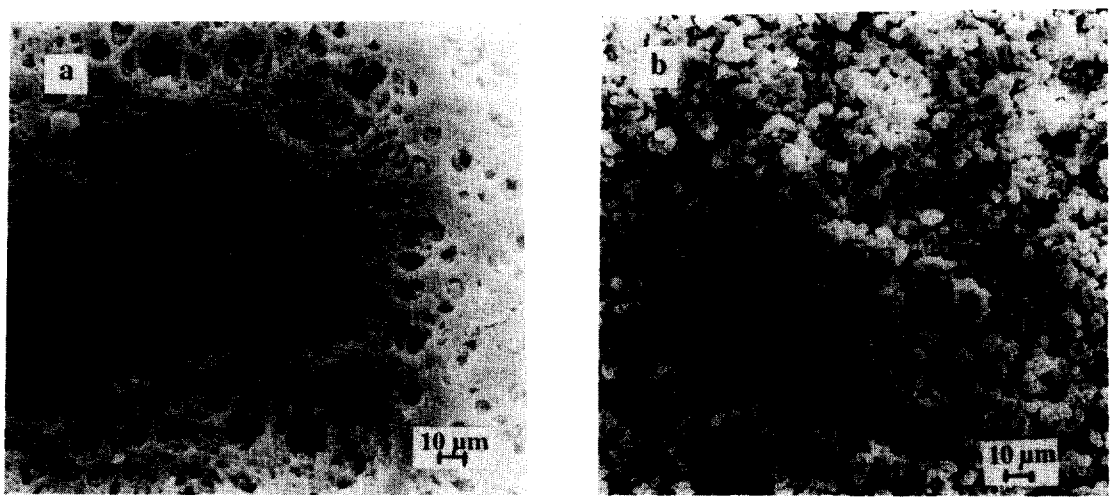

Figure 4 SEM micrographs of the morphology of the polymeric solids formed from microemulsion sample H32 containing 8% SDS: (a) surface facing nitrogen atmosphere and (b) fractured surface

results[14–17]. As the water content was further increased to 40%, the formation of microporous structures is very obvious, as depicted in *Figure 3d*. It can be seen in the micrographs that the dimension of the globular microstructure became smaller on increasing the water content of the precursor systems. The substantial decrease in the size of the spherical aggregates for samples on increasing the water content of the precursor microemulsions showing bicontinuous structures was expected as the monomer to water ratio decreases.

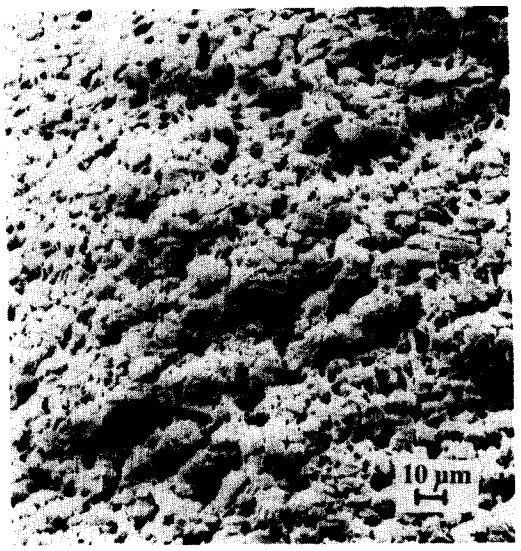

Figure 5 SEM micrograph of the morphology of the polymeric solid formed from microemulsion sample S14 containing 14% SDS

The morphology of fractured surfaces was usually quite different from that of the unfractured surfaces as shown in *Figure 4* for a sample containing 32 wt% water. *Figure 4a* depicts the surface morphology of the sample facing the nitrogen atmosphere, while *Figure 4b* is that of the fractured one. Pores nearly round in shape of dimension ca. 1–10 μm can clearly be seen from *Figure 4a*. These pores might be derived from water domains of the polymerized microemulsion system. *Figure 4b* shows the fractured surface, which is similar to those in *Figures 3c* and *3d*. The microstructure of the fractured surfaces as seen from electron micrographs is more homogeneous than that of the surfaces facing the atmosphere. This may be due to the occurrence of phase separation induced by evaporation of water during polymerization, which leads to the inhomogeneity of the top surface compared with the fractured surface.

The effect of SDS concentration on the morphology for the fracture surfaces of polymeric materials can be obtained by comparing *Figures 4b* and *5*. The former system consisted of 8 wt% SDS (sample H32 in *Table 1*)

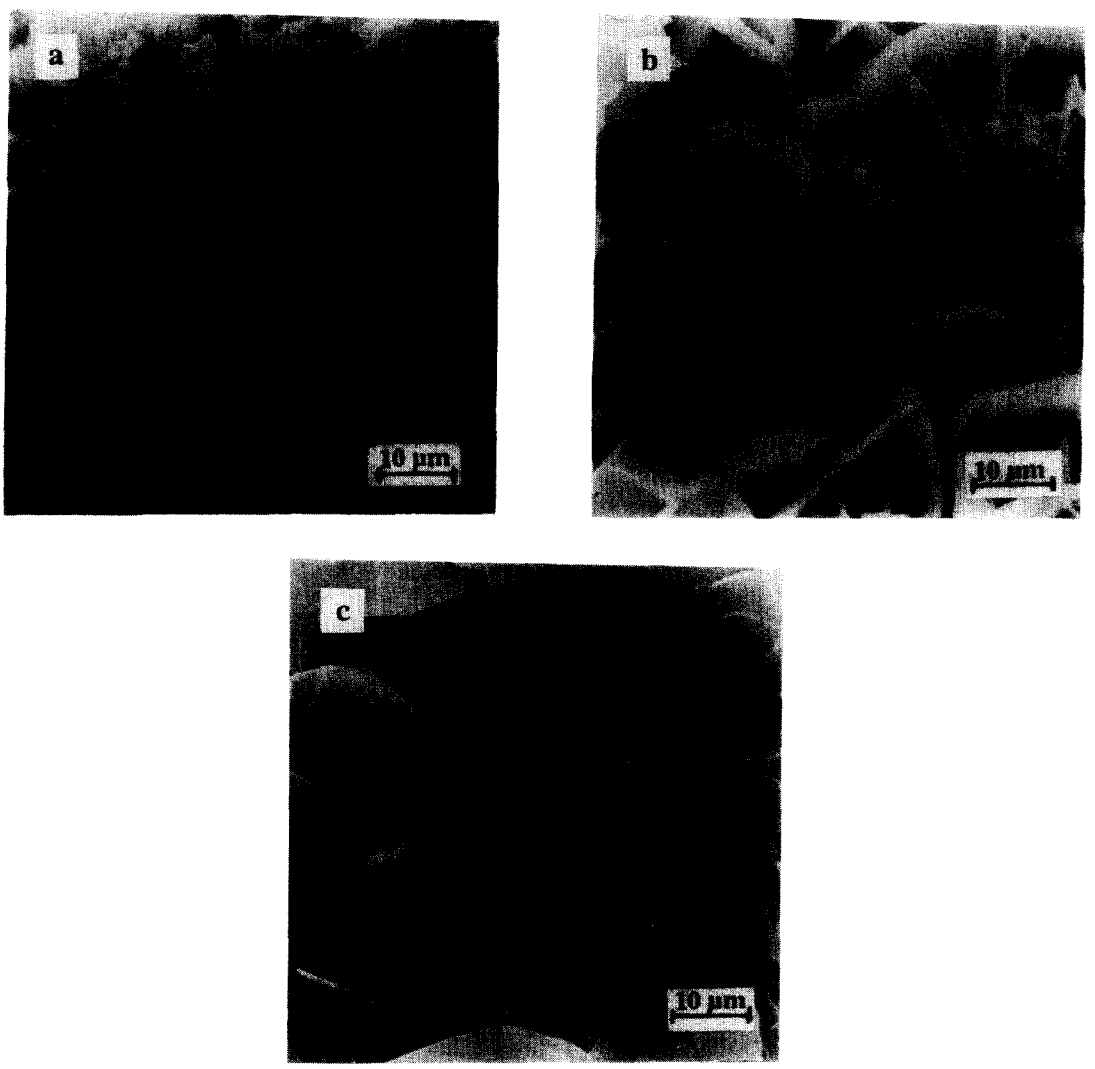

Figure 6 SEM micrographs of the morphology of the polymeric solids formed from precursor microemulsions containing different weight ratio of MMA to HEMA: (a) 5/5, (b) 3/7 and (c) 1/9

while the latter contained 14% (sample S14 in *Table 1*). The globular microstructure of the polymeric materials became less distinctive and they seemed to be more closely packed as the SDS concentration was increased from 8 to 14%. Moreover, some fibrous structure linking the distorted globular structure can also be observed. It has been reported[24] that the coagulation rate of latex particles depends on the concentration of SDS. The reason for this dependence may be due to the great excess of SDS that remained in the aqueous phase, besides that used to stabilize latex particles, which acts as an electrolyte, and increases the ionic strength and reduces the electric double layers of the colloidal particles. This effect facilitates the coagulation of particles, which leads to the formation of more closely packed coagulated globules as observed from the SEM micrograph (*Figure 5*).

A very prominent alteration in the morphology of the polymeric materials can be seen from *Figure 6* with the variation of MMA to HEMA weight ratios. These materials were prepared based on the compositions of samples MH55, MH37 and MH19 as listed in *Table 1*. Their weight ratios of MMA to HEMA are 5/5, 3/7 and 1/9 respectively. The fractured surfaces of the polymeric materials appeared to change from sponge-like, through flake-like to petal-like structures when the weight ratio of MMA to HEMA was decreased from 5/5 to 3/7 to 1/9 respectively. The way the microstructure changes on decreasing the weight ratio of MMA to HEMA is not exactly known.

CONCLUSIONS

The phase behaviour study on the single-phase microemulsions composed of MMA, HEMA, EGDMA, SDS and water indicates the presence of different microstructures at different water contents. It shows the existence of w/o droplet structure at low water content (< 20 wt%), o/w droplet structure at high water content (> 80 wt%) and bicontinuous structure at intermediate water content (20–80 wt%).

Investigation into the morphology of the polymeric materials, obtained by polymerizing the microemulsions, shows that their microstructures are strongly dependent on the composition of the precursor microemulsions (water content, surfactant concentration, and MMA to HEMA ratio). Both the appearance and morphology observations indicate that the initial microstructures are not preserved during polymerization. However, bicontinuous microemulsion polymerization will give rise to the formation of open-cell polymeric materials whereas w/o microemulsion polymerization will lead to the formation of closed-cell polymeric materials.

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