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Polymerization of single-phase microemulsions: dependence of polymer morphology on microemulsion structure

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Polymerization of monomer-containing single-phase Winsor-IV microemulsions was studied and the morphology of the polymer obtained was found to be related to the structure of the microemulsion. The hydrophobic component of the microemulsions was formed with methyl methacrylate together with ethylene glycol dimethacrylate. Methacrylic acid was found to be effective as a polymerizable cosurfactant and was used in formulating the microemulsions, together with sodium dodecyl sulfate which was used as the surfactant. The structure of the single-phase microemulsion was found to vary with change in composition of the system. At concentrations of aqueous surfactant solution below 20%, a droplet structure of water in oil (W/O) existed. Inferential evidence indicated the formation of a bicontinuous structure at aqueous surfactant solution concentrations between 20% and 80%. In the case of aqueous surfactant solution concentrations above 80%, a droplet structure of oil in water (O/W) was obtained. On polymerization, the microemulsions having a W/O droplet structure yielded solids with a closed-cell porous structure. Open-cell porous polymeric solids were obtained by the polymerization of microemulsions with a bicontinuous structure. Stable polymer latices could be formed by polymerization of microemulsions with an O/W droplet structure.

(Keywords: microemulsion; structure; morphology)

INTRODUCTION

Polymerization of thermodynamically stable microemulsion systems is an area which has recently generated considerable research interest[1–6]. The present work represents a continuation of our research in this area. We have earlier reported results on the formation of porous solids by the polymerization of microemulsion systems formed using the weakly amphiphilic nature of acrylic acid[5]. In the present study we examine the use of methacrylic acid (MAA) in the formation of single-phase Winsor-IV microemulsions (thermodynamically stable single-phase microstructured systems made up of oil, water and amphiphile). The monomer methyl methacrylate (MMA) was used as the hydrophobic component together with the crosslinking agent ethylene glycol dimethacrylate (EGDMA). The surfactant sodium dodecyl sulfate (SDS) was used as the amphiphile and methacrylic acid was present as the cosurfactant. The microstructure of the Winsor-IV microemulsions formed was evaluated and the systems characterized based on their microstructure. The polymeric materials obtained on polymerizing the microemulsions were also characterized. This study also investigated the relationship between the microstructure of the microemulsion and the morphology of the polymer obtained on polymerizing the microemulsion.

Studies have been reported on the polymerization of various microemulsion systems which had either a droplet structure[1,7–11] (oil in water (O/W) or water in oil (W/O)) or a bicontinuous structure[2,5,6,12] and the characterization of polymers obtained from them. We considered it of interest to study the nature of the polymer obtained from one particular microemulsion system but with variation in the structure of the precursor microemulsion. The microemulsion structure was varied from droplets of W/O through a bicontinuous structure to an O/W droplet structure by changes in composition. The characteristics of the polymer obtained were studied in relation to the structure of the microemulsion precursor. This study provided results which could be applied to control the morphology of the polymer obtained by varying the structure of the precursor microemulsion. The use of methyl methacrylate containing microemulsions formed with methacrylic acid as the polymerizable cosurfactant offers the possibility of forming copolymers which could have various applications, since the methacrylic acid groups in the copolymer would make it more hydrophilic compared to poly(methyl methacrylate) (PMMA). Copolymers with the desired compositional and morphological features could thus be synthesized by selecting a suitable microemulsion composition as the

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precursor. The possibility of forming stable PMMA microlatices of PMMA copolymerized with MAA has also been investigated.

EXPERIMENTAL

Materials

The monomers MMA and MAA and the crosslinking agent EGDMA were of purity greater than 99%. Monomer samples for polymerization were prepared by vacuum distillation followed by treatment with inhibitor removal columns. The surfactant SDS was 98% pure. The water used for formulating the microemulsions was doubly distilled and deionized. All the chemicals used in this study were obtained from Aldrich.

Phase behaviour studies and microemulsion characterization

The phase behaviour study to determine the Winsor-IV domain was performed by pipetting the required amounts of the various components into glass sample tubes. The amount of EGDMA present in the samples was 4% of the combined weight of MMA and MAA. The sample tubes were hand shaken and equilibrated at 25 ± 0.1°C for 48 h before making measurements. Characterization of the microstructure of the microemulsions was done using conductivity measurements, viscosity measurements, quasielastic light-scattering measurements (QELS) and measurements of the light intensity scattered by the microemulsion at 90° to the incident beam. A 500 mW argon ion laser was used as the light source for the QELS and scattered light intensity measurements. The QELS studies were done using a Brookhaven Instruments BI-DS ECL photomultiplier tube and a BI 2030 AT digital correlator. The scattered light intensity measurements were made using the same light-scattering apparatus but utilizing an RCA 941 photomultiplier tube. The conductivity measurements were made using an Omega PHH-80 conductivity meter and the viscosity measurements were made with a Brookfield LVT digital viscometer. The conductivity, viscosity and light-scattering studies were all done at 25 ± 0.1°C. Additional details pertaining to the phase behaviour studies and microstructure characterization procedures are described in our earlier reports[5,6].

Polymerization procedure

Photoinitiated polymerization of the microemulsions was done after purging the microemulsion samples with nitrogen for 15 min and subsequently adding 0.02 g of the oil soluble photoinitiator azobisisobutyronitrile (AIBN) for 10 g of microemulsion. Polymerization was carried out in a reaction cell using a 450 W ultraviolet source at a temperature of 25 ± 0.1°C for a duration of 1 h.

Morphology observation

The morphology of porous polymeric solids obtained by polymerization of W/O and bicontinuous microemulsions was examined using scanning electron microscopy (SEM). Samples for SEM studies were made by drying the polymer at 55°C and using the freeze fracture technique for sample preparation. The polymer samples were coated using a Polaron E5400 coating machine and an ISI SX 40 scanning electron microscope was used to examine the polymer morphology.

The size of microlatices formed by polymerizing O/W microemulsions was studied by QELS and transmission electron microscopy (TEM). Samples for QELS were made by diluting with water the latex obtained on polymerization to 1% solids content followed by filtration of the latex using a 0.2 μm filter. The QELS measurements were made at 25 ± 0.1°C using the experimental set-up for light scattering described earlier. The samples for TEM observations were made by diluting the polymerized latex to 1% solids content. A drop of the diluted latex was placed on a carbon-coated TEM grid and allowed to dry. The latex particles were then observed using a JEOL JEM 1200-EX II transmission electron microscope.

Pore continuity determination

The continuity in the porous structure of the polymeric solids obtained was evaluated by examining the shape of the drying rate curve obtained from thermogravimetric analysis. Porous solids with an open-cell structure containing water in their pores exhibit a drying rate curve having a linear falling rate period, in contrast to the drying behaviour of closed-cell materials which have an exponentially decreasing falling rate period[3,13–15]. A DuPont Instruments TGA 2950 thermogravimetric analyser was used for the study. The polymer sample, obtained from the polymerization cell, which contained water in its pores was dried in a stream of dry nitrogen at a temperature of 70°C for 300 min. The isothermal drying rate curve for the sample was constructed from the data on the loss in weight of sample as a function of time, as recorded by the thermogravimetric analyser.

RESULTS

The phase behaviour diagram for the microemulsion system formed with MMA, MAA, EGDMA and 20% by weight aqueous SDS solution (SDS/W) is presented in *Figure 1*. The phase diagram shows four regions with

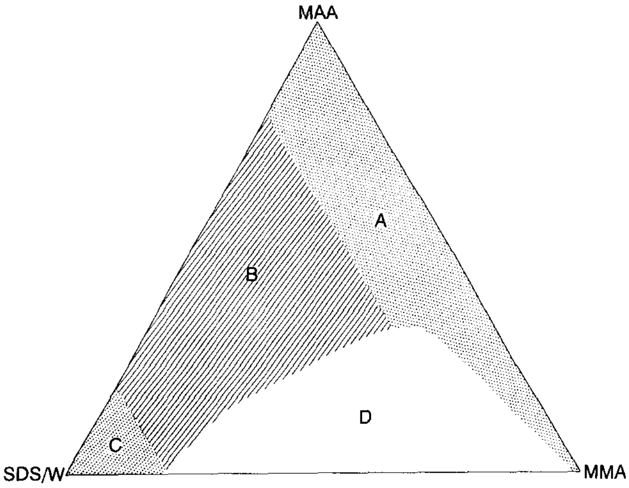

Figure 1 Ternary phase diagram for the system composed of methyl methacrylate (MMA), methacrylic acid (MAA), an aqueous solution of sodium dodecyl sulfate (SDS/W) and ethylene glycol dimethacrylate (EGDMA) at 25 ± 0.1°C. The compositions are on a weight percentage basis and EGDMA is 4% of the combined weight of MMA and MAA: domain A, W/O Winsor-IV microemulsion; domain B, bicontinuous Winsor-IV microemulsion; domain C, O/W Winsor-IV microemulsion; domain D, two-phase region

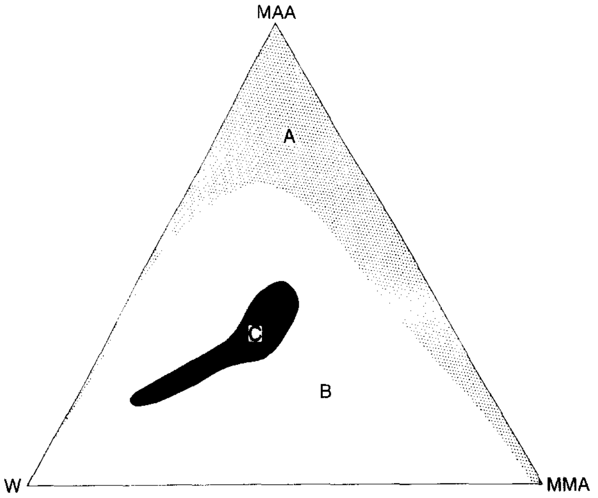

Figure 2 Ternary phase diagram for the system composed of methyl methacrylate (MMA), methacrylic acid (MAA), water (W) and ethylene glycol dimethacrylate (EGDMA) at 25 ± 0.1°C. The compositions are on a weight percentage basis and EGDMA is 4% of the combined weight of MMA and MAA: domain A, single-phase region; domain B, two-phase region; domain C, unstable three-phase region

different microstructural features which were determined from microemulsion characterization studies. The compositions from regions A–C pertain to macroscopically monophasic, transparent, isotropic Winsor-IV microemulsions. The regions A–C were demarcated based on the nature of the microstructure corresponding to the microemulsions from each region. The microemulsions from region A had a W/O droplet structure, while samples from region C had a droplet structure of O/W. The microemulsions from region B of the phase diagram exhibited inferential evidence of a bicontinuous microstructure. The unshaded portion (region D) of the phase diagram represents samples which were not single-phase Winsor-IV microemulsions. The line separating regions A–C from region D represents the boundary between the two-phase region and the Winsor-IV microemulsion systems. Winsor-IV microemulsions with a bluish tinge were observed near the boundary separating the two-phase region from the Winsor-IV microemulsions.

The phase behaviour diagram for the microemulsion system containing MMA, MAA and EGDMA is shown in *Figure 2*. The very small single-phase domain in this system is represented by region A. This single-phase domain is very restricted in size and its extension to compositions with water content greater than about 30% is almost insignificant. The unshaded region B of the phase behaviour diagram corresponds to compositions which are not single-phase microemulsions. In the dark region C of *Figure 2* the formation of three-phase samples consisting of transparent upper and lower phases and a kinetically unstable, coarse white middle-phase emulsion was observed. After a few weeks of equilibration the samples from region C changed to two-phase samples with the white middle-phase emulsion not existing. As the single-phase domain from this system did not include a significantly large composition range, detailed characterization and polymerization studies for this system could not be performed.

Microemulsion structure from characterization studies

Conductivity measurement of microemulsion samples from the Winsor-IV domain was used as one of the techniques to study the microstructure. The study was performed by measuring the conductivity of samples as a function of increasing aqueous content, keeping the relative amounts of the other chemical species constant. The results of the conductivity measurements as a function of aqueous content for samples from the system containing MMA, MAA and SDS/W having an MMA:MAA ratio of 1:1 are presented in *Figure 3*. Three distinct sections of the conductivity–water content curve are observed. There is a small increase in the conductivity of the microemulsions on increasing the aqueous content up to around 20% by weight. A sharp increase in the conductivity of the microemulsions is seen

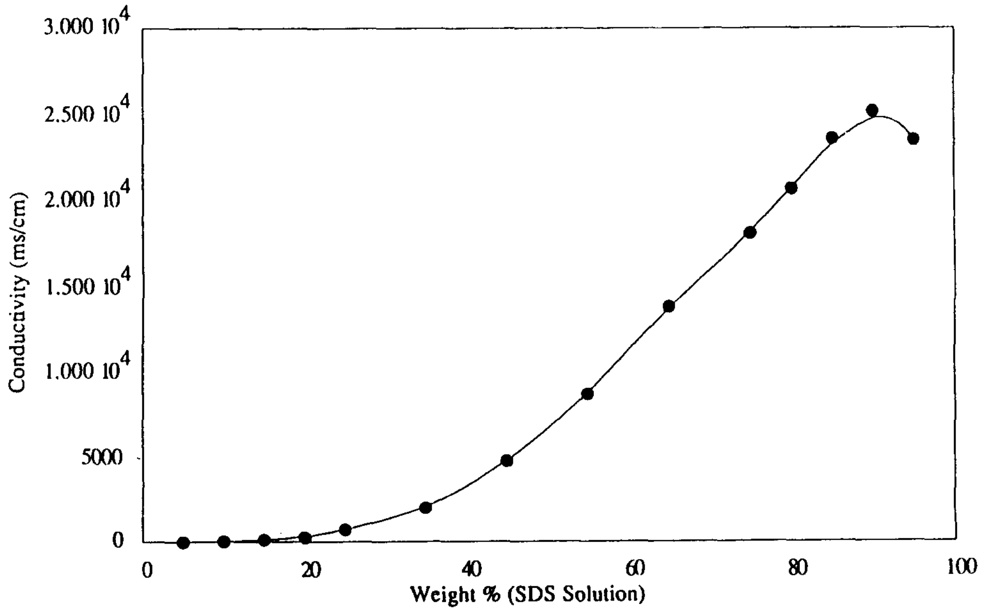

Figure 3 Conductivity as a function of aqueous content for the microemulsion system across the Winsor-IV domain at 25 ± 0.1°C. The MMA:MAA ratio in the microemulsion was maintained at 1:1

above 20% aqueous content and this behaviour is observed up to an aqueous content of around 80%. The conductivity of the microemulsion does not change significantly on increasing the aqueous content above 80%.

The results of viscosity measurements as a function of increasing aqueous content for microemulsions with an MMA : MAA ratio of 1 : 1 are shown in *Figure 4*. The viscosity of the microemulsions does not vary significantly when the aqueous content is less than 20%. A sharp increase in viscosity is observed in the 20–80% aqueous content range. This is followed by a decrease in viscosity at aqueous contents above 80%. The variation in viscosity with aqueous content of the microemulsion exhibits a trend which is qualitatively similar to the variation in conductivity (*Figure 3*).

Quasielastic light scattering (QELS) was used to determine the characteristic length of the microstructure present in the microemulsion samples. QELS measurements were made on microemulsion samples containing an MMA : MAA ratio of 1 : 1 but with increasing aqueous contents. The intensity autocorrelation function for light scattered from microemulsion samples with aqueous contents less than 20% or more than 80% exhibited a single exponential decay. The QELS data for these samples were analysed using the method of cumulants and the equivalent droplet diameter was determined. The QELS measurements on microemulsion samples with aqueous contents in the 20–80% range did not provide an intensity autocorrelation function exhibiting a single exponential decay. The intensity

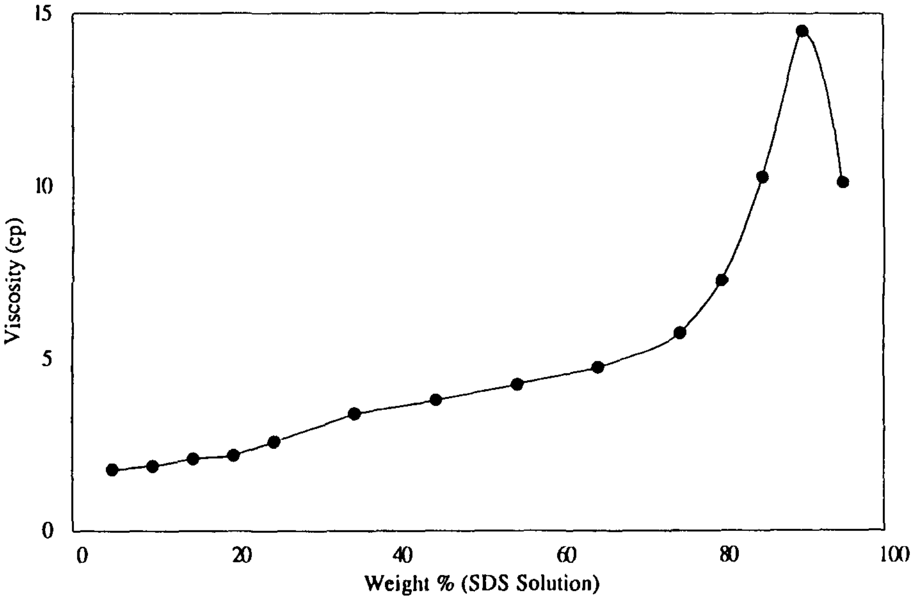

Figure 4 Viscosity as a function of aqueous content for the microemulsion system across the Winsor-IV domain at 25 ± 0.1°C. The MMA : MAA ratio in the microemulsion was maintained at 1 : 1

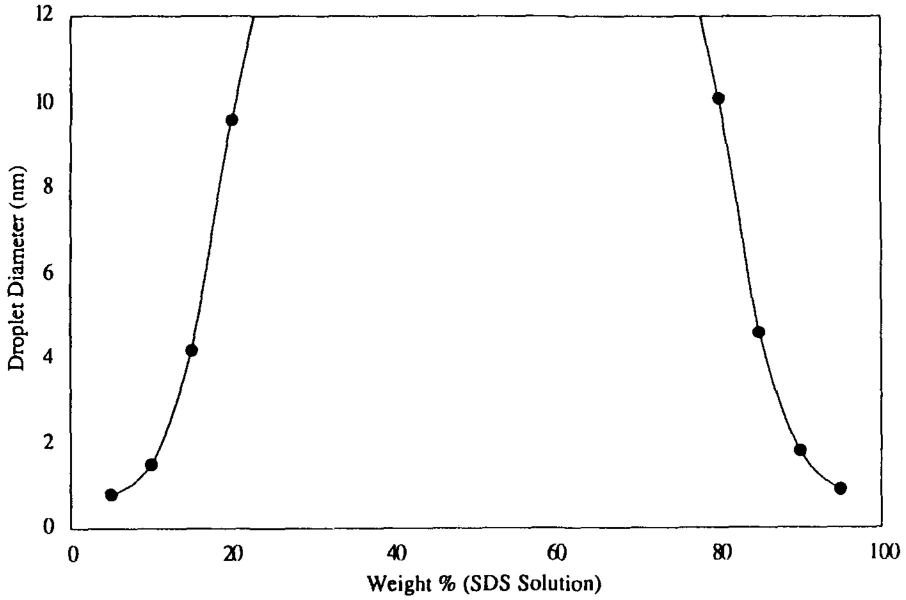

Figure 5 Droplet diameter of the Winsor-IV microemulsion from QELS measurements at 25 ± 0.1°C as a function of aqueous content. The MMA : MAA ratio in the microemulsion was maintained at 1 : 1

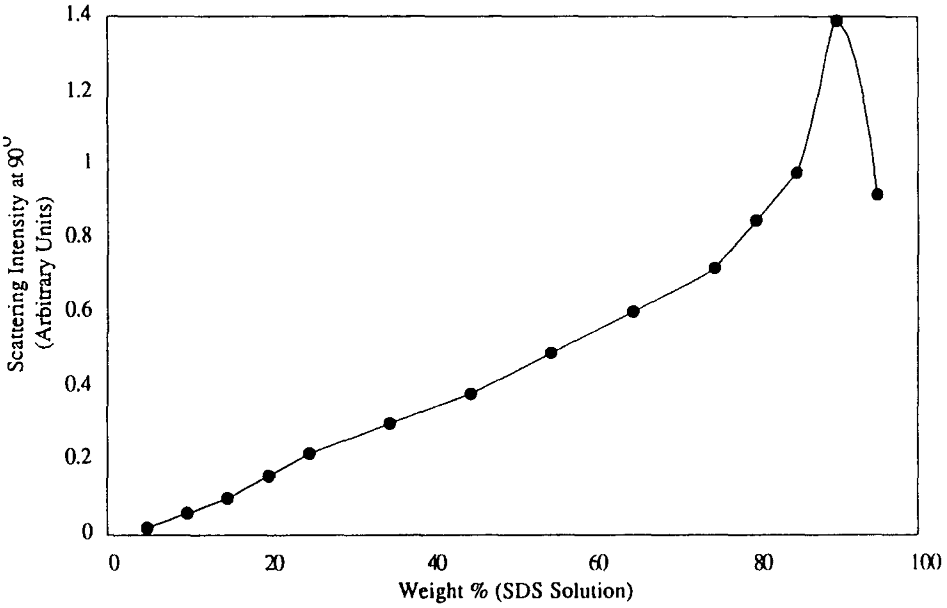

Figure 6 Intensity of light scattered by the Winsor-IV microemulsion, measured at 90° to the incident beam, as a function of aqueous content. The measurements were made at 25 ± 0.1°C and the MMA : MAA ratio was maintained at 1 : 1

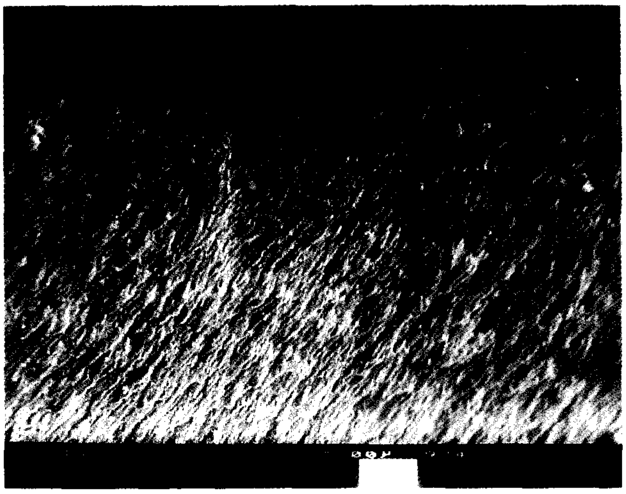

Figure 7 SEM micrograph showing the morphology of the polymer obtained from the microemulsion containing 44% MMA, 44% MAA, 12% SDS/W and EGDMA (4% of combined weight of MMA and MAA)

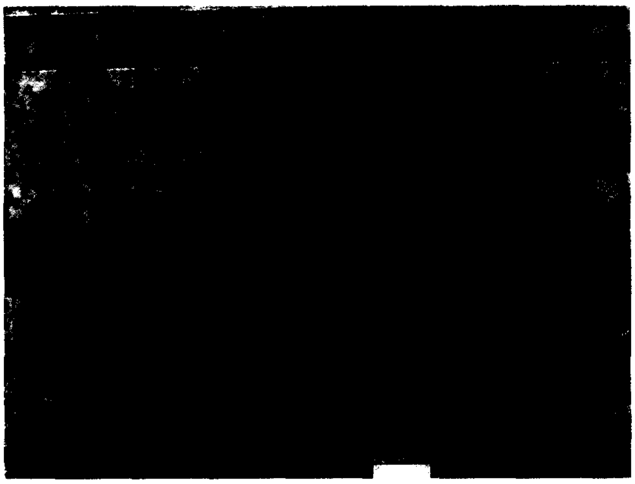

Figure 8 SEM micrograph showing the morphology of the polymer obtained from the microemulsion containing 29% MMA, 29% MAA, 42% SDS/W and EGDMA (4% of combined weight of MMA and MAA)

autocorrelation function for these samples showed a very slow decay, resulting in a long tail. These QELS data could result from systems in which fluctuations in the microstructure occur on a long timescale, making it difficult to utilize QELS to determine the characteristic length. Our earlier studies of QELS measurements from the microemulsion systems formed using acrylic acid[5] as well as potassium undecenoate[6] had resulted in QELS data which were qualitatively similar to those obtained from the present system. The results of the QELS measurements are shown in *Figure 5*. The equivalent droplet diameter increases sharply as the aqueous content of the microemulsion increases up to about 20%. Similarly, the equivalent droplet diameter reduces sharply as the aqueous content is increased above 80%. At intermediate aqueous contents (20–80%) the characteristic length could not be determined using QELS.

The intensity of light scattered from microemulsion samples with an MMA : MAA ratio of 1 : 1, measured at 90° to the incident beam, is presented as a function of the aqueous content of the microemulsion in *Figure 6*. The results indicate a small increase in the intensity of scattered light from microemulsion samples up to an aqueous content of around 20%. This is followed by a sharp increase in the intensity of scattered light with increasing aqueous content to about 80%. A decrease in the scattered light intensity is observed at aqueous contents above 80%. The observed variation in scattered light intensity with aqueous content resembles the variations in conductivity and viscosity observed for this microemulsion system. The results of the

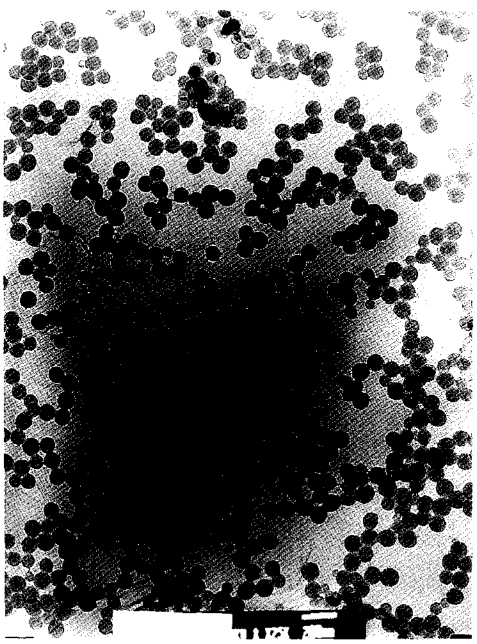

Figure 9 TEM micrograph of the polymer latex obtained from the microemulsion containing 8% MMA, 2% MAA, 90% SDS/W and EGDMA (4% of combined weight of MMA and MAA)

microemulsion characterization studies described above are qualitatively similar to the results of characterization studies which were reported earlier for the acrylic acid[5] and potassium undecenoate[6] based microemulsion systems.

The conductivity, viscosity and light-scattering measurements indicate a variation in microemulsion structure with composition. The microemulsion system appears to be composed of a W/O droplet structure at low aqueous content, a structure bicontinuous in oil and water at intermediate aqueous content and a droplet structure of O/W at high aqueous content.

Characterization of polymer morphology

Rigid polymeric materials were obtained on polymerization of microemulsion samples with compositions pertaining to W/O or bicontinuous structures. The polymeric materials from microemulsions with less than about 60% aqueous content exhibited good mechanical strength. The polymer from bicontinuous microemulsions with aqueous content above 60% was soft and had low mechanical strength. Some of the microemulsion compositions with an O/W droplet structure were polymerized to form stable microlatices. The microlatices formed were transparent, with some having a bluish tinge.

The morphology of polymeric solids was studied using scanning electron microscopy. The polymeric solids were observed to have a porous structure, with the porous morphology related to the structure of the microemulsion system. The microemulsion samples with a W/O structure on polymerization resulted in the formation of porous polymers with a disjointed cellular structure. The pore size of the closed cells was observed to increase with increasing aqueous content. The polymerization of microemulsions exhibiting a bicontinuous structure resulted in polymers having an interconnected porous structure (open cells). The variation in polymer morphology was studied for polymers obtained from microemulsions with an MMA : MAA ratio of 1 : 1. The SEM micrographs for polymers obtained from microemulsions with 12% and 42% aqueous content are shown in *Figures 7* and *8*, respectively. These micrographs are representative of the types of morphology that were obtained from W/O microemulsions and bicontinuous microemulsions. The morphology of the polymer in *Figure 7* is made up of disjointed pockets, while in *Figure 8* the polymer exhibits a structure composed of interconnected pores.

The TEM micrograph in *Figure 9* shows the microlatex particles formed by polymerizing a microemulsion sample containing 8% MMA, 2% MAA and 90% SDS

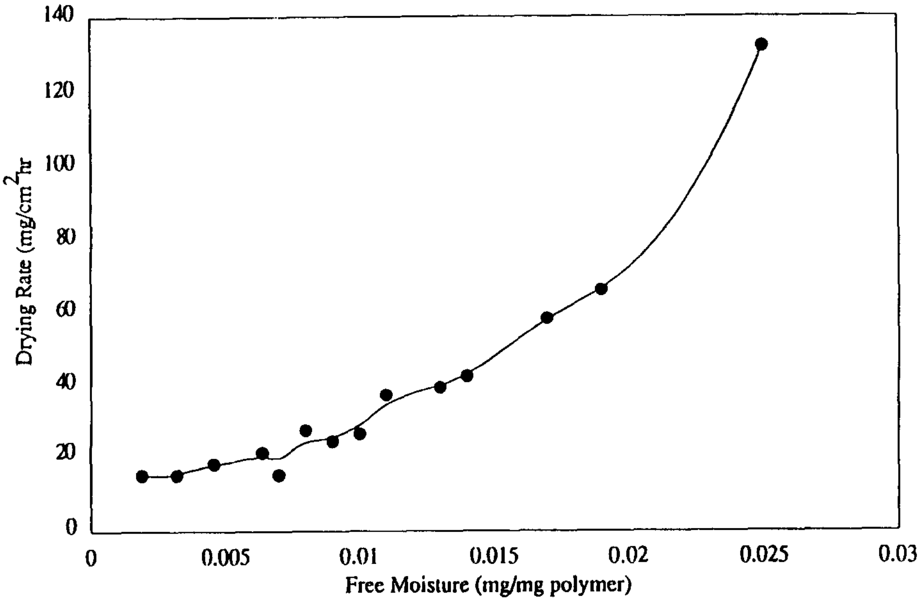

Figure 10 Drying rate curve of the closed-cell porous polymer obtained from the microemulsion containing 44% MMA, 44% MAA, 12% SDS/W and EGDMA (4% of combined weight of MMA and MAA)

solution. The microparticles obtained are relatively monodisperse. QELS measurements of the microlatex indicated the mean particle diameter to be 98 nm. The results of the characterization studies of the precursor microemulsion had indicated the microemulsion structure to consist of O/W droplets. After polymerization, the microemulsion was transformed to a microlatex of relatively monodisperse polymer particles. The microlatex obtained was observed to be transparent and stable. It was observed that polymerization of O/W microemulsions with an MAA content greater than 4% usually resulted in the formation of transparent gels.

Evaluation of pore continuity

Further investigation of the continuity in pore structure in the porous polymeric materials synthesized involved determining the drying rate curves. The drying rate curves were obtained using thermogravimetric analysis. The drying rate curve for the polymer obtained from the microemulsion containing MMA and MAA in the ratio of 1 : 1 with 12% aqueous content is presented in *Figure 10*. The corresponding SEM micrograph for this sample is shown in *Figure 7*. The drying rate plotted as a function of the moisture content in the solid shows an exponential decrease until the equilibrium moisture content is reached. The drying rate curve in *Figure 10* is representative of that obtained from polymer samples synthesized from microemulsions with an aqueous content less than 16%. The characterization studies of the microemulsion structures had indicated these microemulsions to be composed of a W/O droplet structure. The shape of the drying rate curve for these materials agrees closely with the results from published literature[3,13–15] for closed-cell porous materials.

The drying rate curve for the polymer sample from the microemulsion containing an MMA : MAA ratio of 1 : 1 with 42% aqueous content is shown in *Figure 11*. The drying rate results indicate the presence of a linear falling rate period following by a small exponentially decreasing portion until the equilibrium moisture content is reached. The drying rate curves for polymer samples from microemulsions with aqueous contents in the range 22–60% are qualitatively similar to that in *Figure 11*. The microemulsions pertaining to this composition range showed inferential evidence of a bicontinuous structure. The portion of the drying rate curve corresponding to the linear falling rate period increases with increasing aqueous content of the precursor microemulsion. The type of drying rate behaviour observed in these polymer samples is typical of open-cell porous solids with an interconnected pore structure[3,13–15]. The SEM micrograph in *Figure 8* pertains to the polymer sample for which the drying rate curve is shown in *Figure 11*.

DISCUSSION

The phase behaviour diagram for the system containing MMA, MAA, EGDMA and SDS/W indicates the formation of Winsor-IV microemulsions over a large composition range (*Figure 1*). In contrast, the Winsor-IV domain for the system composed of MMA, MAA, EGDMA and water (*Figure 2*) is very small compared to that in *Figure 1*. This suggests that MAA is effective as a cosurfactant when used in conjunction with SDS as the surfactant in the formation of a microemulsion. However, the use of MAA by itself is not effective in the formation of microemulsions. The results of this study, compared with our earlier report on the use of acrylic acid (AA) to form polymerizable microemulsion compositions, indicate MAA to be less effective than AA in forming microemulsions by itself. This could be attributed to the more hydrophobic nature of MAA compared to AA. As cosurfactants MAA and AA are found to be equally effective in microemulsification when used along with SDS.

The results of conductivity measurements on the microemulsions can be related to the variation in

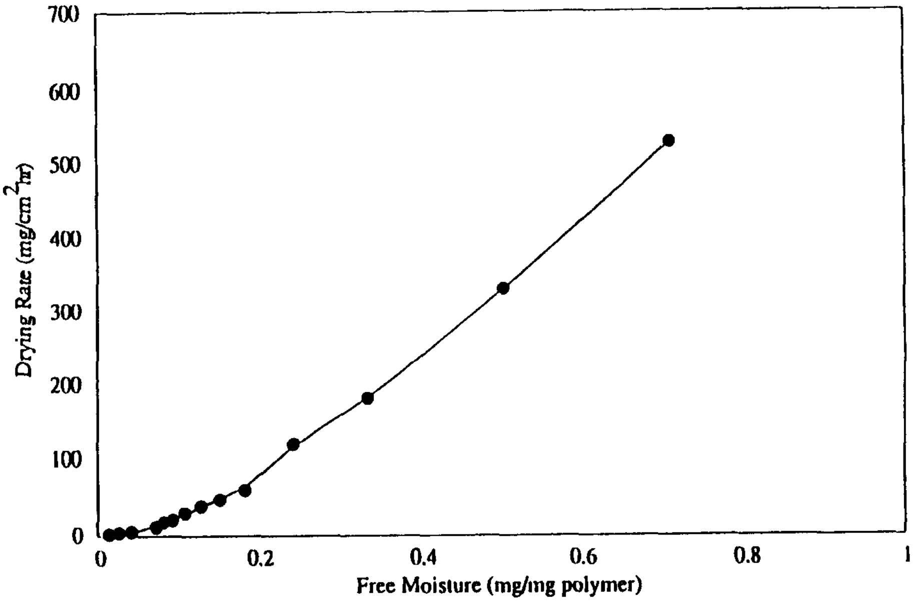

Figure 11 Drying rate curve of the open-cell porous polymer obtained from the microemulsion containing 29% MMA, 29% MAA, 42% SDS/W and EGDMA (4% of combined weight of MMA and MAA)

structure of the microemulsions. The low values of conductivity at low aqueous contents indicate the existence of a microemulsion structure consisting of aqueous droplets dispersed in a continuous oil phase. The lack of a continuous conducting pathway results in low conductivity. On further increasing the aqueous content of the microemulsion a sharp increase in conductivity is observed. The observed conductivity results indicate the aqueous domains as becoming connected. This leads to the formation of a microstructure which is bicontinuous in oil and water. The establishment of continuous conducting pathways leads to the observed sharp increase in conductivity through a percolation-type effect. The conductivity continues to increase with aqueous content in the bicontinuous domain as the available conducting pathways increase. At very high aqueous content (around 80%) the measured conductivity does not change significantly with aqueous content as the microemulsion changes to a droplet structure of O/W. The conductivity measurements on the microemulsion system provide information on the structural details. The microemulsion studied appears to consist of W/O droplets at low aqueous content; with increasing aqueous content the structure becomes bicontinuous in oil and water; and at very high aqueous content an O/W structure is obtained. Similar variations in conductivity with structure of the microemulsion have been reported for other microemulsion systems[5;6,16,17].

The viscosity of the microemulsion system examined is small and does not change significantly at low aqueous contents. The viscosity increases sharply on increasing the aqueous content above 20% and at very high aqueous content (around 80%) a slight decrease in the viscosity is observed. The variation in viscosity of the microemulsion with aqueous content (*Figure 4*) is qualitatively similar to the variation in conductivity that was observed (*Figure 3*). The observed changes in viscosity of the microemulsion with composition can be related to variations in structure. At low aqueous content the existence of a W/O droplet structure results in relatively low viscosity. With the formation of bicontinuous channels at higher aqueous content the viscosity of the system shows a sharp increase. The viscosity continues to increase sharply with aqueous content for bicontinuous microemulsions as more interconnected water channels are formed. The microemulsion structure changes to O/W droplets at very high aqueous content and this leads to a decrease in viscosity. The results of viscosity measurements on the microemulsion system corroborate the structural details inferred from conductivity measurements. Similar reasoning has been used to relate viscosity measurements to the structure of microemulsions in earlier studies[5,18].

QELS studies of microemulsions at low aqueous contents (less than 20%) and high aqueous contents (greater than 80%) provided measurements of the equivalent droplet diameter. The intensity autocorrelation function obtained from QELS for these systems exhibited a single exponential decay and was analysed using the method of cumulants to obtain the equivalent droplet diameter. At intermediate aqueous contents the intensity autocorrelation function from QELS showed a very slow decay and was qualitatively different from that at low or high aqueous contents. The method of cumulants was found to be inappropriate for analysing the intensity autocorrelation function from microemulsions at intermediate aqueous contents. This change in the nature of the QELS measurements indicates the microemulsion structure at intermediate aqueous contents to differ from that at low or high aqueous contents. The information from QELS measurements of microemulsions at low aqueous contents and high aqueous contents shows the existence of a droplet structure. The change in microemulsion structure with composition that is suggested from QELS measurements is in agreement with the information obtained from conductivity and viscosity measurements. These results show the existence of droplet structures in the microemulsions at high and low aqueous contents and the formation of a bicontinuous structure at intermediate aqueous contents. The QELS results obtained from the bicontinuous microemulsions in this study are similar to those reported from other studies[5,6,19,20]. The equivalent droplet diameters determined for W/O and O/W microemulsions are comparable to those reported for similar systems[5,6,21,22].

The intensity of light scattered from the microemulsion, measured at 90° to the incident beam (*Figure 6*), exhibits a variation with composition which is similar to the trends observed in conductivity and viscosity. The intensity of scattered light is dependent on the number of scatterers as well as the size of the scatterers. The small increase in scattered light intensity at low aqueous content could result from an increase in the droplet diameter of the dispersed aqueous droplets and an increase in the number of droplets. With the formation of a bicontinuous structure at higher aqueous content the intensity of scattered light increases. This increase in scattered light intensity could result from the numerous interconnected channels of the bicontinuous structure. The intensity of scattered light continues to increase with aqueous content throughout the bicontinuous region, suggesting an increase in the number of bicontinuous channels, the size of the bicontinuous channels or both. At very high aqueous content the decrease in the intensity of light scattered by the microemulsion represents the change to an O/W droplet structure. The decrease in scattered light intensity with increasing aqueous content in this region is due to the reduction in number and size of the droplets with decreasing volume of the dispersed phase. Similar results on the variation of scattered light intensity with microemulsion composition have been reported from other studies[5,6,17,23].

The information from the studies to characterize the microemulsion structure for the system containing MMA, MAA and SDS/W indicates the existence of droplet structures at low and high aqueous contents. At intermediate aqueous contents, inferential evidence for the existence of a bicontinuous structure is obtained. The observations from each characterization technique used are consistent with those from the others, and combining these results provides useful information on the microemulsion structure.

The polymerization of microemulsions from this system with a W/O structure or bicontinuous structure resulted in the formation of solids. The SEM micrographs (*Figures 7* and *8*) show the variation in polymer morphology with the structure of the microemulsion precursor. The microemulsion with a W/O droplet structure (12% aqueous content) is transformed into a solid with a disjointed cellular structure (*Figure 7*) on polymerization. The connectivity between the pores is observed to be low from the SEM micrograph. The polymer appears to consist of a closed-cell porous structure. Polymerization of the microemulsion with a W/O droplet structure is observed to result in a polymer with a closed-cell porous structure. In contrast, an open-cell porous polymeric solid (*Figure 8*) with a high degree of connectivity between the pores was obtained from the polymerization of a bicontinuous microemulsion (42% aqueous content). The drying rate curves for the polymeric solids provide additional information on the morphology. The shape of the drying rate curves for polymeric solids from W/O microemulsions provides qualitative evidence of the closed-cell structure. This information used in conjunction with the observations from the SEM micrograph confirms the closed-cell morphology of the polymer. Similarly, the drying rate curves for polymers from bicontinuous microemulsions indicate the existence of an open-cell porous structure. Polymerization of microemulsions with a composition close to the transition from a W/O droplet to a bicontinuous structure resulted in polymers with a morphology consisting of both open and closed cells.

The SEM micrographs indicate the polymer morphology to be dependent on the structure of the precursor microemulsion. The closed-cell porous structure could result when the aqueous droplets in the W/O microemulsion are trapped as discrete pockets on polymerization. Similarly, the interconnected aqueous channels in the bicontinuous microemulsion could lead to the open-cell porous structure with a high degree of pore connectivity. However, the dimensions of the porous structures in *Figures 7* and *8* are significantly larger than the length scale of the dimensions characteristic of the precursor microemulsions. This suggests the existence of significant phase separation effects during polymerization of the microemulsion. This phase separation could result in coalescence of the aqueous domains, leading to larger pores. Hence, the polymer morphology has some resemblance to the structure of the precursor microemulsion, but direct preservation of the microemulsion structure by polymerization has not been achieved. The sharp differences between the morphologies of polymers from W/O microemulsions and bicontinuous microemulsions indicate the dependence of the polymer morphology on the structure of the precursor microemulsion.

The polymerization of microemulsions with an O/W droplet structure results in the formation of microlatices (*Figure 9*). The dimensions of the latex particles are significantly larger than the droplet diameter in the precursor microemulsion. This could result from droplet coalescence during polymerization and also from the polymerization of methacrylic acid present in the aqueous phase. The formation of stable microlatices by polymerizing O/W microemulsions further indicates the influence that the structure of the precursor microemulsion has on the polymer morphology.

CONCLUSIONS

Winsor-IV microemulsions were obtained in the system composed of MMA, MAA and a 20% aqueous solution of SDS. Methacrylic acid is effective as a cosurfactant in this system and enables the Winsor-IV domain to extend over a large section of the phase behaviour diagram. The variation in structure of the microemulsion with composition has been studied by combining experimental data obtained from conductivity, viscosity and light-scattering measurements. Corroborative information from these studies indicates the existence of a W/O droplet structure at low aqueous contents, an O/W droplet structure at high aqueous contents and a structure bicontinuous in oil and water at intermediate aqueous contents.

Polymerization of the microemulsions and characterization of the materials obtained has shown the dependence of the polymer morphology on the structure of the precursor microemulsion. Closed-cell porous polymeric solids are obtained by polymerization of W/O microemulsions. Bicontinuous microemulsions are converted to open-cell porous solids on polymerization, and the polymerization of O/W microemulsions results in stable microlatices. The morphologies of the polymeric materials obtained resemble the major structural features of the precursor microemulsions but on a significantly larger length scale. This shows that the exact preservation of microemulsion structure by polymerization has not been achieved, although the major structural features of the microemulsion are retained in the polymer. Additional studies to elucidate the transformation in microemulsion structure during polymerization are in progress in our laboratory. This study also indicates the technological potential of obtaining porous polymeric materials with open-cell pores or closed-cell pores as well as stable microlatex particles by the polymerization of microemulsions.

REFERENCES

1 Antonietti, M., Lohmann, S. and Van Niel, C. *Macromolecules* 1992, **25**, 1139

2 Menger, F. M., Tsuno, T. and Hammond, G. S. *J. Am. Chem. Soc.* 1990, **112**, 1263

3 Sasthav, M., Palani Raj, W. R. and Cheung, H. M. *J. Colloid Interface Sci.* 1992, **152**, 376

4 Jayakrishnan, A. and Shah, D. O. *J. Polym. Sci., Polym. Lett. Edn* 1984, **22**, 31

5 Palani Raj, W. R., Sasthav, M. and Cheung, H. M. *Langmuir* 1991, **7**, 2586

6 Palani Raj, W. R., Sasthav, M. and Cheung, H. M. *Langmuir* 1992, **8**, 1931

7 Guo, J. S., El-Aasser, M. S. and Vanderhoff, J. W. *J. Polym. Sci., Polym. Chem. Edn* 1989, **27**, 691

8 Friberg, S. E., Rong, G., Yang, C. C. and Yang, Y. in 'Polymer Association Structures: Microemulsions and Liquid Crystals' (Ed. M. A. El-Nokaly), ACS Symposium Series No. 384, American Chemical Society, Washington, DC, 1989, p. 34

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

10 Perez-Luna, V. H., Puig, J. E., Castano, V. M., Rodriguez, B. E., Murthy, A. K. and Kaler, E. W. *Langmuir* 1990, **6**, 1040

11 Stoffer, J. O. and Bone, T. *J. Dispersion Sci. Technol.* 1980, **1**, 393

12 Qutubuddin, S., Haque, E., Benton, W. J. and Fendler, E. J. in 'Polymer Association Structures: Microemulsions and Liquid Crystals' (Ed. M. A. El-Nokaly), ACS Symposium Series No. 384, American Chemical Society, Washington, DC, 1989, p. 64

13 Corben, R. W. and Newitt, D. M. *Trans. Inst. Chem. Eng.* 1955, **33,** 52
14 Coulson, J. M. and Richardson, J. F. in 'Chemical Engineering', 2nd Edn, Vol. II, Pergamon Press, New York, 1968, p. 620
15 McCabe, W. L., Smith, J. C. and Harriott, P. in 'Unit Operations of Chemical Engineering', 4th Edn, McGraw-Hill, New York, 1985, p. 716
16 Chen, S. J., Evans, D. F. and Ninham, B. W. *J. Phys. Chem.* 1984, **88,** 1631
17 Auray, L., Cotton, J. P., Ober, R. and Taupin, C. in 'Microemulsion Systems' (Eds H. L. Rosano and M. Clausse) Marcel Dekker, New York, 1987, p. 225
18 Georges, J. and Chen, J. W. *Colloid Polym. Sci.* 1986, **264,** 896
19 Bodet, J. F., Bellare, J. R., Davis, H. T., Scriven, L. E. and Miller, W. G. *J. Phys. Chem.* 1988, **92,** 1898
20 Eric, Y., Sheu, Y., Chen, S. H., Huang, J. S. and Sung, J. C. *Phys. Rev. A* 1989, **39,** 5867
21 Marion, G., Graciaa, A. and Lachaise, J. *J. Phys. Chem.* 1988, **92,** 1553
22 Rushford, D. S., Sanchez-Rubio, M., Santos-Vidals, L. M., Wormuth, K. R., Kaler, E. W., Cuevas, R. and Puig, J. E. *J. Phys. Chem.* 1986, **90,** 6668
23 Friberg, S. E. and Liang, Y. in 'Progress in Microemulsions' (Eds S. Martellucci and A. N. Chester), Plenum Press, New York, 1989, p. 73