

Synthesis of porous polymeric membranes by polymerization of micro-emulsions

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In this study the polymerization of monomer-containing micro-emulsions to yield porous polymeric membranes is demonstrated. A micro-emulsion system composed of methyl methacrylate and acrylic acid as monomers, ethyleneglycol dimethacrylate as crosslinking agent, sodium dodecylsulfate as surfactant and water was studied. An identical surfactant-free system, formed using the same monomers, crosslinking agent and water but without surfactant, was also studied and the micro-emulsions formed at certain compositions were polymerized. Our earlier work with these systems had indicated the porous morphology of the polymer to be dependent on the microstructure of the precursor micro-emulsion. In the present study micro-emulsion compositions which showed inferential evidence of a bicontinuous structure were polymerized to form membranes by using photo-initiated polymerization with ultra-violet radiation. The membranes formed had a thickness of 10–12 μm . The swelling characteristics in water of the polymeric material constituting the membranes was evaluated as a function of pH. The tensile properties of the membranes were also evaluated. The permeability of the membranes was examined using aqueous solutions of acrylic acid. The results indicate the permeability of the membranes to be dependent on the composition of the precursor micro-emulsion due to the relationship between the polymer morphology and micro-emulsion structure. This study conclusively shows the feasibility of synthesizing porous polymeric membranes by utilizing the structure of micro-emulsions.

(Keywords: membranes; porous; asymmetric; micro-emulsions; swelling; permeability)

INTRODUCTION

Micro-emulsions are thermodynamically stable, micro-structured isotropic systems containing hydrophilic, hydrophobic and amphiphilic components. The micro-structure of these systems is dependent on composition and both droplet microstructures and bicontinuous microstructures are known to exist. Substantial research has been carried out in the field of polymerizing monomer-containing micro-emulsions exhibiting droplet microstructures to obtain latices. Interest in polymerizing monomer-containing micro-emulsions which exhibit characteristics indicative of a bicontinuous structure has been relatively recent. Published work in this area indicates the polymerization of micro-emulsions exhibiting bicontinuous characteristics as a potential route for synthesizing porous polymeric materials^{1–11}.

Our research in this area has been focused on the formation of porous polymeric solids from Winsor-IV micro-emulsions (thermodynamically stable single-phase microstructured systems of oil, water and amphiphile) and evaluating the relation between the morphology of the polymer and the microstructure of the precursor micro-emulsion. Our earlier studies using systems consisting of methyl methacrylate (MMA), acrylic acid (AA), ethyleneglycol dimethacrylate (EGDMA), sodium dodecylsulfate (SDS) and water as well as the corresponding surfactant-free system had indicated the formation of open-cell porous solids from micro-emulsions showing

inferential evidence of a bicontinuous structure^{11–14}. Further, it was observed that the morphology of the porous structure in the polymer could be varied through variation in the composition of the precursor micro-emulsion.

The present study represents an extension of this work to evaluate the feasibility of obtaining porous polymeric membranes. This technique could have significant technological importance as it utilizes the microstructure existing in bicontinuous micro-emulsions to form the membranes in a one-step organic solvent-free process starting from monomers. The possibility exists of controlling the permeability of the membranes by varying the pore morphology using changes in the micro-emulsion composition. Further, the surface characteristics of the membrane could be adjusted by formulating the precursor micro-emulsion with suitable comonomers to obtain functionalization of the membrane surface through copolymerization.

The specific objectives of this study were to develop a route to synthesize porous polymeric membranes by photo-initiated polymerization of monomer-containing micro-emulsions. The dependence of the permeability of the membranes on the composition of the precursor micro-emulsion was also evaluated.

EXPERIMENTAL

Materials

MMA, AA and EGDMA were of purity greater than 99%. The surfactant SDS was of 98% purity. The water

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used in the study was doubly distilled and de-ionized. Monomer samples for polymerization were prepared by vacuum distillation followed by treatment with inhibitor-removal columns. The photo-initiator used in this study was 2,2-dimethoxy-2 phenylacetophenone (DMPA). The monomers, surfactant and photo-initiator used were obtained from Aldrich.

Micro-emulsion formation and characterization

The micro-emulsion samples were formed by pipetting the required amount of the various components into glass tubes which were then sealed. The tubes were hand shaken and equilibrated in a water bath at 25°C for 48 h before making measurements. The details pertaining to procedures adopted for the phase-behaviour studies and micro-emulsion characterization were described in the earlier report¹¹. The microstructure of the micro-emulsion systems had been investigated using conductivity and viscosity measurements, quasi-elastic light scattering (QELS) and static light scattering (SLS) studies¹¹ and the Winsor-IV micro-emulsion compositions used in the present study were selected using the phase-behaviour diagrams from the earlier study¹¹ as a guide.

Polymerization procedure

Photo-initiated polymerization of the micro-emulsions was carried out using 0.02 g of DMPA for 10 g of sample. The micro-emulsion samples were purged with nitrogen at a flow rate of 0.56 l h⁻¹ for 15 min and then spread as a film between thin glass plates and polymerized. The glass plates holding the micro-emulsion were placed in a polished aluminium polymerization cell, the temperature of which was controlled by circulating water from a refrigerated bath. The micro-emulsion samples were irradiated using a 450 W ultra-violet lamp for 15 min at a temperature of 25°C to form the membrane.

Swelling measurements

Polymer samples for swelling studies were prepared by photo-initiated polymerization of the micro-emulsion samples in 16 mm diameter sample tubes using the reaction cell described in the earlier report¹¹. The polymer obtained was removed from the sample tube and cut into discs having a thickness of 1 mm. The polymer discs were extracted with distilled water in a Soxhlet extractor for 24 h followed by drying in air at 25°C to constant weight.

They were then placed in aqueous solutions having a pH corresponding to the pH at which the swelling measurement was to be conducted. Aqueous solutions of acrylic acid were used for swelling in acidic media and aqueous sodium hydroxide solutions were used for swelling at a pH of 8. Swelling at pH 7 was determined in distilled water. The measurements were performed at a temperature of 25°C. Periodically the discs were removed from the pH buffer solution, blotted lightly to remove excess surface water and weighed. The swelling of the discs was monitored for a period of 72 h. The extent of swelling was calculated as the percentage increase in weight of the polymer sample due to uptake of the swelling agent relative to the weight of the dry polymer sample prior to swelling.

Permeability studies

The unconverted monomer and surfactant in the membranes from the polymerization step were leached out by washing with distilled water and the conductivity of the effluent water was measured using an Omega PHH-80 conductivity meter. The washing was continued until the effluent had the same conductivity as the fresh distilled water.

The permeability characteristics of the membranes were determined using a 10% by weight aqueous solution of acrylic acid with conductivity and pH values of 2750 $\mu\text{S cm}^{-1}$ and 2.2, respectively. The measurements were conducted using the permeability cell shown in Figure 1. The permeability cell was built of poly(methyl methacrylate) and consisted of two compartments between which the membrane to be tested was held. In one of the compartments of the cell was poured the aqueous acrylic acid solution and in the other compartment was poured distilled water. The two liquids were separated by the porous membrane and the diameter of the membrane across which permeation occurred was 25 mm. The permeability cell was positioned with its axis horizontal and the height of liquids in both chambers was identical to avoid the presence of pressure gradients across the membrane. The thickness of the membranes swollen in water was determined from the weight of a membrane sample of known cross-sectional area swollen in water and the density of a swollen polymer disc of the same composition swollen in water. A conductivity meter was placed in the compartment of the cell containing distilled water and the rise in conductivity due to the transport of acrylic acid across the membrane was monitored as a function of time. The permeability study was conducted at a temperature of 25°C. The liquids in both compartments of the cell were stirred using magnetic stir bars rotating at 100 rev min⁻¹. The increase in conductivity of the pure distilled water could be attributed to the acrylic acid transported across the porous membrane due to the existence of a concentration gradient across the membrane. Hence the rise in conductivity of distilled water in the permeability cell could be considered as a semi-quantitative measure of the permeability of the membrane.

A quantitative representation of the permeability of the membranes was obtained by determining the mass transfer coefficient for transport of acrylic acid across the membrane. The permeability cell used (Figure 1) can be regarded as a dialysis cell, with the membrane to be tested used as the dialysis membrane. The expression for mass transfer coefficient for transport of solute in dialysis cells

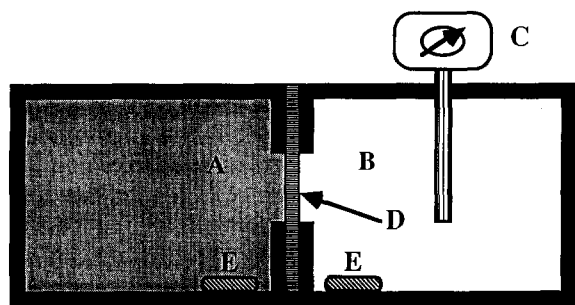


Figure 1 Schematic representation of permeability cell used to evaluate the permeability characteristics of the porous polymeric membranes synthesized. A: Aqueous acrylic acid solution, B: distilled water, C: conductivity meter, D: porous polymeric membrane, E: magnetic stirrer

assuming quasi-steady-state diffusion is well documented in the literature¹⁹⁻²¹ and can be applied to analyse this experiment. The agitation of the liquids in the two compartments was done to minimize concentration gradients within each compartment. Hence the concentration boundary layer adjacent to the membrane surface can be neglected and the mass transfer coefficient can be regarded as a quantitative measure of the permeability. The mass transfer coefficient is given by¹⁹⁻²¹

$$K_0 = \frac{2.303V_1V_2}{A(t-t_0)(V_1+V_2)} \log \frac{(C_1-C_2)_{t_0}}{(C_1-C_2)_t}$$

where K_0 is the mass transfer coefficient, A is the membrane area, C_1 and C_2 are the concentrations of acrylic acid in the compartments upstream and downstream of the membrane, V_1 and V_2 are the volumes of the compartments upstream and downstream of the membrane, t_0 is the initial time and t is the final time. The acrylic acid concentration in the downstream compartment at a given time t , $(C_2)_t$, was experimentally determined by measuring the conductivity of the solution. The acrylic acid concentration in the upstream compartment at time t , $(C_1)_t$, was determined from $(C_2)_t$ by mass balance.

Measurement of tensile properties

The measurements were performed using a Monsanto Tensometer, Model T-10 at a constant crosshead speed of 20 in min^{-1} . A dumbbell-shaped polymer specimen with the dimensions at the narrow section of the dumbbell corresponding to 6 mm length and 33 mm width was cut from the polymerized membrane and the tensile measurements were performed. The polymer sample was stored under water and was mounted between the grips of the tensile tester after lightly blotting the excess surface water. The percentage elongation and tensile strength (nominal) at yield were recorded.

RESULTS

The micro-emulsion samples used in this study were formulated using the phase-behaviour diagrams for the surfactant-free and surfactant-based systems described in our earlier study¹¹ as a guide. The micro-emulsion samples used in this study were from the Winsor-IV domain of the phase-behaviour diagram. The phase-behaviour diagrams for the surfactant-free and surfactant-based systems are reproduced in *Figures 2* and *3*, respectively, to provide information on the extent of the Winsor-IV domain in these systems and the variation of microstructure with composition in the Winsor-IV domain. The earlier study¹¹ pertaining to the characterization of these systems indicated that the micro-emulsions with water contents less than 20% possess a droplet microstructure of water in oil. At water contents above 80%, the microstructure changed over to droplets of oil dispersed in a continuous water phase. In the intermediate water content range, between 20% and 80% water content, there appeared to exist a bicontinuous microstructure. This behaviour was observed in both the surfactant-based and surfactant-free systems.

Our earlier polymerization studies on these systems and the characterization of the polymeric materials obtained indicated the formation of open-cell porous

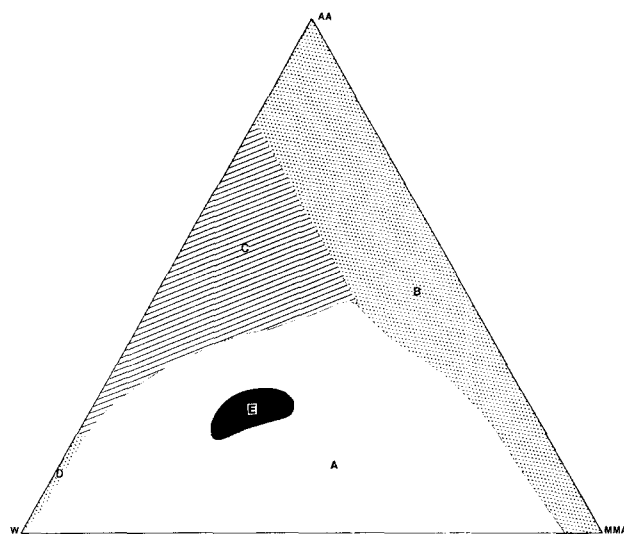


Figure 2 Phase-behaviour diagram for the system, methyl methacrylate (MMA), acrylic acid (AA), water (W) and ethyleneglycol dimethacrylate (EGDMA) at 25°C. Compositions are on a wt% basis and EGDMA is 4% of the combined weight of MMA and AA. Domain A: two-phase region, domain B: W/O Winsor-IV, domain C: bicontinuous Winsor-IV, domain D: O/W Winsor-IV, domain E: unstable three-phase region



Figure 3 Phase-behaviour 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°C. Compositions are on wt% basis and EGDMA is 8% of the combined weight of MMA and AA. Domain A: two-phase region, domain B: W/O Winsor-IV, domain C: bicontinuous Winsor-IV, domain D: O/W Winsor-IV

polymeric materials from the micro-emulsion compositions exhibiting characteristics similar to a bicontinuous structure^{11,12,14}. Micrographs from scanning electron microscopy (SEM) of representative samples of these polymeric materials are reproduced in *Figures 4-7*, to illustrate the significant changes in polymer morphology that can be achieved by varying the composition of the precursor micro-emulsion. *Figures 4-6* pertain to polymer samples from micro-emulsions of the surfactant-free system having an AA:MMA ratio of 1:4. The polymer sample in *Figure 4* was formed from a surfactant-free micro-emulsion containing 10% water and the SEM micrograph shows a morphology which is typical of

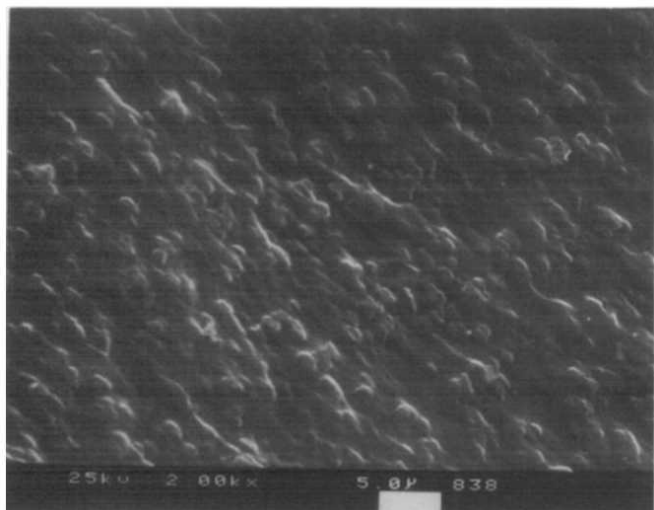


Figure 4 SEM micrograph of polymer sample obtained by polymerizing a micro-emulsion sample from the surfactant-free system with the following composition. MMA: 18%, AA: 72%, water: 10% and EGDMA: 4% of the combined weight of MMA and AA

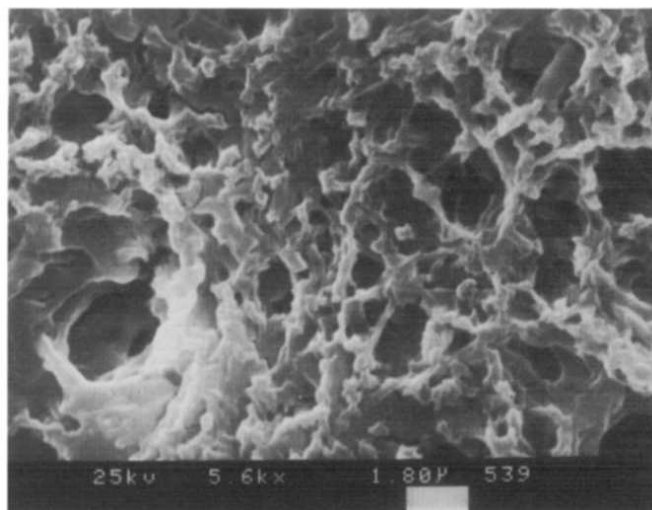


Figure 7 SEM micrograph of polymer sample obtained by polymerizing a micro-emulsion sample from the surfactant-based system with the following composition. MMA: 25%, AA: 20%, SDS-water solution: 55% and EGDMA: 8% of the combined weight of MMA and AA

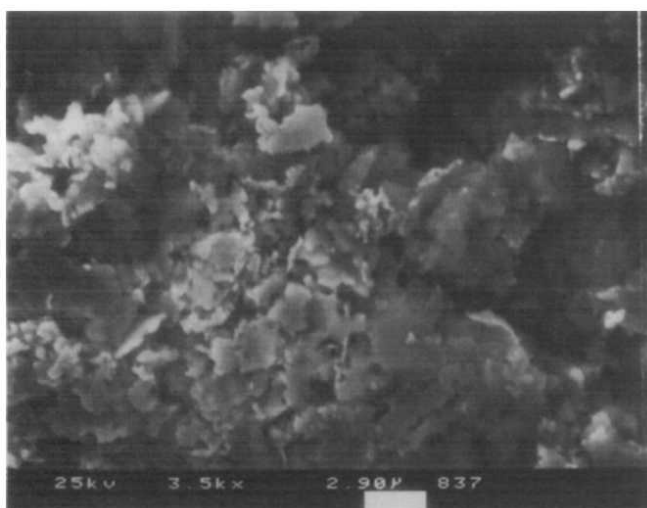


Figure 5 SEM micrograph of polymer sample obtained by polymerizing a micro-emulsion sample from the surfactant-free system with the following composition. MMA: 14%, AA: 56%, water: 30% and EGDMA: 4% of the combined weight of MMA and AA

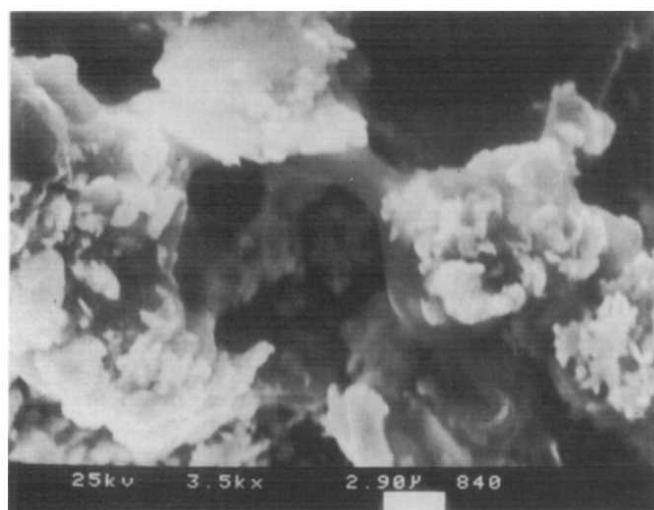


Figure 6 SEM micrograph of polymer sample obtained by polymerizing a micro-emulsion sample from the surfactant-free system with the following composition. MMA: 9%, AA: 36%, water: 55% and EGDMA: 4% of the combined weight of MMA and AA

closed-cell porous polymeric materials. The polymer samples in *Figures 5 and 6* exhibit an open-cell porous structure and were formed from micro-emulsions with water contents of 30% and 55%, respectively. A comparison of *Figures 5 and 6* indicates the pore size in the polymer to increase with increasing water content of the precursor micro-emulsion. *Figure 7* shows the morphology of polymer obtained from the surfactant-based system using a microemulsion sample with an AA:MMA ratio of 1:4 and containing 55% by weight of aqueous SDS solution (20 wt% SDS). This sample also has an open-cell porous structure but the pores of the polymer are better defined compared to polymer from the surfactant-free system (*Figures 5 and 6*).

Detailed studies¹¹⁻¹⁴ involving polymerization of micro-emulsions of different compositions from the phase-behaviour diagram and characterization of the polymer formed using SEM, thermogravimetric analysis, BET adsorption studies and differential scanning calorimetry were performed. Thermogravimetric analysis was used to confirm continuity in the pore structure by studying the drying rate curve obtained on drying the porous materials^{12,13}. Solid materials containing water in interconnected pores exhibit drying rate curves having a linear falling rate period, whereas the drying rate curve for closed cell porous solids has an exponentially decreasing falling rate period. This characteristic feature was utilized to study the porous nature of the polymeric materials synthesized. BET adsorption studies were used to determine the surface area of the porous materials¹³. The surface areas of the closed-cell materials was relatively low compared to the open-cell polymeric materials. The surface area of the open-cell materials exhibited a steady increase with increasing water content of the precursor micro-emulsion. The pore size distribution of the water-saturated open-cell materials was determined by freezing-point depression measurements using a differential scanning calorimeter¹². The depression in freezing point of water was related to the pore size of the material using the Laplace equation and the pore-size distribution obtained. This study indicated an increase in pore size of the open-cell materials with increasing water content of the precursor micro-emulsion.

The results of these characterization studies¹¹⁻¹⁴ conclusively show that polymer samples from water in oil micro-emulsions had a closed-cell porous structure and that micro-emulsions with a bicontinuous structure form open-cell porous materials. Since the object of the present study was to develop porous polymeric membranes, the micro-emulsion compositions used for forming membranes in this study were selected from the bicontinuous region of the phase-behaviour diagrams.

Swelling studies

The swelling of the porous polymer was studied as a function of the water content of the precursor micro-emulsion in aqueous swelling media having pH values of 2, 5, 7 and 8. The studies were performed for polymer samples formed from a set of micro-emulsion samples from the surfactant-free system having an AA:MMA ratio of 4:1 and water content ranging from 10% to 60%. The results of swelling of the samples at the end of a 72 h period are shown in Figure 8. The results indicate the swelling of the polymer to be sensitive to the pH of the swelling medium. As the pH of the swelling medium is increased, the extent of swelling is found to increase. The magnitude of this effect rises sharply for pH values of the swelling medium above 5. It is also observed from Figure 8 that at any given pH the extent of swelling increases with water content of the precursor micro-emulsion, with a sharp increase in swelling for polymer from micro-emulsions having water contents above 40%.

Permeability measurements

The permeability of membranes obtained from micro-emulsions of the surfactant-free system, measured using an aqueous acrylic acid solution of conductivity $2750 \mu\text{S cm}^{-1}$, is shown in Figure 9. The permeability of the membrane is directly related to the increase in conductivity of distilled water in the permeability cell. The results in Figure 9 indicate the permeability of membranes formed from micro-emulsions containing water contents less than 20% to be low compared to membranes from micro-emulsions of higher water contents. A sharp increase in permeability of the membranes to acrylic acid is observed at water contents of the precursor micro-emulsion exceeding 20%. Further, a membrane was formed by polymerizing MMA

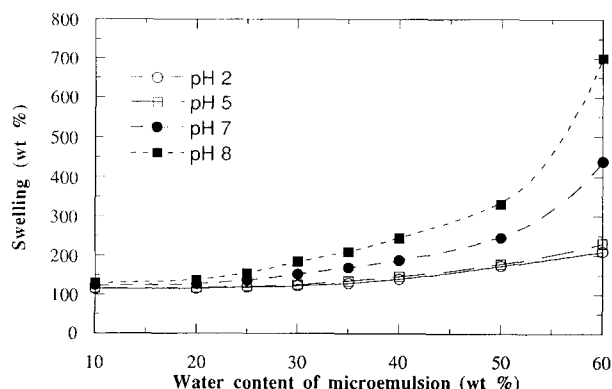


Figure 8 Results of swelling measurements for polymer samples from the surfactant-free system after a period of 72 h in the swelling medium. The results are presented as a function of water content of precursor micro-emulsion with pH of swelling medium as a parameter. The polymer samples were obtained from precursor micro-emulsions having an AA:MMA ratio of 4:1 and water contents ranging from 10% to 60% by weight

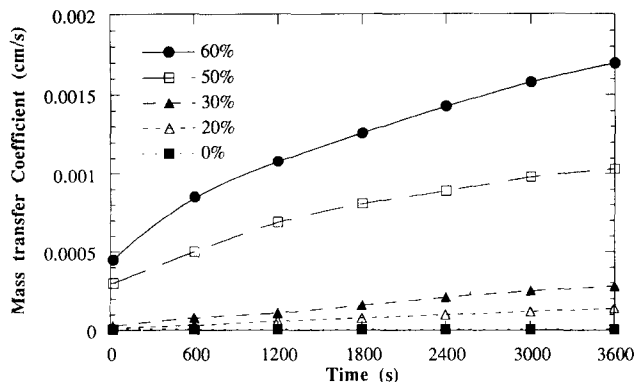


Figure 9 Permeability of membranes formed from micro-emulsions of the surfactant-free system, measured by monitoring the rise in conductivity of distilled water in the permeability cell due to transport of acrylic acid across the membrane. The polymer samples were obtained from precursor micro-emulsions having an AA:MMA ratio of 4:1 and water contents ranging from 0% to 60%

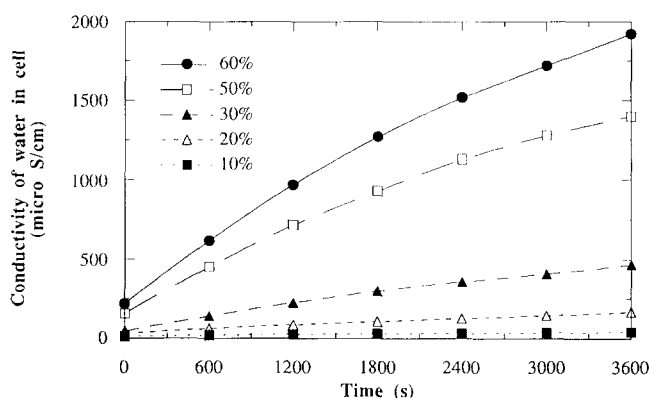


Figure 10 Permeability of membranes formed from micro-emulsions of the surfactant-free system, measured by monitoring the rise in conductivity of distilled water in the conductivity cell due to transport of acrylic acid across the membrane. The polymer samples were obtained from precursor micro-emulsions having an AA:MMA ratio of 4:1 and SDS solution contents ranging from 10% to 60%

containing 4% EGDMA and its permeability evaluated. This crosslinked PMMA membrane showed a negligible increase in conductivity of distilled water compared to the membranes from micro-emulsions under the conditions of this study. Acrylic acid containing 4% EGDMA was also polymerized to form a membrane and its permeability characteristics were found to be very similar to the membrane obtained from the precursor system containing no water (Figure 9).

The results of conductivity studies using membranes formed from micro-emulsions of the surfactant-based system are shown in Figure 10. The studies were conducted using the same experimental conditions as those used with membranes from the surfactant-free system. The conductivity results are qualitatively similar to that obtained with membranes from the surfactant-free system. However, the magnitude of permeability measured by recording the increase in conductivity of the distilled water is significantly higher for the surfactant-based system when compared to the surfactant-free system. The permeability of the membranes formed from micro-emulsions containing less than 20% by weight of the SDS stock solution is quite similar. At SDS stock solution contents above 20% by weight in the micro-emulsion the permeability of the membranes formed is observed to increase substantially.

A comparison of the permeability of membranes from the surfactant-free system and the surfactant-based system as a function of water or SDS solution content of the precursor micro-emulsion is illustrated in Figure 11. This figure shows the conductivity of distilled water in the permeability cell at the end of 1 h. These results were also obtained using an aqueous acrylic acid solution having conductivity of $2750 \mu\text{S cm}^{-1}$. The steep rise in permeability of the membranes with increasing water or SDS solution content of the precursor micro-emulsion in both the surfactant-free system and also the surfactant-based system can be inferred from the conductivity results shown in Figure 11.

The mass transfer coefficient for transport of acrylic acid across the membranes can be regarded as a quantitative measure of the permeability of the membranes. The mass transfer coefficients which were experimentally determined using membranes formed from micro-emulsions of the surfactant-free system are represented in Figure 12. The results in Figure 12 indicate a sharp increase in the permeability of the membranes at water contents of the precursor micro-emulsion exceeding 20%. The results of mass transfer coefficient measurements in Figure 12 are qualitatively similar to the conductivity results for membranes from the surfactant-free system shown in Figure 9.

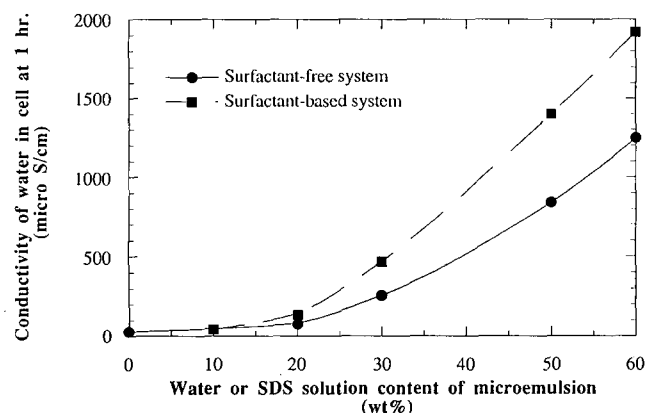


Figure 11 Comparison of the permeabilities of membranes from the surfactant-free system and surfactant-based system as a function of water or SDS solution content of the precursor micro-emulsion. Permeability of the membrane is represented by the conductivity of distilled water in the permeability cell at the end of 1 h

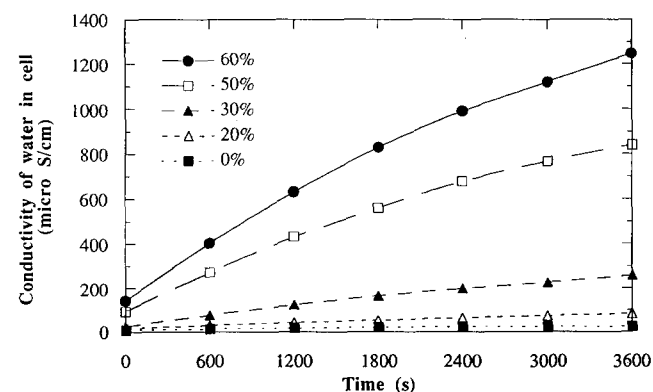


Figure 12 Mass transfer coefficient for transport of acrylic acid across membranes formed from micro-emulsions of the surfactant-free system. The polymer samples were obtained from precursor micro-emulsions having an AA:MMA ratio of 4:1 and water contents ranging from 0% to 60%

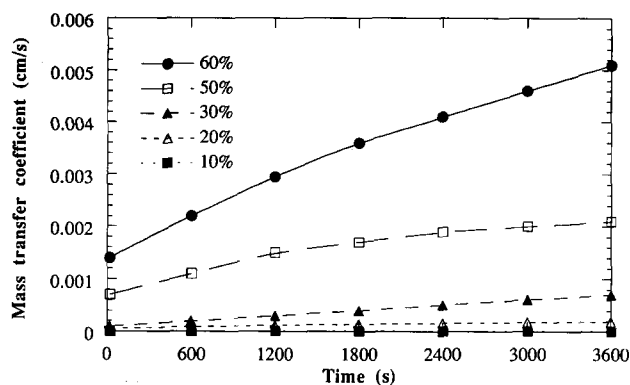


Figure 13 Mass transfer coefficient for transport of acrylic acid across membranes formed from micro-emulsions of the surfactant-based system. The polymer samples were obtained from precursor micro-emulsions having an AA:MMA ratio of 4:1 and SDS solution contents ranging from 10% to 60%

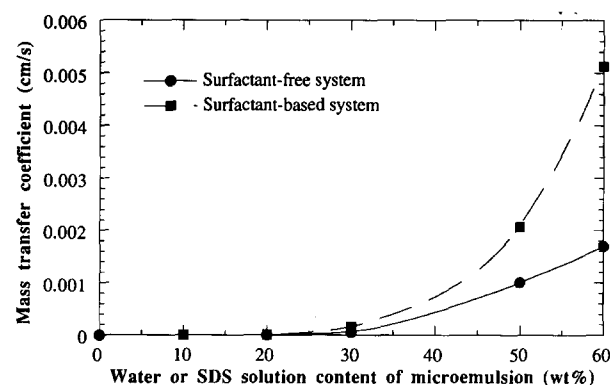


Figure 14 Comparison of the mass transfer coefficients for transport of acrylic acid across membranes from the surfactant-free system and surfactant-based system as a function of water or SDS solution content of the precursor micro-emulsion. The mass transfer coefficients were obtained by conducting experiments for a duration of 1 h using a dialysis cell

The mass transfer coefficients measured using membranes from the surfactant-based system are shown in Figure 13. Those of the membranes are found to increase sharply for SDS solution content of the precursor micro-emulsion greater than 20%. The magnitude of the mass transfer coefficient for membranes from precursor micro-emulsions having less than 20% SDS solution content is similar to that for membranes from the surfactant-free system formed using micro-emulsions with water content less than 20% (Figure 12). The results of mass transfer coefficient measurements in Figure 13 are qualitatively similar to those of conductivity measurement studies for membranes from the surfactant-based microemulsion system shown in Figure 10.

The mass transfer coefficients for membranes formed from the surfactant-free system and the surfactant-based system have been compared in Figure 14 and the mass transfer coefficient after 1 h of dialysis has been plotted as a function of the aqueous content of the precursor micro-emulsion. The results in Figure 14 clearly show the permeability of the membranes from micro-emulsions having an aqueous content less than 20% to be very low for both the systems. At aqueous content of the precursor micro-emulsion greater than 20%, the permeability of the membrane increases sharply. The magnitude of the permeability for membranes from the surfactant-based

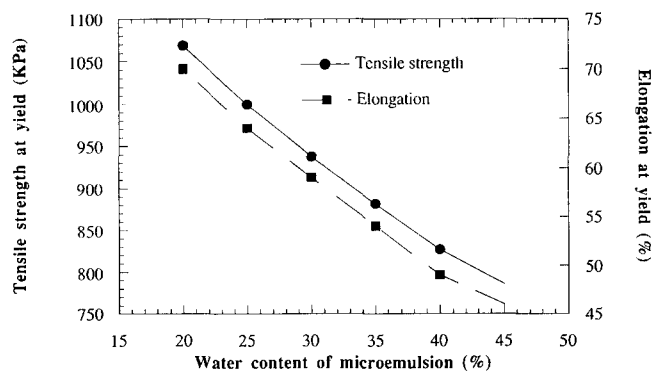


Figure 15 Tensile properties of membranes synthesized from micro-emulsions of the surfactant-free system as a function of water content of the precursor micro-emulsion

system is significantly higher than that of membranes from the surfactant-free system at identical aqueous content of the micro-emulsion.

Tensile measurements

The tensile properties of membranes synthesized from micro-emulsions of the surfactant-free system measured as a function of the water content of the micro-emulsion are shown in *Figure 15*. The results indicate the membranes to be weak and soft and show a decreasing trend in the elongation and tensile strength at yield of the membranes with increasing water content of the precursor micro-emulsion.

DISCUSSION

Swelling behaviour

The degree of swelling of the porous polymeric materials synthesized has been observed to be pH-dependent. The increase in swelling with increase in pH values above 5 is very sharp. This can be explained by the polyelectrolyte effect exhibited by polyacrylic acid which has been extensively studied¹⁵. The carboxyl groups of polyacrylic acid become ionized on increasing the pH of the swelling medium. The ionization results in mutual repulsion between the ionized groups and the hydrophilic nature of polyacrylic acid tends to open the conformation of the polymeric network, leading to swelling. The low degree of swelling observed at pH values below 5 is because of the reduced extent of ionization since the acid ionization constant at the half-neutralization point (pK_a), which equals the pH is 4.75 for polyacrylic acid¹⁶⁻¹⁸.

The increase in the extent of swelling with increasing water content of the precursor micro-emulsion which was used to form the polymer can be explained based on the morphology of the polymer. The SEM micrographs (*Figures 4-7*) and results from our earlier characterization studies¹¹⁻¹⁴ indicate the porosity of the polymer obtained from bicontinuous micro-emulsions to increase with increasing water content of the micro-emulsion. The diameter of the pores and also the number of pores in the polymer were found to increase with water content of the precursor micro-emulsion. The rise in porosity would permit better diffusion of the swelling medium into the pores of the polymer and a higher interfacial area for contact between the polymer and swelling medium. Increasing porosity would also enable the conformation

of the polymer network to open to greater extents on ionization of the carboxyl groups of polyacrylic acid, leading to a higher degree of equilibrium swelling. These effects result in the observed increase in the extent of swelling with increasing water content of the precursor micro-emulsion.

Permeability of membranes

The permeability studies were carried out using aqueous acrylic acid solution of pH 2.2 having a conductivity of $2750 \mu\text{S cm}^{-1}$. Based on the results of the swelling study, it can be postulated that the portion of the polymer membrane in contact with the acrylic acid solution of pH 2.2 would not undergo extensive swelling. Hence the permeability in this section of the membrane could be regarded as representative of the inherent porous characteristic of the membrane. However, the other surface of the membrane is in contact with distilled water of pH 7 contained in the other section of the permeability cell. It can be inferred from the swelling study that the portion of the membrane close to the distilled water would swell to a greater extent compared to that close to the acrylic acid solution. Hence the pore size in the membrane would increase from the acrylic acid side to the distilled water side, resulting in an asymmetric pore morphology under the conditions of the study.

The results of the permeability measurements of the membranes are consistent with the porous characteristics (*Figures 4-7*) observed from the earlier studies of the polymer morphology¹¹⁻¹⁴ and the results of the swelling studies (*Figure 8*). As the water content of the precursor micro-emulsion is increased, the porosity of the membrane obtained also increases. In addition, the extent of swelling of membranes increases with increasing water content of the precursor micro-emulsion. These effects result in an increase in the number and size of pathways through which the diffusion of acrylic acid could occur. The permeability of membranes formed from micro-emulsions with water contents less than 20% is low because the polymer formed from these systems has been shown from our earlier studies¹²⁻¹⁴ to yield closed-cell porous structures (*Figure 4*). The poor continuity between the pores results in a lack of continuous pathways for diffusion, hence the low permeability of these membranes. However, even the membranes formed from micro-emulsions with water contents less than 20% show a marginally increasing trend in permeability with increasing water content. This behaviour is also consistent with the morphology and pore continuity observations from the earlier studies¹²⁻¹⁴ which had shown a gradual increase in connectivity of pores with increasing water content of the micro-emulsion which ultimately leads to an open-cell porous structure at water contents above 20%.

The variation in permeability with SDS solution content of micro-emulsions for membranes formed from the surfactant-based system is similar to the trend in permeability of membranes with water content of micro-emulsion in the surfactant-free system. The permeability of membranes from the surfactant-free system and the surfactant-based system are nearly identical for water and SDS solution contents below 20% in the precursor micro-emulsions. This could be because the predominantly closed-cell porous structure existing in these membranes offers similar resistance to diffusion of acrylic acid since the transport of acrylic acid has to

occur across thin sections of polymer and not through continuous pathways. At higher SDS solution contents of the micro-emulsion, with the creation of an open-cell porous structure in the polymer, the permeability of the membranes formed is higher than that of membranes formed from micro-emulsions of the surfactant-free system at identical water contents. This indicates the resistance to diffusion of acrylic acid to be lower in membranes obtained from the surfactant-based system compared to membranes from the surfactant-free system. The lower resistance to diffusion of acrylic acid in membranes from the surfactant-based system can be explained by scanning electron micrographs (Figures 6 and 7) of the earlier study^{11,14} which showed a more ordered, less tortuous porous structure of polymer obtained from the surfactant-based system compared to the surfactant-free system.

Tensile properties

The results of tensile measurements (Figure 15) indicate the membranes to possess poor tensile properties. The elongation and tensile strength at yield are inversely related to the water content of the precursor micro-emulsion. This could be due to the increasing porosity of the membrane with increasing water content of the precursor and the consequent decrease in the polymer content of the system which is the stress-bearing component. The elongation at yield as also the tensile strength at yield are rather low to permit the application of these membranes directly in separations requiring significant differential pressures to be applied across the membrane. This indicates the need to provide reinforcement to make the membranes suitable for such applications.

CONCLUSIONS

This study indicates the feasibility of forming porous polymeric membranes by polymerizing bicontinuous micro-emulsions. The possibility of varying the porosity of the membrane and thereby its permeability by selecting micro-emulsions of suitable composition has been examined. This technique offers the interesting possibility of developing membranes with modified surface characteristics by functionalizing the surface using polymerizable surfactants or comonomers during the

formation of the micro-emulsion. The development of an asymmetric pore morphology in the membrane depending on the conditions of application can be inferred. Work is currently in progress in our laboratory to apply this technique to develop membranes for specific applications and undertake a precise evaluation of the separation characteristics of the membranes.

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