Microstructured polymers via photopolymerization of non-aqueous organized solutions

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Structurally organized solutions containing monomers in an ethylene glycol (EG) medium were formed and polymerized to produce polymeric solids with various morphologies, and also unique thermal and mechanical properties. Previous research had demonstrated the formation of microemulsions in an aqueous medium containing methyl methacrylate (MMA) and acrylic acid (AA). However, the non-aqueous mixtures of MMA and AA with EG did not yield conventional microemulsions. Molecularly dispersed solutions were formed in the bulk of the phase diagram, while compositions closer to the demixing line exhibited critical behaviour. This paper presents the first account of the use of mixtures exhibiting critical behaviour to produce microstructured polymers. The non-aqueous mixtures did not form any well defined microstructures on polymerization for compositions away from the two-phase boundary. Compositions exhibiting critical behaviour yielded open cell structures and also beaded polymers at high EG contents. This suggests that the microstructure in these mixtures is preserved in the final polymer to a considerable extent. The virgin polymers containing EG had very low glass transition temperatures due to the plasticizing nature of EC. The plasticizing nature of EG was also evidenced in the tensile properties of the virgin polymers.

(Keywords: non-aqueous; microstructure; photopolymerization)

INTRODUCTION

Polymerization of emulsions and microemulsions to produce latices has become an area of intense research in the last decade. However, the potential to synthesize microstructured solids by the polymerization of microemulsions was not recognized until recently[1-6]. This technique has considerable technological significance because it uses the inherent microstructure of microemulsions to produce porous polymers. Polymerizable microemulsions are, however, limited by the need to incorporate high levels of surfactant to achieve thermodynamic stability.

Previously, conventional microemulsions containing monomers were formed in an aqueous medium and then polymerized[5-11]. This paper presents the results of combining the same monomers in ethylene glycol (EG). The non-aqueous mixtures exhibited critical behaviour for certain compositions instead of forming microemulsions.

Observations of critical phenomena in micellar solutions have been reported in the last decade[12]. The structure of the medium can be described as a solution of interacting aggregates dispersed in a continuous (or bicontinuous) phase. Attractive interactions exist between these aggregates. These interactions along with thermal perturbations may be responsible for the short time microstructures observed in some cases.

Photopolymerization of microstructured systems provides a convenient single-step method to produce novel polymers. This study involves the formation of microstructured systems discussed above by using EG as a non-aqueous medium. Little work has been carried out on non-aqueous microemulsion systems and even less has been published on polymerization in such media. The precursor system was characterized by phase diagrams, viscosity, conductivity and light scattering measurements. The characterization of the resulting polymers included scanning electron micrographs, thermal analysis, mechanical testing, solvent extraction and molecular weight measurement.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA), acrylic acid (AA), EG and sodium dodecyl sulfate (SDS) were all obtained from Aldrich (purity >98%). These chemicals were used as received without further purification. The photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (DMPA) was also obtained from Aldrich.

Phase behaviour studies

Samples for phase behaviour were prepared by adding the required amounts of the various components into culture tubes using an Eppendorf micropipet. The SDS-free samples were made by diluting known amounts of MMA and AA with EG. The samples containing SDS were prepared by titrating known amounts of MMA and AA with a stock solution of 5% SDS in EG (by weight).

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The samples were hand shaken and equilibrated in a constant temperature bath for 48 h at $25 \pm 0.1°C$ before making measurements. The criterion for equilibrium was the reproducibility of phase in shaking and standing cycles.

The microstructure of the system was investigated by viscosity, conductivity and static light scattering (s.l.s.) at 90° to the incident beam. Viscosity measurements were made using a Brookfield LVT digital viscometer having a small sample adapter with provision to regulate the temperature. These measurements were made at a shear rate of $79.2\,s^{-1}$ at $25 \pm 0.1°C$. The conductivity measurements were made using an Omega PHH-80 conductivity meter. Samples for s.l.s. were made by filtering the various stock solutions using a $0.2\,\mu m$ Nylon membrane filter. The measurements were made at $25 \pm 0.1°C$ and 1 atm ($1\,atm = 1 \times 10^5\,Pa$). Details of these experimental procedures have been published previously[6–9].

Samples for polymerization were made by purging the mixtures with dry nitrogen at a gas flow rate of $0.56\,l\,h^{-1}$ at 1 atm for 15 min. An initiator concentration of 0.02 g of DMPA per 10 ml of sample was used to initiate the photopolymerization reaction. The samples were placed on a water-cooled aluminium block in order to dissipate the heat of polymerization and also the heat from the u.v. lamp. The samples were irradiated with u.v. light from a 450 W mercury vapour lamp for 1 h to produce a polymer-coated aluminium foil (0.078 mm thick). The polymerization was carried out at $25 \pm 0.1°C$. Dumb-bell-shaped pieces were cut from these sheets according to the dimensions of ASTM D638-89 sample type IV using a standard template and hand press. These specimens were later used to determine the tensile properties.

The polymer morphology was examined using SEM. Both virgin and dried polymer samples were coated in a Polaron E5400 coating machine and the morphology was examined under an ISI SX 40 electron microscope. Glass transition temperatures (T_gs) of the polymers were determined using a DuPont Instruments 910 DSC. The sample was placed in the d.s.c. cell and cooled to $-20°C$. A temperature ramp of $10°C\,min^{-1}$ was applied until 370°C. Tensile testing was performed on a Monsanto Tensometer 10 apparatus. A strain rate of $10\,mm\,min^{-1}$ was used. Molecular weight was determined using an Ubbelohde dilution viscometer by measuring the relative viscosity of polymers dissolved in tetrahydrofuran (THF) at 25°C. Inferential evidence of the pore continuity was determined by solvent extraction.

RESULTS AND DISCUSSION

Phase behaviour

The phase behaviour for the SDS-based system was obtained using MMA, AA and a stock solution of 5% SDS in EG (by weight). In this case, region A corresponds to two-phase samples while region B represents single-phase samples which did not possess any microstructure (*Figure 1*). Most of the samples in region B showed a solution-type behaviour as evidenced by viscosity, conductivity and light scattering measurements. However, samples made with compositions at 1% from the demixing line into the solubility region, exhibited a critical behaviour. This was evident from the total intensity scattering measurements. A similar phase diagram was obtained for the SDS-free system. Again, most of the compositions in region B were solutions

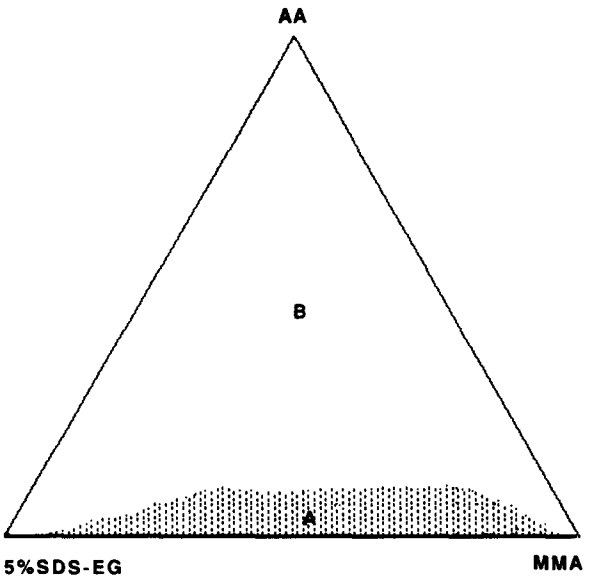

Figure 1 Ternary phase diagram for the system MMA, AA and SDS-EG. Domain A: two-phase region; domain B: macroscopically single phase

whereas samples close to the two-phase boundary exhibited critical behaviour. Due to the low solubility of SDS in EG there was not much difference in the area of the single phase domain in the two systems. The solution behaviour for compositions away from the two-phase boundary may be attributed to the increased solubility of MMA in EG compared to that in water. These observations are similar to those obtained by Kertes[13].

Conductivity is one of the bulk properties which is used in identifying the presence and the nature of microstructured systems. These measurements were conducted mainly on the samples from the single-phase region. The conductivity curves for the SDS-based system show a gradual increase in the conductivity with increasing contents of 5% SDS-EG stock solutions. No sharp increase in the conductivity with increasing SDS-EG contents is observed. Such a behaviour is indicative of a solution-type behaviour. The samples of the SDS-free system showed negligible conductivity at all concentrations. This is obviously due to the low conductivity of EG and the absence of the ionic SDS.

The conductivity curve for the samples of the SDS-based system 1% from the demixing line show the S-shaped curve (*Figure 2*) typically found in aqueous-based microemulsions[6]. This suggests the presence of some microstructure in these samples. Viscosity and light scattering measurements corroborate this result.

Viscosities of all single-phase samples were measured in order to identify the presence of microstructure in all systems. Viscosity data were collected as a function of increasing solvent content at a constant ratio of MMA/AA. The viscosity curves for the two systems do not show a sharp increase with increasing EG contents. This is consistent with the results of conductivity measurements and indicates a solution behaviour. The viscosity curves for samples 1% from the demixing line in the two systems show a gradual increase in the viscosity with increasing EG contents. A comparison of the conductivity and viscosity curves for these samples indicates the presence of unstable or short time microstructures which produce a sharp increase in the conductivity. This could explain the S-shaped curve in

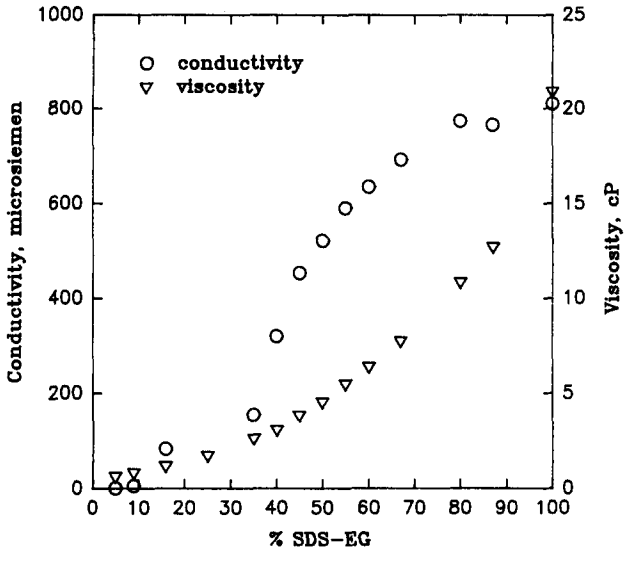

Figure 2 Conductivity and viscosity *versus* SDS-EG content for samples, 1% from the demixing line

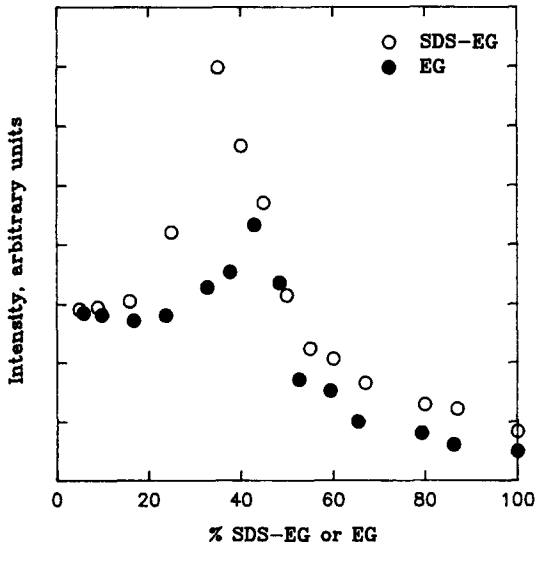

Figure 3 Total scattering intensity *versus* SDS-EG or EG content for samples, 1% from the demixing line

conductivity results. The increase in the viscosity with increasing EG content in this case is not as linear as that found in solutions. This is consistent with the conclusions of short time microstructures found in an earlier study by Ruckenstein[14].

The results of s.l.s. were obtained by plotting the total scattered intensity at 90° as a function of increasing solvent content. The total scattering intensity was measured as a function of increasing EG content in order to detect the presence of any microstructure. Far from the demixing line one obtains a continuous decline in the scattered intensity as the EG content is increased giving further proof of the solution nature of these systems.

Results of the scattering measurements for samples 1% from the demixing line are shown in *Figure 3*. Both the curves show a strong maximum intensity between 35% and 45% EG content. Similar results were also found by Friberg and Sun[15]. Such results confirm the information that mixtures of polar organic substances combined with hydrocarbons do not contain well-defined microemulsion droplets. Instead, typical critical behaviour is found with a maximum in the scattering pattern at the critical point. The critical behaviour is characterized by short time microstructures. These are unstable because the interface between the two immiscible phases is unstable *versus* small thermal perturbations. As a result, conductivity and s.l.s. measurements show a sharp increase with increasing EG content. However, the viscosity measurements are not sensitive enough to detect the critical behaviour.

The Gordon cohesiveness parameter and the solubility parameter of EG are much less than those of water[12]. It has been found in earlier studies that solvents with high cohesiveness parameter and solubility parameter values promote surfactant assembly and hence formation of microstructured systems. The low parameter values of EG results in decreased solubility of the surfactant but increases the solubility of the non-polar monomer (MMA). The aggregates formed in the non-aqueous mixtures are substantially permeated with EG and much more disordered than aqueous mixtures[13]. The conductivity, viscosity and light scattering results of this study are consistent with these earlier observations. Due to the increased solubility of MMA molecularly dispersed solutions are formed at higher EG contents. However, at lower EG contents (closer to the two-phase boundary) associated structures are formed. These aggregates are probably formed on a short time-scale[14].

Photopolymerization

The samples from both systems were photopolymerized to obtain polymeric solids. U.v. polymerization was adopted rather than conventional thermal polymerization in order to greatly enhance the rate of reaction. The reactions were performed at 25°C. The enhanced rate of reaction imposed a kinetic limitation on the thermodynamic tendency of the system to phase separate during polymerization. The objective of the study was to retain the microstructure of the precursor system in the final polymer as much as possible. An attempt was made to freeze the microstructure by the rapid gelation of the precursor system during u.v. polymerization. Gelation occurred in <3 min in general compared to 2–3 h for thermal polymerization. The non-aqueous systems gelled faster (<90 s) than the aqueous systems ($\sim$2–3 min). This is consistent with the observations of Badran *et al.*[16] that addition of EG increased the rate of polymerization.

Characterization of the polymers

The polymers obtained were characterized to determine their molecular weight, morphology, and also their thermal and mechanical properties.

Molecular weight

The polymers did not dissolve in a host of solvents including THF, carbon tetrachloride, acetone and 1-methyl-2-pyrrolidinone. Instead, these polymers swelled in THF and 1-methyl-2-pyrrolidinone indicating the presence of crosslinks. Therefore, for molecular weight measurements the reactions were stopped after reacting for 30 min in a 500 W incandescent lamp (visible light) reactor. The reaction was stopped by adding a 2% NaOH solution. The solution was then washed with methanol and water to precipitate the polymer. The polymer was filtered and dried. Known amounts of the polymer were dissolved in THF and the viscosity of the solution was determined using an Ubbelohde viscometer. The reduced

viscosity (η_{sp}/c) ranged from 0.144 to 0.44 while the inherent viscosities ($\ln[\eta_r]/c$) varied between 0.16 and 0.46. The actual molecular weight was not calculated due to the unavailability of the constant K in the Staudinger equation ($\eta = KM_v^a$).

Scanning electron microscopy

SEM was used to examine the surface morphology of the polymeric solids. The morphological features were related to the composition and microstructure of the precursor systems.

Most of the precursor samples did not exhibit any microstructure as determined by conductivity, viscosity and light scattering measurements. Only polymers with stable structural integrity were examined. EG was extracted from these polymers by repeated washing with distilled water and the solids were then dried in an oven at 50°C for 1 week. Polymers were examined before and after the EG was extracted.

Polymers from both of these systems did not exhibit the distinct characteristics observed in the aqueous systems. Samples formed away from the two-phase boundary (>10% perpendicular distance from boundary) do not show any well defined microstructure. However, samples with compositions closer to the two-phase boundary show a distinct morphology. Both open- and closed-cell structures are observed for such samples depending on their composition. *Figure 4* shows 5 μm sized droplets of polymer coalesced together for MMA/AA = 3/1 and 56% EG. A transition in morphology is quite evident for samples at MMA/AA = 2/1 close to the two-phase boundary. The SEM images of samples with 49% EG content and 55% EG show pores $<1\,\mu$m in size.

Evidence of microstructure was observed in the polymers after extraction with water. The samples with compositions away from the phase boundary did not exhibit any microstructure. The virgin polymer samples did not appear to be affected by the extraction process. However, polymers with >55% EG content lost their structural integrity after extraction as evidenced by the crumbly nature of those solids.

The samples formed at 1% from the demixing line showed critical behaviour in the s.l.s. measurements. The polymer samples from this set were also extracted with water. Only samples with good structural stability after extraction were examined. Samples from both SDS-based and SDS-free systems exhibit well defined microstructures. Samples with EG content between 20% and 40% possess an open-cellular porous structure (*Figures 5* and *6*). *Figure 6* shows polymer with dual porosity indicating a gross phase separation during polymerization which results in the larger pores ($>30\,\mu$m) while the smaller pores ($<1\,\mu$m) are a result of the microstructure present in the precursor system. Similar results were obtained for the SDS-based system. In general the surfactant-based polymers have a more ordered appearance than the SDS-free polymers. Even though no correlation length was measured for the non-aqueous precursors via quasi elastic light scattering (q.e.l.s.), the dimensions of the polymeric micropores are comparable to those found in microporous polymer obtained from the polymerization of water-based microemulsions[6]. This suggests that the samples exhibiting critical behaviour may possess microstructural dimensions of ~10–30 nm or smaller in size. Thus even the short time microstructures suggested by Ruckenstein[14] are preserved to a considerable extent in the final polymer. The microstructure observed in the polymers does not seem to be purely an effect of phase separation but a combination of phase separation and

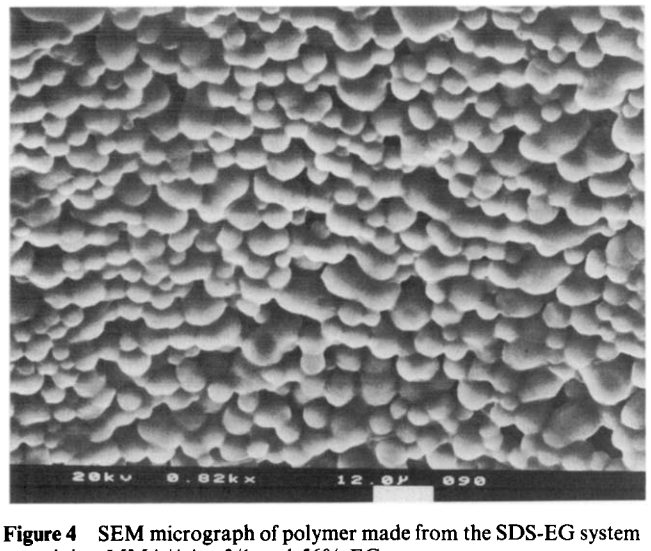

Figure 4 SEM micrograph of polymer made from the SDS-EG system containing MMA/AA = 3/1 and 56% EG

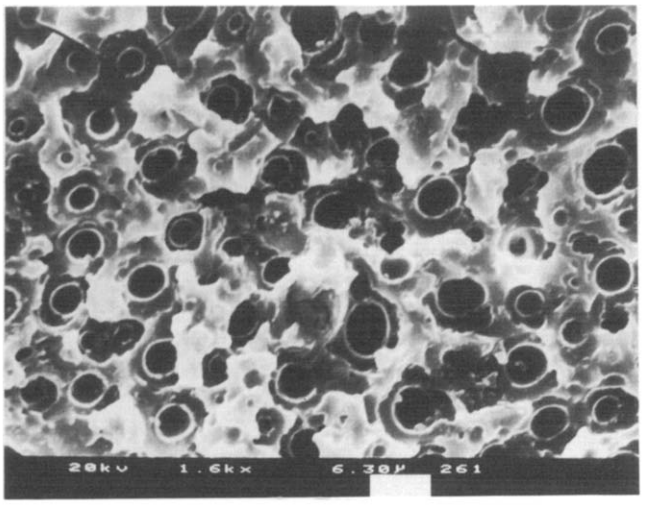

Figure 5 SEM micrograph of (extracted) critical polymer made from the SDS-EG system containing 23.76% EG in original mixture

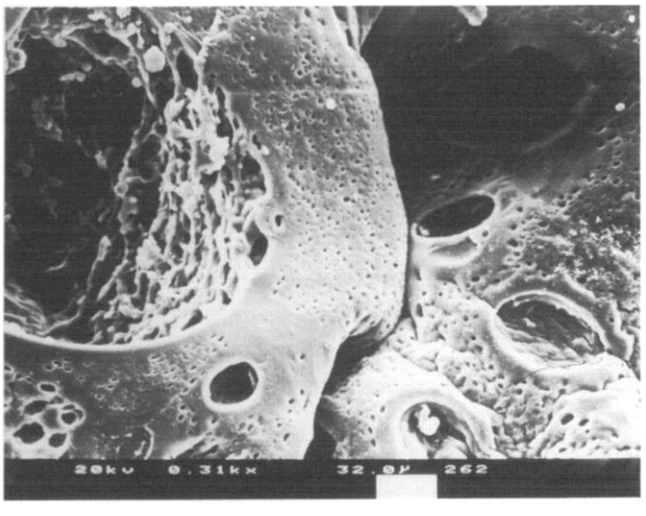

Figure 6 SEM micrograph of (extracted) critical polymer made from the SDS-EG system containing 32.67% in original mixture

the presence of microstructure in the critical region. This preservation of microstructure is mainly due to the rapid gelation (usually <60 s) of the precursors during polymerization.

Extraction studies

The amount of EG and the morphology of these EG domains in the polymer matrix would affect the amount of EG that can be extracted. If the EG is present in closed-cell structures it would be harder to extract it from the matrix compared to the EG present in an interconnected porous network.

This principle was utilized in order to obtain inferential and corroborative evidence of the bulk polymer morphology. *Figure 7* shows the extraction results for the polymers of the SDS-free system. The polymers at low EG contents have very low extraction values compared to the original EG content. This is probably due to the presence of relatively inaccessible EG droplets. At higher EG contents the mass change is almost equal to the original amount of EG. This suggests that at high EG contents (close to the phase boundary) the EG is present in porous channels.

Figure 8 presents the extraction results of the samples formed at 1% from the two-phase boundary and which showed critical behaviour. As expected, almost all of the original EG is extracted. Samples with higher extractions indicate the presence of water-soluble polyacrylic acid (PAA). Thus the polymerization in non-aqueous media produces some homopolymer PAA at higher EG contents. This is consistent with the results obtained with aqueous microemulsion systems because more AA is solubilized in the polar phase and PAA is formed at higher EG contents. However, this interpretation is inferential and more work needs to be done to provide conclusive evidence of the formation of PAA perhaps using n.m.r. or Fourier transform infra-red spectroscopy.

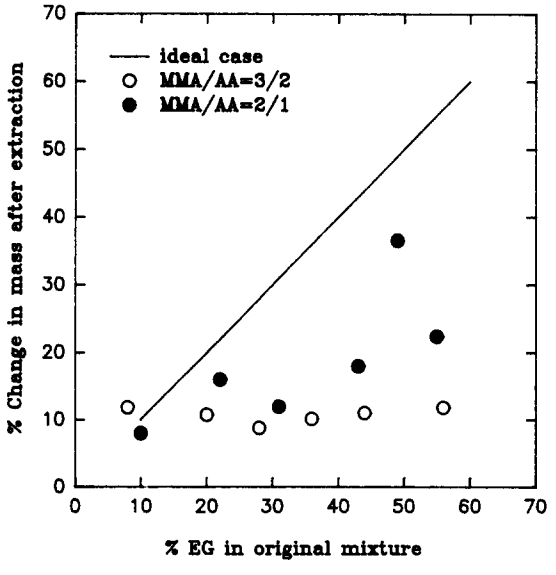

Figure 7 Change in mass of virgin polymers made from the SDS-EG system after extraction plotted as a function of EG content in original mixture

Thermal studies

Even though the samples did not show any evidence of microstructure away from the two-phase boundary, their polymers showed very interesting mechanical properties. Some of the polymers formed were rubbery and tougher than the polymers formed from aqueous microemulsions. EG seemed to act as a plasticizer. In order to study the plasticizing effect of EG on the polymers, the T_g of the virgin polymers was measured. The polymers were cooled to -25°C and heated at a ramp rate of 1°C min^{-1} to 200°C.

The T_g of these polymers at constant MMA/AA ratios was measured as a function of the content of SDS-EG stock solution in the sample. In general the T_g of the polymers decreased with an increase in the SDS-EG content thus confirming the plasticizing effect of EG. The T_g also decreased with increasing AA (lower MMA/AA ratio) content suggesting that more EG was incorporated in to the polymer matrix. The T_g of these polymers was then determined after the EG was extracted. The results are shown in *Figure 9*. These polymers showed two distinct T_gs. The higher T_g probably corresponds to the formation of poly(MMA-*co*-AA) rich in MMA units.

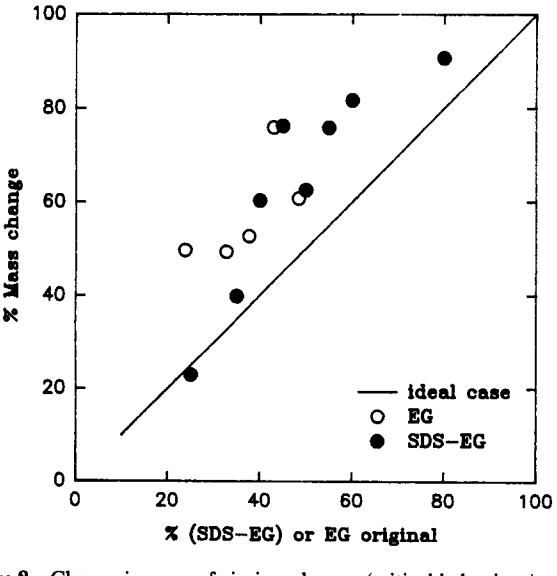

Figure 8 Change in mass of virgin polymers (critical behaviour) made from the EG and SDS-EG systems after extraction plotted as a function of EG or SDS-EG content in original mixture

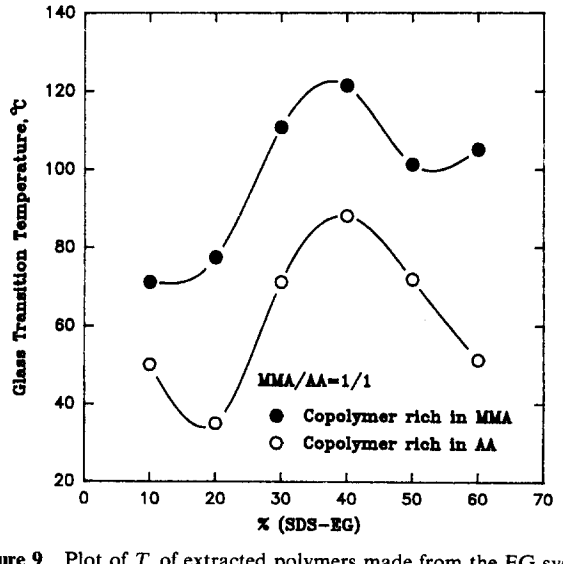

Figure 9 Plot of T_g of extracted polymers made from the EG system as a function of EG stock solution content in original mixture

These T_gs were higher than the T_gs of either homopolymer (PMMA, 105°C and PAA, 106°C). Also, these polymers did not dissolve in a host of solvents even at boiling temperatures. The polymers however swelled in boiling THF and 1-methyl-2-pyrrolidinone indicating crosslinking. The presence of EG increases the solubility of the monomers and thus promotes higher molecular weights or even crosslinks. EG appears to increase the crosslinking effect up to a certain extent when non-porous solids are formed. Above 40–50% EG content the T_g drops due to the loss of connectivity of the polymer matrix (bicontinuous) and a gel-like mass is obtained. Badran *et al.*[16] also found similar increases in the molecular weights in EG mixtures compared to that in a pure aqueous medium. This could explain the higher T_gs of the copolymers.

The lower T_gs observed are probably due to the formation of plasticized PAA or a copolymer rich in AA. As the concentration of EG is increased there is a relative increase in the AA present in the polar phase. This results in the formation of more homopolymer PAA or a copolymer rich in AA. Even though these polymers have been extracted with water and PAA dissolves in water, not all of the PAA is extracted out. The remaining homopolymer has a much lower T_g compared to the usual T_g of PAA (106°C) due to the plasticizing effect of EG. The plasticizing effect of the solvent was not observed in the polymers formed from the polymerization of aqueous microemulsions. This is due to the hosting nature of EG as observed by Badran *et al.*[16].

Tensile testing

One of the most important applications of the porous solids formed in this research could be in the area of membranes. The organized solutions can be polymerized into thin sheets with different pore distributions depending on the initial water or EG content. The mechanical properties of such a membrane would be an important consideration for its application as a self-supporting membrane.

The virgin polymers of the non-aqueous systems showed very interesting elastomeric properties. Dumbbell-shaped polymer strips were tested to study the plasticizing effect of EG. No definite pattern was observed

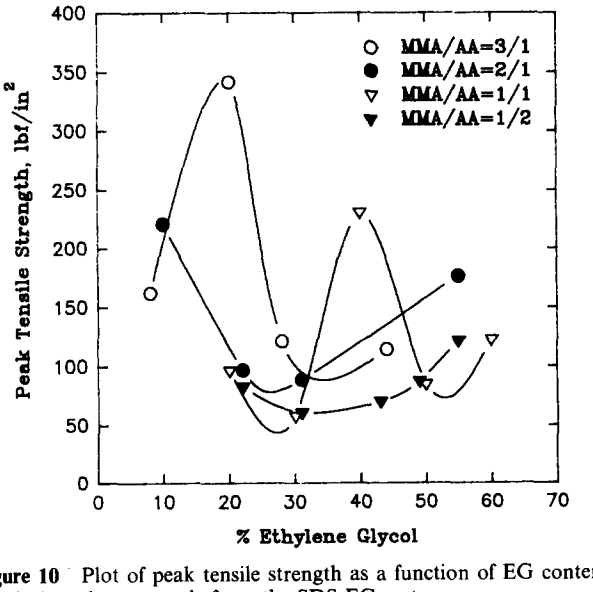

Figure 10 Plot of peak tensile strength as a function of EG content for virgin polymers made from the SDS-EG system

but elongations as high as 95% were obtained even in the absence of a crosslinking agent. In general the elongation increased with EG content but as the EG content approached ~35–40% the solids started losing their structural integrity and hence a drop in elongation was observed. Higher AA contents (low MMA/AA) improved the compatibility of EG in the polymers (reduced phase separation) and hence the elongation at break increases. The peak tensile strength is reduced with increasing EG and AA content (*Figure 10*). This is expected because of the plasticizing effect of EG which reduces the hardness of the solids. These results agree with the earlier observations which suggest that with increasing EG content the pores become bigger and the cell walls become thinner. As a result there is a drop in values of elongation at break at high EG contents (>45%). The tensile properties are a complex function of the EG content and the morphology.

CONCLUSIONS

Organized solutions containing monomers were formed and polymerized to form polymeric solids with different morphologies, and also unique thermal and mechanical properties. An attempt has been made to find a direct correlation between the nature of the microstructured systems and its effect on the resulting polymers. The non-aqueous mixtures of MAA and AA did not yield conventional microemulsions even in the presence of a highly surface active surfactant, SDS. The aggregates formed in the non-aqueous mixtures are substantially permeated with EG and much more disordered than aqueous mixtures. The conductivity, viscosity and light scattering results of this study are consistent with these observations. Due to the increased solubility of MMA, molecularly dispersed solutions are formed at higher EG contents. However, at lower EG contents (closer to the two-phase boundary) associated structures are formed. These aggregates are probably formed on a short time-scale[14]. The synthesis of polymeric solids from the aqueous[6–9] and non-aqueous mixtures is dependent on the nature and composition of the precursors. The non-aqueous mixtures did not form any well defined microstructures on polymerization for compositions away from the two-phase boundary. However, compositions exhibiting critical behaviour yielded open cell structures and also beaded polymers at high EG contents. The size of the pores in these solids does not appear to be a manifestiation of phase separation. However, phase separation during polymerization does exist as evidenced by the dual porosity in some of these polymers. The increased rate of reaction as evidenced by lower gelation times is probably due to the increased solubility of MMA in EG. The polymers obtained from the EG systems are crosslinked as evidenced by the swelling behaviour in THF while the polymers formed from water-containing microemulsions did not form crosslinks in the absence of ethylene glycol dimethacrylate. This effect could be utilized to control the crosslinking in these polymers by using a mixture of water and EG. The porous polymers can be used in forming membranes with specific pore sizes by varying the solvent content. The virgin polymers containing EG had very low T_gs due to the plasticizing nature of EG. The presence of two T_gs in some of the polymers suggests the formation of two copolymers, one rich in MMA and the other rich in AA. Corroborative evidence

of this is found in extraction measurements. Higher EG contents promote the formation of PAA due to the increased solubility of AA. The plasticizing nature of EG was also evidenced in the tensile properties of the virgin polymers. This study presents the first account of using mixtures exhibiting critical behaviour to produce microstructured polymers. This is of technological significance because critical behaviour in multicomponent mixtures is probably more prevalent and these systems are easier to formulate than microemulsions. The compositional range of critical behaviour is, however, limited and not as extensive as most microemulsions.

REFERENCES

1 Bone, T. and Stoffer, J. O. *J. Dispersion Sci. Technol.* 1979, **1**, 37
2 Haque, E. and Qutubuddin, S. *J. Polym. Sci., Polym. Lett. Edn* 1988, **26**, 429
3 Qutubudin, S., Haque, E., Benton, W. J. and Fendler, E. J. *Am. Chem. Soc. Symp. Ser.* 1989, **384**, 64
4 Menger, F. M. and Tsuno, T. *J. Am. Chem. Soc.* 1990, **112**, 1263
5 Sasthav, M. and Cheung, H. M. *Langmuir* 1991, **7**, 1378
6 Palani Raj, W. R., Sasthav, M. and Cheung, H. M. *Langmuir* 1991, **7**, 2586
7 Sasthav, M., Palani Raj, W. R. and Cheung, H. M. *J. Colloid Interface Sci.* 1992, **152**, 376
8 Palani Raj, W. R., Sasthav, M. and Cheung, H. M. *J. Appl. Polym. Sci.* 1993, **47**, 499
9 Palani Raj, W. R., Sasthav, M. and Cheung, H. M. *Langmuir* 1992, **8**, 1931
10 Palani Raj, W. R., Sasthav, M. and Cheung, H. M. *Polymer* in press
11 Palani Raj, W. R., Sasthav, M. and Cheung, H. M. *J. Appl. Polym. Sci.* in press
12 Roux, D. and Bellocq, A. M. in 'Micellar Solutions and Microemulsions' (Eds S.-H. Chen and R. Rajagopalan), Springer-Verlag, New York, 1990, p. 251
13 Kertes, A. S. in 'Micellization, Solubilization and Microemulsions' (Ed. K. L. Mittal), Vol. 1, Plenum Press, New York, 1976, p. 445
14 Ruckenstein, E. *Am. Chem. Soc. Symp. Ser.* 1985, **272**, 21
15 Friberg, S. E. and Sin, W. M. *Colloid Polym. Sci.* 1990, **268**, 755
16 Badran. A. S., Abd El-Hakim, A. A., Ayoub, M. M. H. and Younan, A. F. *J. Appl. Polym. Sci.* 1992, **45**, 333