

# Humidity-Responsive Polymeric Films Based on AOT-Water Reverse Microemulsions

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**ABSTRACT:** Hydrophobic polymer films, having an aqueous phase distributed throughout the matrix, were formed by polymerizing a solution of dodecyl acrylate and 1,6 hexanediol diacrylate containing nanometer-sized drops of water stabilized by sodium bis(2-ethylhexyl) sulfosuccinate (AOT). Photopolymerization-induced aggregation of the water drops and/or phase separation occurred, as the initially clear solutions became opaque films. The polymerized films became

clear, as the relative humidity was reduced. Clear films still contained 20–50% of the initial water. The transition from opaque to clear films was reversible provided that the film did not become completely dry and form cracks. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1957–1963, 2007

**Key words:** reverse microemulsion; photopolymerization; phase separation

## INTRODUCTION

Microemulsions are thermodynamically stable mixtures of oil, water, and surfactant that consist of nanometer-sized micelles. The nanometer-sized micellar droplets are incapable of scattering visible light and thus the mixtures are optically transparent. A surfactant is used to form a bridge between the two immiscible fluids, allowing the formation of a macroscopically homogeneous but microscopically heterogeneous system.<sup>1</sup> The spontaneous formation of a single-phase system from two otherwise immiscible components is a unique characteristic of microemulsions.

Microemulsions are thermodynamically stable because the surfactant sufficiently reduces the interfacial tension between the oil and water phases, which, in turn, lowers the energy required to increase the surface area, and spontaneous droplet formation occurs.<sup>2,3</sup> Typically, microemulsions have an oil phase dispersed in a continuous aqueous phase. Reverse microemulsions are characterized by nanometer-sized drops of water distributed throughout an oil phase.<sup>4–9</sup> The most common water-in-oil

(w/o) reverse microemulsions use the anionic surfactant sodium bis(2-ethylhexyl) sulfosuccinate (Aerosol-OT, AOT), which exhibits varied aqueous phase behavior including dense droplet, vesicular, lamellar, bicontinuous cubic, and reverse hexagonal liquid crystalline phases.<sup>2</sup> AOT, with its double tail, forms stable reverse microemulsion (water in oil) with many different organic substances.<sup>2</sup>

Because of the stability and small droplet size of microemulsions, they are capable of producing coatings that overcome many shortcomings of traditional solvent-based processes.<sup>10–12</sup> Polymerization of a microemulsion is commonly used to produce large molecular weight polymer particles ( $10^5$ – $10^7$ ) of small size (10–1000 nm) that are polymerized within the micelles of an aqueous or nonaqueous medium.<sup>10,11</sup> To date, investigations of polymerization involving inverse water-in-oil microemulsions have only focused on the synthesis of water-soluble monomers in the aqueous phase.<sup>12</sup>

We describe the creation of hydrophobic polymer films with an aqueous phase distributed throughout the matrix as droplets. The inspiration of this work comes from polymer-dispersed liquid crystals (PDLCs) that are biphasic networks created by polymerizing a homogeneous liquid crystal and monomer mixture, which upon polymerization forms phase-separated liquid crystal droplets.<sup>13</sup> The aqueous droplets dispersed throughout the crosslinked film are produced by the polymerization of a monoacrylate/diacrylate mixture in which an aqueous

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TABLE I  
Composition of Microemulsions

Water concentration wrt monomer (%)	Weight composition (%)				
	Water	AOT	DDA	HDDA	Initiator
5	4.51	10.57	80.01	4.84	0.06
10	8.13	18.35	69.26	4.17	0.09
15	11.35	24.27	60.57	3.73	0.08
20	14.26	28.75	53.68	3.25	0.07
25	16.93	32.26	47.83	2.92	0.06
30	19.52	34.90	42.89	2.64	0.05

component is initially dispersed as a reverse microemulsion.

### EXPERIMENTAL

Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) (>96%) from Aldrich, dodecyl acrylate (DDA) (90%) from Sartomer, 1,6-hexanediol diacrylate (HDDA) (>99%) from Cytec Surface Specialties and Irgacure 369 from Ciba Specialty Chemicals were used as received.

#### Preparation of microemulsion solutions

All microemulsions were prepared according to the following procedure: For the preparation of a microemulsion with 10% water relative to the monomers, 11.07 g (0.025 mol) of AOT was added to 50 mL of a monomer mixture, consisting of 41.8 g (0.17 mol) of DDA and 2.5 g (0.11 mol) of HDDA. The solution was allowed to stir for up to 24 h, or until all the AOT was fully dissolved. Next, the deionized water was added (4.92 mL) to form microemulsions with a water-to-surfactant ratio,  $W$ , of 10. The composition of 5.7 wt % of crosslinker, HDDA, with respect to DDA was kept constant for all formulations. Other microemulsions with different water contents were prepared in a similar manner. In each case, the amount of AOT was varied so that the water-to-surfactant ratio was kept constant to assure the same initial micelle size of the water droplets. Finally, the photoinitiator, Irgacure 369, in the amount to give 3 mM concentration relative to the monomers was added. The final compositions of the prepared microemulsions are listed in Table I.

#### Polymerization of films

The films were prepared between two glass microscope slides. The thickness of that formed cell was determined with either a microscope cover glass (Fisher Scientific 12-540-B) placed between two glass slides for thicker films or a 10-micron glass spacers for thin films. Samples were photopolymerized with a small handheld ultraviolet light source (365 nm) (light intensity  $2.3 \text{ mW cm}^{-2}$ ). Exposure time was 1 min on

each side of the film. The films' names are formed from the amount of weight percent water content in relation to the monomers in microemulsion, for example, "25% film" means a film that was prepared from microemulsion containing 25% water relative to the organic phase. Films used for experiments with UV-vis were prepared between two quartz slides from ChemGlass (CGQ-0640-02), and before the experiment was started one of the slides was removed.

#### Humidity measurements

Humidity measurements were made using an Omegaette HH314 humidity/temperature meter. The following conditions were used in the experiments: "open," "desiccator," and "saturated" atmospheres. A condition designated as "open" atmosphere refers to the laboratory atmosphere with a relative humidity ranging from 50 to 55%. The relative humidity for a "desiccator" atmosphere was achieved over a drying agent ( $\text{CaCl}_2$ ) and was equal to 12%. A closed jar with few milliliters of water created 100% relative humidity and is referred to as "saturated" atmosphere. All experiments were carried out at ambient temperatures and pressure.

#### Instruments

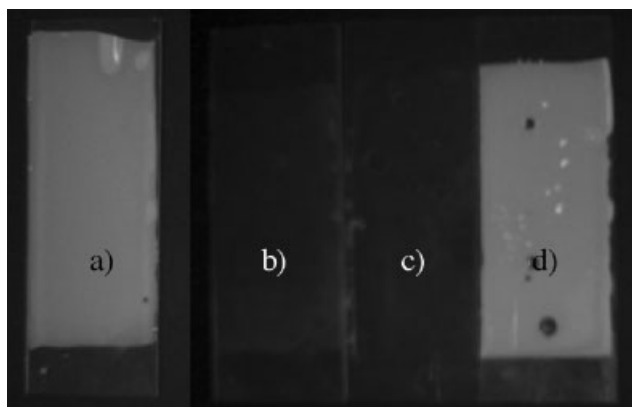
Thermal gravimetric measurements were obtained using a TGA 2050 Thermogravimetric Analyzer from TA instruments. The heating rate was  $5^\circ\text{C min}^{-1}$  from 20 to  $500^\circ\text{C}$ . The percent transmission of 500-nm light was recorded on a UV-2401PC Shimadzu double-beam instrument in time-acquisition mode. ATR-FTIR spectra were obtained using a Nicolet Nexus 470 FTIR spectrometer with Omnic computer software.

All measurements were repeated three times, and the standard deviation was less than 5%.

## RESULTS AND DISCUSSION

### Polymerization-induced aggregation

Two optically transparent microemulsion solutions were prepared. Both solutions contained DDA, and



**Figure 1** Films prepared from a microemulsion with 25% water (relative to monomers) and  $W = 10$ . (a) An opaque film immediately after polymerization; (b) The same film after 24 h exposure to the open atmosphere; (c) A film kept in a desiccator for 24 h; (d) A film kept in the saturated atmosphere.

HDDA, AOT, a photoinitiator (Irgacure 369), and either 10 or 25% deionized water. When both solutions were exposed to UV light, a rapid photopolymerization occurred, producing opaque films, which indicated that the nanometer-sized drops of water in the reverse microemulsion aggregated when the polymeric film formed.

$$\Delta G_{\text{form}} = \Delta A\gamma_{1,2} - T\Delta S_{\text{conf}} \quad (1)$$

This can be understood in terms of eq. (1), where  $\Delta G_{\text{form}}$  is the free energy change for the formation of the microemulsions,  $\Delta A$  is change in interfacial area,  $\gamma_{1,2}$  is the interfacial tension between phases 1 and 2,  $\Delta S$  is change in entropy, and  $T$  the temperature. The entropy term,  $\Delta S$ , is reduced upon polymerization because the number of possible combinations of arranging the drops is reduced. When the monomer is present, there is a constant dynamic exchange between water droplets. Thus, the entropy of mixing is large. Upon polymerization, as with a PDLC, the entropy of mixing is greatly reduced. This results in an overall free energy increase. The only way to reduce free energy is by the reduction of the surface area through the aggregation of the water droplets. (It is assumed that the surface energy of the AOT-water interface between the polymer-monomer solutions is the same as for the pure monomer.) In another words, when the monomer polymerizes, the polymer molecules force the water droplets to combine.<sup>14</sup>

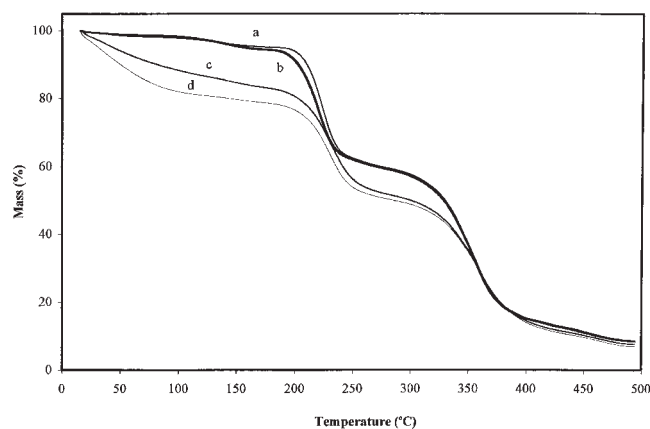
Xia et al. showed that adding a polymer to decane in a reverse microemulsion could cause phase separation.<sup>15</sup> However, in our systems, the organic phase itself is polymerizing. Therefore, the aggregation of the initially nanometer-sized water drops to domains larger than the wavelength of visible light could be

caused by the polymerization shifting the size distribution of the microemulsion to larger sizes. It is likely that both a perturbation of the microemulsion and phase separation occurred simultaneously. The rapid polymerization could be trapping the water into large domains before complete phase separation occurs. Small angle neutron scattering studies are underway to determine the morphology and will be reported at a later date.

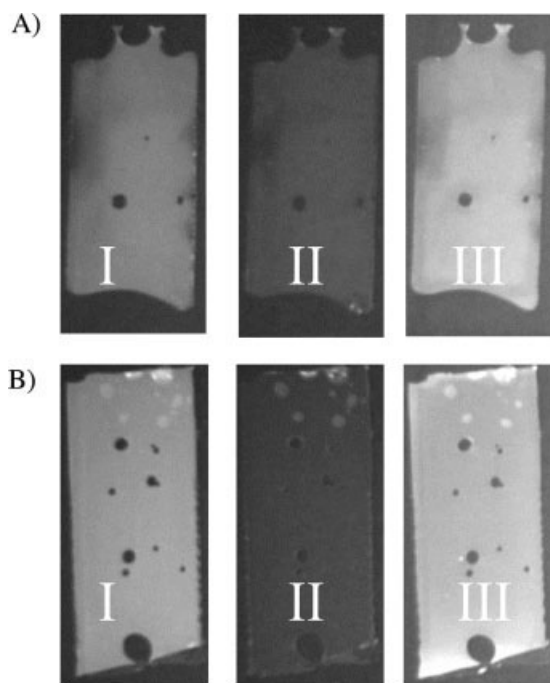
### Opacity as a function of humidity

Although both films prepared from microemulsions with 10 and 25% water were analyzed, in this section, we only present results for the film produced from the microemulsion with 25% water. Upon polymerization, the film has an opaque, milky-white color [Fig. 1(a)]. The initial (right after polymerization) opacity was greater for films formed from microemulsion with higher water content. The difference in opacity in 10 and 25% films right after polymerization can be seen in pictures I in Figure 3. When the polymerized films were exposed to environment with humidity less than 100%, they began to lose opacity and eventually became transparent [see Fig. 1(b,c)]. Films exposed to the lab atmosphere and kept in the desiccator became equally transparent. However, if the films were kept in the saturated atmosphere, they absorbed water, as demonstrated for the film in Figure 1(d), where the opacity actually exceeds that of the film right after polymerization.

Thermal gravimetric analysis (TGA) plots presented in Figure 2 confirm that the transparent films from the desiccator and open atmospheres still contained a significant amount of water. For example,



**Figure 2** TGA analysis of films kept at different humidity conditions and prepared from the microemulsion with 25% of water content relative to monomers (water is 18% relative to total mass); (a) film exposed to open atmosphere for 40 h, (b) film kept in the desiccator for 40 h, (c) film right after polymerization, and (d) film kept in the saturated atmosphere for 40 h.



**Figure 3** Images of films formed from microemulsion with 10% water (A) and film with 25% water (B) under three conditions; (I) right after polymerization; (II) one hour after polymerization exposed to open atmosphere; (III) after exposure to saturated atmosphere for 80 min.

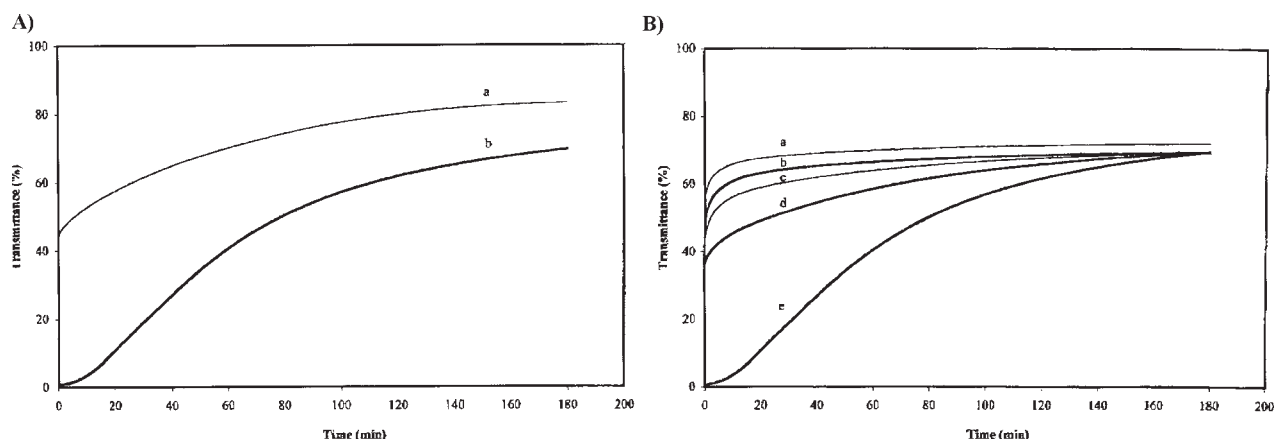
the film [Fig. 1(a)] right after polymerization showed 11% water content (plot c in Fig. 2). The TGA plot of the same film exposed for 40 h in the open atmosphere [Fig. 1(b)] indicated that there was still 2% water remaining (plot a in Fig. 2). The same result was obtained for the film kept in the desiccator for 40 h (plot b in Fig. 2). It was also proved that the film exposed to saturated atmosphere gained water. The film that was exposed to a saturated atmosphere for 40 h [Fig. 1(d)] after polymerization had gained

water (plot d in Fig. 2); the mass fraction of water increased from 11 to about 19%.

### Quasi-reversible hydration

Films prepared from the 10 and 25% microemulsions were allowed to “dry” in the open atmosphere for 48 h followed by an exposure to the saturated atmosphere for 80 min. The appearance of both films changed from transparent to opaque as they regained water (Fig. 3). The cyclic process of drying and rehydrating from clear to opaque exhibited in Figure 3 can be performed many times. However, if the film loses all the water, by placing in the desiccator for an extended time period, its surface cracks; it is not possible to resaturate such a film.

The change in opacity of 10 and 25% films was followed by the change in visible light transmittance (Fig. 4). The films were prepared in a controlled manner, with the same thickness, time of polymerization. Figure 4(A) shows the change in transmittance of two films right after polymerization. The films were placed in the spectrometer immediately after polymerization, and the transmittance in the open atmosphere was recorded as a function of time. At zero time, the films showed significant difference in transmittance, which can also be seen in Figure 3(I). The 10% film is transparent (44% transmittance) when the 25% film has a transmittance of about 1% with an induction period, where the transmittance does not change for few minutes. This variation of the two films’ transmittances has to do with different water amounts and possibly different water aggregation sizes. The films reached a plateau in transmittance after about 120 min; however, they still showed different final transmittances, which relates to the films’ initial compositions. When all films prepared from all microemulsions were



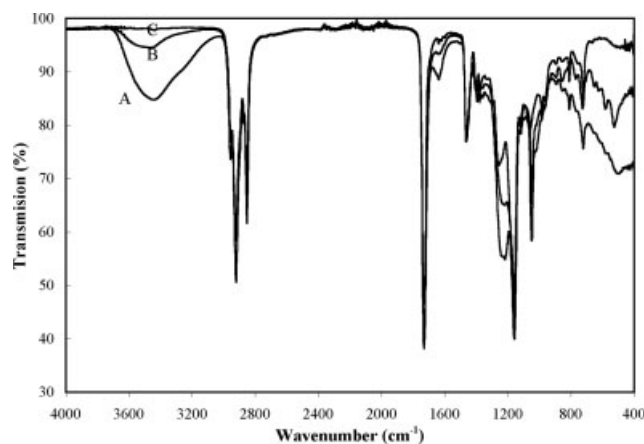
**Figure 4** Transmittance of 500-nm light as a function of time. A: Change in transmittance after polymerization for 10% (trace a) and 25% (trace b). B: Change in transmittance for 25% film right after polymerization (e) and after exposure to different times in saturated atmosphere: (a) 10, (b) 20, (c) 30, and (d) 80 min.

compared, (for clarity data is not presented), they demonstrated trends falling in logical transmittance response. The 5% film had the highest transmittance (right after polymerization 74%, and a final value of 88%), and the 30% film exhibited the lowest transmittances (0.6% at the beginning and 65% at the end). In addition, the 30% film showed the longest induction period, where the transmittance changed very little over about 20 min.

Figure 4(B) shows the plots of the resaturation process for the 25% film. When the transmittance of the film had reached a plateau (at least 180 min), the film was removed from the spectrometer and placed in the saturated atmosphere for different periods of time (10, 20, 30, or 80 min) to resaturate the film with water by exposing it to 100% relative humidity. The sample was then removed from the saturated atmosphere and immediately repositioned in the spectrometer. The change in transmittance was then recorded in the open atmosphere as a function of time. The resaturated films show the initial transmittance values of 56, 49, 44, and 36% corresponding to times in the saturated environment of 10, 20, 30, and 80 min, respectively. As expected, when the sample was exposed to the longest saturation time, it became the most opaque with transmittance of only 36% and exhibited the longest time to reach the final transmittance (70%). In each case, after the film was removed from the saturated atmosphere and placed in the spectrometer (i.e., the open environment), the film eventually attained a transmittance of 70%.

### Presence of water

Infrared spectra of the films under several conditions were recorded to interpret the results from the previous section. IR spectra were recorded for an opaque film immediately after polymerization prepared from the microemulsion with 10% water, for the same film in a transparent state after 24 h of exposure to the open atmosphere, and for a film prepared from the same microemulsion that was allowed to completely dry in the desiccator to the point of cracking (Fig. 5). The decrease in the peak at  $3500\text{ cm}^{-1}$  indicates that the amount of water in the initially hydrated film decreased with time. The most water is present in the freshly photocured film (Fig. 5, trace A) as demonstrated by the peak in the water region with the highest absorbance. When the film had been allowed to dry to the point of cracking, it could not be rehydrated. The IR spectrum for the film in such state (Fig. 5, trace C) shows no presence of water. However, if the film was allowed to become transparent, but not to the point of cracking, the water peak in IR spectrum (Fig. 5, trace B) was smaller than for the freshly polymerized, but still shows the presence of water in the film, as con-



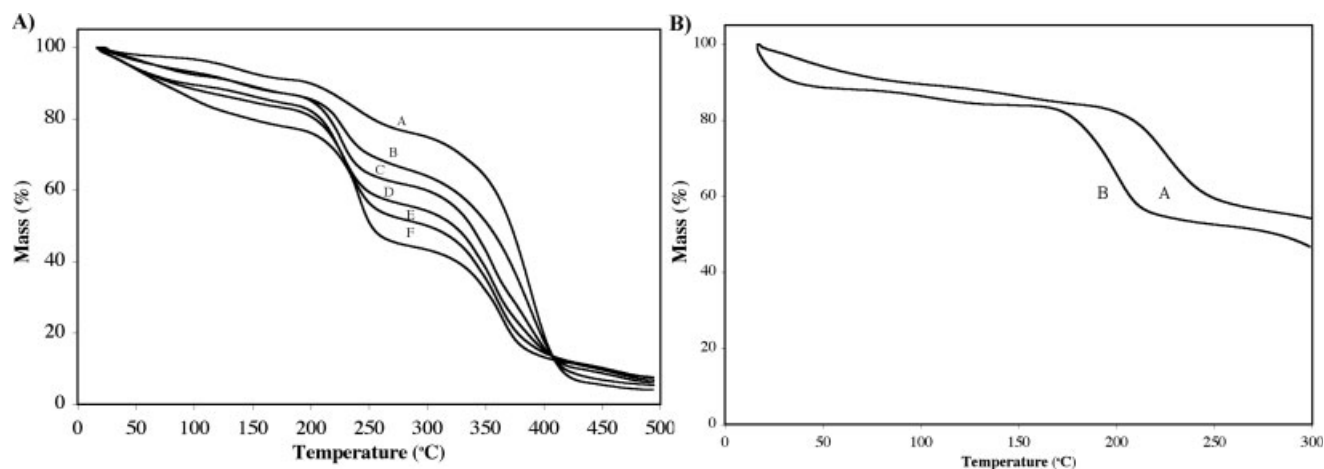
**Figure 5** IR spectra comparing opaque and transparent films prepared from microemulsion with 10% water.

firmed by TGA (Fig. 2, plot a and b). Such films could be resaturated.

### Determination of water content by TGA

We attempted to determine amounts of water in films prepared from microemulsions containing different water contents ranging from 5 to 30% by TGA. Samples were analyzed immediately after polymerization to minimize evaporation of water from the films. We used a dynamic temperature ramp with the heating rate of  $5^{\circ}\text{C min}^{-1}$  from room temperature to  $500^{\circ}\text{C}$ . The resulting mass loss versus temperature plots are presented in Figure 6. The results in Figure 6(A) show that water is present in each of the films after the polymerization. The trends are consistent with the initial composition of the microemulsions. The water loss occurs from the starting temperature to above  $100^{\circ}\text{C}$ . Unfortunately, the determination of the water content was complicated by the fact that at about  $140^{\circ}\text{C}$  the unreacted monomers leave the film (confirmed by TGA analysis of a pure film prepared from 5% HDDA/95% DDA mixture). For films with higher water contents of 25 and 30% (plots e and f on Fig. 6, respectively), these two events overlap without giving a well-defined plateau for water loss. In addition, kinetic effects associated with the heating rate make the evaluation of the precise amount of water difficult. Changing the heating rate to  $1^{\circ}\text{C min}^{-1}$  shifted the final plateau to  $150^{\circ}\text{C}$  [Fig. 6(B)] from  $200^{\circ}\text{C}$  for the sample heated at  $5^{\circ}\text{C min}^{-1}$ . For the lower heating rate, water leaves at very low temperature (below  $80^{\circ}\text{C}$ ); however, the unreacted monomer evaporation also occurs at lower temperature and extends over a  $40^{\circ}$  range (between 80 and  $120^{\circ}\text{C}$ ) possibly overlapping with the remaining water evaporation.

We next point out that in each of the films, the surfactant decomposition occurs at about  $225^{\circ}\text{C}$ . The



**Figure 6** TGA of films (A) Films with different water content but the same water-AOT ratios; each ramped  $5^{\circ}\text{C min}^{-1}$  from room temperature to  $500^{\circ}\text{C}$ . Percent water (wrt monomers) (a) 5%, (b) 10%, (c) 15%, (d) 20%, (e) 25%, and (f) 30%; (B) Film with 25% water (wrt monomers) at different heating rate from room temperature to  $300^{\circ}\text{C}$ ; (a)  $5^{\circ}\text{C min}^{-1}$ , (b)  $1^{\circ}\text{C min}^{-1}$ .

decomposition of sodium bis(2-ethylhexyl) sulfosuccinate occurred at lower temperatures for scans at  $1^{\circ}\text{C min}^{-1}$ . For example, for the freshly polymerized films from 25% water microemulsion the temperature of AOT decomposition shifted from  $229^{\circ}\text{C}$  for a heating rate of  $5^{\circ}\text{C min}^{-1}$  to  $198^{\circ}\text{C}$  for  $1^{\circ}\text{C min}^{-1}$ .

To determine the origin of the weight loss at temperatures greater than  $350^{\circ}\text{C}$ , a film of 5% HDDA/95% DDA was tested to determine if the weight loss occurring at higher temperature is a result of DDA/HDDA network decomposition. For a pure film without surfactant or water, the network decomposes at  $380^{\circ}\text{C}$ . It is clear from the results in Figure 6(A) that depending on the water content, the onset of the network decomposition occurs at different temperatures. This may be due to acrylate hydrolysis or change in network structure or morphology.

#### Mass loss of water as a function of water content

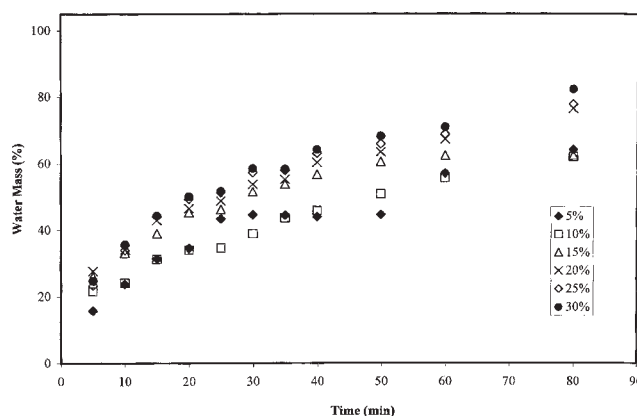
To further investigate the loss of water with time, films containing different amounts of water, but with the same water-to-AOT ratio ( $W = 10$ ), were weighed immediately after photopolymerization and exposed to the open atmosphere.

Each film was then weighed as a function of time to construct a graph of mass fraction lost as a function of time at  $25^{\circ}\text{C}$  (Fig. 7). The films became transparent within 80 min. The data demonstrate that the films lose up to 80% of the total water present within 80 min, suggesting that a significant amount of water exists unbound to the surfactant.

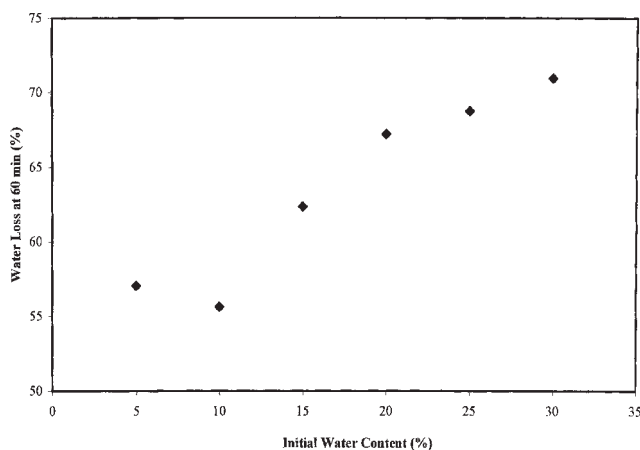
It has been shown that in reverse (*w/o*) microemulsions, water is present in three solubilized states.<sup>16</sup> Below  $W = ([\text{H}_2\text{O}]/[\text{AOT}]) < 4$ , water associates with the ionic head groups of the surfactant. Swollen micelles are formed when  $W$  is between 4

and 12. In this state, the extra water hydrogen bonds with the hydrated head groups of the surfactant. Finally, when  $W > 12$ , the excess water builds up in the core of the micelles and is referred to as "bulk water." Thus, we propose that in our films the water left in the films, after they become transparent, is the water associated with the surfactant's ionic head groups. Interestingly, the films with higher initial water content (25 and 30%) lose water with higher rates than films with lower initial water content.

In addition, there is a relationship between the initial water content and the fraction of water lost (Fig. 8). Even though the microemulsions were prepared with the same water-to-surfactant ratio, which predicts the size of the initial micelles, polymerization-induced aggregation formed aggregates with different water content. The water leaving the film at room temperature is the "free" water of the droplets, which is loosely bound to the AOT. The films containing initially more water must form water aggre-



**Figure 7** Percentage loss of water as a function of time for films at room temperature open to 50% relative humidity. Initial amount of water is relative to monomer.



**Figure 8** Mass fraction of water lost as a function of initial percentage water at room temperature after 60 min.

gates with larger fractions of that water. It also shows that 20–45% of water stays bound to the surfactant.

### CONCLUSIONS

We report for the first time the preparation of films by the photopolymerization of a reverse microemulsion. The organic phase consisted of DDA and 1,6-hexanediol diacrylate with water drops in separate phase stabilized with anionic surfactant sodium bis(2-ethylhexyl) sulfosuccinate (Aerosol-OT, AOT). The solution before polymerization was clear, but upon photopolymerization, the films formed were opaque. The opacity is a result of water droplet aggregation from nanosized micelles in the microemulsion into micron-sized aggregates in the film.

The films become clear upon exposure to less than 100% relative humidity, and the films can be resaturated by exposure to 100% humidity. Even when the film is clear, water remains in the film for an extended period of time. This suggests that water

exists in two states. In the first state “bulk” or “free” water is loosely bound and leaves the film at room temperature. In the second state, water is bound to the surfactant’s head groups. The AOT-bound water represents 20–50% of the initial water. The amount of bulk water is related to the initial composition of the microemulsion; the highest amount is found in the films formed from microemulsions with the highest water content.

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