

# Formation of Polymeric Microspheres Using Electron Beam Radiation

DALE C. McHERRON and GARTH L. WILKES\*

Polymer Materials and Interfaces Laboratory & Department of Chemical Engineering,  
Virginia Polytechnic Institute, Blacksburg, Virginia 24061

## SYNOPSIS

Polymeric particulates are currently being produced by a variety of different techniques. This new approach illustrates the formation of cross-linked polymeric microspheres by incorporating trimethylolpropane propoxylate triacrylate (a radiation-sensitive monomer) into a polyaphron system and exposing it to electron beam radiation. Polyaphrons are essentially a collection of droplets encapsulated in a very thin aqueous film dispersed in an aqueous matrix. This film gives extreme stability to the system, which allows for extremely high dispersed-phase concentrations. The formation of polyaphrons requires the presence of a surfactant in both the dispersed (monomer) and continuous (aqueous) phases. The effects of monomer-phase concentration, monomer- and aqueous-phase surfactant concentration, aqueous-phase surfactant type, and preparation temperature were studied to gain an understanding of the conditions that promote the formation of polymeric microspheres with a narrow size distribution. Polymeric microspheres ranging from 2 to 40 microns in diameter were formed with monomer concentrations as high as 67 vol % without any aphron bridging occurring or need for agitation to keep the monomer-phase dispersed in the aqueous matrix. In addition, the ability to reduce the wettability of the microspheres is demonstrated through incorporation of a polymerizable fluorinated acrylate in the dispersed phase.

## INTRODUCTION

Polymeric microspheres have been produced by a variety of different techniques. Emulsion polymerization of vinyl polymers is probably the most well-known process.<sup>1</sup> More recently, several investigators have described the formation of polymeric microspheres using radiation processes. Yoshida et al.<sup>2</sup> have reported on the formation of polymeric microspheres by gamma irradiation of a homogeneous solution of diethylene glycol dimethacrylate in methyl orthoformate. Rembaum et al.<sup>3</sup> also demonstrated the formation of microspheres by a gamma radiation emulsion polymerization technique.

The investigation reported in this paper illustrates the formation of cross-linked polymeric mi-

crosheres utilizing a polyaphron system and electron beam radiation. This method possesses several advantages over past or current techniques that have been reported. The polyaphron system facilitates formation of microspheres in an aqueous medium with monomer concentrations as high as 67 vol %. In addition, electron beam radiation allows for reaction times on the order of seconds, as opposed to gamma radiation, where reaction times are on the order of hours. Hence, electron beam radiation is well suited for continuous web line processing, which would be easily adapted to this application for polymeric microsphere production.

At the onset of this work, the formation of polymeric particulates was attempted using trimethylolpropane propoxylate triacrylate (a radiation curable monomer) in an emulsion system coupled with electron beam radiation. This scheme posed numerous processing difficulties, and the resulting product was quite disperse in size. To circumvent these problems, an attempt was made to incorporate the monomer

---

\* To whom correspondence should be addressed.

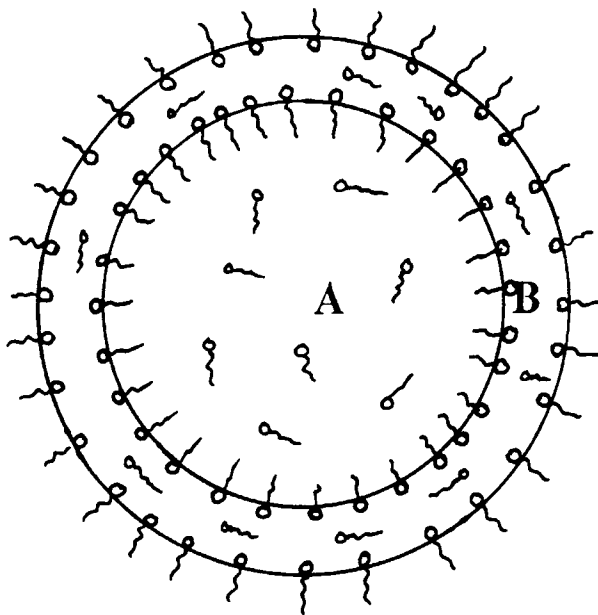
into a polyaphron system, which, as will be shown in this paper, is a successful approach.

Polyaphrons were discovered by Sebba, who also developed all the current theories for these systems and coined the term "aphron" from the Greek word for foam.<sup>4</sup> In addition, he invented a continuous polyaphron generator, which may make it possible to design a continuous process for the formation of solid polymeric microspheres, although this scheme has yet to be reduced to practice. Sebba's work deals with strictly liquid systems, although he does mention the possibility of making polymerizable aphrons, which is the focus of this work.

According to Sebba, an aphron is a phase that is encapsulated in a thin soapy film.<sup>4</sup> Polyaphrons (a collection of a large number of aphrons) are similar to foams in that they consist of a continuous aqueous phase with a second phase (of greater volume) dispersed throughout the aqueous matrix. Instead of a gas being dispersed, as with a foam, an immiscible liquid constitutes the dispersed phase. Each droplet of this immiscible liquid is encapsulated in a thin soapy film that imparts extremely high stability to the system. This stability allows for the existence of high concentrations of the dispersed phase with no coalescence or need for agitation. Obviously, aphrons are structurally very different from emulsion droplets. Emulsion systems consist of two distinct phases with an electrical double layer at the interphase, which stabilizes the droplets. On the other hand, aphron systems contain three distinct phases (continuous, dispersed, and encapsulating phases), where the third encapsulating film phase imparts some unique and desirable characteristics to the system (see Fig. 1).

The mechanism of aphron formation requires the ability of each phase to spread on the other. This is achieved through the presence of a surfactant in both phases. In order for an aphron to form, the liquid to be dispersed must spread on an aqueous surface. A large aqueous surface area can be obtained by foaming the water prior to contact with this second phase. This large surface area allows the liquid to spread into a very thin film on the aqueous interface. As the film becomes very thin, and the contact angle becomes low enough, the aqueous phase spreads over this liquid film. As the film spreads, local disturbances eventually cause the film to break up into tiny globules and these globules become encapsulated by the aqueous phase. Hence, each thin film forms a single layer of aphrons.<sup>4</sup>

As is evident from the proposed aphron formation mechanism, the creation and resulting size distribution of a system of polyaphrons will be strongly



**Figure 1** Physical structure of an aphron. It is composed of (A) the core phase, which contains the monomer solution, and (B) the aqueous shell, which encapsulates and stabilizes the core, preventing coalescence. This is distinctly different from an emulsion droplet, which has no permanent physical barrier that prevents coalescence, and relies on a surfactant monolayer (and possibly another stabilizer) for stabilization.

dependent on the spreading phenomena that occurs when two immiscible phases come in contact with each other. Aphron formation requires the ability of each phase to spread on the other, as previously mentioned. Thus, the surfactant concentration in both phases should be sufficient such that the resulting spreading coefficients (or surface pressures) are approximately equal. If the coefficients are substantially different, one of the phases will have difficulty spreading on the other, resulting in inefficient (or total lack of) aphron formation. If the nonpolar phase has a significantly higher spreading coefficient than does the water phase, it will be able to spread easily on the water surface. However, the water will not be able to spread over the top of this phase as easily, which is necessary for aphron formation. On the other hand, if the spreading coefficient of the water phase is significantly higher than is the nonpolar phase, there will be a large aqueous surface area, but the nonpolar phase will have difficulty spreading on it, due to the high surface pressure (compared to its own surface pressure).

The above discussion suggests many factors that will affect the formation of aphrons and the underlying spreading phenomena that is occurring, some

of which include<sup>4</sup> (a) nature and concentration of the water-soluble surfactant, (b) nature and concentration of the nonpolar-phase-soluble surfactant, (c) equilibrium surface pressure on the water surface [related to (a) above], (d) preparation temperature, and (e) viscosity of the phases. Although this list is by no means a complete listing of all the factors affecting spreading, it does provide a basis for this study.

This paper addresses the effects of the aqueous surfactant type, monomer- and aqueous-phase surfactant concentration, and the formation temperature on a polyaphron system containing a radiation-sensitive monomer as the dispersed liquid phase that is subject to electron beam radiation to form cross-linked polymeric microspheres. Obviously, due to the nature of the aphron formation process, a distribution of aphron sizes will be produced. The objective of studying these variables is to determine what conditions influence the size distribution of polymeric microspheres, with an attempt to produce small microspheres with as narrow a size distribution as possible. In addition to this size-distribution study, the ability to modify the surface characteristics (i.e., wettability) of the microspheres is illustrated through use of a polymerizable surfactant (a fluorinated acrylate) in the monomer phase.

## EXPERIMENTAL

### Materials

- Distilled water.
- Trimethylolpropane propoxylate triacrylate (TMPPTA) (Henkel Corp.).
- Sodium dodecyl benzene sulphonate (NaDBS) water-soluble anionic surfactant (Tennessee Chemical Co.).
- Sodium didodecyl disulfonated diphenyloxide (Dowfax 2A1) water-soluble anionic surfactant (Dow Chemical Corp.).
- Alkyloxypolyethyleneoxyethanol (Tergitol 15-S-3) oil-soluble surfactant (Union Carbide Corp.).
- 2-(*N*-ethylperfluorooctane-sulfonamido) ethyl acrylate (FX-13 Fluororad) fluorochemical acrylate (3M Corp.).

### Aphron Formation

A specified amount of aqueous surfactant solution is placed in a closed vessel and shaken vigorously to create a foam. Several drops of the monomer (with

the specified amount of surfactant) is added to the foam and shaken vigorously for approximately 20 s. This facilitates the spreading and breakup of the monomer film with subsequent aphron formation. This process is repeated until the desired concentration of monomer is obtained. During this process, the solution slowly transforms from a conventional foam (only gas is dispersed in the aqueous solution) to a biliquid foam (only the monomer is dispersed in the aqueous matrix). After several milliliters of monomer has been added, it is possible to add increasing amounts of monomer in a single step. Aphron formation requires the presence of a large aqueous surface area. However, the surface of an aphron works just as well as does an aqueous film in this respect. Therefore, once a significant number of aphrons have been produced, increasing amounts of monomer may be added at one time. For reasons to be discussed, the final concentration of monomer dispersed in the aqueous solution was 67% for most samples prepared in this study. To gain an understanding of how various factors affect the particulate formation, several variables were systematically manipulated to determine their influence on the final product. The following variables were considered:

- (a) Monomer-phase concentration. Four aphron samples were prepared with a 1.0% NaDBS aqueous solution and 0.4% Tergitol 15-S-3 in TMPPTA in a monomer-to-water ratio of 1 : 1, 2 : 1, 3 : 1, and 9 : 1 to determine the effect of monomer concentration on the resulting product.
- (b) Monomer-phase surfactant concentration. Surfactant concentrations of 0.04, 0.07, 0.4, 0.8, and 1.0 vol % of Tergitol 15-S-3 in TMPPTA were used with various aqueous solutions to determine the effect of the monomer-phase surfactant concentration on the final product.
- (c) Aqueous-phase surfactant type and concentration. Aqueous solutions containing 0.5% and 1.0% of NaDBS or Dowfax 2A1 were prepared for use as the continuous phase of the aphron systems to determine what effect this has on the final product.
- (d) Temperature. Various aphron samples containing different combinations of the specified aqueous and monomer solutions were prepared at 25°C and 75°C to determine the effect of formation temperature on the final product since the viscosity and surface tension of the phases are dependent on this parameter.

### Surface Modification

Alteration of the wettability of polymeric microspheres has been considered by substituting the fluorinated acrylate surfactant, FX-13, for the nonionic surfactant, Tergitol 15-S-3, in the monomer phase. In addition to preparing microspheres containing this compound, thin films were made with varying concentrations of FX-13 to facilitate contact-angle measurements on this material, which complements the wettability measurements made on the microspheres. The wettability of the microspheres was determined by placing 15 mg of the particles on the surface of a series of solutions containing increasing amounts of isopropanol in water and visually observing when the particles sank into solution. Contact-angle measurements were made on thin films using small droplets of deionized distilled water and measuring the advancing contact angle at ambient conditions.

### Radiation Curing

The aphron samples were cured to form cross-linked polymeric microspheres under the following conditions: A small amount of biliquid foam was placed on an inert semicrystalline polyester substrate, PET, and spread to a thickness of 5 mil (maximum thickness allowed to ensure uniform radiation dosage) using a wet film applicator. Samples that had been made more than 1 or 2 days prior to curing tended to settle out, forming a clear aqueous layer on the surface of the polyaphron phase. This aging posed no problem; the liquid was simply shaken to restore homogeneity and ensure a representative sampling. All wet film samples were cured at ambient temperatures under a nitrogen atmosphere with electron beam radiation. The electron beam source utilized was an Energy Sciences Inc. CB150 Electrocurtain operating at 175 kV, with a beam current of 2.4 mamps and a conveyor speed of 40 ft/min. This resulted in a total radiation dose of 4 Mrad. This dosage is slightly above the manufacturer's recommended dose for film curing (3 Mrad). After curing, the particles were washed in acetone, filtered, washed in water, filtered, then washed in acetone and filtered again, then placed under vacuum for at least 24 h prior to analysis.

### Analysis

Particle analysis was performed using a Cambridge Instruments Stereoscan 200 scanning electron microscope and a Shimadzu SA-CP3 centrifugal par-

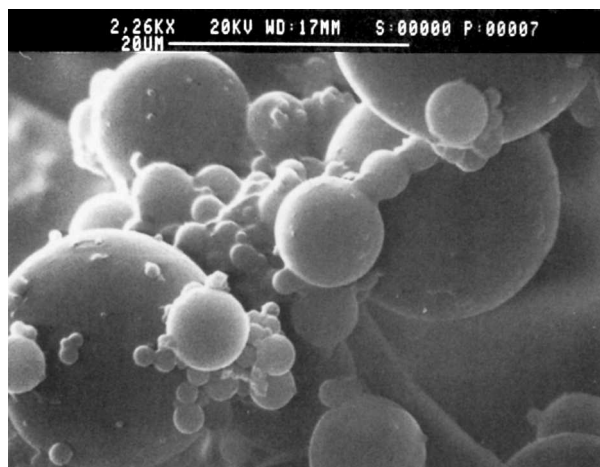
ticle-size analyzer to obtain information on the size, shape, and size distribution of the cross-linked microspheres. The particle-size analyzer is based on the sedimentation method for particle-size determination and measures the particle concentration photometrically. Accelerated sedimentation of small particles is facilitated by a rotating sample holder that exerts a centrifugal force on the colloid solution. All distributions shown represent an average of three runs made on the analyzer, which were performed using a 30 vol % solution of glycerol in distilled water with Dowfax 2A1 as a dispersant. To obtain an indication of the error associated with these distributions, three solutions of one polyaphron sample were prepared and analyzed. In addition, three polyaphron samples of the same composition were prepared and analyzed. This allowed the error associated with the aphron preparation and the particle analysis to be qualitatively separated.

To obtain information on the mechanical properties and degree of cure of these particles, thin films were formed from the monomer under the same radiation conditions and analyzed using dynamic mechanical analysis (Automated Vibron, Toyo Baldwin Inc.) at a frequency of 11 Hz and differential scanning calorimetry (Seiko Instruments). FT-IR spectroscopy was attempted on the particles, but this did not produce a good-quality spectra with the apparatus available, due to the low transmittance (large degree of scatter) of the IR beam. This same method was applied to the thin films with success, since the smooth surface of film did not scatter the beam as the particles did.

Surface tension values were measured using the Du Nouy ring method of surface tension determination. To obtain a quantitative measurement of the relative foam stability of the aqueous surfactant solutions, 10 mL of each solution was placed in a capped 100 mL graduated cylinder and shaken vigorously to create a foam. The foam was allowed to sit for 20 s, and the volume of drained water was measured as an indication of this property.

## RESULTS AND DISCUSSION

As previously mentioned, the formation of polymeric particulates was first attempted by introducing TMPPTA into an emulsion with glycerol, water, and Dowfax 2A1 constituting the continuous phase. The emulsion was subjected to electron beam radiation to form solid polymeric microspheres. This system required extensive stirring prior to processing to sufficiently disperse the monomer phase, and the

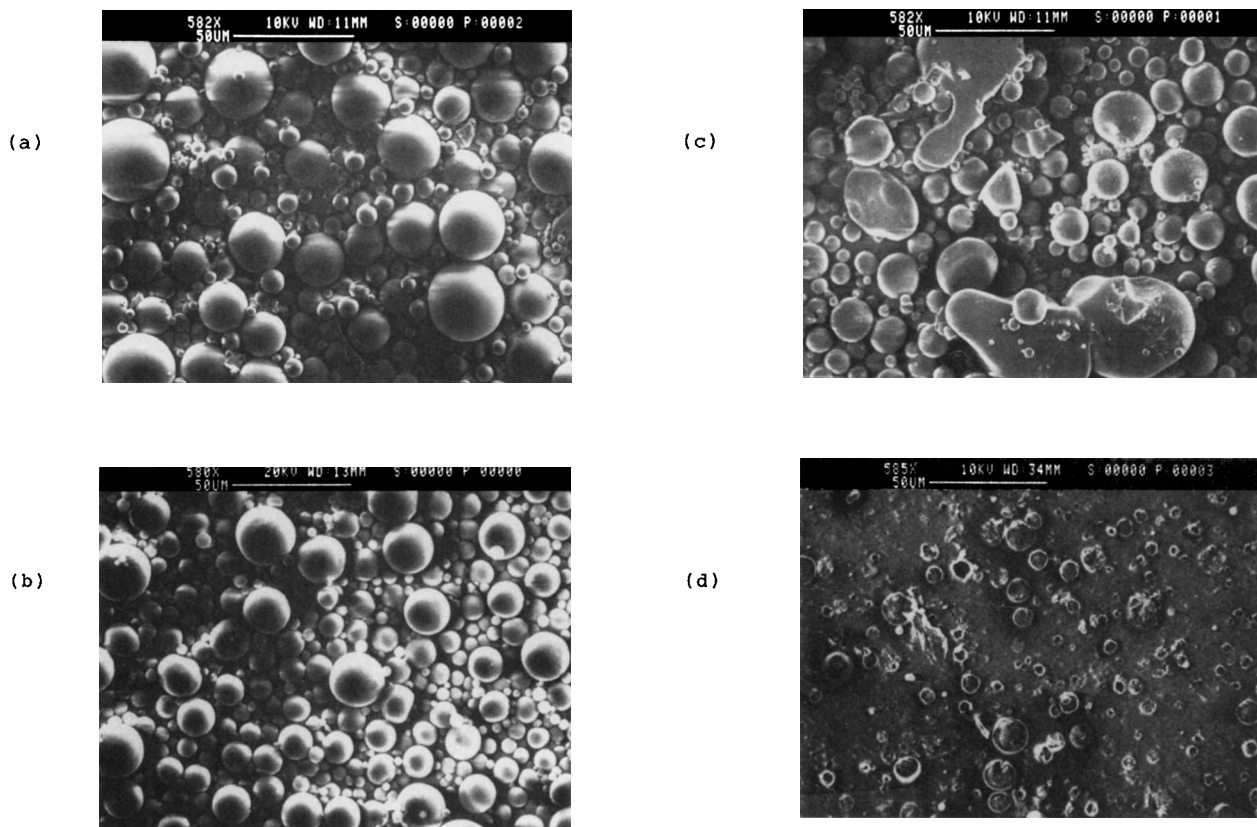


**Figure 2** Polymeric microspheres formed via irradiation of an emulsion system containing TMPPTA.

monomer concentrations had to be kept fairly low (about 5 vol %). The resulting product was quite disperse in size (see Fig. 2) and required extensive purification, which resulted in the production of a

large amount of byproduct (i.e., the reaction medium). As mentioned earlier, these difficulties were eliminated by developing a polyaphron system with TMPPTA incorporated into the dispersed phase.

Electron beam irradiation of the polyaphron samples did result in the creation of polymeric microspheres, but their formation was strongly dependent on the monomer concentration. Figure 3 (a-d) illustrates the effect of monomer concentration on the formation of microspheres. At monomer concentrations of 50 and 67 vol %, polymeric microspheres are produced with very little (if any) production of other geometric structures [see Fig. 3 (a) and (b)]. In addition, there does not appear to be any difference in the size distribution of particles between these two concentrations. However, as the monomer concentration is increased to 75%, the production of irregular fragments (in addition to microspheres) becomes significant [Fig. 3(c)]. In fact, at a monomer concentration of 90%, irradiation of the sample results in the formation of a continuous film [Fig. 3(d)]. Apparently, as the monomer concentration approaches 75% or higher, the



**Figure 3** Polymeric microspheres obtained by irradiation of a polyaphron system containing (a) 50%, (b) 67%, (c) 75%, and (d) 90% TMPPTA dispersed in an aqueous matrix.

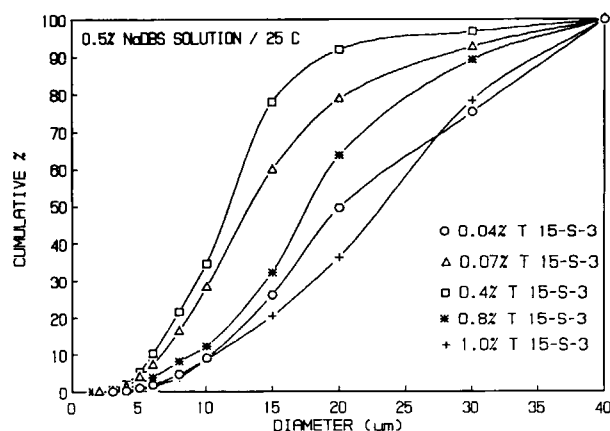
aphrons become so close to one another that the encapsulating soap film around the individual aphrons does not prevent monomer in one aphron from coalescing with monomer in neighboring aphrons, under the reaction conditions specified in this study. It should be noted that at a concentration of approximately 75% of the dispersed phase, Sebba<sup>5</sup> has reported that liquid aphrons begin to lose their spherical character and take on a polyhedral structure due to the close packing of aphrons. In light of this, the production of irregular fragments at a monomer concentration of 75% should become evident. Because of the lower yield of microspheres and an increase of undesirable structures created at this monomer concentration, all subsequent aphron samples to be discussed were produced using a monomer concentration of 67 vol %.

By varying the concentration of the monomer-phase surfactant, it is possible to change the size distribution of the resulting microspheres. Although the end points of the size distribution (i.e., the largest and smallest spheres produced) are not dramatically affected by the monomer-phase surfactant concentration, the relative distribution of particle sizes between the end points is significantly dependent on this variable (see Fig. 4). It should be noted that an error analysis was performed on the sample containing 1.0% Tergitol 15-S-3 in TMPPTA. The results show an overall average error of  $\pm 14\%$  for all data points greater than 10 cumulative %. Below this value, the percent error was somewhat greater, due to the small average value used in the calculations. This represents the error associated with both the aphron preparation and the size analysis. The

average error associated with the size analysis alone was determined to be  $\pm 12\%$ . Although this error analysis was performed on only one composition, it is indicative of the error associated with all the distributions shown.

As illustrated in Figure 4, varying the monomer-phase surfactant concentration from 0.04 to 1.0% results in a minimum average particle size at 0.4%. Increasing the surfactant concentration in the monomer phase from 0.04 to 0.4 vol % results in a significant decrease in the average particle size, which may be attributed to the Gibbs effect. The Gibbs effect applies to thin films or small volumes that contain a surfactant and can be described as follows: If a fixed volume of a liquid contains a surfactant and the surface area is increased (as in spreading), then surfactant molecules will move to the surface in accordance with the Gibbs adsorption isotherm and reduce the surface tension of this new surface. However, if the surfactant concentration becomes so low that the liquid surface already contains a significant portion of the total amount of surfactant, then there may not be enough surfactant available to reduce the surface tension of this new surface. The net effect is to produce a restoring force that resists further thinning of the liquid surface. Hence, as the surfactant concentration is increased, the monomer phase can form thinner films prior to breaking up and being encapsulated in the soap film, thus forming smaller aphrons. However, as the surfactant concentration is increased further (to 0.8 and 1.0 vol %), the average particle size increases.

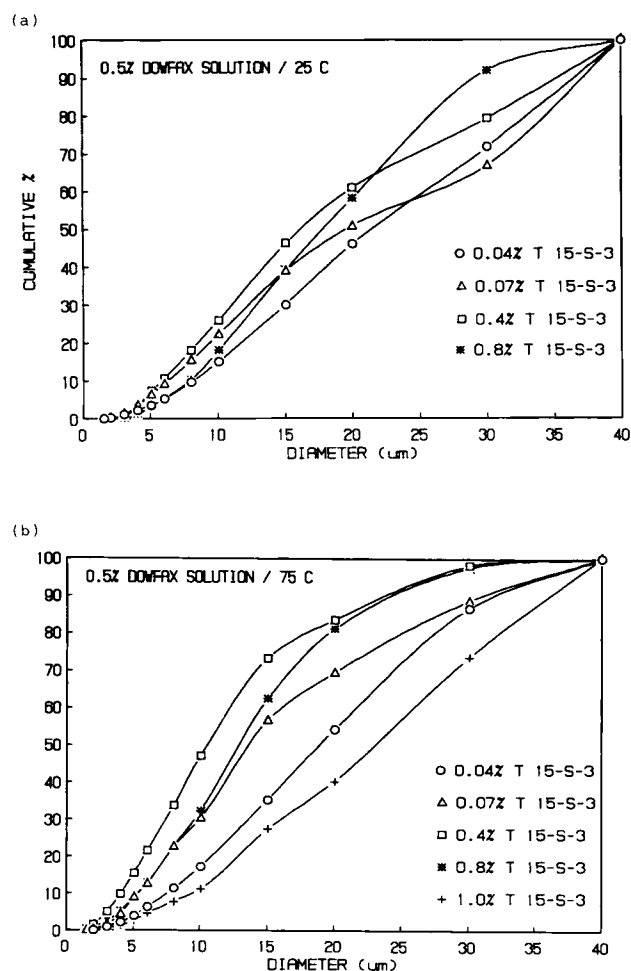
The increase in average particle size at the higher monomer-phase surfactant concentrations may have several origins. One possibility is that at high concentrations the surfactant may be forming complex micellar structures in the monomer phase that may be very stable and not break down readily as the surface area is increased. Thus, the surfactant molecules may not be able to diffuse to the surface, allowing the Gibbs effect to occur. A second possible explanation is related to the Marangoni effect. This effect is similar to the Gibbs effect except that it is not restricted to thin films. If a liquid contains a surfactant and its surface area is increased, this new surface area will have a greater surface tension than the surface that was already present. This is a non-equilibrium condition because the Gibbs adsorption isotherm requires that surfactant molecules must diffuse to the surface from the bulk to reduce the surface tension to its equilibrium value. Although this diffusion time is very small, the momentary increase in surface tension produces a restoring force preventing the extension of the surface, thus causing



**Figure 4** Effect of the Tergitol 15-S-3 concentration in TMPPTA on the particle-size distribution of microspheres formed at 25°C with a 0.5% NaDBS solution as the continuous phase.

a surface elasticity. If the concentration of the surfactant is very high, this diffusion time will be very small. Hence, the surface will have minimal elasticity, and the film may become unstable. This instability could cause the monomer film to break up and become encapsulated by the soap film before it is able to thin sufficiently, thus producing larger aphrons. A third possibility is that the high surfactant concentration produces a spreading coefficient that is substantially "out of balance" (as discussed earlier) with the spreading coefficient of the aqueous phase, thus causing inefficient formation of aphrons due to the hindered ability of the aqueous phase to spread over the monomer phase.

Figure 5 (a) illustrates the variation of the particle-size distribution with monomer-phase surfactant concentration for a series of polyaphrons formed using the Dowfax 2A1 aqueous surfactant.



**Figure 5** Effect of the Tergitol 15-S-3 concentration in TMPPTA on the particle-size distribution of microspheres formed at (a) 25°C and (b) 75°C with a 0.5% Dowfax 2A1 solution as the continuous phase.

Note that there is no apparent trend here with respect to particle-size distribution and the monomer-phase surfactant concentration (as was discussed previously for the polyaphron systems utilizing the NaDBS aqueous surfactant). This indicates that other factors may be present here that essentially override the ability of the monomer-phase surfactant concentration to control the resulting particle-size distribution. The reduced foamability of the Dowfax solution (compared to the NaDBS solution, see Table I) may account for this apparent lack of control. The Dowfax solution produces less aqueous surface area for the monomer to spread on, which may affect the aphron formation process. However, if the preparation temperature is increased to 75°C, the trends discussed with the systems containing the NaDBS solution is established [see Fig. 5(b)]. Table I shows that the main effect of the temperature increase is to reduce the viscosity and surface tension of the monomer phase. Both of these physical property changes will improve the ability of the monomer to spread, so the surface area produced with the Dowfax solution may now be sufficient for the Gibbs effect (or other effects previously discussed) to govern the aphron formation process.

These points lead one to consider the effects of the aqueous-phase surfactant type and concentration on particulate formation and properties. Figure 6 illustrates these effects on the particle-size distribution for a series of aphron systems formed at 75°C with a Tergitol 15-S-3 concentration of 0.07% in the monomer phase. An increase in the aqueous surfactant concentration increased the average particle size for both NaDBS and Dowfax 2A1 surfactants. Increasing the surfactant concentration produces a higher surface pressure on the aqueous film, which increases the resistance to spreading of the monomer film. This will produce a thicker monomer film, which will lead to the formation of larger aphrons when the film breaks up and becomes encapsulated in a thin soapy film. However, if the Tergitol 15-S-3 concentration is increased to 1.0%, the average particle size decreases with increasing aqueous-phase surfactant concentration. This trend reversal at high monomer-phase surfactant concentrations strongly supports the fact that a "balance" between the spreading coefficients (or spreading pressures) is necessary for the efficient production of small aphrons.

SEM analysis of the cross-linked particles has shown some differences among the shape of various microspheres that appears to be related to the aqueous-phase surfactant type. It should be noted that SEM sample preparation was facilitated by us-

**Table I** Some Physical Properties of the Surfactant Solutions Used in Aphron Preparation

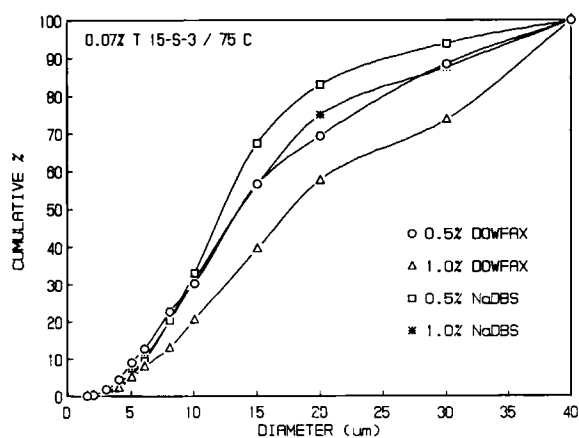
Material	Apparent Surface Tension (dyne/cm)		Viscosity (cps)		Foam Stability (vol %) <sup>a</sup>
	25°C	75°C	25°C	75°C	
TMPPTA (all Tergitol concentrations)	37	32	140	32	—
n0.5% NaDBS aqueous solution	33	32	—	—	25
0.5% Dowfax 2A1 aqueous solution	33	32	—	—	50

<sup>a</sup> Vol % of water drained in 20 s after foaming solution.

ing double-sided adhesive tape to secure the specimen to the SEM stub. Some microspheres may appear to be semicircular, where actually they are imbedded in the adhesive layer. Figure 7(a) and (b) shows SEM micrographs of polymeric microspheres formed with 0.5% Dowfax 2A1 and 0.5% NaDBS solutions, respectively, with equal concentrations of Tergitol 15-S-3 in the monomer phase. The micrographs show the presence of some indentations on the surface of the larger microspheres formed with the NaDBS solution. These distortions were not found on all the samples prepared from the NaDBS solution, but they were present to a much larger extent than were the microspheres produced with the Dowfax 2A1 solution. Sebba<sup>4</sup> has reported that increasing the ionic strength of the encapsulating film

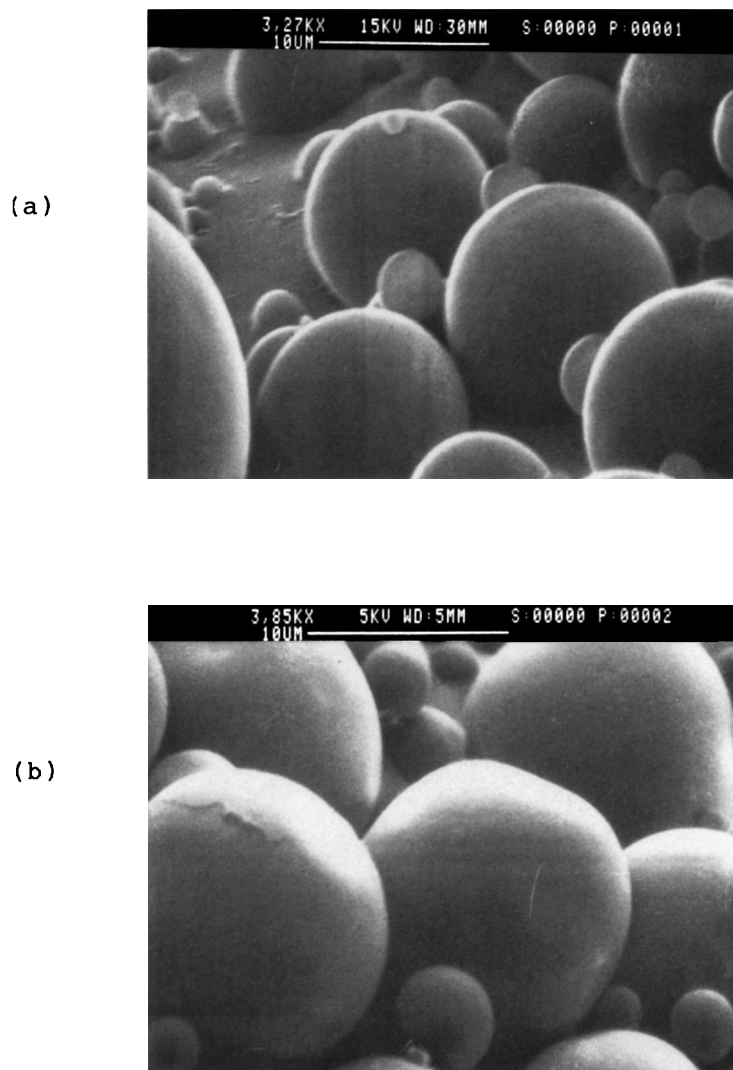
(i.e., by increasing the surfactant concentration or strength) increases the attractive forces between aphrons and the smaller aphrons will tend to adhere to the surface of larger aphrons and distort their sphericity. This is a likely cause of the surface distortions seen on the microspheres formed with the NaDBS solution. However, it is expected that some shrinkage of the monomer phase occurs during curing as a result of the polymerization through double-bond moieties. This shrinkage can induce stresses that may affect the curvature of the larger microspheres to a greater extent, due to the larger volume, but this does not account for the apparent surfactant-type dependence. Hence, we discount this latter explanation as the cause for the lack of particle sphericity.

As previously discussed, increasing the aphron preparation temperature produces a significant decrease in the monomer viscosity and surface tension, as well as a slight decrease in the surface tension of the aqueous solution. As illustrated in Figure 8, this temperature increase causes a decrease in the average particle size over the entire range of monomer-phase surfactant concentrations studied. The reasons for this should be obvious. A reduction in the monomer surface tension will promote more spreading since the surface energy is lower. The same holds true for the aqueous phase, but to a much lesser extent. A reduction in the monomer viscosity obviously promotes better spreading, but this will also reduce the diffusion time of the surfactant molecules to the surface as spreading occurs. This may cause the monomer film to become stable for a longer period of time (allowing for more film thinning) as the surfactant molecules become depleted from the



**Figure 6** Effect of the aqueous-phase surfactant type and concentration on the size distribution of microspheres formed at 25°C with 0.07% Tergitol 15-S-3 in TMPPTA.



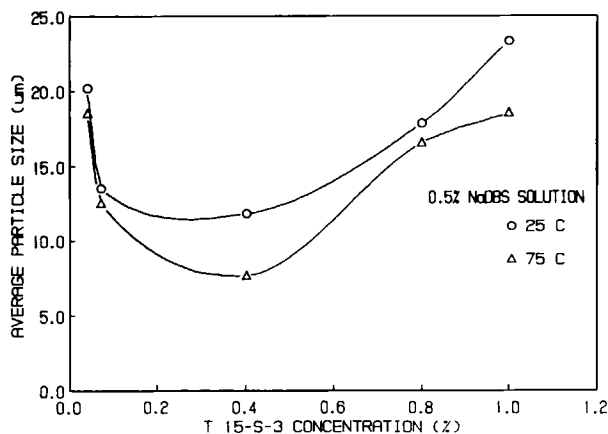


**Figure 7** SEM micrographs depicting the effect of the aqueous-phase surfactant type on the shape of the resulting microspheres.

bulk and the diffusion paths (or diffusion times) become longer. It should be noted from Figure 8 that the reduction in particle size with increasing temperature appears to be dependent on the monomer-phase surfactant concentration. The reasons for this are not entirely clear, but it may be related to the relative balance of spreading coefficients that exists in each system and the extent to which temperature may affect this condition.

Since the objective of this investigation has been to gain an understanding of the conditions that promote the production of small polymeric micro-

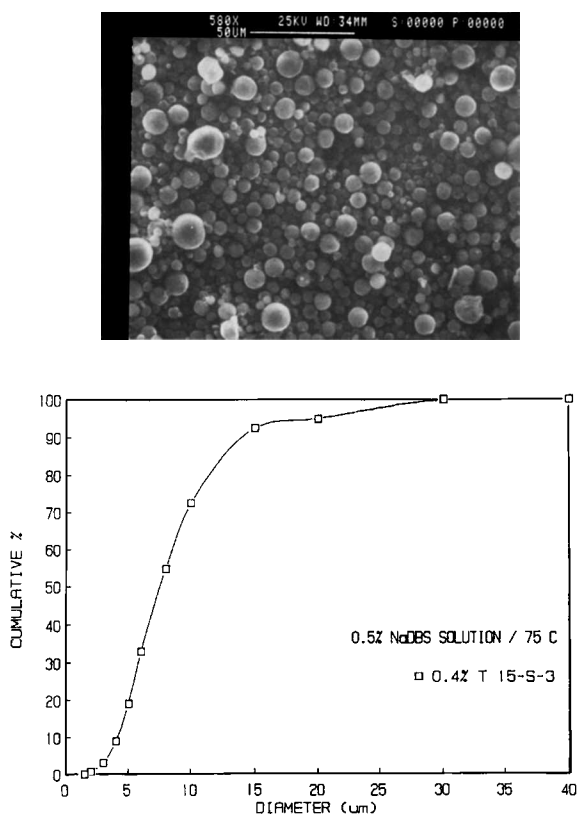
spheres with a narrow size distribution, it is worthy to highlight the best and worst cases found in this respect. Figure 9 shows the SEM micrograph and particle-size distribution for the smallest polymeric microspheres obtained in this study. The average particle size is approximately 7 microns with 90% of the particles between 3 and 18 microns. Although this is not an extremely narrow size distribution, it is a significant improvement over many of the samples obtained in this study and it does illustrate which conditions decrease the dispersity of the size distribution. These microspheres were produced us-



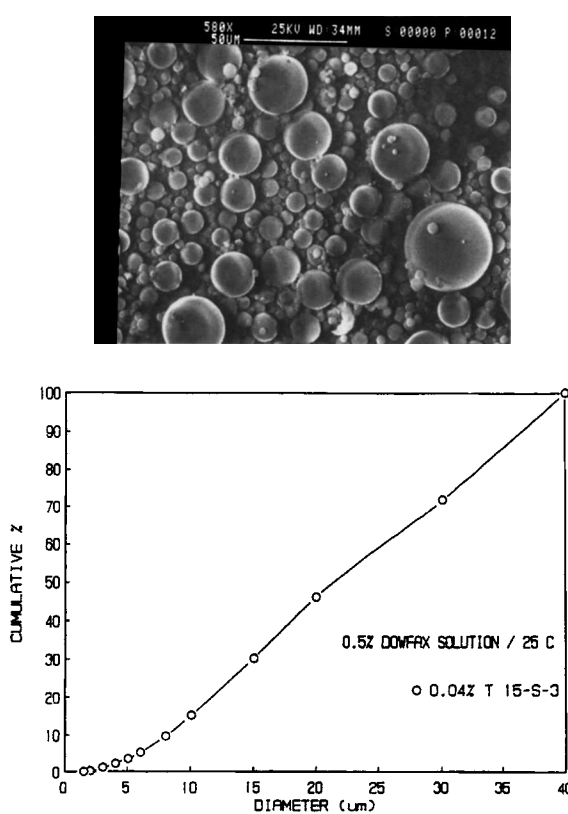
**Figure 8** Effect of aphron formation temperature on the average particle size of microspheres formed with varying amounts of Tergitol 15-S-3 in TMPPTA.

ing 0.4% Tergitol 15-S-3 in TMPPTA and a 0.5% NaDBS aqueous solution prepared at 75°C. Figure 10 depicts one of the worst cases. The microspheres

in Figure 10 have an average particle size of 24 microns with 90% of the particles between 5 and 38 microns. These particles were formed at 25°C with 0.04% Tergitol 15-S-3 in TMPPTA and the 0.5% Dowfax 2A1 aqueous solution. In contrast, a similar “worst case” was obtained by forming microspheres at 25°C with 1.0% Tergitol 15-S-3 in TMPPTA and a 0.5% NaDBS aqueous solution. The average size of these microspheres was 23 microns with 90% of the particles between 7 and 40 microns. These best and worst cases illustrate some of the conditions that will promote (and hinder) the production of polymeric microspheres with a narrow size distribution. The best case illustrates that a higher preparation temperature facilitates a narrower distribution. The two worst cases further support the need for a delicate balance between the surfactant concentrations in both phases: Either too much or too little surfactant in the monomer phase can have a detrimental effect on the production of small microspheres with a narrow size distribution.



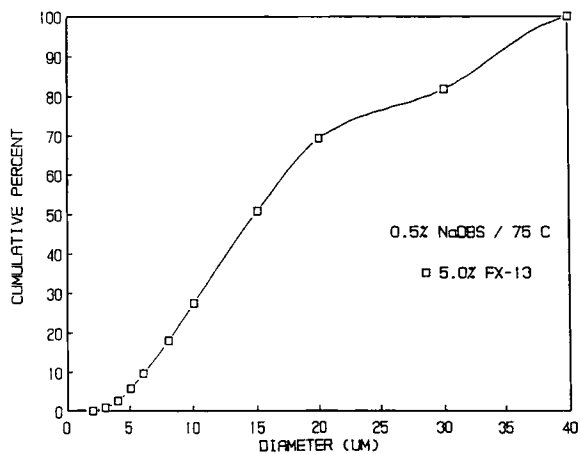
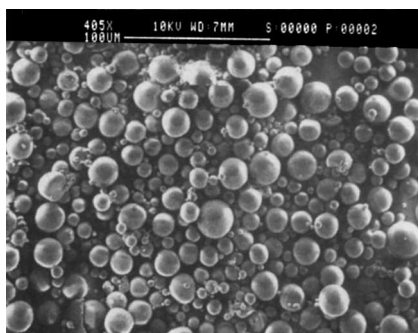
**Figure 9** SEM micrograph and particle-size distribution of microspheres obtained from irradiation of a polyaphron system formed at 75°C with 0.4% Tergitol 15-S-3 in TMPPTA and a 0.5% NaDBS aqueous solution (a “best case”).



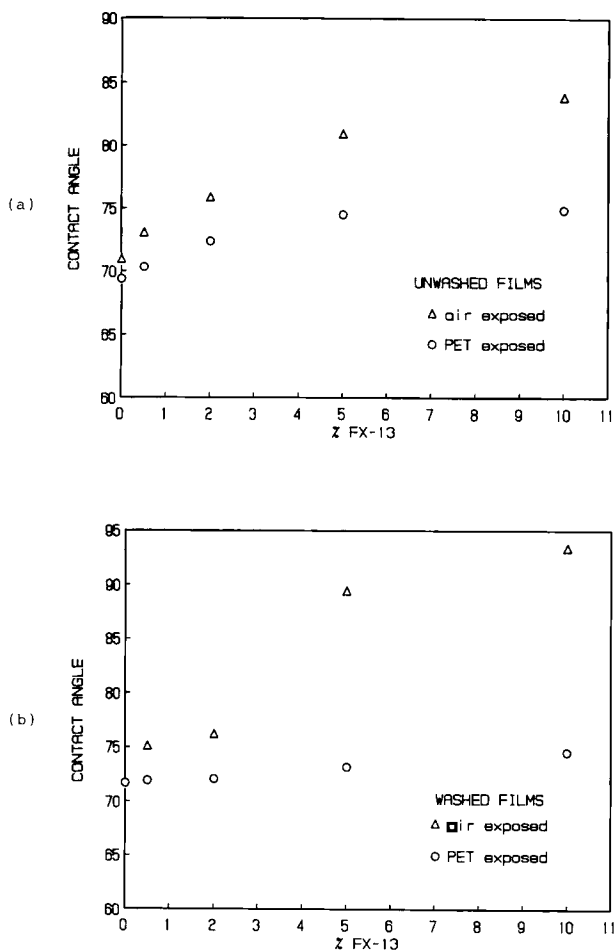
**Figure 10** SEM micrograph and particle-size distribution of microspheres obtained from irradiation of a polyaphron system formed at 25°C with 0.04% Tergitol 15-S-3 in TMPPTA and a 0.5% Dowfax 2A1 aqueous solution (a “worst case”).

**Surface Modification via a Fluorinated Acrylate Surfactant**

The process scheme that has been discussed here has also been modified to produce microspheres with reduced wettability. The only change necessary is the substitution of FX-13 for Tergitol 15-S-3 in the monomer phase. Figure 11 shows the resulting product with 5.0% FX-13 in TMPPTA with a 0.5% NaDBS solution as the continuous phase that was prepared at 75°C. It was possible, however, to produce microspheres with as little as 0.5% FX-13 in the monomer phase. To analyze the relative wettability of these particles, a series of isopropanol-water solutions were prepared to determine the maximum liquid surface tension that would wet the particles (see Experimental section for details). The particles containing the Tergitol 15-S-3 surfactant sank into a solution of pure water; the particles produced with 5.0% FX-13 remained on a water surface for several days. A solution of 12% isopropanol in water was needed for these particles to sink into the mixture and become wetted.



**Figure 11** SEM micrograph and particle-size distribution of microspheres obtained from irradiation of a polyaphron system formed at 75°C with 5.0% FX-13 in TMPPTA and a 0.5% NaDBS aqueous solution.



**Figure 12** Effect of the FX-13 concentration on the advancing contact angle of water on TMPPTA films (a) before and (b) after washing in acetone.

As a supplement to the wettability study on the microspheres, thin films were prepared with concentrations of FX-13 ranging from 0% to 10% in TMPPTA for contact-angle measurements. Figure 12(a) and (b) shows the effect of FX-13 concentration on the advancing contact angle of distilled, deionized water on the TMPPTA film. Results for both the TMPPTA-air and TMPPTA-substrate (PET) interfacial surfaces (during curing) both before [Fig. 12(a)] and after washing [Fig. 12(b)] in acetone are given. The trend shows increasing contact angle with increasing FX-13 concentration; however, there are some differences between the two surfaces. First, the side of the film exposed to the atmosphere during curing has a higher contact angle than does the side exposed to the PET substrate. This is in accord with the results obtained by Torstensson et al.<sup>6</sup> who reported information regarding various thin films modified with fluorinated acrylate

surfactants. Torstensson et al. proposed that this is due to the preferential adsorption of the surfactant toward the less polar phase (i.e., air) since this is more energetically favorable than is adsorption toward the PET surface. Also note that at a concentration of 0.5% FX-13 has no effect on the contact angle at the PET-exposed surface. This also was reported by Torstensson et al., which indicates that at low concentrations the hydrophobic moiety of FX-13 is even less compatible with the PET substrate than with the bulk TMPPTA, thus preferentially desorbing at the PET-TMPPTA interface. Another interesting point is the effect of the acetone wash, which seems to cause an increase in the advancing contact angle, even when no FX-13 is present. This may suggest that the acetone wash causes a reduction in the surface energy of the film, thus increasing the contact angle.

### Analysis of Material Properties

Several techniques were utilized to obtain information on the modulus, glass transition behavior, and extent of cure of the irradiated material: differ-

ential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and FT-IR spectroscopy. These analyses were done at least 1 week after curing to reduce the possibility of trapped free radicals reacting as the sample is heated, which can cause a broadening of the glass transition range.<sup>7,8</sup> The results from DSC show a wide glass transition range somewhat above room temperature, as illustrated in Figure 13. A glass transition beginning slightly above room temperature may indicate that vitrification occurred in this system during curing. As a network is formed by cross-linking reactions, in this case, principally through the polymerization of double bonds, the glass transition temperature of the material increases as a result of an increase in the cross-link density. If the glass transition temperature reaches the reaction temperature, the polymerizable units lose mobility and are unable to react due to this restriction. If this occurs before the reaction has reached completion, a certain amount of sol fraction will be left in the network, which can be detrimental to the physical properties of the material. If the material formed is a rubbery network, this is of no concern since the glass transition tem-

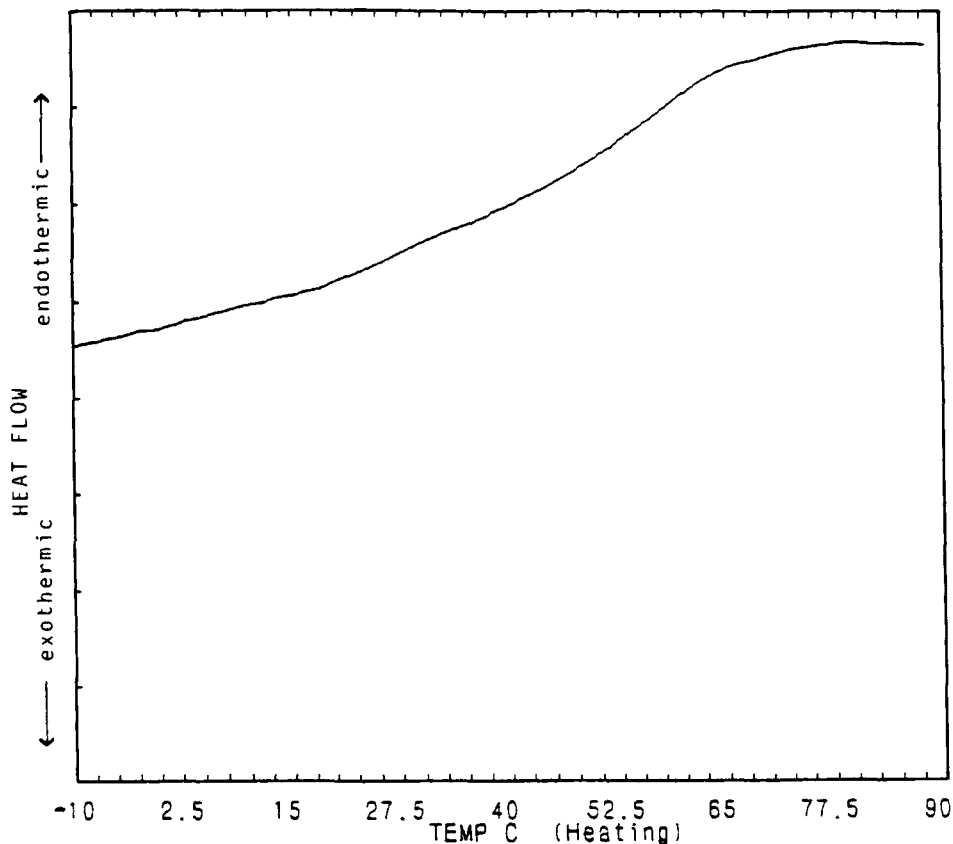


Figure 13 DSC scan of TMPPTA with a heating rate of 15°C/min.

perature will not ever reach the reaction temperature. However, TMPPTA forms a glassy network, so there is a strong possibility that vitrification will occur. Although the material was cured at room temperature, heat effects from the electron beam radiation will heat the reaction medium, which accounts for a glass transition somewhat above room temperature. Gillham et al.<sup>9,10</sup> have described this phenomena in terms of a time-temperature-transformation (TTT) diagram that graphically illustrates the physical state of a reactive polymeric medium as a function of time and reaction temperature. More recently, Kim and Wilkes<sup>11</sup> extended this treatment for electron beam initiated systems in terms of a time-temperature-energy (TTE) diagram. The TTE diagram describes the physical state of a cross-linking network in terms of the reaction temperature, time, and energy imparted to the system from the electron beam radiation. Graphical interpretation of these diagrams show that vitrification will indeed occur if the reaction temperature is below the glass transition temperature associated with the completely reacted system, as previously discussed.

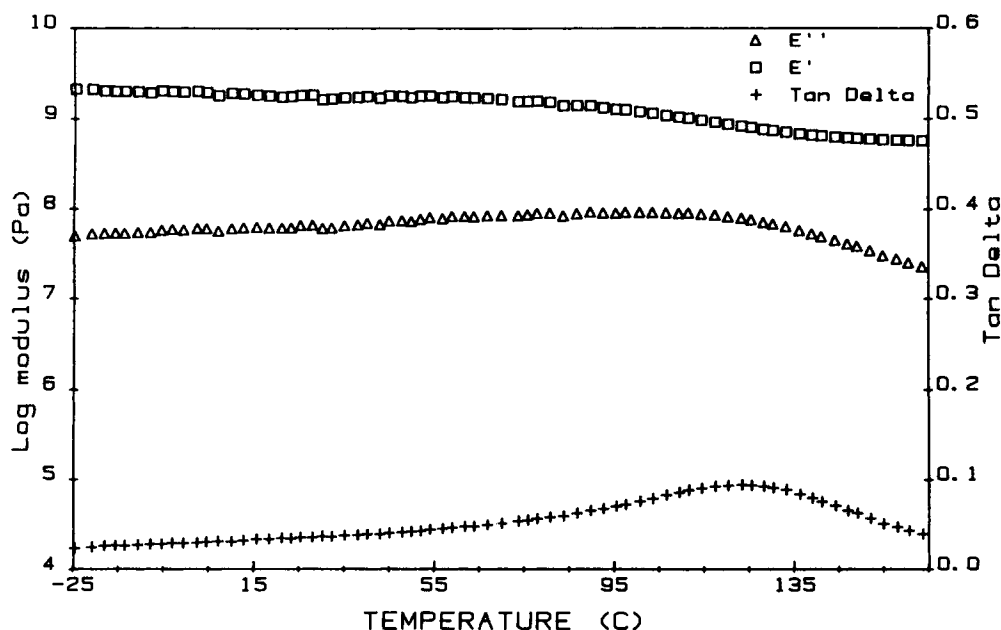
The DMA results show the onset of the glass transition at approximately 40°C (see Fig. 14), which is in agreement with the DSC results. However, the DMA results indicate a broader transition, with a maximum in the tan delta peak at about 125°C. The modulus decreases slightly over this temperature range, from about 2.00 GPa to about

0.63 GPa, which is to be expected for a highly cross-linked material.

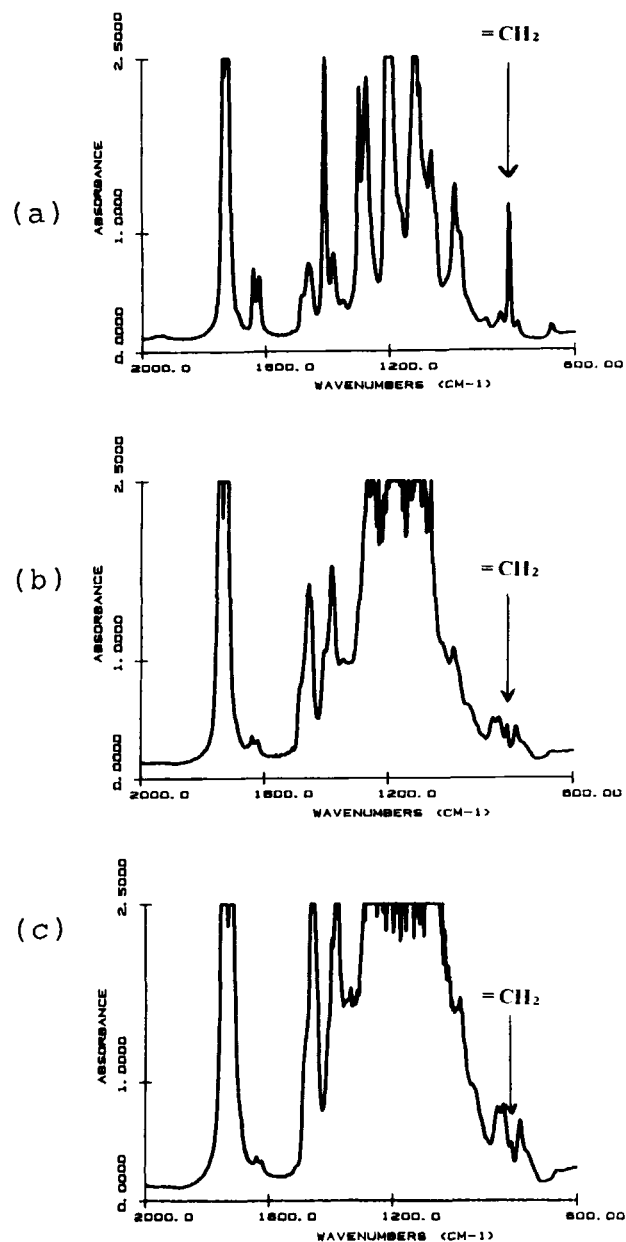
To confirm the possibility of vitrification occurring, FT-IR spectroscopy was used to determine the residual double-bond content. Comparison of the normalized double-bonded methylene peak at 810  $\text{cm}^{-1}$  (normalized against the peak at 3550  $\text{cm}^{-1}$ , which remained unchanged during irradiation) between the monomer and the film irradiated at 25°C show a residual double-bond content of approximately 15% [see Fig. 15(a) and (b)]. This gives further evidence that vitrification did indeed occur. To ensure that this was not simply the minimum attainable residual double-bond content, FT-IR was carried out on a thin film irradiated at 50°C [see Fig. 15(c)]. The residual double-bond content for this sample was approximately 9%, indicating that vitrification did occur in the sample cured at room temperature. However, no sol percentage could be extracted from the irradiated material, so it is likely that the residual double bonds are only present as dangling ends in the cross-linked network.

## SUMMARY AND CONCLUSIONS

This work has illustrated the successful incorporation of TMPPTA into a polyaphron system for the production of cross-linked polymeric microspheres



**Figure 14** DMA of a TMPPTA film with a frequency of 11 Hz and a heating rate of 2°C/min.



**Figure 15** FT-IR spectra of TMPPTA (a) monomer, (b) film cured at 25°C, and (c) film cured at 50°C with a 4 Mrad dose.

using electron beam radiation. Spherical particulate formation is facilitated at a solids content as high as 67 vol %, with complete conversion and no agitation necessary. There are several parameters that

affect the particle-size distribution that include preparation temperature, the relative concentrations of the monomer- and aqueous-phase surfactants, and the aqueous-phase surfactant type. It is also possible to form polymeric particulates with reduced wettability by utilizing a polymerizable surfactant in the monomer phase. These microspheres are glassy materials at room temperature that contain a small amount of unreacted double bonds, due to vitrification occurring during the curing process. However, there is no soluble fraction that can be extracted from the irradiated material, indicating that conversion is nearly complete.

The financial support of 3M Corporation for this work is gratefully acknowledged. The authors would also like to thank Dr. James Wightman for his helpful discussions.

## REFERENCES

1. I. Piirma, *Emulsion Polymerization*, Academic Press, New York, 1982.
2. M. Yoshida, M. Asano, J. Katsu, and Y. Morita, *Radiat. Phys. Chem.*, **30**, 39 (1987).
3. A. Rembaum, R. C. K. Yen, D. H. Kempner, and J. Ugelstad, *J. Immunol. Methods*, **52**, 341 (1982).
4. F. Sebba, *Foams and Biliquid Foams-Aphrons*, Wiley, New York, 1987.
5. F. Sebba, *Chem. Indust.*, **10**, 367 (1984).
6. M. Torstensson, B. Ranby, and A. Hult, *Macromolecules*, **23**, 126 (1990).
7. D. Thompson, J. H. Song, and G. L. Wilkes, *J. Appl. Polym. Sci.*, **34**, 1063 (1987).
8. H.-C. Kim, Ph.D. Dissertation, Virginia Polytechnic Institute and State University, Department of Chemical Engineering (1989).
9. X. Peng and J. K. Gillham, *J. Appl. Polym. Sci.*, **30**, 4685 (1985).
10. C. C. Chan and J. K. Gillham, *J. Appl. Polym. Sci.*, **29**, 3307 (1984).
11. H.-C. Kim and G. L. Wilkes, *Polym. Prepr.*, **30**, 250 (1989).

Received December 10, 1990

Accepted December 20, 1990