Poly(divinylbenzene-*alt*-maleic anhydride) Microgels: Intermediates to Microspheres and Macrogels in Cross-Linking Copolymerization

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ABSTRACT: Three distinct copolymer morphologies were observed during the cross-linking copolymerization of divinylbenzene-55 and maleic anhydride at low monomer concentrations in methyl ethyl ketone/heptane mixtures: microspheres, microgels, and macrogels. These morphologies depended primarily upon solvent composition and changed from microspheres and microgels to macrogels with increasing methyl ethyl ketone volume fractions. The effects of solvent composition and cross-linker concentration on the observed morphologies were investigated using electron microscopy, viscosity, and light scattering experiments. Microgels were found to be precursors to both macrogels and microspheres, and mechanisms for the formation of each morphology are proposed.

Introduction

Since the 1970s, interest in polymer microgels has grown dramatically in both the scientific and industrial communities due to their interesting properties. Microgels are a unique type of polymer that are considered intermediate to branched polymers and macroscopic polymer networks.[1] Specifically, Funke et al. defined microgels as intramolecularly cross-linked polymer molecules with a globular structure in the colloidal size range (10−1000 nm).[2]

Historically, the earliest reports of polymer microgels described them as precursors to macroscopic polymer networks. However, the best known example of these cross-linked polymer molecules was reported by Staudinger in 1934 where they were observed as a byproduct of the solution polymerization of styrene that contained small amounts of divinylbenzene as an impurity.[3] Subsequently, Staudinger showed that it was possible to prepare divinylbenzene microgels by dilute solution polymerization of divinylbenzene in good solvents such as benzene.[4]

Initially considered a problem in solution copolymerization, microgels were recognized to have useful properties, which include lower solution viscosity than their linear counterparts, and excellent film-forming properties. The surface coatings industry soon incorporated microgels into their formulations to increase solids loading while reducing solvent emissions and maintaining viscosity. With regards to film formation, microgels have been shown to produce less brittle films than cross-linked linear polymers without affecting desirable film properties like gloss and durability.[2,5]

From an academic standpoint, polymer microgels offer a convenient route to the study of polymer networks. The internal structure of microgels is similar to that of macroscopic networks and so reflect their properties, especially their swelling behavior which can be determined using classical methods such as light scattering. In addition, microgels are much easier to purify than macroscopic gels, using conventional precipitation techniques.

Microgels are typically prepared by one of two routes: dilute solution polymerization, as in the case of Staudinger, and emulsion (or microemulsion) polymerization. Dilute solution polymerization can produce microgels because the probability of intramolecular cross-linking and cyclization are increased at high dilution, as described by the Ziegler dilution law, while intermolecular reactions are inhibited. Emulsion polymerization, on the other hand, can lead to microgels because the polymerization takes place in the restricted volume of the surfactant micelles, thereby preventing macrogelation. Antonietti categorized these two classes of microgels as type A (dilute solution) and type B (emulsion) microgels.[6] In addition to these classical examples, newer techniques to prepare microgels have been reported that involve anionic polymerization,[7−9] end-linking of polymer chains,[10,11] and step-growth cross-linking reactions.[12,13]

Our interest in microgels stems from our earlier study of the preparation of copolymer microspheres by precipitation polymerization of divinylbenzene-55 (DVB-55), either by itself[14−16] or with maleic anhydride (MAn).[17,18] In these precipitation polymerizations, the reaction mixture is initially a homogeneous solution of monomer and initiator. As the reaction proceeds, the polymer formed becomes insoluble and precipitates from solution. In contrast to classical precipitation polymerizations that result in polydisperse, irregular particles and aggregates, the use of low monomer loadings together with marginal solvents led to narrow disperse, polymer microspheres in the micron and submicron size range. During our DVB-55/MAn study, some reactions resulted in low-viscosity, opalescent microgel dispersions. Apparently, the solvency in these cases was too high to permit the internal phase separation necessary to produce microspheres. These microgels proved to be interesting new functional materials that may also provide further insight into precipitation copolymerizations.

To better understand the driving forces for the polymerization-induced precipitation of polymers, the basic thermodynamics of these system must be considered. Precipitation and solution polymerization both start as homogeneous mixtures of monomers in suitable solvents but differ mainly in the fate of the forming polymer. Gibb's free energy of mixing **(**1**)** may be used to describe

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the ability of the forming polymer to remain in solution.

$$\Delta G_{\mathrm{mix}} = \Delta H_{\mathrm{mix}} - T\Delta S_{\mathrm{mix}} \tag{1}$$

Here, there are two contributions to the dissolution of polymer chains: an enthalpic term and an entropic term. Classical precipitation polymerizations involve monofunctional monomers that are soluble in the reaction solvent while the newly formed polymer is not. This polymer desolvates because polymer–polymer interactions are more favorable than polymer–solvent interactions; i.e., ΔH_{mix} is large, and hence ΔG_{mix} is positive. Accordingly, this process can be described as enthalpic desolvation. The second driving force for desolvation is described by the entropy term in **(1)**. In the case of polymerization reactions that include cross-linking monomers, entropic desolvation can occur due to the cross-linking reaction itself. Cross-linking causes a large decrease in the entropy of mixing in a system of this type, which can again lead to a positive ΔG_{mix} and thus cause polymer precipitation.

This paper reports our study of the effects of solvent composition (enthalpic desolvation), cross-linker concentration (entropic desolvation), and monomer loading on the morphology of the products of the cross-linking copolymerization of divinylbenzene and maleic anhydride, with emphasis on microgel formation and the transitions between the three morphologies observed.

Experimental Section

Materials. Maleic anhydride (MAn, 99%, Aldrich) was recrystallized from chloroform prior to use. Divinylbenzene (DVB-55, 55% mixture of isomers, technical grade, Aldrich) was used as received. The cosolvents, methyl ethyl ketone (MEK) and heptane (Hp), were both reagent grade and used as received from Caledon Laboratories. 2,2′-Azobis(isobutyronitrile) (AIBN, Eastman Kodak) was also used without further purification.

Synthesis. A typical procedure for the preparation of DVB/MAn microspheres/microgels was as follows:

Maleic anhydride (0.40 g, 4.1 mmol) was dissolved in 16 mL of MEK in a 25 mL scintillation vial. After dissolution of the maleic anhydride, 4 mL of heptane and 0.36 g (4.3 mmol of vinyl groups) of DVB-55 were added. The vial was placed on a set of heated horizontal stainless steel rollers contained in a thermostatically controlled polymerization reactor set to 70 °C, and the vial was rolled at a rate of 5 rpm for 24 h.

Purification. Sol/gel separation, in the case of microspheres and microgels, was carried out by repeated washing/centrifugation steps using MEK as the wash solvent. Particle and polymer yields were determined gravimetrically.

Characterization. a. Electron Microscopy. Transmission electron microscopy (TEM) samples were prepared by diluting the reaction mixtures with a 20-fold excess of MEK and placing a drop of the resulting dispersion onto a carbon-film-coated 200 mesh copper grid. The grids were allowed to air-dry, and images were obtained on a Philips CM12 transmission electron microscope.

Sample solutions for environmental scanning electron microscopy (ESEM) were prepared in the same manner as for TEM. Aluminum ESEM stubs were modified by adhering a small piece of a glass microscope coverslip to the stub using double-sided adhesive tape. A drop of the diluted sample solution was placed on the glass surface and allowed to air-dry. The stubs were sputter-coated with an 8 nm gold film to ensure conductivity and the samples were then imaged on a Philips Electroscan 2020 environmental scanning electron microscope.

b. Particle Sizing. Particle sizing was carried out in MEK using a Coulter LS230 particle sizer which operates on the principles of Fraunhofer diffraction for large particles (>0.4 μm) and polarization intensity differential scattering (PIDS) for small particles (<0.4–0.8 μm).

c. Viscosity. Dilute solution viscosity measurements were carried out using an Ubbelohde-type viscometer in a temperature-controlled water bath held at 25 °C. A series of solutions were prepared for each sample ranging in concentration from approximately 0.1 to 0.001 g/dL.

Results and Discussion

A. Reaction Solvent Effect on Product Morphology. In our earlier work on the precipitation copolymerization of divinylbenzene-55 and maleic anhydride to prepare copolymer microspheres, mixtures of a good solvent, methyl ethyl ketone ($\delta = 19.0$ MPa$^{1/2}$), and a poor solvent, heptane ($\delta = 15.1$ MPa$^{1/2}$), were employed, allowing the reaction solvency to be adjusted by varying the ratio of the two solvents. In that study, four distinct copolymer morphologies were observed as a function of solvent composition: coagulum, microspheres, macrogels, and microgels. Coagulum was formed under the poorest solvency conditions, at less than 20 vol % MEK in the solvent mixture. Macrogels (space-filling gels) were formed under the best solvency conditions, at MEK levels of greater than 95 vol %. Microspheres and microgels were formed at intermediate MEK concentrations of approximately 40 vol % MEK and 80 vol % MEK, respectively.

We observed earlier that the size of the DVB-55/MAn microspheres decreased with increasing proportions of MEK. It appeared that microgels were formed at greater than about 50 vol % MEK. However, it was not clear whether this involved a smooth transition from the microsphere to the microgel morphology or whether a critical solvency condition led to a sharp change in polymer network solvation and hence the observed change in morphology. One of the goals of the present study was to accurately identify the conditions under which the transitions from microspheres to microgels and from microgels to macrogel took place.

The Microsphere to Microgel Transition. Figure 1 shows a series of transmission electron microscopy (TEM) images of DVB-55/MAn copolymer particles prepared in MEK/Hp mixtures with the MEK concentrations increasing from 40 to 80 vol %. The transition from hard, spherical particles to soft, irregular microgels is clearly visible in these images.

All the copolymerizations were carried out at a constant total monomer loading of 4% (w/v) and typically gave polymer yields of greater than 95%. Parts a, b and c of Figure 1 show microspheres in the 0.1–0.5 μm diameter range, formed in 40, 50, and 60 vol % MEK, respectively. The smaller microgel particles in Figure 1d,e, formed in 70 and 80 vol % MEK, appear to be connected by thin copolymer strands, reflecting the significant swellability of these microgel products.

Figure 2 shows the dry particle diameters as measured by TEM as well as the swollen diameters of the same particles dispersed in neat MEK measured by light scattering on a Coulter LS230. While the samples prepared in 70 vol % MEK still retain a semispherical shape in the TEM images, the microgels formed in 80 vol % MEK were clearly nonspherical when dried, and consequently, diameters from TEM were only estimated for this sample.

Both the diameters for dry and swollen particles showed a dramatic decrease with increasing solvency of the polymerization medium, corresponding to the transition from the microsphere to microgel morphology

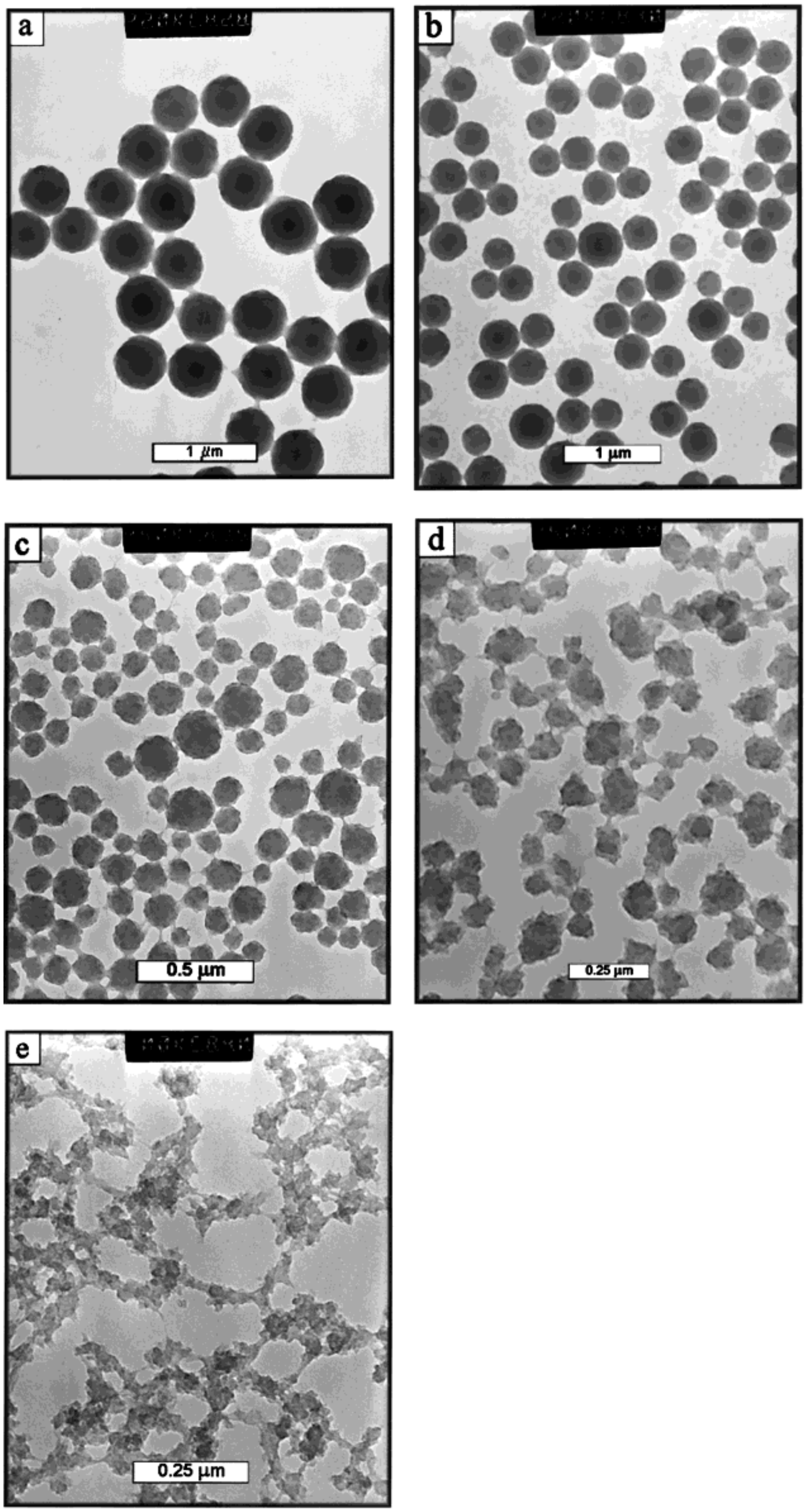

Figure 1. TEM images demonstrating the effect of reaction solvency on DVB-55/MAn copolymerization products: (a) 40% MEK/60% heptane, (b) 50% MEK/50% heptane, (c) 60% MEK/40% heptane, (d) 70% MEK/30% heptane, (e) 80% MEK/20% heptane.

between 40 and 60 vol % MEK. This transition is likely caused by increased solvation of the growing oligomeric species, inhibiting cross-linking and also preventing entropy-driven phase separation.

The Microgel to Macrogel Transition. At approximately 95 vol % MEK, we observed the transition from microgels to macroscopic gels. However, this transition could not be easily studied using the techniques we have discussed previously. In particular, electron microscopy became more difficult since the resulting macroscopic gels and their immediate precursors tend to be homogeneous and hence show little contrast. Consequently, dilute solution viscosity was used to study this transition. Figure 3 shows the viscometric results obtained for a series of DVB-55/MAn microgels which were prepared at different levels of MEK, as indicated in the figure. The viscosity measurements themselves were carried out in neat MEK, and the data are displayed as Huggins plots. The Huggins equation (2) relates the reduced viscosity of a polymer

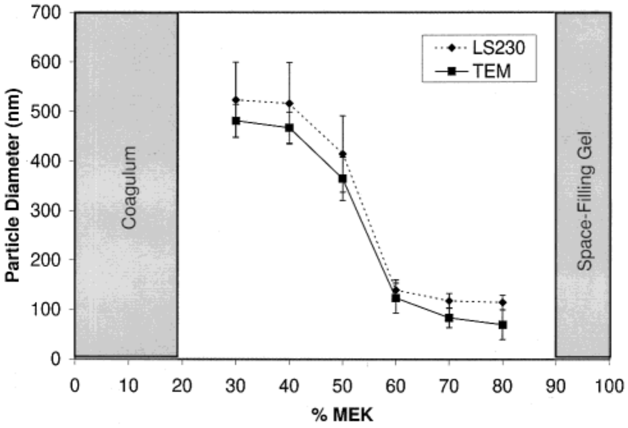

Figure 2. Effect of reaction solvency on particle diameter for DVB-55/MAn reactions as determined by TEM and LS230.

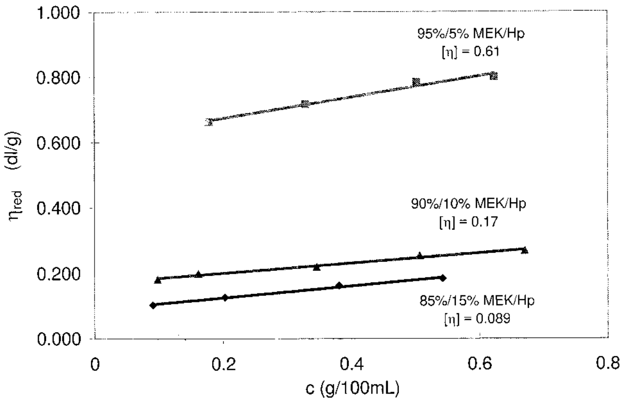

Figure 3. Viscometric behavior of DVB-55/MAn microgels prepared in 85%, 90%, and 95% MEK (Huggins plots).

solution, η_{red}, to both the intrinsic viscosity, $[\eta]$, of the polymer and its concentration, c.

$$\eta_{\text{red}} = \frac{1}{c}\left(\frac{\eta}{\eta_0} - 1\right) = \frac{1}{c}\left(\frac{t}{t_0} - 1\right) = [\eta] + k_{\text{H}}[\eta]^2 c \quad (2)$$

For dilute solutions, the ratio of the viscosity of the polymer solution and the pure solvent, η and η_0, respectively, is approximated by the ratio of the flow time of each liquid in the viscometer, t and t_0. The constant k_{H}, termed the Huggins coefficient, is typically around 0.3 for linear polymers in good solvents. This term can be affected by a variety of conditions including solvency, branching, and the width of the molecular weight distribution.[19] When viscometric methods are applied to the present system, they clearly demonstrate the onset of macrogelation, which is observed as a large increase in the intrinsic viscosity for microgels prepared in 95 vol % MEK, the immediate precursors to macrogels. This increase in viscosity is caused by intermolecular cross-link formation between microgels, resulting in a dramatic increase in the molecular weight of these species. Good solvency conditions, i.e., more than 85% MEK, has a 2-fold effect on the growing microgels. First, the swelling of the microgels is increased, which reduces the distance between the dispersed microgels, enhancing intermolecular reactions. Second, better solvency further reduces the cross-linking efficiency, which also leads to a higher degree of swelling. These effects cause the microgels to exceed the critical overlap conditions described by DeGennes,[20] resulting in intermolecular reactions with other microgels that lead to macrogelation. Of note here is the absence of the so-called "excluded volume effect" which has been used to describe the suppression of macrogelation under near ideal solvency conditions.[21] In such cases, microgels are formed even under the best solvency conditions, while macrogelation resulted in slightly poorer solvents. This phenomenon was explained by the fact that intermolecular cross-linking reactions require the displacement of neighboring solvent molecules from the vicinity of the microgels which is more difficult when polymer−solvent interactions are strong. The absence of this effect in the DVB-55/MAn system suggests that neat MEK, although a good solvent, is not an ideal solvent for the copolymer. To determine the validity of this statement, the δ-parameter, or Hildebrand parameter, has been used to estimate the polymer/solvent interactions. A good solvent for a particular polymer typically has a comparable δ-parameter, within about 4 MPa$^{1/2}$.[22] Using group contribution theory, the δ-parameter for styrene−maleic anhydride copolymer was calculated to be approximately 26 MPa$^{1/2}$.[23] Compared to the δ-parameter for MEK of 19.0 MPa$^{1/2}$, the difference of 6 MPa$^{1/2}$ suggests that MEK is, as expected, not an ideal solvent for the copolymer.

B. Cross-Linking Effects on Polymer Morphology. As mentioned previously, we expected that increasing the MEK content of the reaction mixture would decrease the efficiency of the cross-linking reaction. In an attempt to separate the effects of solvency and cross-linking, we carried out copolymerizations at constant solvent compositions but with varying DVB cross-linker concentrations. The cross-linker concentration was adjusted by using 4-methylstyrene as a monovinyl diluent for DVB-55 such that mixtures containing from 5 to 36 mol % DVB, referred to as DVB-5, DVB-11, DVB-24, and DVB-36 hereafter, were prepared and copolymerized with maleic anhydride.

Two solvent mixtures were chosen for this study, 40 vol % MEK/60 vol % Hp (microsphere domain) and 80 vol % MEK/20 vol % Hp (microgel domain). It was expected that varying the cross-linker concentration in each of these systems would cause morphology changes equivalent to those observed upon changing the reaction solvent quality. Figure 4 shows scanning electron micrographs for a series of samples, all prepared in 40 vol % MEK but with various amounts of divinylbenzene. For DVB-55/MAn, typical, hard microspheres are observed while at lower cross-linker concentrations down to DVB-5/MAn, soft particles are produced. However, all particles formed in this series had comparable diameters of approximately 0.5−0.7 μm.

In an analogous series carried out at 80 vol % MEK, the diameter of the polymer particles formed increases with decreasing cross-linker concentration. Examples of the other samples are shown in Figure 5.

We attribute this increase in particle size to more effective intermolecular reactions in the mixtures containing less DVB since the polymer chains will be much more highly swollen in these cases. Only soluble products are formed in the DVB-5/MAn reaction, and hence no image is shown for this sample. However, when the MEK proportion is decreased to 70 vol %, very soft, semispherical structures are formed as shown in Figure 6.

The conversion to particles for all reactions incorporating 55 mol % DVB are nearly quantitative at >90%. This value falls to approximately 60% for the DVB-5

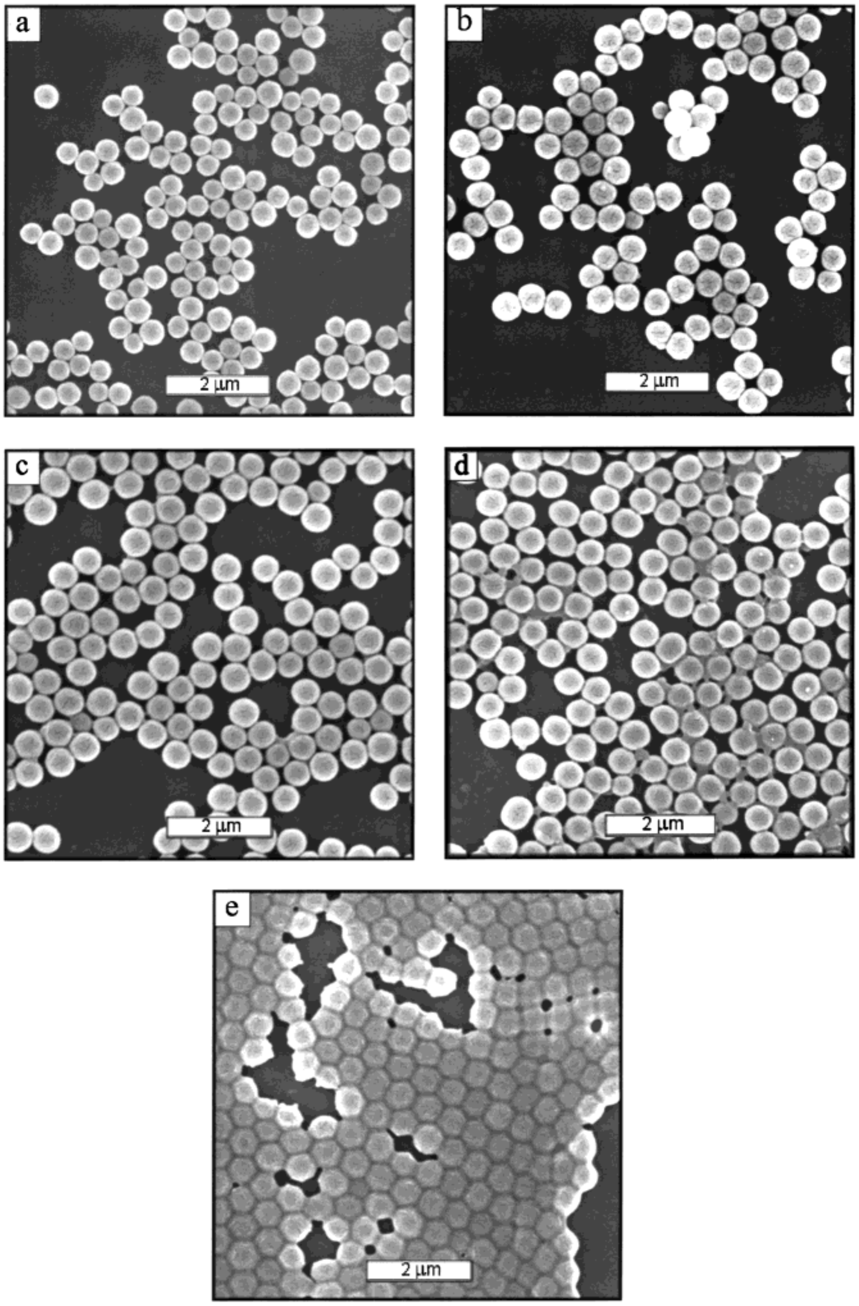

Figure 4. ESEM images illustrating the effect of DVB content on particle morphology for DVB/MAn copolymerization in 40% MEK: (a) DVB-55, (b) DVB-36, (c) DVB-24, (d) DVB-11, (e) DVB-5.

reactions while the total polymer yield remains at greater than 90%, showing an increase in soluble material. This result is expected since the divinyl monomer has been shown to play a significant role in particle growth as it is necessary to capture oligomers from solution.[16]

C. Effect of Monomer Concentration on Particle Size. Total monomer concentration represents the third dimension of the reaction parameter system reported here. Figure 7 illustrates the effect of changing the total monomer concentration on the average volume of the individual particles for two series of DVB-55/MAn reactions at 40 and 80 vol % MEK as measured using the Coulter LS230.

At 40 vol % MEK, the particle volume increases quickly with increasing monomer concentration in a nonlinear fashion. This suggests that the number of particle nuclei produced in these reactions is not proportional to the monomer concentration. In contrast, at 80 vol % MEK, there seems to be little effect of monomer concentration on particle volume. These results suggest that there are two different nucleation mechanisms for these species which are explained below.

D. Mechanistic Aspects of Microgel and Microsphere Formation. As mentioned previously, the preparation of microgels by polymerization of cross-linking monomers in dilute solution has been demonstrated many times in the past.[11,24,25] This work illustrates an example of microgel preparation with relatively high cross-linker concentrations where subtle changes in solvency can lead to different morphologies. The key question here concerns the cause of the morphology transition from microspheres to microgels. This question can be answered on the basis of differences in the mechanisms of nucleation for these two morphologies.

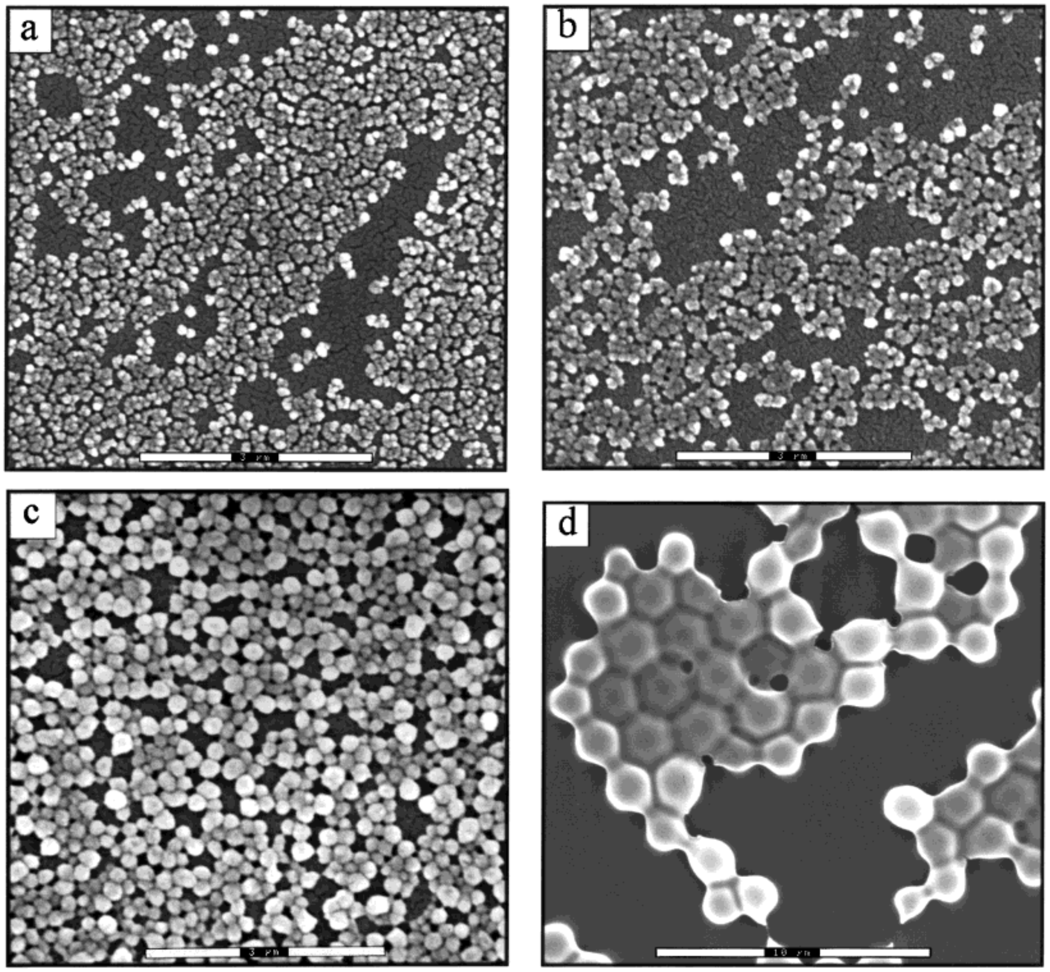

Figure 5. ESEM images illustrating the effect of DVB content on particle morphology for DVB/MAn copolymerization in 80% MEK: (a) DVB-55, (b) DVB-36, (c) DVB-24, (d) DVB-11.

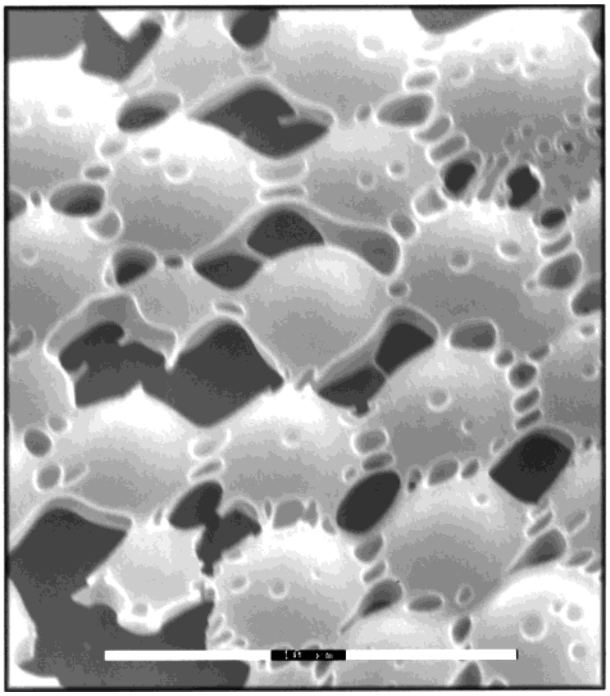

Figure 6. ESEM image of microgels prepared from DVB-5/MAn in 70% MEK.

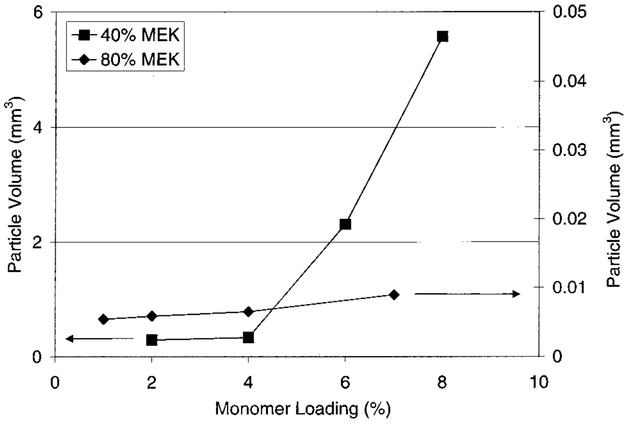

Figure 7. Effect of total monomer loading on particle diameters measured by light scattering (LS230) for reactions in 40% and 80% MEK.

Microsphere Formation Mechanism. A proposed mechanism for the formation of microspheres (40 vol % MEK) is shown in Figure 8. The reaction proceeds in three stages: oligomer formation, nucleation, and particle growth. The oligomer formation stage involves just conversion of monomer to oligomer as in a classical solution polymerization. These oligomers can then undergo three processes: continued growth by intermolecular reactions, intramolecular cross-linking, and cyclization. All three of these processes cause a decrease in the entropy of mixing and hence contribute to the entropic desolvation of the oligomers. The insoluble

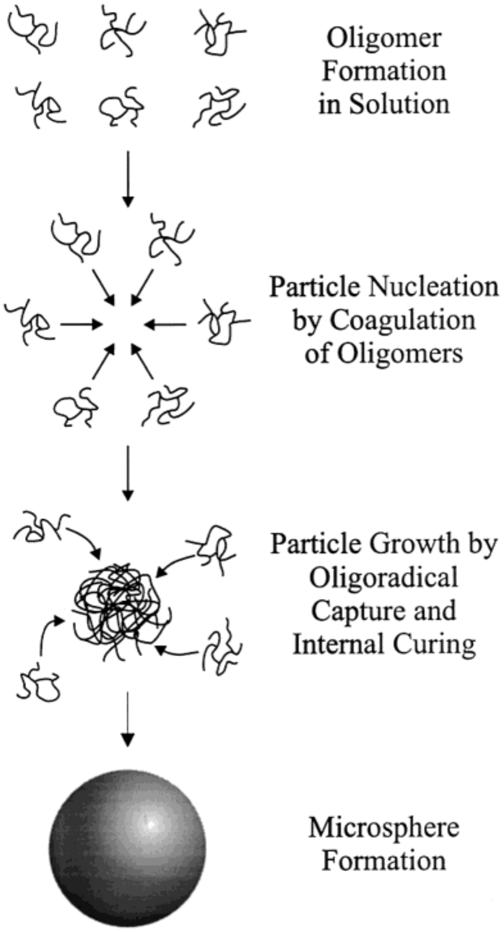

Figure 8. Mechanism of microsphere formation in 40% MEK.

oligomers then homocoagulate to form particle nuclei (particle nucleation step in Figure 8).

As discussed earlier, the ultimate particle volume for DVB-55/MAn microspheres does not scale linearly with monomer concentration (see Figure 7). This supports the existence of a homocoagulation step which would be expected to be concentration dependent. At higher monomer concentrations, homocoagulation would be more pronounced and produce a proportionally smaller number of particle nuclei. These nuclei would then ultimately result in the larger final particles observed at higher monomer concentrations. Particle nucleation continues only until there are enough particles to capture all newly formed oligomers from solution. Capture of oligomers from solution has two effects: growth of the particles and steric stabilization. The newly captured oligomers form a solvated layer on the surface of the growing particles that prevents them from coagulating. This gel layer then continues to cross-link and desolvates to become another layer on the particle core. Simultaneously, more oligomers are captured from solution to regenerate the gel layer. In the case of the DVB-55/MAn system, these processes continue until effectively all the monomer is consumed. A marginal solvent mixture such as 40% MEK/60% Hp is necessary in these systems to swell the gel layer yet still permit its subsequent cross-linking and desolvation.

Microgel Formation Mechanism. There are a number of key observations for the microgel systems that differ from the reactions that produce microspheres. When the effect of monomer concentration was studied for a reaction solvent composition of 80 vol % MEK, the final microgel volumes were not affected by changes in the monomer concentration, in contrast to the results at 40 vol % MEK. Consequently, there cannot be a concentration-dependent homocoagulation step at the particle nucleation stage of the microgel reactions. In the absence of homocoagulation, a linear relationship between microgel volume and monomer concentration is expected. However, the microgel volume remained constant in this case, which indicates that another effect is acting on this system that prevents the microgels from growing beyond their final diameter of ~100 nm. The proposed mechanism of microgel formation in these systems is outlined in Figure 9.

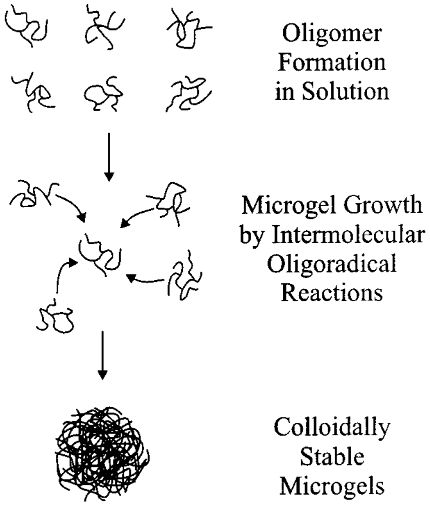

Figure 9. Mechanism of microgel formation in 80% MEK.

In this case, the reactions occur in only two stages: oligomer formation and microgel growth. Oligomer formation is similar to that in the microsphere formation mechanism with the exception that the oligomers are more swollen in 80 vol % MEK. The microgel growth stage occurs by intermolecular reactions between oligomers. In addition to these bimolecular reactions, intramolecular cross-linking and cyclization also occur. Under conditions of increased solvency such as in 80 vol % MEK, it is expected that cyclization will be extensive since internal cross-linking will be inhibited by the highly swollen nature of the forming polymer network. Consequently, the reduced internal cross-linking may not be sufficient to cause the growing microgels to desolvate. Instead, these species continue to react with oligomers until they reach this limiting diameter of ~100 nm, at which point growth ceases. The cessation of growth may be caused by a predominance of cyclization that reduces the number of vinyl bonds at the microgel's surface below the level necessary to permit further growth.

Another key difference between the microgel and microsphere mechanisms is that this limiting diameter would suggest that, for all the monomer to be consumed, new microgels must be formed throughout the course of the reaction. This continuous nucleation is in clear contrast to the distinct nucleation period of the microsphere-forming reactions.

Conclusions

The cross-linking copolymerization of divinylbenzene and maleic anhydride can be used to prepare different polymer morphologies by varying the reaction solvency and cross-linker concentration. Coagulum results under the poorest solvency conditions while the space-filling macrogel is formed in the best solvents. The two most interesting morphologies, microspheres and microgels, are formed at intermediate solvencies and by significantly different mechanisms. Microsphere nucleation appears to occur through a concentration-dependent coagulative process that stops early in the polymerization. Microgel nucleation, on the other hand, continues throughout the polymerization, leading to a constant final microgel diameter that is independent of monomer loading. Varying the cross-linker concentration has little effect under conditions of poor solvency, such as 40 vol % MEK, where the polymer enthalpically desolvates to form microspheres. Conversely, varying the cross-linker concentration under conditions of good solvency, i.e., 80 vol % MEK, dramatically affects the resulting morphology through control of the swelling of the forming microgels. Presumably, there is an intermediate solvency where a decrease in the cross-linker concentration would induce the microsphere to microgel transition.

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