

Experimental Study of Emulsion Polymerization with Crosslinking

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ABSTRACT: Herein is reported the results of an extensive experimental investigation of the kinetics of emulsion polymerization as affected by crosslinking in the polymer particles. The model monomer system, methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA), was chosen for this study due to its earlier comprehensive investigation in bulk polymerization. Standard recipes with sodium dodecylsulfate (SDS) as anionic emulsifier and potassium persulfate (KPS) as initiator were used for the batch emulsion polymerizations. Results, which clearly show the effect of crosslinking on the kinetics, are discussed in detail. These include swellability of polymer particles by monomer; polymer particle nucleation rates, below and above the critical micelle concentration (CMC); average number of radicals per particle; and gel–sol levels. It was found advantageous to use electron spin resonance (ESR) to follow radical concentrations during crosslinking in polymer particles. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 935–957, 1997

Key words: emulsion polymerization; crosslinking; kinetics; electron spin resonance; methyl methacrylate

INTRODUCTION

Polymer latices and emulsion polymerization are commercially important with applications in the manufacture of adhesives, protective coatings, synthetic rubbers, engineering thermoplastics, and substrates for biochemical and medical technology. In addition to the solids content, pH, and ionic strength, the applications of polymer latices are dominated mainly by the polymer and particle properties, such as particle size distribution, molecular weight distribution, long chain branching, and crosslinking density. The particle size distribution influences the latex dispersion stability,

the relationship between suspension viscosity and particle concentration, shear rate, and coagulated film properties (particle packing density, mechanical, and optical properties). The polymer chain properties affect film properties that include adhesion and cohesion in addition to film mechanical and optical properties.

A fundamental understanding of the synthesis mechanism and critical parameters governing the above-mentioned polymer and particle properties will lead to improved design and control of latex manufacturing processes and to superior polymer product properties. In this investigation, the focus is on the kinetics of emulsion polymerization with crosslinking. To date, a comprehensive investigation of the effects of crosslinking on emulsion polymerization kinetics has not been done. In this study, extensive experimentation has been carried out with the aim of elucidating the effects of crosslinking on emulsion polymerization kinetics.

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The model monomer system chosen for this study was methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA) as the comonomer and crosslinker.

LITERATURE SUMMARY

Preparation of Crosslinked Polymer Particles

Microgels are crosslinked polymers in small polymer particles. The chains are crosslinked, but due to the small particle size, Flory's \bar{M}_w criterion for gelation is not satisfied. The overall dimensions of microgels are comparable to high molecular weight linear chains ($\sim 10^6$ g/mol). However, their internal structure resembles a typical network. Microgels can dissolve or swell in suitable solvents with a finite limit, depending on the crosslinking degree of their sponge-like structure. Therefore, the definition has been extended from the submicroscopic particles in the size range of 1–100 nm² to the colloidal dispersions of crosslinked polymer particles.¹

Funke et al.^{2–4} prepared and characterized reactive microgels formed in emulsion polymerization of divinyl benzene (DVB). Not all carbon–carbon double bonds of multifunctional monomers participated in network formation for steric reasons. Residual reactive groups (e.g., pendant double bonds and trapped polymeric radicals) were available at their surface and interior for further reaction.³ For the DVB monomer, the number of microgel particles formed is about 6–9 times higher than that for a standard styrene emulsion polymerization.³ They also found that the ratio of vinyl–divinyl monomer played a very important role in emulsion polymerization.² Low crosslinker levels produce macrogels, and very high crosslinker levels produce both microgels and agglomerates. The pendant double bonds on the microgel surface can be changed to other functional groups, such as carboxyl, hydroxyl, sulphate, amino, or halogen. They might also further react with various monomers to get network structures of desired heterogeneity.

Characteristics of Emulsion Polymerization that Crosslinking Might Influence

From the point of view of crosslinking kinetics, the microenvironment for emulsion polymerization with and without crosslinking is different. For example, crosslinking can reduce equilibrium

swelling of a polymer particle by monomer. This can reduce the rate of surface area growth rate in stage I and thereby increase the micellar nucleation rate of polymer particles.

High levels of crosslinking in polymer particles may cause a significant increase in the average number of radicals per particle due to diffusion-controlled termination. Crosslinking may also retard the diffusion rate of monomer within the particle, causing significant monomer concentration gradients. Polymerization of the divinyl monomer in the aqueous phase also alters the structure of oligomer radicals. This may cause a change in the nucleation mechanism, which might change the major particle nucleation path and the stability of the suspension. These effects may give rise to significantly altered kinetic phenomena in the emulsion polymerization process.

Effect of Divinyl Monomer Type and Concentration on Polymerization Kinetics

Investigations of the kinetics of vinyl–divinyl monomer polymerization and, in particular, diffusion-controlled reactions, gel-point conversion, and crosslinking density, and procedures for fitting experimental data to obtain rate parameters, have been reported by several workers.^{5–9} Li et al.¹⁰ reported extensive experimental data on the kinetics of MMA–EGDMA bulk polymerization, covering a wide range of divinyl–vinyl monomer ratios, and the effect of chain transfer agent concentration on the gel-point conversion. The temperature control in ampoule reactors, radical concentration and radical trapping, radical decay, and diffusion control of rate parameters have been reported by Zhu et al.^{11–14}

Salovey et al.^{15–18} published procedures for the synthesis and characterization of crosslinked monodispersed polymer beads and microbeads for applications as fillers for polymer composites by emulsion polymerization in the absence of emulsifiers. For the styrene–divinyl benzene (St–DVB) monomer system, they found that DVB reacts more rapidly than styrene at low monomer conversions. In batch polymerization, the crosslinking density, as well as T_g of the polymer, decreased with increase in conversion.

Capek^{19–21} published experimental data on the effects of divinyl monomer structure on the emulsion polymerization of ethyl acrylate. Generally, it is expected that if the distance between two double bonds in the divinyl monomer is greater and the connection is more flexible, a looser gel

structure would form. Small species such as monomer and initiator radicals could diffuse more easily within this network, and the polymerization rate would be similar to that without crosslinking (at least in the early stage of the gelation period). Comparing the results of ethyl acrylate, ethyl acrylate–4.9 wt % divinyl benzene, and ethyl acrylate–4.9 wt % 1,6-hexamethylene diacrylate, they found that divinyl benzene decreased both the polymerization rate and the mean polymer particle size (increase particle number), while 1,6-hexamethylene diacrylate increased both the reaction rate and the size of polymer particles slightly.

Particle Nucleation and Particle Number and Size Development

The development of particle morphology in emulsion polymerization is an important area to consider. For vinyl and divinyl monomer systems, crosslinked polymer latex particles with different internal structure can be prepared by seeded,²² emulsifier-free,^{15–18} and micellar nucleation processes.^{20,21}

Nomura and Fujita²³ studied particle nucleation in the emulsion copolymerization of divinyl monomers. They first clarified the nature of particle formation for the styrene–divinyl benzene (St–DVB), and St–EGDMA monomer systems. They found that for a particular monomer recipe, the final particle number increased sharply at the CMC of the emulsifier used (SDS: 0.75 g/L at the ionic strength used). This means that, above the CMC, particles are almost all formed via micellar nucleation. This was confirmed in their experiments²³ by changing the EGDMA monomer fraction in the St–EGDMA monomer feed. Their results showed that for up to 70 wt % EGDMA, the polymer particle number increased with an increase in the EGDMA fraction. Also, the polymer particle number remained constant for most of the monomer conversion range (from about 20 to about 95 wt % total monomer conversion). It was found that the effects of initiator and emulsifier levels on particle number were the same for both systems (with and without crosslinking).

Pendant Double Bond Conversion and Phase Separation

In the polymerization of vinyl–divinyl monomers, the network formed is swellable but not soluble in the monomer medium so that some microphase

separation may occur, and this causes phase heterogeneity in the polymer particle. Very recently, Mallamace et al.²⁴ verified that in the bulk polymerization of MMA–EGDMA, there were microscopic segregation processes and build up of localized heterogeneity in the gel structure. This phenomenon was observed when the EGDMA fraction in the monomer mixture is greater than 3 wt % ($f_2 = 0.015$). In emulsion polymerization, this microscopic segregation produces partitioning of monomer between sol–gel polymer domains within the particle. This syneresis phenomenon explains why one can produce porous particles.

Sheu et al.^{25,26} noticed this phenomenon even on a macroscale. Using it, they produced uniform nonspherical latex particles by seeded emulsion polymerization of styrene onto crosslinked monodispersed styrene latex particles. At first, they found that there was a critical DVB concentration (0.03% wt) required to give a crosslinked network. Increasing crosslinking density of St–DVB seed increases the degree of phase separation and the number of phase domains of final polymer particles.

Free Radicals in Emulsion Polymerization

Information on radical concentration development during polymerization is most useful for any kinetic study on free radical polymerization, including emulsion polymerization. In a typical oil-in-water emulsion polymerization process, the thermal decomposition of the initiator (e.g., KPS) generates primary radicals (e.g., sulfate radical anions) in the water phase, which propagate in the water phase to give oligomeric radicals, which can transfer into polymer particles where higher monomer concentrations cause rapid polymerization. In emulsion polymerization with crosslinking, the fate of these radicals in the polymer particles is responsible for much of the unusual kinetic behavior of these systems.

Termination in a polymer particle is a complicated process, particularly when radical centers are located on or attached to crosslinked chains. In latex particles, polymer concentrations are high, and polymer self-diffusion with many chain entanglement points is operative. Radicals attached to the polymer network can move only by propagation. With highly crosslinked systems, termination is almost exclusively by reaction diffusion. Instantaneous termination is not valid, and many radicals per particle is the usual result.

ESR Application in Free Radical Polymerization

The advent of modern electron spin resonance (ESR) has provided a powerful direct method for measurement of radical type and concentration. For bulk polymerization, Bresler et al.²⁷ used ESR to study the homogeneous polymerization of MMA and vinyl acetate and, to some extent, solved the problems of how to detect rapid changes in free radical concentration during the pre- and post-gel effect periods.

In the late 1980s, the application of ESR techniques has improved to cover a broad range of studies of bulk polymerization kinetics. Kamachi et al.^{28,29} reported the results on ESR observation of propagating radicals of vinyl acetate in a stationary state and of conformation of propagating radicals of triphenylmethyl methacrylate. Shen et al.³⁰ used ESR to study the propagation rate constant and radical concentration for bulk polymerization of MMA.

More recently, a comprehensive study using *in-situ* ESR technology for bulk polymerization has been reported by Zhu et al.¹¹⁻¹⁴ The radical trapping and termination in free radical polymerization of MMA; the radical concentration in free radical copolymerization of MMA-EGDMA; the termination of trapped radicals at elevated temperatures during copolymerization of MMA-EGDMA; and the conformation, environment, and reactivity of radicals in copolymerization of MMA-EGDMA have been investigated. These investigations are unique in that both conversion-time and radical concentration measurements have been coupled to provide a deeper understanding of the polymerization kinetics phenomena and a better estimate of rate parameters.

For emulsion polymerization without crosslinking, Smith-Eward Case II kinetics might apply, with the average number of radicals per polymer particle ($\bar{n} = 0.5$). Thus, the total free radical concentration $[R^*]$ is 10^{-9} to 10^{-8} (mol/L) when the particle concentration (N_p) is 10^{15} to 10^{16} particles per liter. For a typical ESR spectrometer, the detection limit is about 10^{-7} (mol/L). Much higher radical concentrations might be expected during the course of polymerization, particularly during the period of auto-acceleration in rate. The heterogeneous nature of an emulsion polymerization renders difficult the direct application of an *in-situ* ESR technology (rapid flow technology). The presence of liquid water always places a severe restriction on the ESR sample size because its dielectric properties tend to reduce the quality

factor of ESR cavity and, therefore, leads to weaker ESR signal intensity to an impracticably low value. This makes it difficult to directly measure radical concentrations by doing emulsion polymerization in the cavity of an ESR.

EXPERIMENTAL

The experimental polymerizations were carried out in a batch reactor. The following data were collected: (1) total monomer conversion versus polymerization time; (2) monomer volume fraction in the polymer particles versus time; (3) polymer particle size and number versus time; (4) conversion of pendant double bonds versus time; (5) radical concentration in the polymer latex versus time; and (6) glass transition temperature (T_g) and internal heterogeneity of polymer particles free of monomers.

Materials

MMA and crosslinking agent EGDMA (Aldrich Chemical Co.) were purified by vacuum distillation. Potassium persulphate (KPS) (Fisher Chemical, certified) and sodium dodecyl sulphate (SDS) (BDH Chemicals, analytic reagent) were used without further purification.

Experimental Design

The polymerization conditions, such as monomer feed composition, levels of emulsifier (sodium dodecyl sulfate), and initiator ($K_2S_2O_8$ /KPS), were considered important factors to examine. In this experimental investigation, the temperature was set at 50°C. We would like to reduce the number of radical types in ESR measurements, so we decided not to use a redox initiation system. The concentrations of emulsifier, initiator, and EGDMA ratio in the monomer feed were chosen as important variables to study. The basic experimental conditions selected in the present study were as follows:

Recipes	Reactor
Water: 650 g	1 liter ($H:D = 1.6$)
Monomer: 100 g (EGDMA 0-25 wt %)	300-350 rpm (agitation)
SDS: $(3.5-10) \times 10^{-3}$ (mol/L H ₂ O)	$50 \pm 0.2^\circ\text{C}$
$K_2S_2O_8$: $(2.2-8.8) \times 10^{-3}$ (mol/L H ₂ O)	Vacuum sample outlet

A typical recipe for an emulsion polymerization in the present investigation includes 650 g water and 100 g monomer. The monomer-to-water ratio is not very high in order to isolate the crosslinking effect from other external influences, such as agitation. Most of the experiments were in the low to middle EGDMA concentration range (from 0 to 25 wt %), while two experiments were done with pure EGDMA monomer, at low and high SDS concentration separately to explore limiting conditions. KPS concentrations were about $(2.2\text{--}8.8) \times 10^{-3}$ mol/L H_2O , and this covered a fairly wide concentration range. SDS concentrations were at both below and above the CMC, $(3.5\text{--}10) \times 10^{-3}$ mol/L H_2O .

Polymerization

Polymerizations were conducted in a 1 L glass reactor with a height to diameter ratio of about 1.6 and with a stainless steel four-bladed flat paddle type stirrer of 65 mm diameter. The reactor was fitted with a nitrogen inlet, a water-cooled condenser with wash bottle trap filled with oil to prevent back-contamination by air. A vacuum sample outlet was also fitted at the dished bottom of the reactor.

After the desired levels of water, monomer, and emulsifier were added to the reactor, a small amount of sodium hydroxide solution was added to adjust the pH to about 7. Several drops of pH 7 buffer solution were also added at this time. Then, oxygen in the reactor system was removed by bubbling nitrogen gas (UHP grade) for more than 30 min. The nitrogen bubbling was carried out at room temperature in order to reduce the loss of monomers by evaporation.

The polymerization was started by injecting about 30 mL aqueous KPS solution that had also been deoxygenated by bubbling nitrogen gas through it. At this time, the nitrogen gas was switched to another inlet above the liquid surface. The nitrogen gas flow rate was monitored by the bubbling extent in the wash bottle trap to just keep a nitrogen gas blanket. The polymerization temperature was controlled at $50 \pm 0.2^\circ\text{C}$ for all runs. The agitation speed was set to 300–350 rpm.

Polymer and Particle Characterization

(1) Total Monomer Conversion

Total monomer conversion and polymer mass–time history was determined by gravimetry using

methanol as precipitant for the polymer. The sampling time interval was about 10 min. An ice water bath was used to quench the polymerization in each sample. The vacuum oven temperature was kept at 30°C .

(2) Particle Size Determination by Dynamic Light Scattering

Polymer particle size distribution was measured by Semi-micro Particle Sizer, model 370 with version 5.0 Nicomp software. The measurement error of the instrument was estimated by using two monodispersed polystyrene latex particle standards obtained from Polysciences Inc., U.S.A.: Cat. no. 00876, 110 ± 3 nm; Cat. no. 08691, 60 ± 2 nm. Particle number concentrations were estimated using measured particle size distribution data and polymer concentration.

(3) Equilibrium Swellability of Particles

The equilibrium swellability of polymer particles was also measured by the dynamic-light scattering (DLS) method. Polymer particles sampled at different polymerization conversions were washed and centrifuged several times. The particle size was then measured. Then, the concentrated samples at the bottom of the centrifuge tube were diluted with the solvent. In the present study, acetone and MMA monomer were used as swelling agents. The swelling process was carried out at 25°C for 72 h. The sample was stirred during the swelling process with a magnetic stirrer. The size of the equilibrium swollen polymer particles was measured again by DLS to get the equilibrium volume increase of the polymer particles.

(4) Differential Scanning Calorimetry Measurement of Pendant Double Bond Conversion

Conversion of pendant double bond (PDB) and glass transition temperature (T_g) were determined using Dupont 910 Differential Scanning Calorimeter with a Thermal Analysis 2000 System. The heating rate used was 10°C min for all tests. The samples taken at different times were washed and dried before DSC testing. The conversion of PDB was estimated from the exothermic peak in the first heating process. After the sample was cooled down, it was heated again.

(5) ESR Measurement of Free Radical Concentration in Crosslinked Polymer Particles

In the present experiments, the polymeric radical concentrations during emulsion polymerization

Table I ESR Measurement Conditions

Parameter	Quantity	Units
Temperature	150, 170	K
Microwave power	20	dB
Microwave frequency	9.46	Ghz
Modulation intensity	4.0	Gpp
Modulation frequency	100	KHz
Modulation gain	1×10^6	—
Scan center	3380	G
Scan time	1000	s
Scan size	1	K
Scan width	300	G

were measured by a Bruker ER100D ESR spectrometer equipped with a TE 110 cavity. The spectrometer was connected to an IBM PC with EPRware software. The polymer latex was sampled at present different polymerization conversions through a specially designed closed-loop vacuum sampling line. These samples were instantaneously quenched by liquid N_2 in a 3 mm od ESR tube when the latex flowed into it. Thus, polymerization was stopped immediately, and free radicals in the samples were frozen in preventing further termination. The sample latex was then sealed ready for ESR testing. In the experiments, the sampling process was done in less than 10 s.

The ESR signal was set up autocollecting by a computer. In order to increase the signal–noise ratio, the ESR signal was accumulated for 1000 s and then double integrated to get the improved total signal intensity. With the solution of 2,2-diphenyl-picrylhydrazyl hydrate (DPPH) in MMA for signal calibration, the absolute polymeric radical concentration was obtained. The ESR measurement conditions are listed in Table I.

RESULTS AND DISCUSSION

(1) Monomer Conversion Histories and Rate of Polymerization

Effect of EGDMA Level in Recipe

Figure 1 (a) shows the total monomer conversion histories with different EGDMA levels in the monomer feeds. The SDS concentration was 3.47×10^{-3} mol/L H_2O , which is below the critical micelle concentration (ca. CMC_{SDS} , @20°C $\approx 8.0 \times 10^{-3}$ mol/L H_2O ³¹). The initiator (KPS) concentration was 2.2×10^{-3} mol/L H_2O . Figure 1 (b)

shows the total monomer conversion histories with different EGDMA levels in the monomer feeds. In this case, the SDS concentration was 10×10^{-3} mol/L H_2O , which is above the CMC.

It can be seen in Figure 1 (a) that when the SDS concentration was below the critical micelle concentration (CMC), there was not much difference in the polymerization rate for the systems with different EGDMA levels (from 0 to 10 wt %). The reason could be that under this condition, because of its very low water solubility, EGDMA did not copolymerize with MMA to form oligomer chains for the homogenous particle nucleation. The newly formed primary particles mainly contain MMA repeat units in oligomer chains. EGDMA started to play a role in polymerization only in the later stages by diffusing into those stabilized primary particles.

Therefore, it can be understood that, in this case, the low EGDMA solubility in water makes its effect on particle nucleation negligible. This can be verified further by observing the pure EGDMA conversion data. The polymerization rate is extremely slow, and the particle suspension is not stable. The reason is that those precipitated primary particles cannot coalesce to increase the surface charge density to stabilize themselves because they are glassy particles.

On the other hand, in Figure 1 (b), one can see that when polymerization was carried out with SDS concentration above its CMC, there is a very clear effect of EGDMA or crosslinking level on polymerization rate. In the present experiments, the polymerization rate increased with an increase in the EGDMA level to about 10 wt %, then the polymerization rate for 25 wt % EGDMA is slower than that for 10 wt % and decreases with further increase in EGDMA concentration.

These conversion–time histories are very different from those observed in a bulk polymerization of MMA–EGDMA. In the bulk polymerization, all the rate data showed that the polymerization rate was a monotonous increasing function of EGDMA concentration in the monomer feed.¹⁰ In emulsion polymerization with crosslinking, a change in the divinyl monomer concentration can have two opposite effects on the polymerization rate. On one hand, increasing the EGDMA concentration in the recipe produces more crosslinking, and this causes an increase in polymer particle viscosity and a decrease in the termination rate. This increases the number of free radicals per particle and so increases polymerization rate.

On the other hand, high crosslinking of poly-

mer particles lowers their free volume. From the mass transfer rate and swelling equilibrium point of view, the higher the EGDMA level, the lower the monomer concentration in the polymer particle. This in turn reduces the polymerization rate per polymer particle. This reduction in polymerization rate (especially in Stage I) lowers the surface area increase rate of the formed polymer particles. Thus, more micelles are consumed to form new polymer particles than to cover growing surface area, generating a higher concentration of polymer particles; and this favors a higher polymerization rate.

Experimental studies on the bulk polymerization kinetics of MMA and alkyl glycol dimethacrylate have been reported.^{32–34} It was found that gelation occurred at low conversions with increase in $(-\text{CH}_2-)_n$ units in the ester group beyond two ($n > 2$). This result was attributed to the suppression of intermolecular termination between the growing polymer radicals having loop structure due to intramolecular cyclization.

Effect of Initiator Concentration

Figure 1 (c) shows the effect of initiator concentration on conversion–time history. EGDMA is 10 wt %, and SDS is 10×10^{-3} mol/L H_2O . It can be seen that initiator concentration affects the initial time period of polymerization. The final total monomer conversion, a similar limiting conversion in both cases, was reached after about 35 min. This is the result of the glassy effect. The final particle size and number were also reached about this time as expected. The SDS concentration is above the CMC, and the nucleation process is micellar.¹⁹ The higher the initiator concentration, the more rapid the polymer particle nucleation rate. The conversion rate (slope in the linear range in both profiles) is about 2.4 and 5.8 for low and high initiator concentrations, respectively.

Effect of Emulsifier Concentration

Figure 1 (d) shows the effect of SDS concentration on the polymerization rate. The A1 and B1 lines show the system with low SDS concentration 3.47×10^{-3} mol/L H_2O , while A2 and B2 lines show the system with high SDS concentration 10×10^{-3} mol/L H_2O , above CMC. Group A lines are for the 10 wt % EGDMA, while group B lines are for pure EGDMA. A faster polymerization rate, especially in the early stage, can be seen for the high SDS concentration case (comparing A1 and

A2), with A1 having a clearly visible auto-acceleration in the rate.

The reason is that the particle nucleation process is different. MMA has a moderate water solubility (50°C , 1.43 ± 0.08 g $100/\text{g}$ H_2O). When the SDS concentration is below the CMC, the nucleation process is homogeneous with MMA involved almost exclusively. When the SDS concentration is above the CMC, the nucleation process is micellar. Micellar nucleation generates polymer particles at a much faster rate than homogenous nucleation. An additional additive effect is that although EGDMA has a very low water solubility, micelles contain a substantial level of EGDMA, which causes early crosslinking, low monomer concentrations, and low surface area growth rates, which lead to a greater fraction of micelles forming polymer particles.

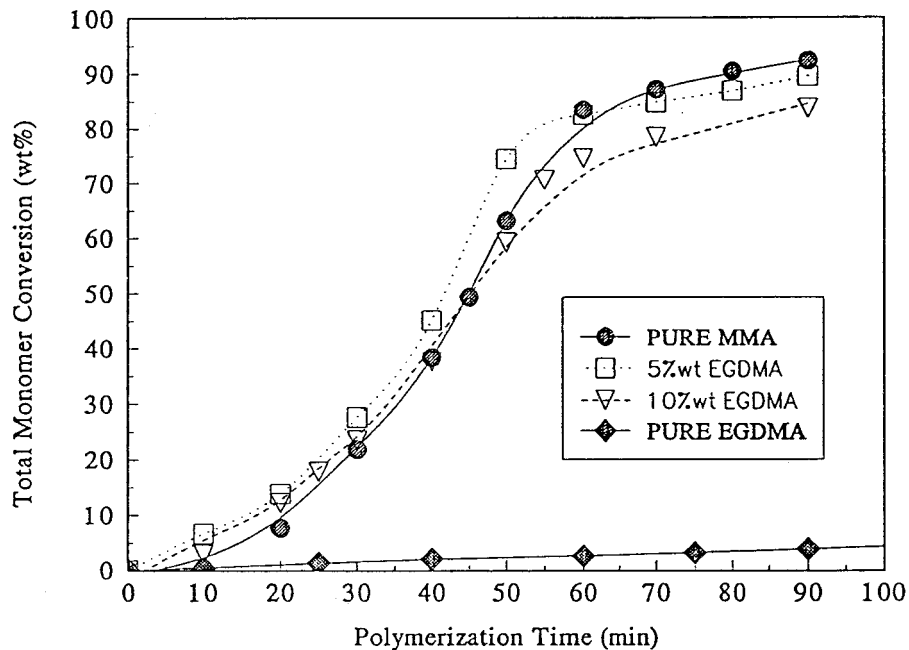
However, at extreme levels of EGDMA and crosslinking [see B2 in Figure 1 (d)], monomer swellability is so low that polymer particles may be almost glassy soon after their formation; and, of course, this reduces the polymerization rate close to zero, with perhaps most occurring in surface layers on the particles.

(2) Polymer Particle Nucleation and Polymer Particle Number and Size Development

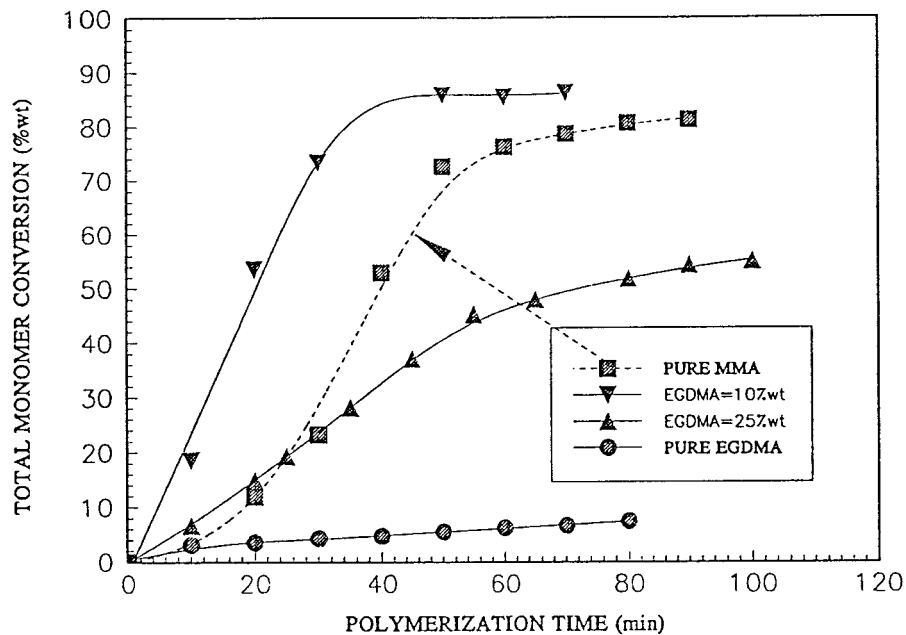
Micellar and Homogeneous Nucleation

Figure 2 (a) shows the effect of SDS concentration on the particle number history with 10 wt % EGDMA in the recipe. As a reference, the total monomer conversion at each related polymerization time are also shown in this figure. In this figure, the two solid lines show the total monomer conversion, and the two open symbols show the polymer particle concentrations. The SDS concentration for the two triangle symbols (both solid and open) is above the CMC, while the SDS concentration for the two circle symbols (both solid and open) is below the CMC. Other conditions were kept the same. A conclusion that can be made is that with SDS above the CMC, polymerization is fast initially, with a large number of polymer particles produced.

The polymerization carried out at a high SDS concentration (above CMC) has smaller particle size with more particles than that carried out under low SDS condition. It is also evident that polymer particles produced at the high SDS concentration are more stable because no particle coagulation trend can be seen in Figure 2 (a). The total



(a)



(b)

Figure 1 (a) Experimental results showing the effect of EGDMA monomer level on total monomer conversion history in MMA-EGDMA emulsion polymerization at low emulsifier concentration. SDS: 3.47×10^{-3} mol/L H_2O ($< CMC$). KPS: 2.2×10^{-3} mol/L. $T = 50^\circ C$. (b) Experimental results showing the effect of EGDMA monomer level on total monomer conversion history in MMA-EGDMA emulsion polymerization at high emulsifier concentration. SDS: 10×10^{-3} mol/L H_2O ($> CMC$). KPS: 2.2×10^{-3} mol/L. $T = 50^\circ C$. (c) Experimental results showing the effect of KPS concentration on total monomer conversion history in MMA-EGDMA emulsion polymerization. EGDMA-MMA: 10/90 wt %. SDS: 10×10^{-3} mol/L H_2O . $T = 50^\circ C$. (d) Experimental results showing the effect of SDS concentrations on total monomer conversion history in MMA-EGDMA emulsion polymerization. KPS: 2.2×10^{-3} mol/L H_2O . $T = 50^\circ C$. A1, B1: SDS = 3.47×10^{-3} mol/L H_2O (below CMC). A2, B2: SDS = 10×10^{-3} mol/L H_2O (above CMC).

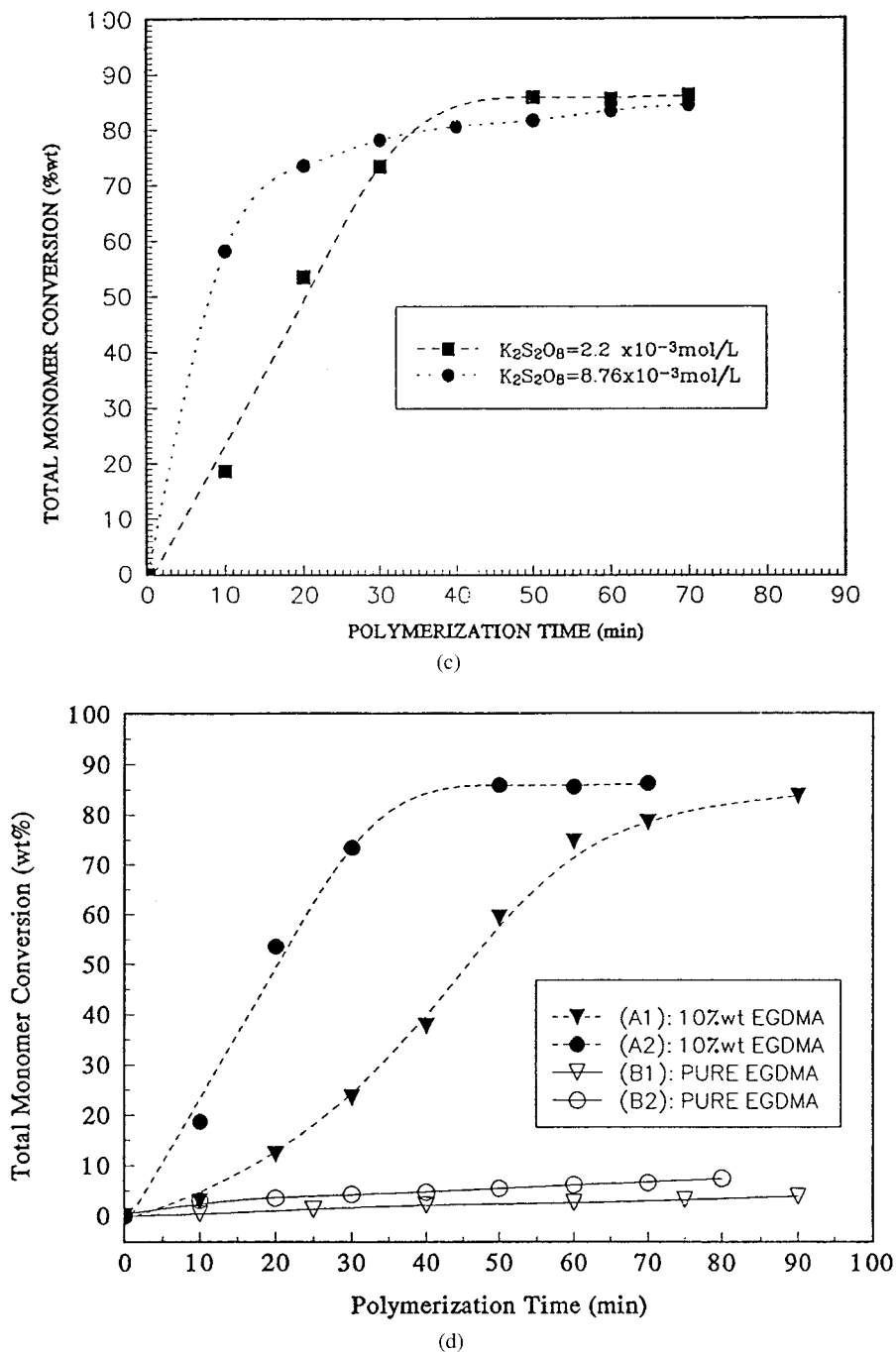


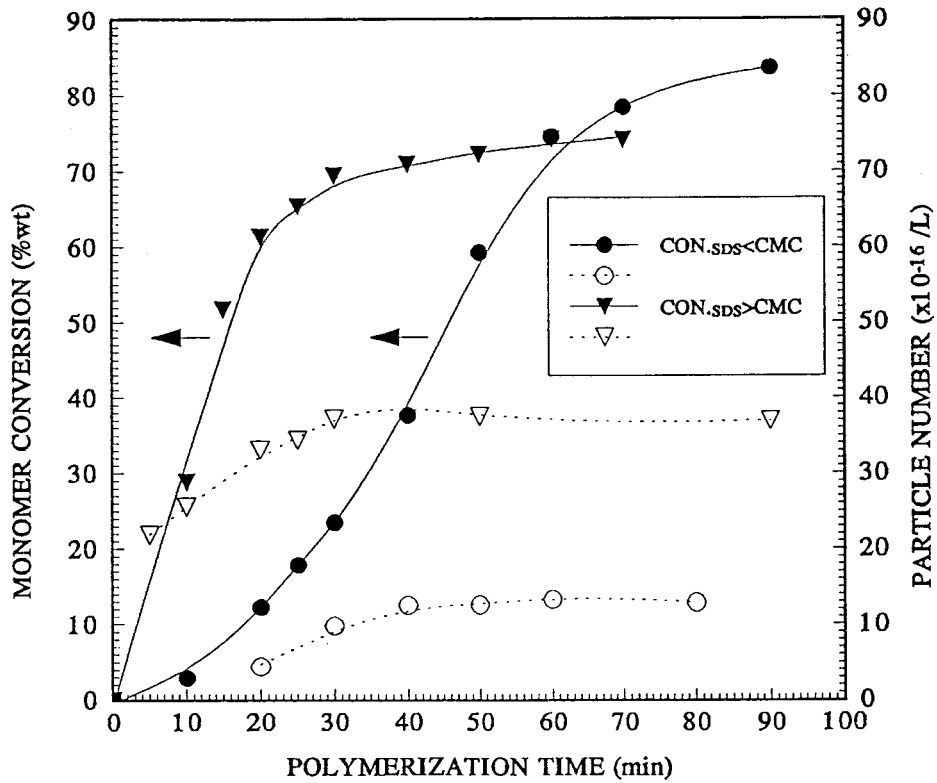
Figure 1 (Continued from the previous page)

number of polymer particles reaches a plateau and remains constant with time. This is true for both low and high SDS concentrations.

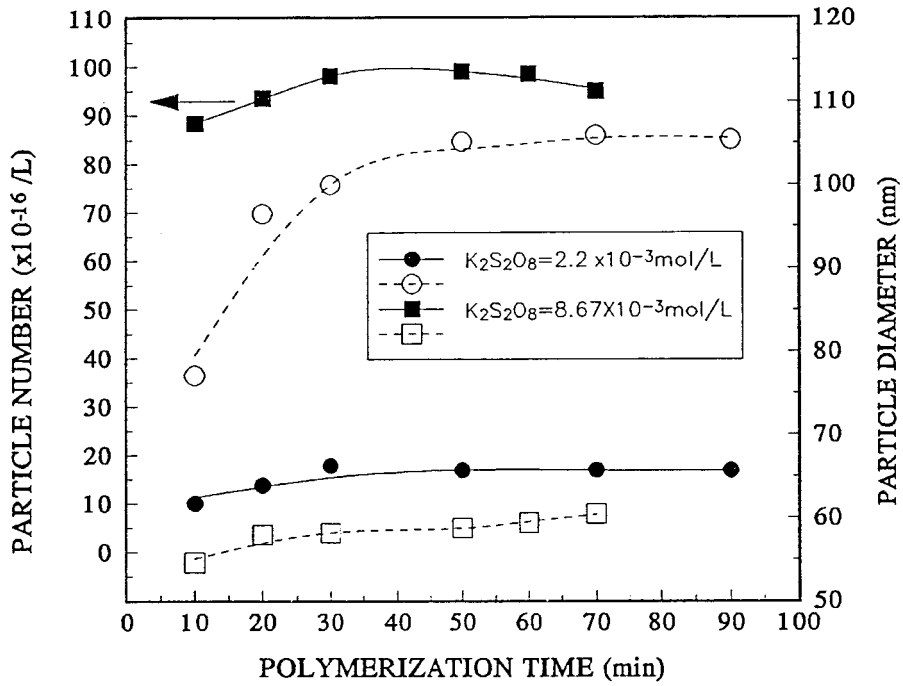
Effect of Initiator Concentration

The micelle nucleation mechanism was studied further by checking the effect of initiator concentration.

A system with 10 wt % EGDMA and 10×10^{-3} mol/L H_2O SDS was considered (above the CMC). Figure 2 (b) shows the particle size and particle number history at two different initiator levels. The solid lines represent the particle concentrations. The short dash lines show the particle diameters. Circular symbols (both solid and open) are for the low initiator concentration case. It can be seen that

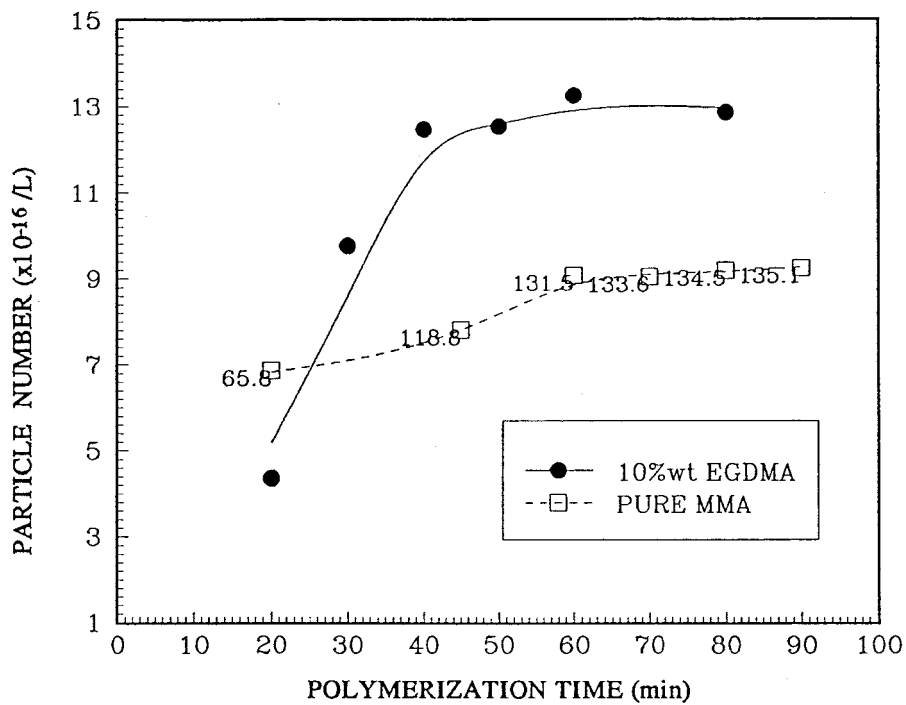


(a)

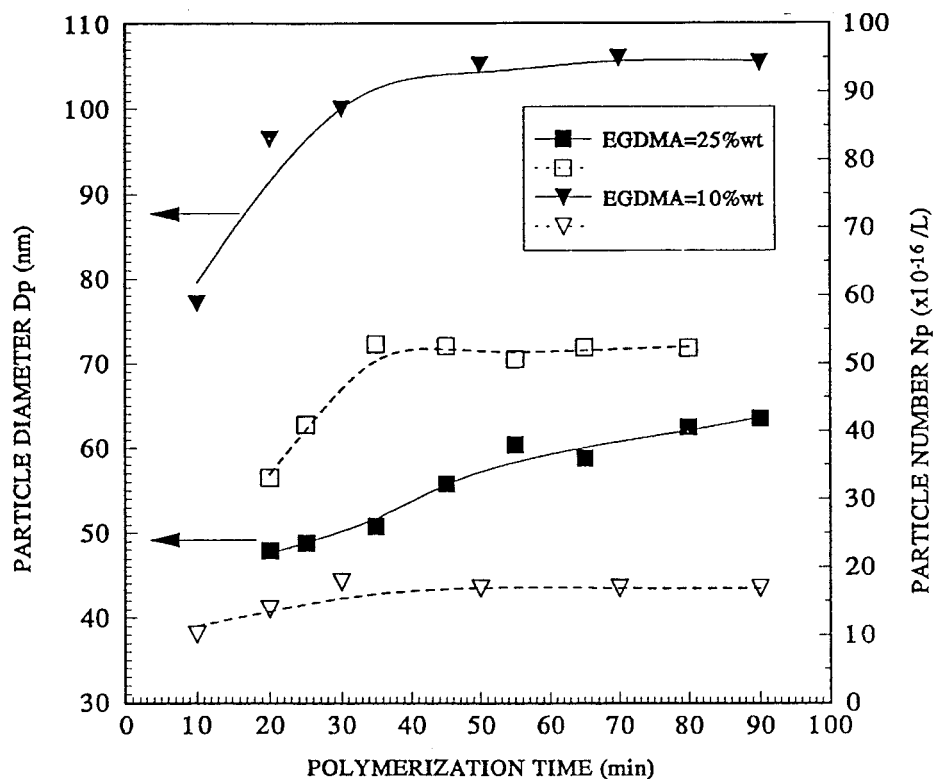


(b)

Figure 2 (a) Effect of SDS concentration on polymer particle nucleation. EGDMA–MMA: 10/90 wt %, KPS: 2.2×10^{-3} mol/L H₂O. $T = 50^\circ\text{C}$. SDS: 3.47×10^{-3} and 10×10^{-3} mol/L H₂O. (b) Effect of initiator (KPS) concentration on polymer latex particle diameter and number versus history. EGDMA–MMA: 10/90 wt %. SDS: 10×10^{-3} mol/L H₂O (above the CMC). $T = 50^\circ\text{C}$. (c) Effect of EGDMA monomer level on polymer



(c)



(d)

Figure 2 (Continued from the previous page)

latex particle diameter history. SDS: 3.5×10^{-3} mol/L H₂O (below CMC). KPS: 2.2×10^{-3} mol/L H₂O. $T = 50^\circ C$. (d) Effect of EGDMA monomer level on polymer latex particle number and diameter history. SDS: 10×10^{-3} mol/L H₂O (above CMC). KPS: 2.2×10^{-3} mol/L H₂O. $T = 50^\circ C$.

the initiator concentration affects the early stage of polymerization (initial 35 min). When the initiator concentration was increased by about four times, the particle diameter was reduced by about a factor of two, while the particle concentration was increased by about a factor of six.

An interesting observation is that the final diameter of particles prepared at the higher initiator concentration (8.76×10^{-3} mol/L H₂O) is just a little larger than the diameter of monomer solubilized micelles. It is likely, therefore, that the majority of monomer swollen micelles were stung to nucleate polymer particles and that the particles did not undergo a significant growth in size during the whole polymerization. This clearly suggests that a high level of crosslinking existed in the particles, giving a very low monomer concentration in the particles; as a consequence, a very slow volume and surface area growth rate for newly formed polymer particles occurs. This, in turn, reveals a micellar nucleation domain that can be confirmed by recalling the results shown in Figure 1 (c).

Effect of Divinyl Monomer Concentration at Low SDS Concentration

Because of the effect of different SDS levels on the polymer particle size and number mentioned in the above section, two experiments were done at low and high SDS concentrations in order to isolate the effect of EGDMA. At first, the particles were produced at SDS concentrations below the CMC. Figure 2 (c) shows the effect of EGDMA level on the particle number history at the same initiator concentration. The open square symbols are for pure MMA monomer. The number near these symbols is the related polymer particle diameter in nm for pure MMA polymerization under the same conditions. This result is used as the base case (i.e., no crosslinking).

For the pure MMA system, both particle size and number continually increase up to 60 min, then remain essentially constant thereafter. This indicates a long nucleation period (about 60 min). However, for the system having 10 wt % EGDMA monomer, there is a sharp increase in particle number in the initial stage of polymerization up to 30 min. After this point, the polymer particle number remains constant until about 60 min, corresponding to the final polymerization conversion about 75 wt %. This is a typical stable particle growth period.

The reason is that for a homogenous nucleation

process, the existence of EGDMA in the water phase produces oligomeric chains that are more hydrophobic. The critical chain length for precipitation is smaller; as a consequence, homogeneous nucleation rates are larger, resulting in more polymer particles being nucleated.

With this recipe, the SDS concentration is below the CMC; and after a certain time, with continuous growth of polymer particle surface area, the surface charge density is not large enough to stabilize the particle suspension, and modest levels of particle agglomeration occur. It should be understood that at the conversion where agglomeration occurs, the particles are glassy at the polymerization temperature used, so that this aggregation does not involve coalescence but is more like a loose flocculation.

Effect of Divinyl Monomer Concentration at High SDS Concentration

In Section (1), it was mentioned that when polymerization was carried out at the high SDS concentration, an increase in the EGDMA monomer level in the recipe lowers the surface area growth rate of the freshly formed polymer particles. Thus, more micelles are consumed in particle nucleation, leading to higher particle concentrations. In other words, a greater fraction of micelles forms polymer particles. In theory, the highest concentration of polymer particles results when every micelle becomes a polymer particle.

The present experimental data confirm the above explanation. Figure 2 (d) shows the effect of EGDMA concentration on the change of polymer particle diameter and number history for higher levels of crosslinker. In this figure, the two solid lines are for the polymer particle diameter, while the two dotted lines are for the particle number. Square symbols (both solid and open) are for the highest EGDMA concentration level (25 wt %). Triangle symbols (both solid and open) are for the low EGDMA level (10 wt %).

First, one can see that for 25 wt % EGDMA, particle size is about half of that for 10 wt % EGDMA, while particle concentration is two times higher than for 10 wt % EGDMA. Secondly, after the nucleation stage, the particle number remains constant for both EGDMA monomer levels. This suggests that at this SDS concentration, the latex is a stable dispersion, with sufficient emulsifier molecules adsorbed on the surface to stabilize them electrostatically. Also, for the 25 wt % EGDMA level, particle size increases only slightly.

This recipe should give polymer particles with a highly crosslinked structure.

(3) Swellability of Crosslinked Polymer Particles

In the present study, the swelling ratio is defined as the ratio of particle diameter before and after equilibrium swelling using an inert swelling solvent, which is a good solvent for the linear chains.

Effect of Initiator Concentration on Swellability

Figure 3 (a) shows the present results for equilibrium swelling ratio versus total monomer conversion for particles produced at different initiator concentrations. Acetone was used as the swelling solvent. It is clear that at both levels of initiator, the swelling ratio is a monotonous decreasing function of monomer conversion, but with different rates. Particles prepared at a low initiator concentration have a higher swelling ratio. Higher initiator levels clearly give higher crosslinking densities for the polymer chains in the particle.

The rate of change of the swelling ratio with monomer conversion is greater at higher conversion levels, with evidence of a possible transition point, which may be a result of some structural change in the polymer particles. The higher the level of initiator, the earlier is the transition point. Figure 3 (b) shows the change of liquid volume fraction in polymer particles with total monomer conversion calculated using these swelling ratio data. In this figure, open symbols (square and circle) are for swelling with acetone as the solvent. Solid squares are for MMA swelling. Square symbols (both solid and open) show the swelling with polymer samples produced using high initiator concentration.

Again, it is clear that the solvent volume fraction has a similar pattern as that of the swelling ratio based on particle diameter ratio. The liquid volume fraction in polymer particles initially remains a stable value to certain monomer conversion and decreases abruptly thereafter. The lower the initiator concentration used in the preparation of polymer particle samples, the higher the stable value and the later this transition point does appear. It is understandable that the swellability reflects particle size at low conversions and crosslinking density and internal structure of polymer particles at higher conversions. It has been mentioned in Section (2) that the initiator

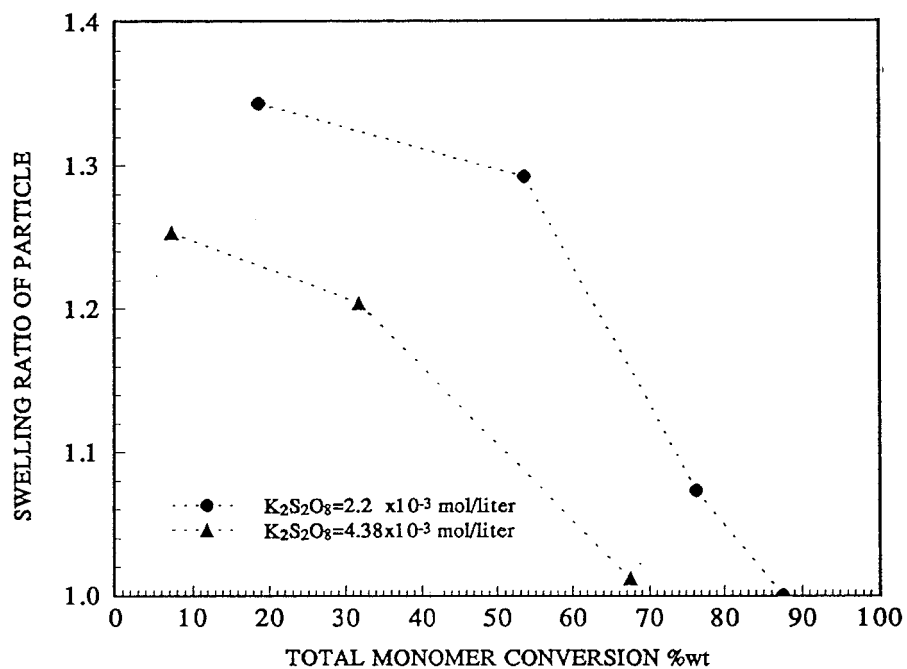
concentration has a clear effect on the development of size and number of polymer particles.

Recall results shown in Figure 2 (b) and the interesting observation that the final diameter of particles decreases with increase in initiator concentration (from 2.2 to 8.76×10^{-3} mol/L H_2O). It is likely, therefore, that with the increase of initiator concentration, more and more monomer swollen micelles were stung to nucleate polymer particles. As a result, with the increase of the initiator concentration, the particles undergo a less significant volume growth during the whole polymerization. This clearly suggests that a high level of crosslinking exists in the particles with a low monomer concentration with the higher initiator concentration. The swelling experimental results confirm this conclusion. An alternative explanation is to involve the effect of surface energy per unit volume on the chemical potential of monomer with smaller particles having a lower equilibrium level of monomer.

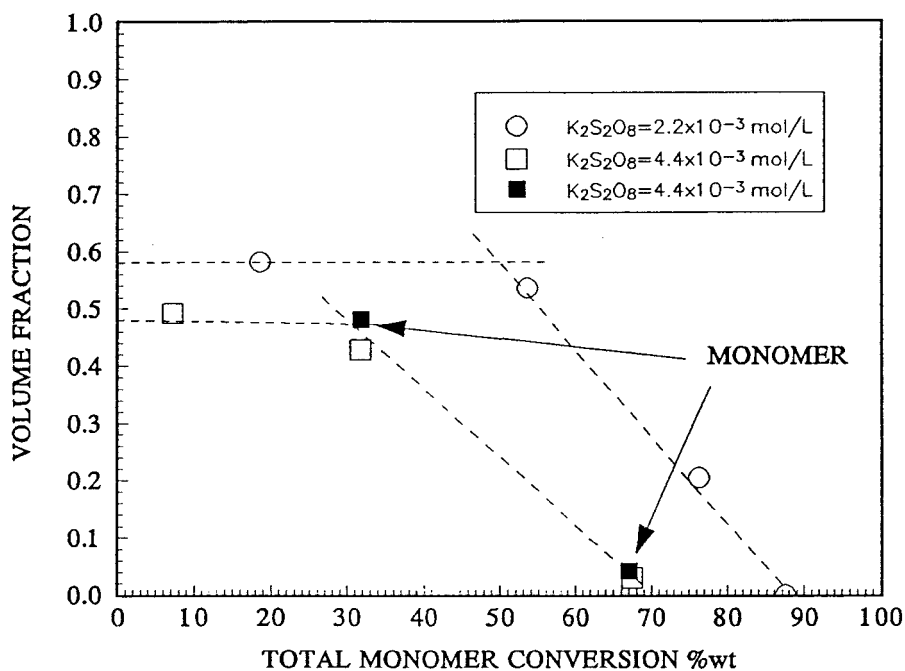
Effect of Solvent Type on Swellability

The effect of solvent type on the change of solvent volume fraction in polymer particles versus total monomer conversion. Acetone and pure MMA were used as swelling solvents for the polymer sample produced at the same initiator concentration (about 4.4×10^{-3} mol/L H_2O). It can be seen that for this polymer sample, the solvent and/or monomer volume fraction in the polymer particles keep a relative constant value 0.48 up to about 35 wt % total monomer conversion. The swelling ratios reported in this study are smaller than those reported by Tobita et al.³⁵

The reason for this may be that in these experiments, a higher initiator concentration was used. This dependence on initiator concentration was shown in Figure 3 (b). For conversions up to about 40 wt %, the solvent volume fraction remains almost at about 0.48 for particles prepared at the higher initiator concentration (4.4×10^{-3} mol/L H_2O) and about 0.58 for particle prepared using the lower initiator concentration (2.2×10^{-3} mol/L H_2O). Tobita³⁵ reported a value of 0.56 using 2.3×10^{-3} mol/L H_2O . As is mentioned above, not only this initial liquid volume fraction but also the transition point is strongly influenced by the initiator concentration in the emulsion polymerization among the other things. This clearly reflects the effect of crosslinking density on polymer particle swelling.



(a)



(b)

Figure 3 (a) Effect of KPS concentration on swelling ratio of polymer particles. Polymerization conditions are as follows. EGDMA–MMA: 10/90 wt %. SDS: 10×10^{-3} mol/L H₂O. $T = 50^\circ\text{C}$. Swelling conditions: acetone, at 25°C for 72 h. (b) Swelling of polymer particles made at different initiator levels with two solvent types. Polymerization conditions are as follows. EGDMA: 10 wt %. SDS: 10×10^{-3} mol/L H₂O. $T = 50^\circ\text{C}$. Swelling conditions are as follows. Swelling at 25°C for 72 h (swelling solvents: pure acetone and MMA monomer).

(4) Pendant Double Bond Conversion and Glass Transition Temperature (T_g)

To reveal the effect of shielding, if any, on the reactivity of pendant double bonds, one needs to measure pendant double bond (PDB) concentration with time. Besides the normal chemical analysis methods, Raman³⁶ and nuclear magnetic resonance (NMR)^{37–42} spectroscopy are extensively applied for this purpose. For conversions before the gelation point, ¹H NMR is normally used.^{22,37–39}

DSC Measurements of PDB

In the present research, differential scanning calorimetry (DSC) was used to measure the content of residual double bonds in polymer samples. Figure 4 (a) shows DSC spectra of MMA–EGDMA polymer samples prepared by emulsion polymerization. Every DSC measurement was repeated once. The reproducibility appeared to be very good. The figure shows that at different monomer conversions, the heat flow profile for residual double bonds has only one peak. The relationship between total monomer conversion and integrated total heat flow for residual or unreacted double bonds in these samples is a monotonous decreasing function of total monomer conversion. In the present experiments, the samples were washed and dried to remove unreacted monomers before DSC measurement. The heat flow profiles for polymer samples can be used to estimate residual PDB. In the present study, the DSC testing began after the sample was cooled to room temperature, whereupon it was heated. No other reaction peaks were detected.

PDB Conversion

Figure 4 (b) is the profile of PDB conversion and glass transition temperature (T_g) versus total monomer conversion. In this figure, open symbols represent T_g . Solid symbols show PDB conversion. Triangle symbols (both solid and open) are for polymerization conditions with low SDS concentration. Regarding the PDB conversion, it can be seen that under both high and low SDS concentrations, the plots are monotonous increasing functions with total monomer conversion. A sharp change in slope is observed, and this may reflect a change in microstructure of polymer network. For the system having the higher SDS level, PDB conversion levels are higher.

It has been shown in Section (1) that for emulsion polymerization at a high SDS concentration,

micelle nucleation gives smaller particles with a lower monomer concentration. Therefore, a high EGDMA content might be expected in both free monomer and copolymer chains. These conditions favor a higher rate of PDB conversion. Considering the data for pendant double bond conversion mentioned above, one can understand that the crosslinking density of these polymers would vary differently with conversion. This phenomenon is an outcome of the different characteristics in emulsion polymerization mentioned above. Smaller particles have a lower monomer concentration. When one considers an active radical in the particle, the competition between propagation with monomer and reaction with PDB is clear. However, in this case, reaction with PDB is more favorable; thus, crosslinking in small polymer particles occurs at a higher level than that for large particles. A second explanation might be that for the system at a high SDS concentration and above the CMC polymer chains formed at earlier time have more EGDMA units. The glass transition temperature measurements for these samples further confirmed that this explanation is also possible. In the absence of micelles, copolymer chains produced in the water phase would be lean in EGDMA because of its very low water solubility.

Glass Transition Temperature (T_g)

In the present study, glass transition temperature is defined as the onset point of glass transition. In Figure 4 (b), the glass transition temperatures of those two polymer samples are shown as a function of monomer conversion. The only difference in the synthesis of these two samples is the SDS concentration used in the polymerization process. This figure shows that SDS concentration in the emulsion polymerization does have an effect on the polymer T_g . It is clear that samples prepared at higher SDS concentration have a higher T_g than those prepared at low SDS level. For samples prepared at higher SDS concentrations, T_g is initially close to that of a pure EGDMA polymer³⁰ then decreases with conversion.

For samples prepared at low SDS, at low conversions, T_g has values typical of polymers prepared by bulk polymerization with 0 and 25% EGDMA in the monomer feed.⁴³ Then it increases a little with conversion. The difference of T_g between these two samples narrows with conversion as chains with higher MMA levels are produced later in the polymerization when synthesized above the CMC. As mentioned in Section (2),

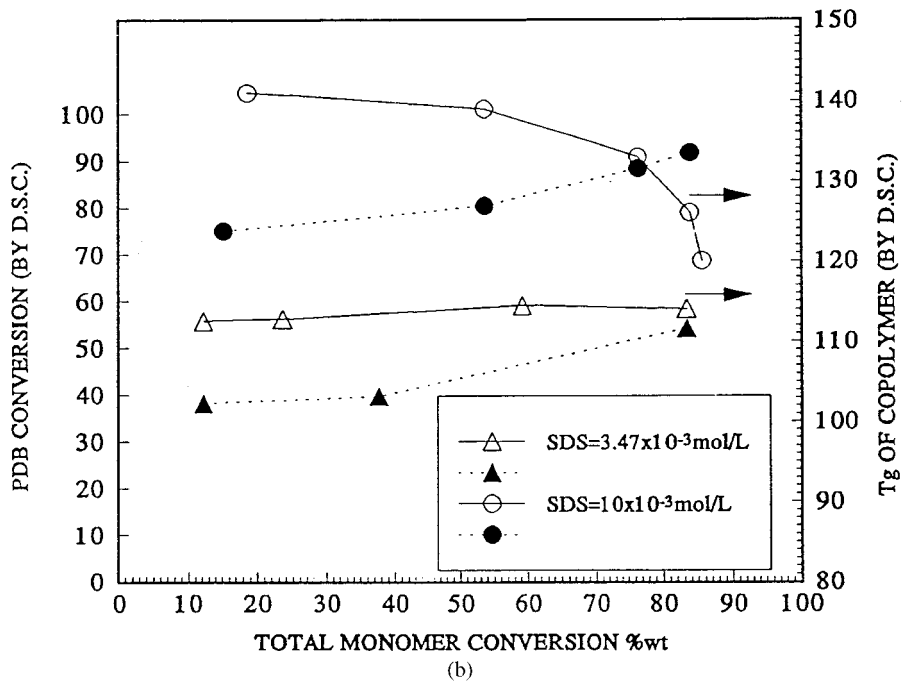
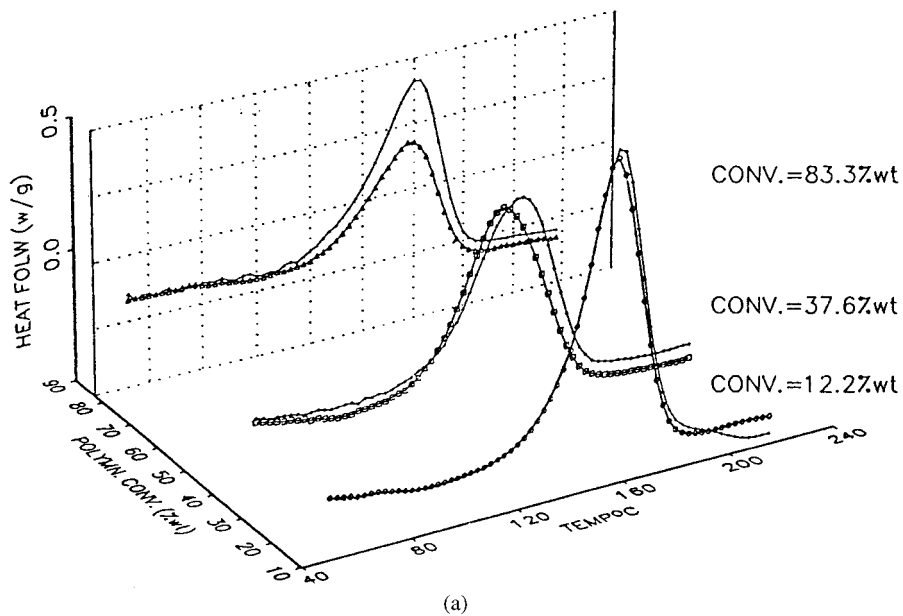
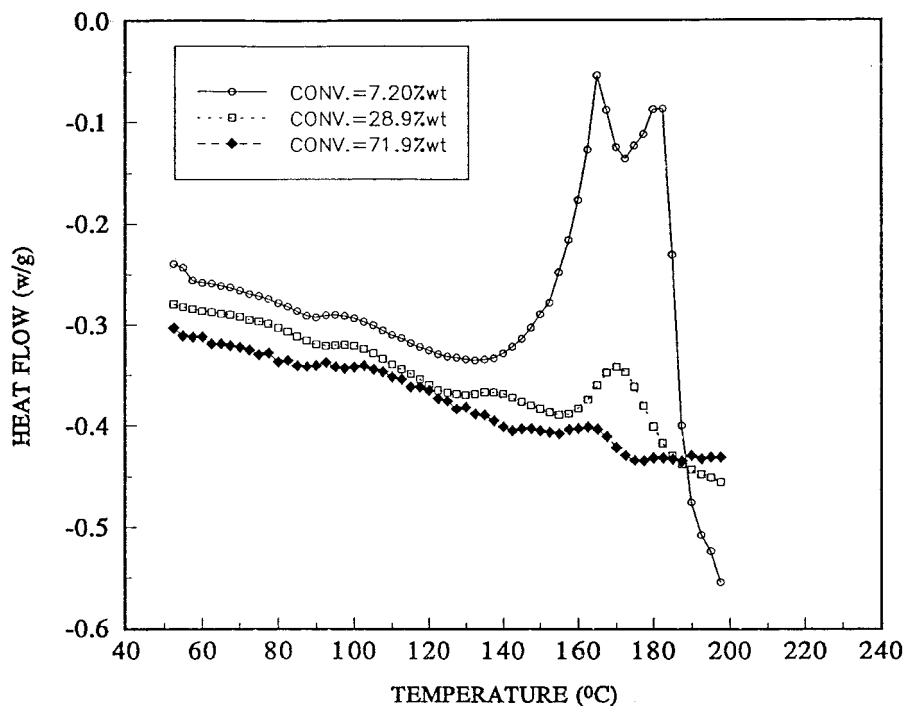
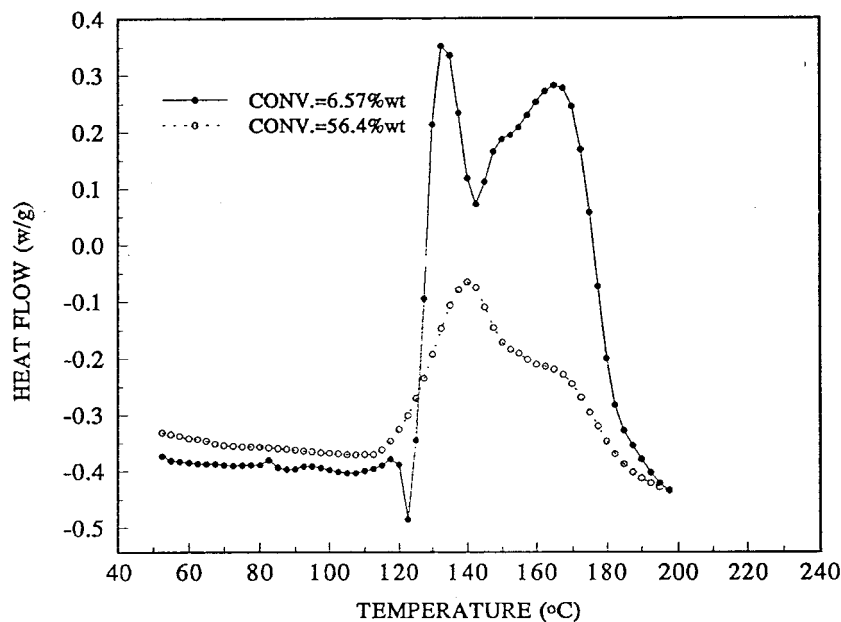


Figure 4 (a) 3-D Experimental results of DSC spectra for MMA-EGDMA copolymer recovered from the latex. Polymerization conditions are as follows. EGDMA-MMA: 10/90 wt %; KPS 2.2×10^{-3} mol/L H₂O. SDS: 3.47×10^{-3} mol/L H₂O. $T = 50^\circ\text{C}$. (b) Effect of SDS concentration on residual double bond content and glass transition temperature in MMA-EGDMA copolymer recovered from the latex. Polymerization conditions are as follows. EGDMA-MMA: 10/90 wt %; KPS 2.2×10^{-3} mol/L H₂O. $T = 50^\circ\text{C}$ (T_g = open symbols, PDB = solid symbols). (c) DSC spectra showing internal phase heterogeneity in MMA-EGDMA copolymer recovered from the latex. Polymerization conditions are as follows. EGDMA-MMA: 10/90 wt %; KPS: 4.4×10^{-3} mol/L H₂O. SDS: 10×10^{-3} mol/L H₂O. $T = 50^\circ\text{C}$. DSC spectra showing internal phase heterogeneity in MMA-EGDMA copolymer covered from latex. Polymerization conditions are as follows. EGDMA-MMA: 10/90 wt %. KPS: 2.2×10^{-3} mol/L H₂O. SDS: 10×10^{-3} mol/L H₂O. $T = 50^\circ\text{C}$.



(c)



(d)

Figure 4 (Continued from the previous page)

when SDS concentration is above its CMC, the solubilization of micelles has a significant effect on the availability of EGDMA monomer for polymerization. Polymers formed in the early stage of polymerization have more EGDMA monomer units and higher crosslinking density. They also

have higher double bond conversions and higher glass transition temperatures.

When SDS concentration is below the CMC, there are no micelles in the polymerization system. The homogeneous particle nucleation process makes larger particles. Chains precipitated

out of the water phase to form particles are much richer in MMA. The large particles are simply agglomerates of primary particles; hence EGDMA levels in the chains are smaller, giving lower crosslinking levels and T_g values.

Evidence for Internal Heterogeneity in Polymer Particles

Recalling the result in Section (1) that under high SDS concentration the polymerization rate with 25% EGDMA is lower than that with 10% EGDMA, and the effect of initiator concentration on the swellability of polymer particles in Section (3), attention was directed to the microinternal heterogeneity of polymer particles. This directly reflects the effect of crosslinking on microenvironment in polymerization. In the present study, DSC was used to study this phenomenon.

Figure 4 (c) shows the DSC spectra for polymers produced at the higher SDS concentration (10×10^{-3} mol/L H_2O), 10 wt % EGDMA, and KPS (4.4×10^{-3} mol/L H_2O) in the recipe. One can see that the polymer formed in the early stage shows two reaction peaks overlapping in the DSC spectra. It suggests that the polymer formed in the early stage of polymerization experiences microphase separation. This phase separation effect gradually reduces in intensity. These measurements reveal that the internal structure changes with conversion and that the shielding effect on trapped pendant double bonds might also change in intensity with conversion.

Figure 4 (d) shows the DSC spectra for polymers produced at SDS concentration (10×10^{-3} mol/L H_2O), 25 wt % EGDMA, and KPS (2.2×10^{-3} mol/L H_2O) in the recipe. Phase separation occurs again. At the higher EGDMA level, microphase separation situation showed more intensity and lasted longer. The effect of crosslinking on monomer swelling is more pronounced, PDB conversion slows, and radical trapping and diffusion control of propagation become distinct possibilities. This phase separation effect gradually decays with total monomer conversion as the system approaches the glassy state.

(5) Free Radical Concentration in Crosslinked Polymer Particles

There are only a few publications on the use of ESR to measure radical concentration in emulsion polymerization.⁴⁴⁻⁴⁹ All these publications considered emulsion polymerization in batch and semi-

continuous processes. MMA and styrene homopolymerizations, and butyl acrylate-MMA-methacrylic acid (8 : 91 : 1 wt %) copolymerizations were covered; but to date, the use of ESR to study emulsion polymerization with crosslinking has not been reported. In this section, the discussion of the direct measurement of the concentration of propagating free radicals in MMA-EGDMA emulsion polymerization coupled with the monomer conversion, the measurement accuracy involved in the ESR testing, the time profiles of free radical concentrations in the emulsion polymerization of MMA-EGDMA, the kinetic analysis of polymerization mechanism elucidated using ESR data, and the free radical trapping in polymer latex particles and glassy reactive polymer particles are included.

Characteristics of ESR Spectra in MMA-EGDMA Emulsion Polymerization

Figure 5 (a) shows the ESR spectra of polymer latex sampled from the reactor at different polymerization times. Polymerization conditions in the recipe were as follows: EGDMA-MMA, 10 : 90 wt %; SDS, 10×10^{-3} mol/L H_2O ; and KPS, 8.76×10^{-3} mol/L H_2O . It can be seen that the spectra gradually develop the characteristics of PMMA (5 + 4)-line hyperfine structure.

In bulk polymerization of MMA-EGDMA, Zhu et al.¹¹⁻¹⁴ observed an interesting ESR spectra transition from 13-line to 9-line in a 15 wt % EGDMA bulk polymerization near the final conversion. It was suggested that a 13-line signal structure indicated that the MMA radicals in the reaction mass were in a liquid environment, while a 9-line signal structure was contributed from the EGDMA radicals and/or the MMA radicals in a glass matrix.

In the above example measurement, because the sample quenching technology is always used before ESR testing, the 13-line spectrum cannot be expected, but the final 9-line structure is very clear. This revealed the accumulation of trapped radicals in polymer particles and change to a more heterogeneous radical structure as the glassy state transition is approached. The 9-line ESR spectrum of PMMA radicals in a solid-state matrix was probably first reported by Bowden and O'Donnell.⁵⁰ Ballard et al.⁴⁴ also reported that the 9-line spectrum was found in the latex sample taken from the reactor at the final conversion range of polymerization. In the above-mentioned semi-continuous emulsion polymerization of

monomer feed containing 98 wt % MMA, this 9-line spectrum was detected as well.

Radical Concentration and Total Monomer Conversion

Figure 5 (b) shows the change of total radical concentration and total monomer conversion versus polymerization time. The numbers in brackets are the total polymer particle numbers. The measurement shows two regions. Total radical concentration is almost constant in the early stage of polymerization and then increases dramatically. No radical concentration level off can be observed.

In the above-mentioned seeded MMA emulsion polymerization experiment,⁴⁴ the concentrations of PMMA propagating radicals in latex samples were measured by ESR. The radical concentration versus polymerization time curve showed a sigmoidal shape. It displayed three regions for radical concentration corresponding to the polymerization rate curve: (1) a low radical concentration value (ca. 10^{-7} mol/L) during stage II of the polymerization (i.e., in the absence of particle nucleation wherein the growth of the seed latex particles proceeds in the presence of monomer droplets); (2) a rapid radical concentration increase during the period of accelerating region in Stage III of polymerization (i.e., polymerization of monomer within the latex particles after exhaustion of monomer droplets), and a final level-off limiting radical concentration value about 10^{-5} mol/L near complete conversion.

Kinetic Analysis of Mechanism

The two regions for radical concentration versus polymerization time is related to the two stages in total monomer conversion change and total particle number change periods that could be kinetically analyzed to deduce the polymerization mechanism. During the rapid monomer consumption period, total particle number increases, but total radical concentration is constant. It is clear that monomers are mainly consumed in this period so that radicals produced in the water phase are primarily consumed in particle nucleation.

It can be understood that in this stage, the spectra should have an EGDMA-type character due to predominance of EGDMA-based radical centers. The EGDMA monomer has lower water solubility than MMA. EGDMA molecules transfer directly from the monomer droplet to polymer particles. Because the EGDMA monomer has a higher propagation rate constant ($k_{p22,p} \approx 2k_{p11,p}$), at this

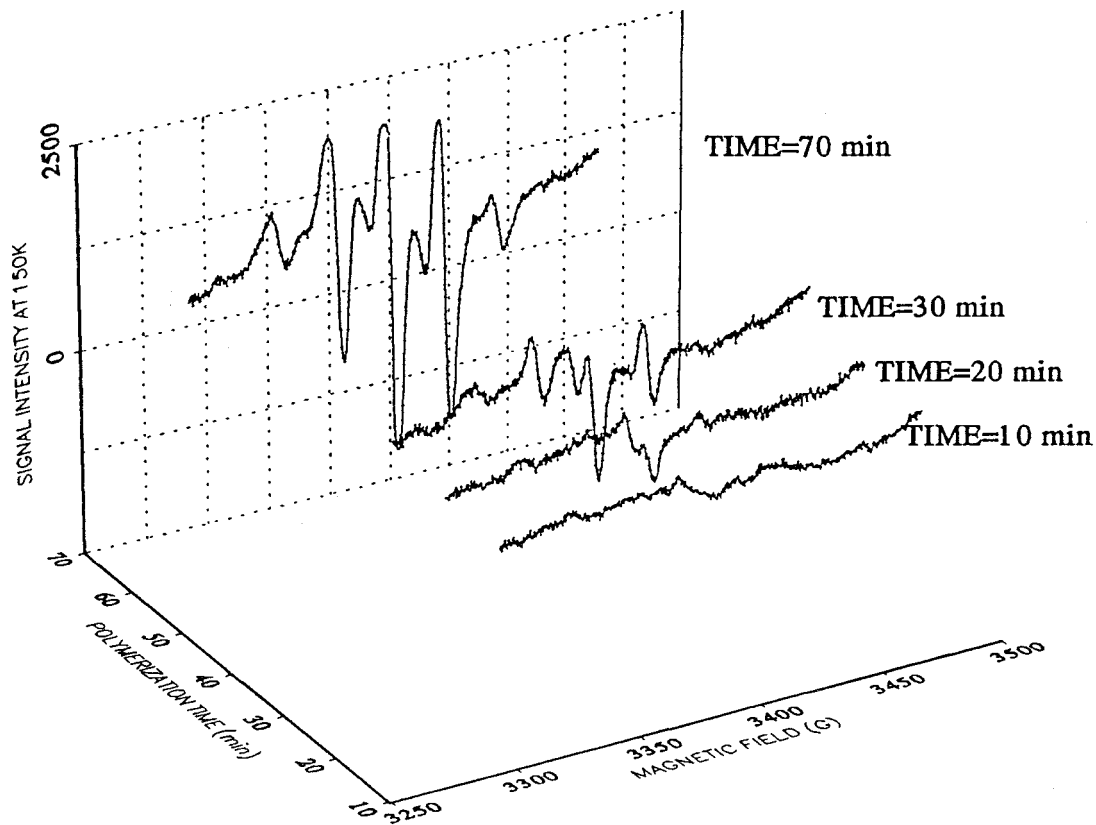
early stage, the copolymer chains are richer in EGDMA monomer units. The EGDMA-based radicals have a higher concentration than MMA-based radicals in the polymer latex.

In the second stage, total monomer conversion and particle number do not seem to change with time. However, in this period, the total radical concentration continues to increase, and the ESR spectra gradually evolve to that of PMMA chains. In this stage, oligomeric radicals entering the particle would experience instantaneous termination due to the small size of recently nucleated polymer particles and/or, most likely, they are immediately trapped by the high crosslinked network before further propagation with monomers or with PDB in particles. Based on the critical chain-length-controlled radical entry explanation, the oligomeric radicals that form in water phase basically consist of a KPS end group and a few MMA monomer units.

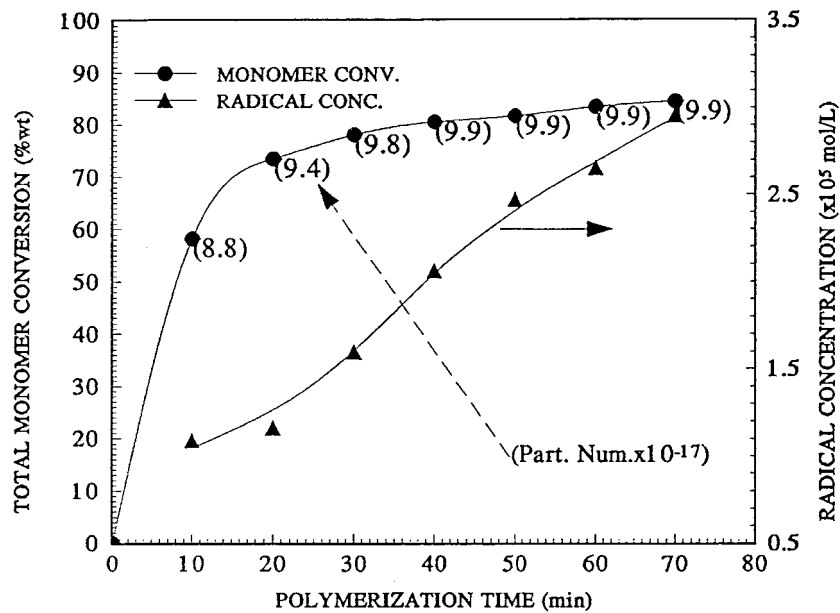
In the present MMA-EGDMA emulsion polymerization, that slight drop in radical concentration has not been observed. The reason is that the decrease in total radical concentration in bulk polymerization is attributed to the a dramatic reduction in initiator efficiency because of the cage effect. However, in emulsion polymerization, since radicals are generated from initiator decomposition in the water phase, the initiator efficiency likely does not change over most of the conversion range. The efficiency may fall, however, when the concentration of monomer in the water phase is close to zero.

Free Radical Trapping and Glassy Reactive Polymer Particles

To verify the assumption that the ESR signal is for the trapped radicals in the polymer particles rather than oligomeric radicals frozen in the water phase, the decay in radical concentration in the network was measured. At the end of the polymerization (polymerization was stopped at time = 70 min), the reactor temperature was reduced below the polymerization temperature (to about ambient temperature). The reactor was then opened to the atmosphere. Five days later, latex was sampled and measured again under the same conditions as before. The intensity of these two spectra is almost unchanged within the tolerance measurement error range. This means that the radicals trapped in the polymer were not consumed. If the radicals measured at the end of emulsion polymerization (time = 70 min) in-



(a)



(b)

Figure 5 Three-dimensional ESR spectra time profiles showing structure developing with polymerization time in MMA-EGDMA polymer latex. Polymerization conditions are as follows. EGDMA-MMA: 10/90 wt %. KPS: 8.76×10^{-3} mol/L H₂O. SDS: 10×10^{-3} mol/L H₂O. $T = 50^\circ\text{C}$. (b) Radical concentration and monomer conversion time

cluded those in the water phase; after 5 days in the presence of oxygen, it is certain that water-phase radicals would have reacted with oxygen.

At the ambient temperature, the polymer particles are in the glassy state. According to the result of ESR study on permeation of oxygen in cross-linked polymers⁴³ at 110°C, the permeability of oxygen (DH) is around 10^{-16} ($\text{cm}^2 \text{s}^{-1} \text{Pa}^{-1}$) in a MMA-EGDMA polymer network. The activation energy of permeation for oxygen in temperatures below T_g is 7.3 kJ/mol. The following estimation could be made:

$$\ln\left(\frac{DH_{110^\circ\text{C}}}{DH_{25^\circ\text{C}}}\right) \approx \frac{7300}{8.314} \left[\frac{373 - 298}{373 \cdot 298} \right] = 0.59 \quad (1)$$

The permeability of oxygen at room temperature ($DH_{25^\circ\text{C}}$) is 5×10^{-17} ($\text{cm}^2 \text{s}^{-1} \text{Pa}^{-1}$). Assuming a polymer particle with $0.1 \mu\text{m}$ diameter, under 10^5 Pa pure oxygen atmosphere condition,⁴³ a charac-

teristic diffusion time (t_{oxy}) could be estimated as follows:

$$t_{\text{oxy}} \approx \frac{(0.1 \times 10^{-4})^2}{5 \times 10^{-17}} = 2 \times 10^6 \text{ (s)} \approx 23.2 \text{ (day)} \quad (2)$$

It could be understood that at room temperature and 10^5 Pa pure oxygen atmosphere condition, over a five-day period, the diffusion of oxygen into polymer particles with a crosslinked network could be around $(5 : 23.2) \approx 21.5\%$. However, considering the oxygen content in the normal atmosphere (about 21%), this effect could be neglected.

Also, the diffusion of trapped (not chemically bonded) radicals from the polymer particles into water phase can also be neglected. It is clear that radicals in polymer particles are not consumed during this 5-day delay. The signal measured after 5 days represents that of trapped radicals

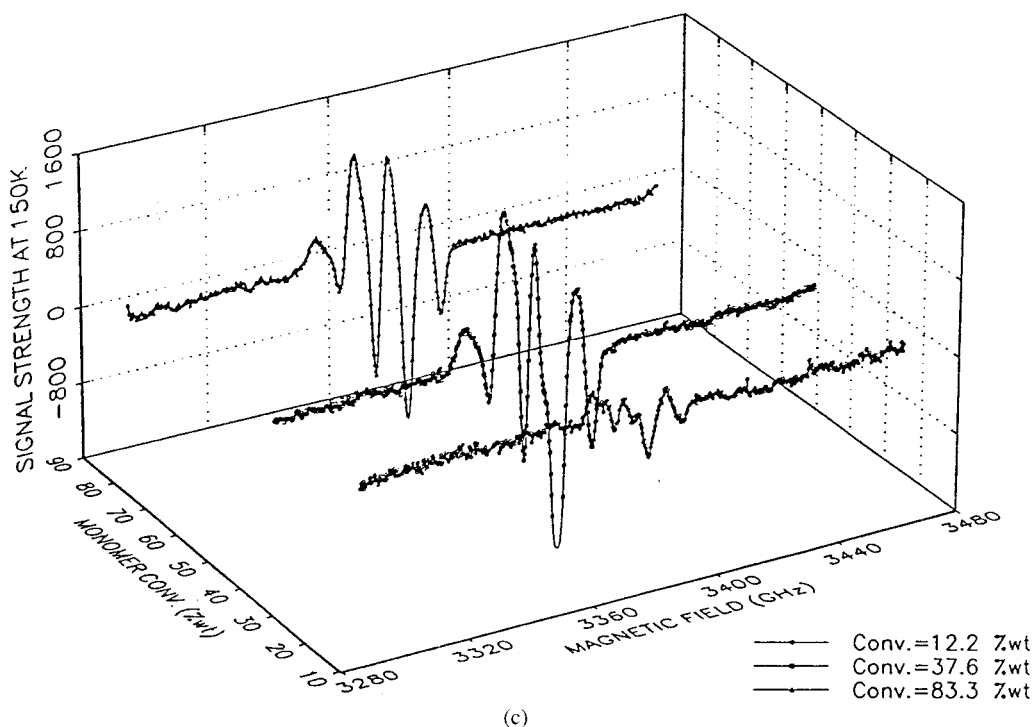


Figure 5 (Continued from the previous page)

profiles in MMA-EGDMA polymer latex. Polymerization conditions are as follows. EGDMA-MMA: 10/90 wt %. KPS: 8.76×10^{-3} mol/L H_2O . SDS: 10×10^{-3} mol/L H_2O . $T = 50^\circ\text{C}$. (c) Three-dimensional spectra conversion profiles showing structure developing in MMA-EGDMA polymer sampled at different monomer conversion and after being dried in a vacuum oven. Polymerization conditions are as follows. $T = 50^\circ\text{C}$. EGDMA-MMA: 10/90 wt %. KPS: 2.2×10^{-3} mol/L H_2O . SDS: 3.47×10^{-3} mol/L H_2O .

at the end of polymerization. The major structure of the spectrum was found unchanged. However, the center line structure has changed somewhat. The reason might be that due to the long relaxation time of the network after polymerization, the microenvironment of trapped radicals has changed.

In Section (4), results of DSC measurement of PDB for EGDMA 10 wt % system was reported. DSC spectra showed only one reaction peak. The total area of those peaks was a monotonous decreasing function of total monomer conversion. As has been mentioned, all these samples were washed and vacuum dried at 30°C to remove the residual monomer. Besides DSC testing, all these samples were tested by ESR for trapped residual radicals. Figure 5 (c) shows a typical spectrum. It could be clearly seen that after careful sample cleaning, these samples still have a very high radical concentration (about $0.4\text{--}6.0 \times 10^{-5}$ mol L). It could be deduced from these data that the reaction peak tested by DSC at elevated temperatures really involves pendant double bonds and free radicals. Both of them were trapped in highly crosslinked polymer particles during the emulsion polymerization process. Based on these experimental results, it should be clear that one kind of chemically reactive, highly crosslinked nanopolymer latex particle has been prepared that may have a potential application in synthetic rubber, engineering plastics, polymer modification, and controlled chemical release substrate areas.

CONCLUSIONS

The results of a comprehensive experimental study on kinetics of emulsion polymerization with crosslinking are reported. In the micellar nucleation domain case, solubilization by micelles caused a fast initial polymerization rate, a higher polymer particle concentration, and a smaller polymer particle size with higher initial PDB conversion and T_g . When polymerization was carried out at higher emulsifier concentrations (above the CMC), the EGDMA level in the monomer feed caused a very obvious crosslinking effect on the kinetics of emulsion polymerization. The polymerization rate increased with increase in EGDMA content to about 10 wt %. However, the polymerization rate at 25 wt % EGDMA level was lower than that at 10 wt %. This is a result of two opposing effects, the lower monomer concentration and the smaller polymer particles, the negative effect;

and the higher radical concentration in the polymer particles, the positive effect. Internal heterogeneity was detected by DSC in polymer particles prepared at higher initiator concentration and higher EGDMA monomer levels. This complex microenvironment for polymerization suggests that the shielding effect of pendant double bonds in the polymer particles is a most complex phenomenon. Time profiles of propagating radical concentration have two regions. A relative constant radical concentration region couples with a rapid monomer conversion rate and polymer particle concentration increase. A dramatic radical concentration change appears when monomer conversion rate and polymer particle concentration level off. These indicate a trapping of radicals within crosslinked polymer network during emulsion polymerization. Radical trapping is further confirmed by ESR testing of solid polymer samples coupled with DSC testing of residual PDB in the same samples. These results indicate the achievement of reactive, highly crosslinked nanopolymer particles, which might have many potential applications in the manufacture of specialty polymer-based products.

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