

# Study on Copolymer Emulsion Containing an Epoxy Group

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## SYNOPSIS

Methyl methacrylate, butyl acrylate, acrylic acid, and various amounts of glycidyl methacrylate (GMA) were copolymerized by a semicontinuous seeded emulsion copolymerization to be a four-component copolymer emulsion; the copolymers were characterized using swelling capacity, transmission electron microscopy (TEM), etc. The effect of glycidyl methacrylate and its content on the properties of emulsion and copolymer films was studied. The self-crosslinking reaction of the copolymer was investigated by FTIR and DSC. It was found that the swelling capacity of the crosslinked copolymer films decreased with increase of the glycidyl methacrylate content, the morphology showed a core-shell structure, and the copolymer emulsion possessed a self-crosslinking property. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Acrylate copolymers containing functional group emulsion as coatings, adhesives, and handling agents of spinning and weaving are produced and used widely.<sup>1-3</sup> But the properties of copolymer emulsion affects its application greatly. Sundardi and Zubir<sup>4</sup> prepared the emulsion with epoxy and carboxyl groups using radiation emulsion polymerization and investigated the influence of the irradiation dose rate and emulsifier. The glycidyl methacrylate copolymer emulsion without carboxyl groups was prepared by Zurkova et al.<sup>5</sup> and Okubo et al.<sup>6</sup> The existence of functional groups at the surface layer of the latex particle is very significant. The reactivity of the oxirane ring toward various nucleophiles is helpful for chemical modification of the basic polymer for various novel end uses. Copolymers based on glycidyl methacrylate (GMA) are, thus, of great value for binding enzymes and other biologically active species.<sup>7-9</sup> The oxirane-containing latex can be modified by a number of polymer-analogous reactions such as hydrolysis, ammonolysis, and aminolysis and by reaction with hydrogen sulfide in an aqueous solution, consequently obtaining active compounds.

In a previous article,<sup>10</sup> it was found that the methyl methacrylate-butyl acrylate-acrylic acid-*N*-

butoxymethylacrylamide copolymer emulsion possessed a self-crosslinking property; in this report, the methyl methacrylate-butyl acrylate-acrylic acid-GMA copolymer emulsion was prepared by seeded emulsion polymerization so that the functional groups were at the surface of the latex particle as far as possible. We turned our attention to the preparation of latexes containing epoxy groups and carboxyl groups and to the self-crosslinking property and morphology of the latex particle. The properties of copolymer emulsion were studied by various methods; investigated mainly were the effects of the functional groups on properties.

## EXPERIMENTAL

### Materials

Monomers such as butyl acrylate, acrylic acid, methyl methacrylate, and GMA were distilled in a stream of inert gas at a reduced pressure and stored in a refrigerator; sodium dodecyl sulfate and non-ionic emulsifier OS-15 were of analytical grade and were used without further purification; sodium persulfate was of analytical grade and was recrystallized. The aqueous phase was prepared with redistilled water, and all the polymerizations were conducted in a nitrogen atmosphere.

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**Table I** Recipe for Seeded Emulsion Polymerization

Ingredients	Amount
Methyl methacrylate	15
Butyl acrylate	25
Acrylic acid	3
Nonionic emulsifier OS-15	1.3
Sodium dodecyl sulfate	2.6
Water	160
Sodium persulfate	0.5
Ethylene glycol	2

### Preparation of Copolymer Emulsion

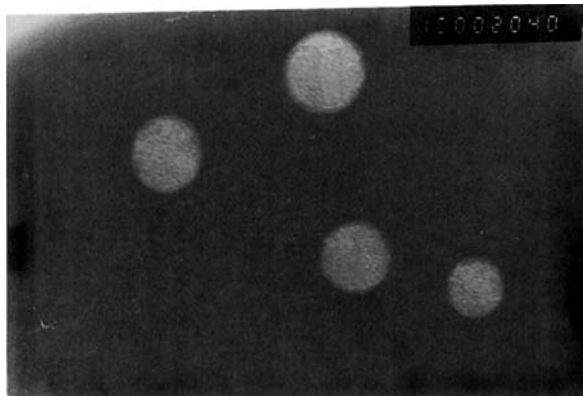
Polymerizations were carried out in a 0.5 L reactor equipped with stirrer, reflux condenser, sampling device, and inlet system for nitrogen. Seeded emulsions were prepared in a batch process using the recipes given in Table I and the polymerizations were carried out at 70°C for 1 h; then, the latexes were heated to 80°C and this temperature was maintained for 3 h. The recipes are given in Table II for the second stage of the seeded emulsion polymerization. The GMA content was changed but not the other ingredients' contents in the different samples. By semibatch emulsion polymerization, the seeded particles were allowed to swell with the mixture of the ingredients in Table II in a glass bottle by tumbling or by stirring for 24 h at room temperature prior to the polymerization; the polymerization was then carried out at 80°C and this temperature was maintained for 3 h. By semicontinuous emulsion polymerization, however, the polymerizations were carried out by dripping the mixture of ingredients in Table II to a seeded emulsion at 80°C; this temperature was maintained for 3 h after completing the addition of the ingredients.

### Transmission Electron Microscopy

Latex particle morphologies were determined by transmission electron microscopy (TEM) using a

**Table II** Recipe for Preparation of Copolymer Emulsion

Ingredients	Amount
Glycidyl methacrylate	X
Butyl acrylate	55
Acrylic acid	1
Water	80
Sodium persulfate	0.3

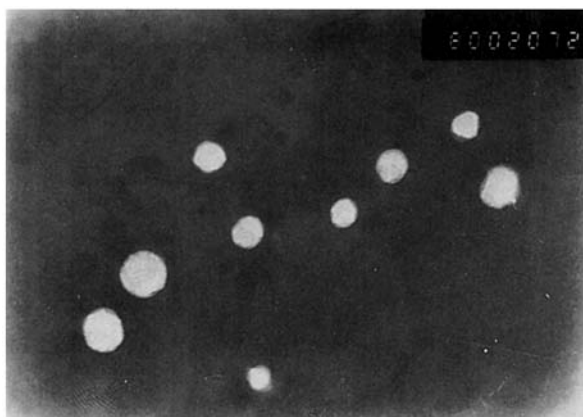


**Figure 1** Transmission electron micrograph of the 4% GMA composite particles prepared by semibatch emulsion polymerization (magnifying object  $8 \times 10^4$  diameters).

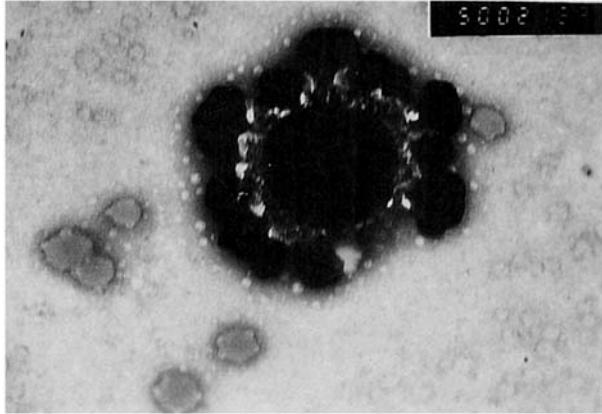
100-sx TEM. TEM has been extensively used in earlier studies of the morphology of submicron-size composite particles.<sup>11,12</sup> Internal particle morphologies were examined by drying samples of each latex, and the sections were stained with phosphotungstic acid ( $H_7[P(W_2O_7)_6 \cdot xH_2O]$ ) aqueous solution.

### Self-Crosslinking Property

The copolymer emulsions were dried at room temperature on polytetrafluoroethylene (PTFE) dishes to make the copolymer films; the films were characterized by ALPHACENTRIFT-IR. The IR spectra of the copolymers in different conditions were recorded. The variations in the extent of the reaction with temperature were measured at a heating rate of 2.5°C/min from room temperature to 220°C. Dif-



**Figure 2** Transmission electron micrograph of the 4% GMA composite particles prepared by semicontinuous emulsion polymerization (magnifying object  $8 \times 10^4$  diameters).

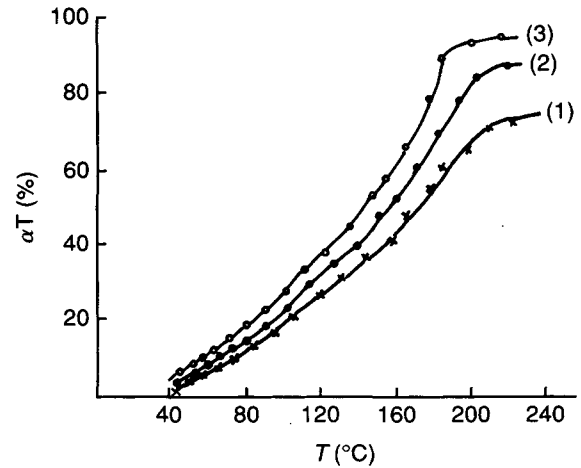


**Figure 3** Transmission electron micrograph of the 6% GMA composite particles prepared by semicontinuous emulsion polymerization (regative-dyeing).

ferential scanning calorimetry (DSC) was done in CDR-1-type instrument, and 10–20 mg specimens were scanned at a heating rate of 10°C/min in a nitrogen atmosphere.

**Swelling Capacity**

Copolymer emulsions were precipitated in methol and treated at 140°C for 45 min; then, the cross-linked copolymers were immersed in solvent at room temperature for more than 20 days so as to attain a swelling equilibrium. The specimens were immediately weighed after the solvent, which had attached onto the surface, was wiped off. The densities of

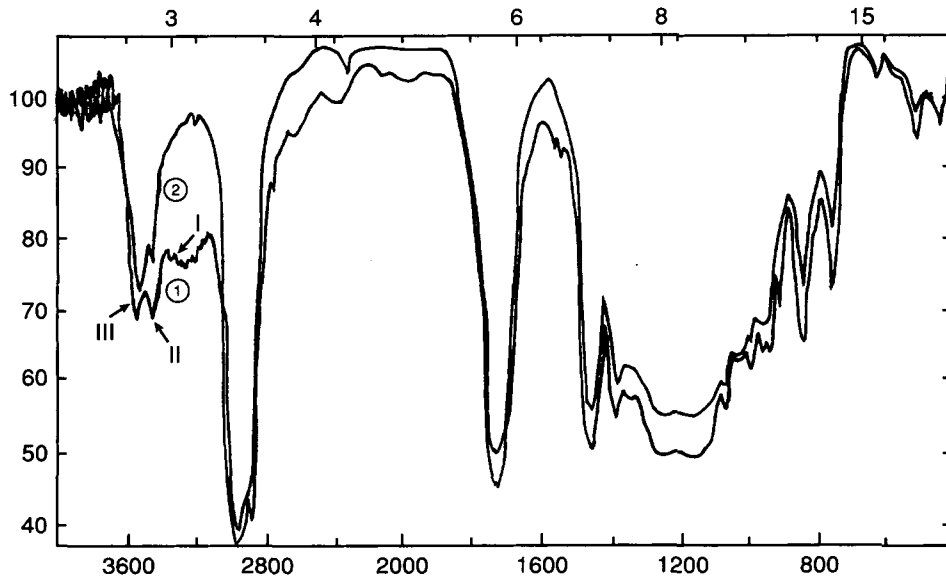


**Figure 5** The conversion rate of the epoxy group in the copolymer as a temperature function: (1) 3.5% GMA; (2) 3.9% GMA; (3) 4.2% GMA.

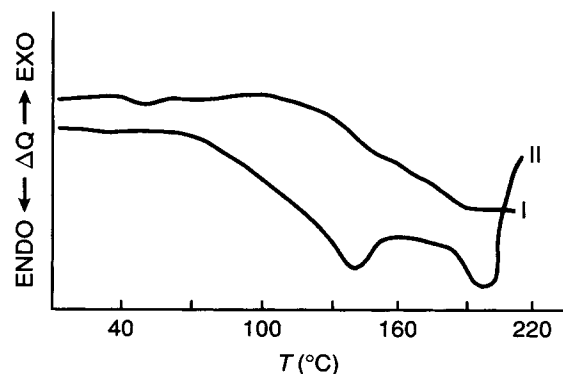
specimens were measured by a hydrometer method. The swelling capacities were calculated from the following equation:

$$Q = \left( \frac{W_1}{\rho_1} + \frac{W_2}{\rho_2} \right) / \frac{W_2}{\rho_2}$$

where  $W_1$  and  $W_2$  are the weight of solvents which are, respectively, in the swollen copolymer and specimen,  $\rho_1$  and  $\rho_2$  are, respectively, the density of the solvent and specimen which are not swelled.



**Figure 4** The absorption of the characteristic band decreased with increasing temperature: (1) 30°C; (2) 170°C.



**Figure 6** The DSC curve of copolymer films: (I) 4% GMA (it has been heated); (II) 4% GMA.

## RESULTS AND DISCUSSION

### Morphology of Composite Particle

The properties of a processed polymer compound depend to a major extent on the degree of mixing of its components. In the case of copolymer compounds prepared via core-shell latex technology, uniting the shell with the core can be controlled by polymerization parameters as well as by interfacial functional groups; the united degree of shell and core is directly reflected in the micromorphology of the final product.

Figure 1 shows the composite particles prepared by semibatch emulsion polymerization, and Figures 2 and 3 shows the composite particles prepared by semicontinuous emulsion polymerization. Figure 3 shows the composite particles which were treated by a negative-dyeing technology. Comparison of all micrographs has led to the following conclusions: (1) the morphology of the composite particles was of a core-shell structure, (2) the diameter of the particles which were prepared by semibatch emulsion polymerization was bigger than that prepared by semicontinuous emulsion polymerization and the sample has a narrow-size distribution, and (3) the composite particles have a streaky transitive layer between core

and shell. Attention was paid to the polymerization process, polymerization sites, and active functional groups. Considerations are focused on clarifying the difference between the two polymerization sites, i.e., at the surface or in the interior of the seeded particles. In semibatch emulsion polymerization, the monomer enters the interior of the seeded particles and swell the seeded particles; the majority of the monomer is concentrated in the interior of the particles. The polymerization took place mainly in the interior of the particles. The number of monomer molecules in the seeded particles was larger, but the number of monomer molecules in different seeded particles was almost the same; also, the rate and degree of polymerization in different particles were almost the same. Thus, the diameter of the emulsion particles was bigger and the size distribution was narrower. In semicontinuous polymerization, it is, contrarily, that the polymerization at the surface of the seeded particles was faster than that in the interior of the seeded particle. This might result from a higher monomer and radical concentration at the surface than that in the interior of the particles. The polymerization at the surface was affected by surface phenomena such as radical adsorption and desorption; the monomer concentration at different surfaces of the particles was different for the diffuseness of the monomer. The rate and degree of increase in the seeded particles were smaller and these, moreover, were different in different seeded particles. There was generation of a new crop of secondary particles. Therefore, the diameter of the emulsion particles was smaller and the size distribution was larger. Figure 3 shows that the composite particles has a streaky transitive layer between core and shell. The monomer accessed the surface of the seed particles during the emulsion polymerization, and the carboxyl groups at the surface of the seed particles might react to the epoxy groups contained in GMA, so there existed an opening-ring reaction accompanying the radical propagation re-

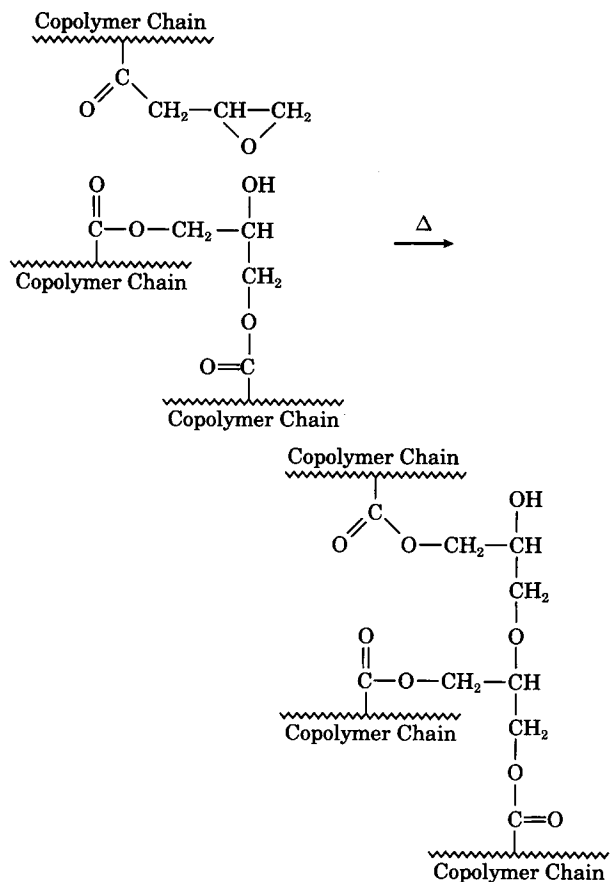
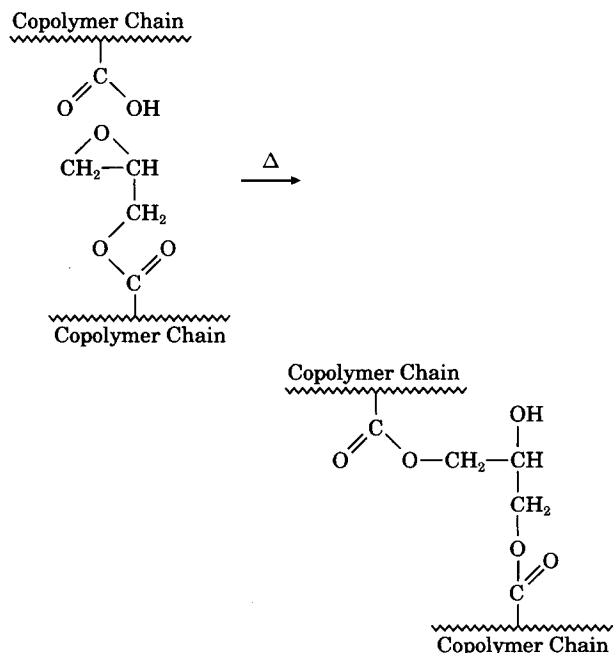
**Table III** Swelling Capacities of Crosslinked Copolymers in Different Solvents

Sample	Acrylic Acid Content (%)	GMA Content (%)	Swelling Capacities			
			THF	<i>n</i> -Heptane	DMF	<i>p</i> -Xylene
G-1	4	2	12.34	1.68	8.99	9.90
G-2	4	4	10.70	1.56	6.93	8.79
G-3	4	6	6.60	1.45	4.49	5.94
G-4	4	8	6.57	1.38	4.48	5.24
G-B	4	15	3.60	1.20	3.38	2.81
G-D	0	4	15.35	1.75	3.73	12.05

action; on the other hand, grafting copolymerization may have existed. Therefore, a complex crosslinking structure was produced in the interfaces of the core and shell.

### Self-Crosslinking Property

In IR spectra, we took the epoxy absorption at  $909\text{ cm}^{-1}$  as the characteristic band and the C—H bending vibration absorption at  $1452\text{ cm}^{-1}$  as the internal standard to analyze the reaction; we paid attention to the  $3600\text{--}3100\text{ cm}^{-1}$  region which was a mixture of the absorption bands of both carboxyl and hydroxyl groups; the hydroxyl groups were from epoxy groups opening in the emulsion polymerization. The epoxy group absorption band decreased and disappeared when the sample was heated from room temperature to  $220^\circ\text{C}$  (Fig. 4); simultaneously, band I in the  $3600\text{--}3100\text{ cm}^{-1}$  region disappeared, and the ratio of the band II area to the band III area in  $3600\text{--}3100$  was changed. This indicated that the epoxy group in the copolymer reacted to carboxyl groups and produced hydroxyl groups; the hydroxyl groups might also react to epoxy groups at higher temperature. The reaction was between the composite particles and between the copolymer chain sections. Furthermore, the crosslinked point is produced; it formed a crosslinked network structure. On heating, the copolymers containing epoxy groups, carboxyl groups, and hydroxyl groups might react as follows:



The conversion rate of epoxy groups at varied temperatures was calculated using the following equation:

$$a_T = \left[ 1 - \frac{(A_{909} \div A_{1452})T}{(A_{909} \div A_{1452})Tr} \right] \times 100\%$$

where  $A_{909}$  and  $A_{1452}$  are the absorption band area at frequency of  $909$  and  $1452\text{ cm}^{-1}$ , respectively.  $T$  and  $Tr$  are the measurement temperature and room temperature, respectively.

When the copolymer was heated from room temperature to  $220^\circ\text{C}$ , the conversion rate of epoxy groups was measured as a temperature function (Fig. 5). Figure 5 indicates that the conversion rate was smooth after  $200^\circ\text{C}$  and the conversion rate increased with the increasing temperature before  $200^\circ\text{C}$ ; although the content of GMA was different, the changes of the conversion rate at higher temperature ( $140\text{--}200^\circ\text{C}$ ) is bigger than that at lower temperature ( $40\text{--}120^\circ\text{C}$ ); this phenomenon is obvious as the content of GMA is higher.

Figure 6 shows the DSC results where curve I is the DSC curve of the film heated at  $140^\circ\text{C}$  for 45 min and curve II is the DSC curve of the film dried at room temperature. There are thermal phenomena

in curve II, which shows that the self-crosslinking reaction takes place when the copolymer film is heated. The endothermal process may accompany the self-crosslinking reaction. The thermal phenomenon is hardly observed as the copolymer film has been heated (curve I) prior to the DSC experiment.

The films of copolymers were heated at 140°C for 45 min, and the functional groups in copolymers reacted to each other and formed a crosslinked network structure. The crosslinked copolymer should not be dissolved but it swelled in some solvents; the more the copolymers were crosslinked, the more they swelled. The GMA content was found to have a considerable effect on the swelling capacity of crosslinked copolymers (Table III); the swelling capacity decreased with increase of the GMA content due to the increase of crosslinked density in the copolymer.

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