

# Crosslinking Reaction of Polyacrylate Soap-Free Hydrosol with Zirconium Chelate

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**ABSTRACT:** The crosslinking reaction mechanism of polyacrylate copolymer (monomer mass ratio of methyl methacrylate/butyl acrylate/acrylic acid = 48.77:46.69:4.54) hydrosol with triethanolamine chelate of zirconium isopropoxide was studied with IR spectroscopy, NMR spectroscopy, differential scanning calorimetry, and ultraviolet spectroscopy. The instrumental analyses on the copolymer mix-

ture heated at different temperatures were investigated, and we proved that the crosslinking adduct had amino groups that were provided by the chelate. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3605–3609, 2004

**Key words:** curing of polymers; water-soluble polymers; hydrophilic polymer; crosslinking

## INTRODUCTION

The change from an organic solvent to an aqueous system in ink formulations requires the development of new ink binders. The use of alkali-soluble emulsions has been increasing steadily because at high pH, the polymer particles disintegrate, the emulsion turns into a water solution, and the alkaline solution behaves similarly to a traditional polymer solution in a solvent-based system.<sup>1,2</sup> The most popular characteristic of the alkali-soluble emulsion is its reverse solubility. The resolubility of the ink is the ability of the dry polymer in the cell and roller to be redispersed by the wet ink, which is essential for high-speed printing. However, the properties of the inks formed from such emulsions are usually inferior to those from polymer solutions when considered in terms of resistance to water and organic solvents, general mechanical properties, and drying and blocking properties.

To overcome these drawbacks, new types of polymers have been developed, and an extensive amount of fundamental research has focused on the study of the particle size, size distribution, film formation, drying behavior, and shape of the emulsion particles.<sup>3–9</sup> However, little attention has been paid to the delayed crosslinking reaction in the drying film, which can keep the emulsion reverse solubility within 10s of seconds and retain film water resistance. On the basis of this more “micro” point

of view, our research was directed to improve emulsion film water resistance through a crosslinking reaction.

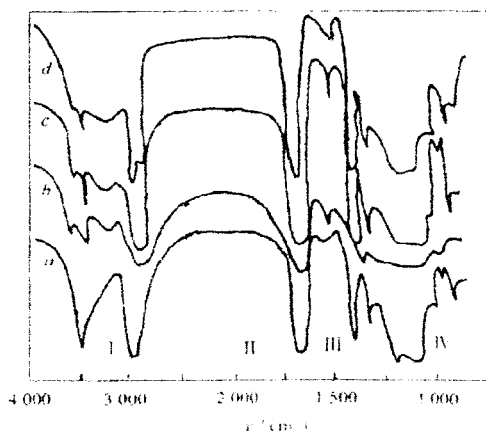
According to Nagila et al.,<sup>10</sup> in polyacrylate ionomers, the zirconium has the necessary physicochemical properties for durable binding to carboxylate and other oxygen donor sites; moreover, the zirconium is generally environmentally favored and has gained approval for use in foodstuff packaging. In this study, a polyacrylate copolymer [methyl methacrylate (MMA)/butyl acrylate (BA)/acrylic acid (AA)] soap-free hydrosol was used as the alkali-soluble emulsion, and the water-soluble triethanolamine chelate of zirconium isopropoxide (ZrE) was used as the crosslinking agent. It has been found<sup>11</sup> 2% chelate decreased the water uptake of a hydrosol film from 4.5–0.6%; meanwhile, the hydrosol with ZrE kept good reverse solubility (the film dried at room temperature for an hour solved in the wet phase within 30 s). In this study, the mechanism of this improvement is investigated.

## EXPERIMENTAL

### Materials

The copolymerization of the polyacrylate (monomer weight ratio of MMA/BA/AA = 48.77:46.69:4.54) was conducted in a homogeneous-phase isopropyl alcohol (IPA) solution, and it was neutralized with 25% aqueous ammonia and then dispersed in water, forming a soap-free hydrosol. The hydrosol solid content was 30% at pH 8 with 10% IPA as the cosolvent. ZrE was provided by Dupont (Wilming-

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**Figure 1** IR spectra of the films: (a) copolymer hydrosol dried at 120°C, (b) hydrosol with ZrE dried at 80°C, (c) hydrosol with ZrE dried at 100°C, and (d) hydrosol with ZrE dried at 120°C.

ton, DE) and was used as received. The chelate was  $\text{Zr}(\text{TEA})_2(\text{OR})_2$  abbreviated as ZrE, where R represents an isopropyl group.

#### Preparation of films

We prepared the films were prepared by spreading polymer hydrosols with or without chelate on polytetrafluoroethylene dishes and evaporating them to dryness over a period of half an hour at different temperatures.

#### IR spectroscopy

Infrared spectra were measured with a Nicolet 205 FT instrument over a range of 4000 to 400  $\text{cm}^{-1}$ . Measurements were performed on films prepared from hy-

drozol with 2% chelate ZrE dried at different temperatures and purified by soaking in alkali solution and washing with deionized water till neutral.

#### Film water resistance

The water resistance of the hydrosol film was judged by the water uptake ( $U_w$ ) after the tested samples soaked in water. We weighed the film ( $m_1$ ), soaked it in water for 24 h, cleaned the film surface water with paper tissue, weighed it again ( $m_2$ ), and calculated the weight increment percentage, or  $U_w$ , as follows:

$$U_w = \frac{m_2 - m_1}{m_1} \times 100\%$$

#### Differential scanning calorimetry (DSC)

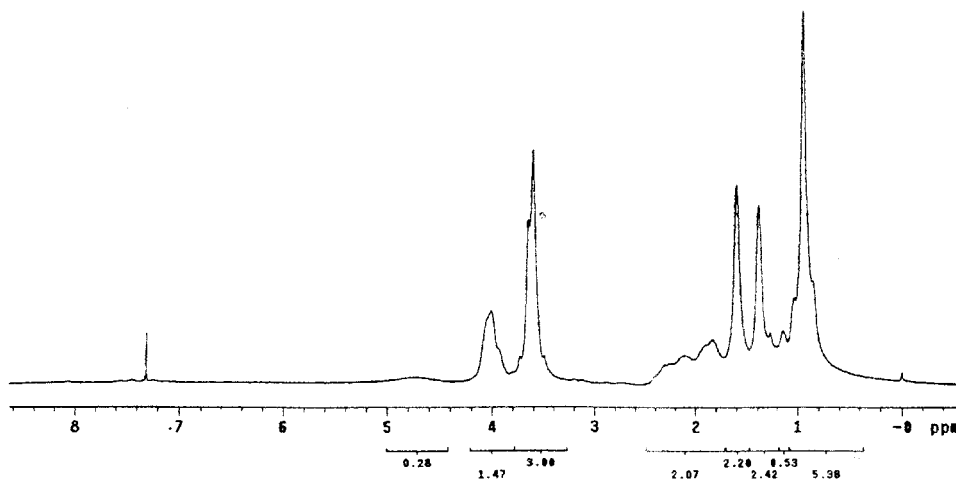
DSC was used to determine the glass-transition temperatures ( $T_g$ ) and the reaction mechanism<sup>12</sup> of the film samples. A PerkinElmer DSC-2C was performed from -20 to 150°C, and the heating rate was 10°C/min.

#### Ultraviolet visible (UV-vis) spectrophotometry

An UV-vis UV 240 spectrophotometer was used to detect the existence of the chelate ring in the hydrosol under different heating temperatures.

#### NMR spectroscopy

A jedl EX90Q Fourier transform NMR spectrometer (Varian, USA) was used to study the crosslinking behavior of the copolymer with chelate. The samples were purified as in IR analysis.



**Figure 2**  $^1\text{H}$ -NMR spectrum of the copolymer with ZrE dried at 80°C for 30 min.

TABLE I  
NMR Analysis of Films of the Copolymer with or Without ZrE

<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>H</i>	Assignment
No notable	7.320	7.264	7.309	—OH	N(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>2</sub>
4.001	4.004	4.007	3.999	—OCH <sub>2</sub> —	BA
3.644	3.542	3.644	3.645	—OCH <sub>2</sub>	MMA
1.600	1.599	1.601	1.601	—CH <sub>2</sub> —	BA
1.386	1.381	1.383	1.383	—CH <sub>2</sub> —	BA
1.030	1.029	1.029	1.029	—CH <sub>3</sub>	BA
0.942	0.943	0.943	0.947	—CH <sub>3</sub>	MMA

## RESULT AND DISCUSSIONS

### IR spectroscopy analysis

Figure 1 shows the IR spectra of films cast from the copolymer hydrosol dried at 120°C [Fig 1 (a)] and the hydrosol with ZrE dried at 80, 100, and 120°C, respectively [Fig. 1 (b–d)]. The band at 3441.8 cm<sup>-1</sup> in Figure 1 (a), due to the hydroxy groups, shifted to a lower frequency just a little bit in the spectra in Figures 1(b)–1(d), but for the copolymer with chelate, there appeared a new band at 3250.0 cm<sup>-1</sup>, which was assigned to N—H vibration in the copolymer. As the free chelate was water soluble and was cleaned off in the purification process, the NH groups were from the crosslinked copolymer. The IR bands due to the  $\nu_{CO}$  stretching frequency were clearly visible at 1727.1 cm<sup>-1</sup> [Fig. 1 (a)] but moved to 1718.2, 1716.8, and 1716.4 cm<sup>-1</sup> [Fig. 1 (b–d)].

### <sup>1</sup>H-NMR analysis

The chemical compositions of the hydrosols with chelate dried at 80, 100, and 120°C were studied with

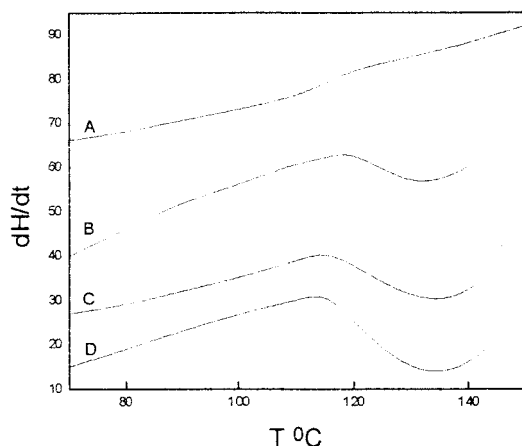
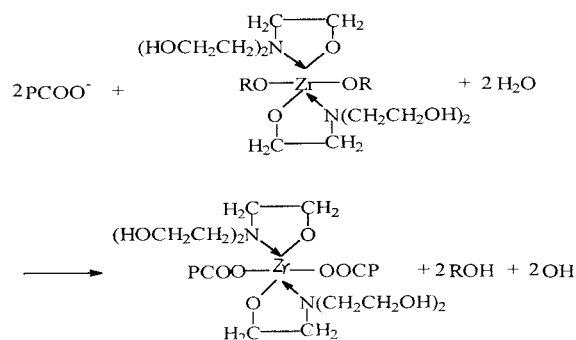


Figure 3 DSC of the films of the (A) copolymer hydrosol dried at 120°C, (B) hydrosol with ZrE dried at 120°C, (C) hydrosol with ZrE dried at 100°C, and (D) hydrosol with ZrE dried at 80°C.

<sup>1</sup>H-NMR. Figure 2 shows the spectrum of the copolymer with the chelate dried at 80°C. All of the samples with chelate had similar NMR spectra; the chemical shift data are listed in Table I. The chemical shift of —NH of the chelate agent was  $\delta$  7.3, and appeared in the three samples with ZrE dried at different temperatures, but no such chemical shift appeared in the copolymer without the chelate. That means N—H bonding was found in the copolymer with ZrE, which was consistent with the IR results.

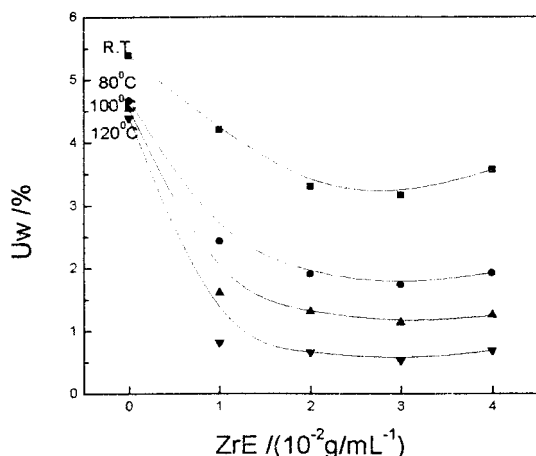
From IR and <sup>1</sup>H-NMR results, we inferred the crosslinking reaction between copolymer and ZrE as follows:



The existence of isopropanol (ROH) could oppress the reaction. It was evident that when the copolymer hydrosol with ZrE was heated at a higher temperature, the evaporation of ROH was favorable for the crosslinking reaction. We expected the crosslinking of the hydrosol with ZrE at 120°C would be more complete than that at 80°C.

### DSC analysis and film water resistance

Figure 3 shows that exothermic peaks existed in curves D, C, and B, but no such peak occurred in curve A. That means the crosslinking reactions took place continuously in the hydrosol films with ZrE. Furthermore, the peak area decreased from 80 to 120°C. That means the crosslinking reaction had already taken place more completely at the higher temperature. This

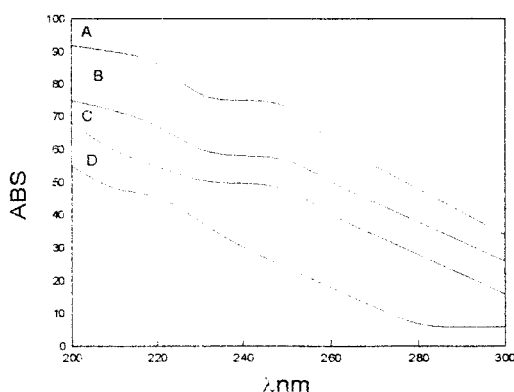


**Figure 4** Effect of the amount of ZrE and the drying temperature on the film water resistance.

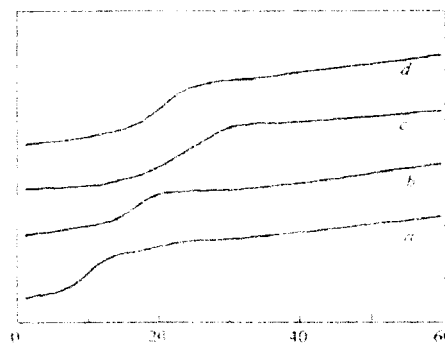
was consistent with the results detected for the water resistance of hydrosol films dried at different temperatures (Fig. 4). The  $U_w$  value of the 120°C film was evidently lower than the 80°C dried film due to more crosslinked polymer in 120°C sample.

#### UV spectroscopy analysis

The ultraviolet (UV) studies of the heated hydrosols with chelate ZrE diluted to a solid content of  $10^{-4}$  wt % are shown in Figure 5. ZrE had a characteristic absorbance at 240 nm [Fig. 5 (A)], which was related to the ZrE ring structure. When ZrE was blended in the copolymer hydrosol, the characteristic peak was still visible in Figure 5 (B) and shifted a little bit in Figure 5 (C) for the 80°C heated sample but was absent in Figure 5 (D). The UV evidence, therefore, suggested that there was a ring structure from ZrE in the hydrosol at 80°C, but at 130°C, most of the ring structure



**Figure 5** UV spectra of the (A) ZrE, (B) hydrosol with ZrE, (C) hydrosol with ZrE heated at 80°C for 30 min, and (D) hydrosol with ZrE heated at 130°C for 30 min.

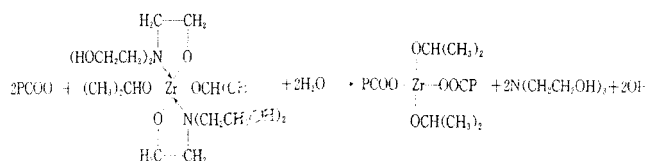


**Figure 6**  $T_g$  values of the films of the (a) copolymer hydrosol dried at 120°C, (b) hydrosol with ZrE dried at 120°C, (c) hydrosol with ZrE dried at 100°C, and (d) hydrosol with ZrE dried at 80°C.

was broken. This deduction was further proven by the copolymer glass-transition temperature ( $T_g$ ) results as shown in Figure 6.

#### $T_g$ values of the copolymer with or without the zirconium chelate

$T_g$  values of a series of films formed from the hydrosol containing 2% chelate and dried at different temperatures were determined by DSC. An examination of Figure 6 showed that the samples with the chelate had higher  $T_g$  values than the precursor copolymer. The  $T_g$  value for the hydrosol with 2% chelate dried at 80°C was 18°C, 5°C higher than that found for the copolymer without ZrE. This was expected, as ZrE was expected to result in a crosslinked film; this is generally associated with a decrease in the segmental mobility of the polymer. However, there was an interesting phenomenon as we compared the  $T_g$  of the copolymers with ZrE dried at different temperatures. The  $T_g$  value of the 120°C dried film was a little bit lower than that of the 80°C film. It was probable that at 120°C, there was another crosslinking reaction, and according to the UV results, the crosslinking site was probably related with the broken chelate ring. This crosslinking reaction may be displayed as follows:



Because the crosslinked copolymer had a less hard ring structure, the  $T_g$  correspondingly decreased.

#### CONCLUSIONS

This study on the films of carboxyl polyacrylate with zirconium chelate by IR and NMR, spectroscopy

showed that the polyacrylate copolymer could crosslink with the chelate ZrE to produce a crosslinking polymer with amino groups provided by the chelate. The crosslinking reaction took place more completely at higher temperatures. This was proven by the results of DSC, UV analysis, and water resistance tests of the hydrosol films dried at different temperatures.

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