

Studies on Coordination-Crosslinking of Soap-Free Polyacrylate Hydrosol and Metal Ion

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Received 12 November 1996; accepted 7 May 1997

ABSTRACT: A new soap-free water-borne coating (solid content ca. 35 wt %) has been obtained by adding the coordination-crosslinking agent $M(\text{NH}_3)_4^{2+}$ into the $-\text{COO}^-$ -containing polyacrylate hydrosol ($\text{P}-\text{COO}^-$). The transmission electron microscope analysis has been used to investigate the coordination-crosslinking process of the polyacrylate hydrosol with $\text{Zn}(\text{NH}_3)_4^{2+}$ in the water-borne coating of low concentration (solid content ca. 0.05 wt %). The existence of the coordination-crosslinking polymer ($\text{P}-\text{COO}^-)_n\text{M}^{2+}$ both in the water-borne coating of low concentration (solid content ca. 0.3 wt %) and in the coating film has been detected by the linear sweep voltammetry polarographic analysis, ultraviolet-visible spectrographic analysis, and IR spectrographic analysis. All the experimental results show that the polyacrylate hydrosol ($\text{P}-\text{COO}^-$) can take the coordination-crosslinking reaction with metal ion M^{2+} to form the coordination polymer $[(\text{P}-\text{COO}^-)_n\text{M}^{2+}]$. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 2457–2463, 1997

Key words: coordination-crosslinking; coordination polymer; soap-free hydrosol; water-borne coating; coating film

INTRODUCTION

Water-borne coating, with water as the main solvent or dispersion medium, has the advantage of low pollution, low price, and good quality in comparison with the traditional organic coatings, such as acrylate coating crosslinked by isocyanate with methylbenzene or acetic ether as organic solvent (DuPont Company 660S product). According to the features of the crosslinking-curing mechanism, the water-borne coating is divided into two types: self-crosslinking coating and coating with added crosslinking agent. The curing of the first type takes place through the crosslinking reaction between the active groups (e.g., methylol, alkyl methylol, and amido) inherent in the macromolecules in the coating, while the curing of the second type through the crosslinking between the func-

tional groups (e.g., hydroxyl and carboxyl) of the macromolecules and those groups (e.g., metal ion, amino, isocyanate) of the added crosslinking agents. Usually the crosslinking interaction is stronger for the second type, leading to reduction of the curing temperature ($\leq 120\text{--}150^\circ\text{C}$),^{1,2} lower than the curing temperature of the first type ($\cong 160\text{--}180^\circ\text{C}$).³

In recent years, many articles have been written about the crosslinking reaction between the metal ion and the $-\text{COO}^-$ -containing polymer in the emulsion coating at low temperature,^{4–8} but no such works for the soap-free hydrosol coating are reported. The property of the soap-free hydrosol coating, which does not contain the additional emulsifier, is better than the emulsion coating with additional emulsifier in two respects: (1) the particle diameter of the hydrosol (0.01–0.1 μm) is much smaller than that of the emulsion ($\geq 0.1 \mu\text{m}$), so that the hydrosol has better freeze-thaw stability. (2) Since no added emulsifier is left in the soap-free hydrosol coating film, the film has better lustre, water resistance, and mechani-

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Journal of Applied Polymer Science, Vol. 66, 2457–2463 (1997)
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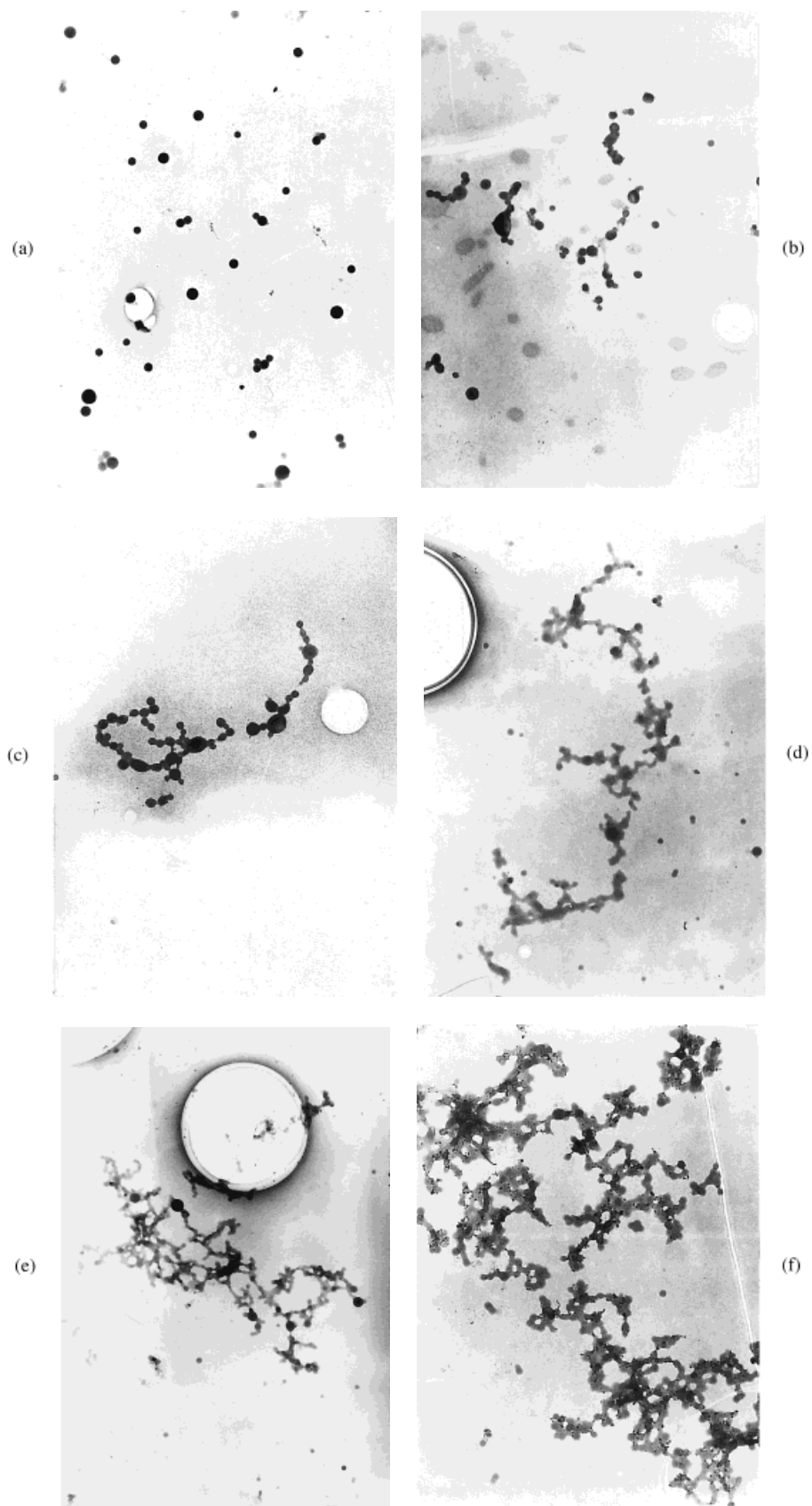


Figure 1 TEM photos of water-borne coating with $\text{Zn}(\text{NH}_3)_4^{2+}$ as coordination-cross-linking agent at 80°C (8000 times): (a) $t = 0$, (b) $t = 20$ min, (c) $t = 40$ min, (d) $t = 60$ min, (e) $t = 90$ min, (f) $t = 120$ min.

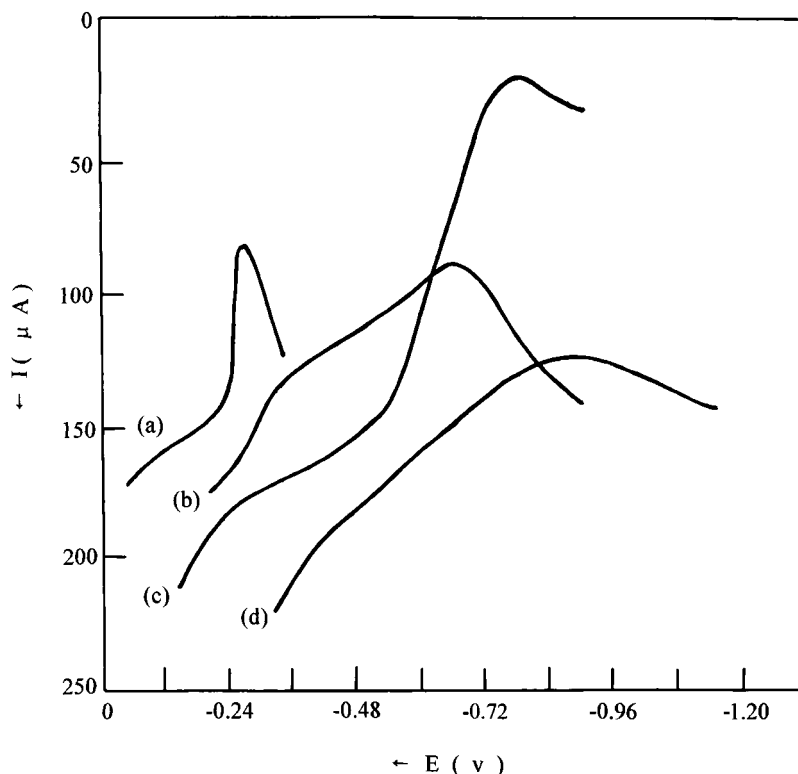


Figure 2 The linear sweep voltammetry polarograms of Cu^{2+} in various coordination states: (a) free Cu^{2+} , (b) $(\text{CH}_3\text{COO}^-)_2\text{Cu}^{2+}$, (c) $\text{Cu}(\text{NH}_3)_4^{2+}$, (d) water-borne coating heated at 80°C for 30 min.

cal properties. But on the other hand, there are some complications for the soap-free hydrosol system. The soap-free hydrosol coating is stabilized by self-emulsification, while the emulsion coating is stabilized by the added emulsifier. Therefore, in the soap-free hydrosol coating, the functional group (e.g., $-\text{COO}^-$) in the polymer has to emulsify (or stabilize) the coating through its own hydrophilicity and also has to deemulsify (or cure) through its reaction with the added curing agent. How to control these two opposite processes is a rather complex problem.

In the present work, a soap-free polyacrylate

Table I E_p and $\log K_s$ of Cu^{2+} in Various Coordination States

Coordination State	$E_p(\text{v})$	$\log K_s$
Free Cu^{2+}	-0.27	—
$(\text{CH}_3\text{COO}^-)_2\text{Cu}^{2+}$	-0.67	2.7 ¹⁰
$\text{Cu}(\text{NH}_3)_4^{2+}$	-0.78	12.5 ¹¹
$(\text{P-COO}^-)_n\text{Cu}^{2+}$	-0.91	> 12.5

hydrosol containing $-\text{COO}^-$ (P-COO^-) has been prepared by the reaction of the acrylate copolymer (acrylic acid/butyl acrylate/methyl methacrylate/styrene) with amine. The metal amino complex $\text{M}(\text{NH}_3)_4^{2+}$, used as the added curing agent, is added into the hydrosol to form a soap-free water-borne coating. It is expected that before curing, M^{2+} in $\text{M}(\text{NH}_3)_4^{2+}$ form cannot react with P-COO^- completely, leaving some $-\text{COO}^-$ free to stabilize the hydrosol, and in forming the coating film by heating at not too high temperature, M^{2+} can set free from the NH_3 ligand to join the coordination-crosslinking reaction with P-COO^- , forming the more stable coordination-crosslinking polymer $[(\text{P-COO}^-)_n\text{M}^{2+}]$. It is very probable that this soap-free polyacrylate hydrosol coating can be cured below 100°C and can be used to paint the surface of metal, such as electrical equipment and automobile, for protection and decoration. This work is undertaken to investigate the coordination-crosslinking process for the soap-free polyacrylate hydrosol/metal ion system and the existence of the coordination-crosslinking polymer.

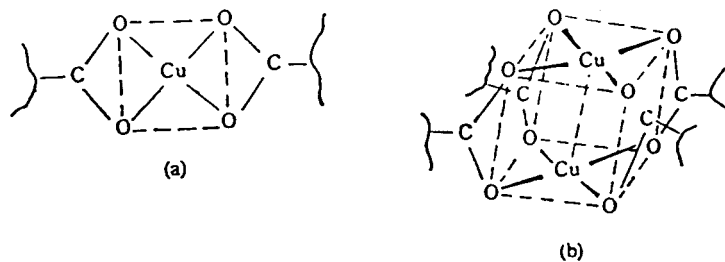


Figure 3 Two basic coordination units of $(P'-COO^-)_nCu^{2+}$ coordination polymer.

EXPERIMENTAL

Preparation of Soap-Free Polyacrylate Hydrosol

The copolymer of acrylic acid (AA), butyl acrylate (BA), methyl methacrylate (MMA), and styrene (St) were synthesized by solution polymerization in the mixed solvent of isopropanol (IP) and diethylaminoethyl alcohol (DEAE), then neutralized with amine and diluted with water to form $-COO^-$ -containing soap-free polyacrylate hydrosol ($P-COO^-$).⁹

TEM Analysis

The photos were taken by a transmission electron microscope (TEM) (HITACHI HU-12A Transmission Electron Microscope, Japan).

Linear Sweep Voltammetry Polarographic Analysis

The peak exponentials of Cu^{2+} (ca. $10^{-3}M$) were measured with a JP3-oscilloscopic polarograph (the Seventh Telecommunication Factory of Shandong, China). The working electrode was a glass

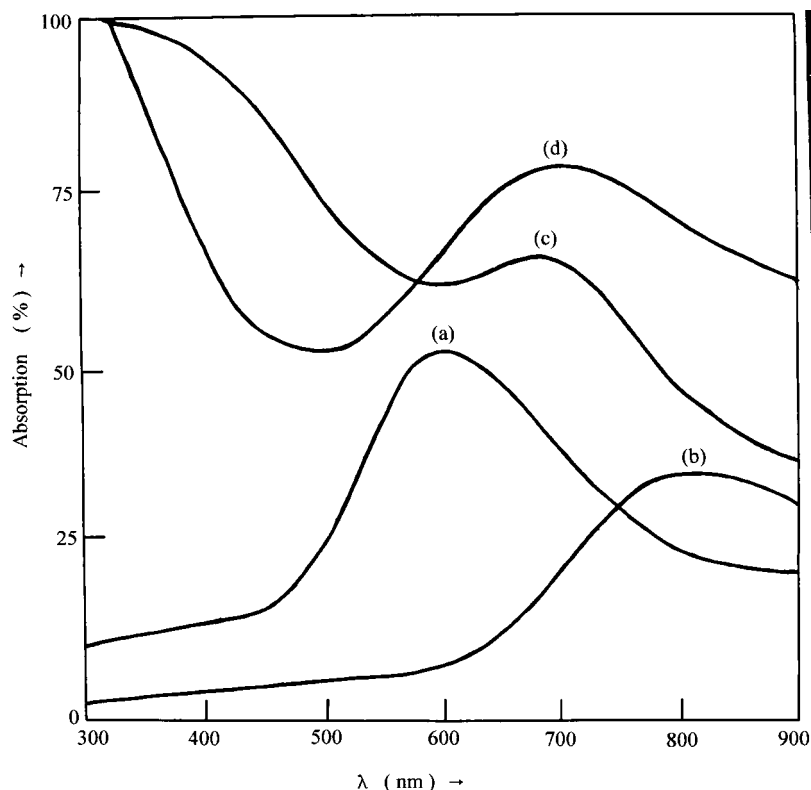


Figure 4 Ultraviolet-visible spectra of Cu^{2+} in various coordination states: (a) $Cu(NH_3)_4^{2+}$, (b) $(CH_3COO^-)_2Cu^{2+}$, (c) water-borne coating heated at $80^\circ C$ for 30 min, (d) solid coating film.

carbon electrode, the comparison electrode was a Ag/AgCl (saturated KCl solution) electrode, and the auxiliary electrode was a Pt electrode. The supporting electrolyte solution was a 0.10M NaClO₄ solution.

Ultraviolet-Visible Spectrographic Analysis

The samples were examined by UV spectroscopy (UV-240, Shimadzu, Japan) and scanned from 300 to 900 nm.

IR Spectrographic Analysis

Infrared (IR) spectra were recorded with a Nicolet 205 FTIR spectrometer (USA).

RESULTS AND DISCUSSION

TEM Analysis

The crosslinking process of the polyacrylate hydrosol in forming the network structure with Zn(NH₃)₄²⁺ in the water-borne coating at low concentration (solid content ca. 0.05 wt %) has been investigated by TEM. The TEM photos taken by heating at 80°C for different times are shown in Figure 1. When the hydrosol is just mixed with Zn(NH₃)₄²⁺ (photo a), the hydrosol particles can well disperse as the spherical particles in the wa-

ter-borne coating. At this moment, P—COO⁻ cannot take the coordination-crosslinking reaction with Zn²⁺ on account of the NH₃ ligand, so the shapes of the particles are not affected, that is, —COO⁻ can still act as the emulsifier to stabilize the hydrosol. However, if the water-borne coating has been heated, Zn²⁺ will be set free from NH₃ ligand and join the coordination-crosslinking reaction with P—COO⁻. As a result, the shapes of the particles will change.

When the water-borne coating has been heated at 80°C for 20 min (photo b), the particles begin to aggregate and their boundaries are not as clear as photo (a). After 40 min, the particles begin to crosslink into the branched structure and their boundaries become dimmer (photo c). After 60 min, the particles have been crosslinked into the network structure and their boundaries cannot be found out (photo d). After 90 min, the particles have crosslinked into the network in large area (photo e) and this implies that the coordination-crosslinking reaction is going up to the end. After 120 min, there is a larger crosslinking network in photo (f) than in photo (e), and no phase-separated structure exists. It indicates that the process of coordination-crosslinking of the hydrosol P—COO⁻ and Zn²⁺ has finished. It must be emphasized that the higher concentration the water-borne coating is, the less time this process requires.

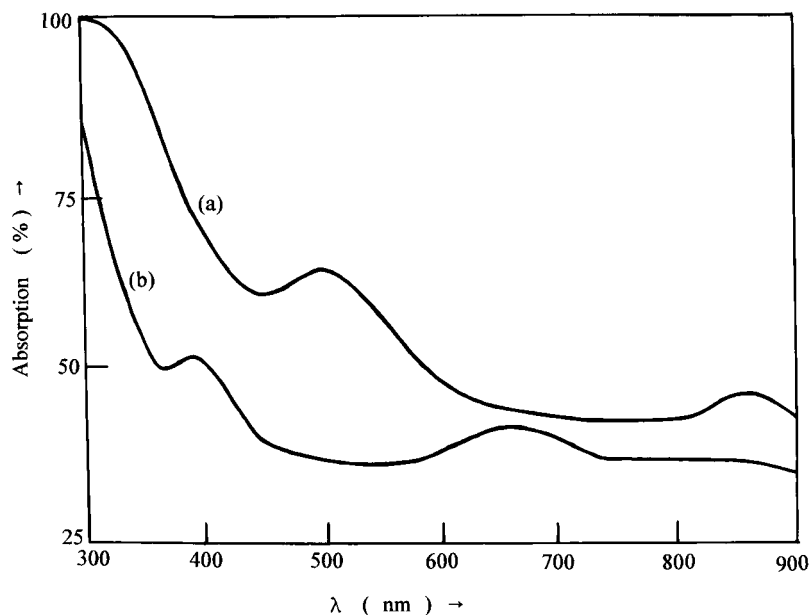


Figure 5 Ultraviolet-visible spectra for solid coating films with different M(NH₃)₄²⁺ as coordination-crosslinking agents: (a) with Co(NH₃)₄²⁺, (b) with Ni(NH₃)₄²⁺.

Linear Sweep Voltammetry Polarographic Analysis

The linear sweep voltammetry polarographic analysis has been used to study the coordination-crosslinking of Cu^{2+} (ca. $10^{-3}M$) and $\text{P}-\text{COO}^-$ in the low concentration water-borne coating (solid content ca. 0.3 wt %). The polarograms of Cu^{2+} in various coordination states are shown in Figure 2. The peak potential (E_p) of Cu^{2+} in coordination state (curves b–d) becomes more negative than that of free Cu^{2+} (curve a). When the water-borne coating has been heated at 80°C for 30 min, NH_3 ligand vaporizes and Cu^{2+} can join the coordination-crosslinking reaction with $\text{P}-\text{COO}^-$ to form the coordination polymer $[(\text{P}-\text{COO}^-)_n\text{Cu}^{2+}]$. Therefore, there is a wide polarographic wave (curve d) which is attributed to the slow electrode reaction resulted from the slow diffusion of the voluminous $(\text{P}-\text{COO}^-)_n\text{Cu}^{2+}$.

The peak potentials of Cu^{2+} are shown in Table I. As the larger stability constant (K_s) corresponds to the more negative E_p , then it can be inferred that $\log K_s$ of $(\text{P}-\text{COO}^-)_n\text{Cu}^{2+}$ formed by heating at 80°C for 30 min should be larger than 12.5, that is, $(\text{P}-\text{COO}^-)_n\text{Cu}^{2+}$ is more stable than $(\text{CH}_3\text{COO}^-)_2\text{Cu}^{2+}$ and $\text{Cu}(\text{NH}_3)_4^{2+}$, which is very favorable for Cu^{2+} to form the coating film through coordination-crosslinking.

The structure of $(\text{P}-\text{COO}^-)_n\text{Cu}^{2+}$ can be deduced from Wang et al.'s study¹² on fluorine-containing coordination polymer $(\text{P}'-\text{COO}^-)_n\text{Cu}^{2+}$. Their results indicate that there are two basic coordination structure units in the coordination polymer (Fig. 3). The first is a square planar coordination structure of Cu^{2+} with four oxygen atoms from two carboxylate groups. The coordination number of Cu^{2+} is four and the bond distance of $\text{Cu}^{2+}-\text{O}$ is ~ 0.196 nm. The second is a binuclear coordination structure of $\text{Cu}^{2+}-\text{Cu}^{2+}$ ionic pairs with eight oxygen atoms from four carboxylate groups. In this structure, the bond distance of $\text{Cu}^{2+}-\text{O}$ is ~ 0.196 nm and the bond distance of $\text{Cu}^{2+}-\text{Cu}^{2+}$ is ~ 0.264 nm. We suppose there may be also two basic coordination structure units similar to Figure 3 in the coordination polymer $(\text{P}-\text{COO}^-)_n\text{Cu}^{2+}$ studied in this article. Just because $(\text{P}-\text{COO}^-)_n\text{Cu}^{2+}$ has so strong complex coordination-crosslinking network structure, it is more stable than the low molecular coordination complex $(\text{CH}_3\text{COO}^-)_2\text{Cu}^{2+}$ and $\text{Cu}(\text{NH}_3)_4^{2+}$.

Ultraviolet-Visible Spectrographic Analysis

The ultraviolet-visible spectrographic analysis has also been used to study the coordination-

crosslinking of Cu^{2+} (ca. $10^{-3}M$) and $\text{P}-\text{COO}^-$ in the low concentration water-borne coating (solid content ca. 0.3 wt %). The ultraviolet-visible spectra of Cu^{2+} in various coordination states are shown in Figure 4. The maximum absorption wavelength (λ_{max}) of $\text{Cu}(\text{NH}_3)_4^{2+}$ solution is ~ 600 nm (curve a) and λ_{max} of $(\text{CH}_3\text{COO}^-)_2\text{Cu}^{2+}$ is ~ 800 nm (curve b). When the water-borne coating has been heated at 80°C for 30 min, a small absorption peak appears at ~ 700 nm (curve c), which indicates that $(\text{P}-\text{COO}^-)_n\text{Cu}^{2+}$ has primarily formed. And there is a large absorption peak at the same position for the solid coating film of $(\text{P}-\text{COO}^-)_n\text{Cu}^{2+}$ (λ_{max} ca. 700 nm, curve d). It will be concluded that $(\text{P}-\text{COO}^-)_n\text{Cu}^{2+}$ has already formed as the stable coordination polymer at this moment.

We also use the ultraviolet-visible spectra to study the existence of coordination polymers in solid coating films with other $\text{M}(\text{NH}_3)_4^{2+}$ as coordination-crosslinking agents. The results are shown

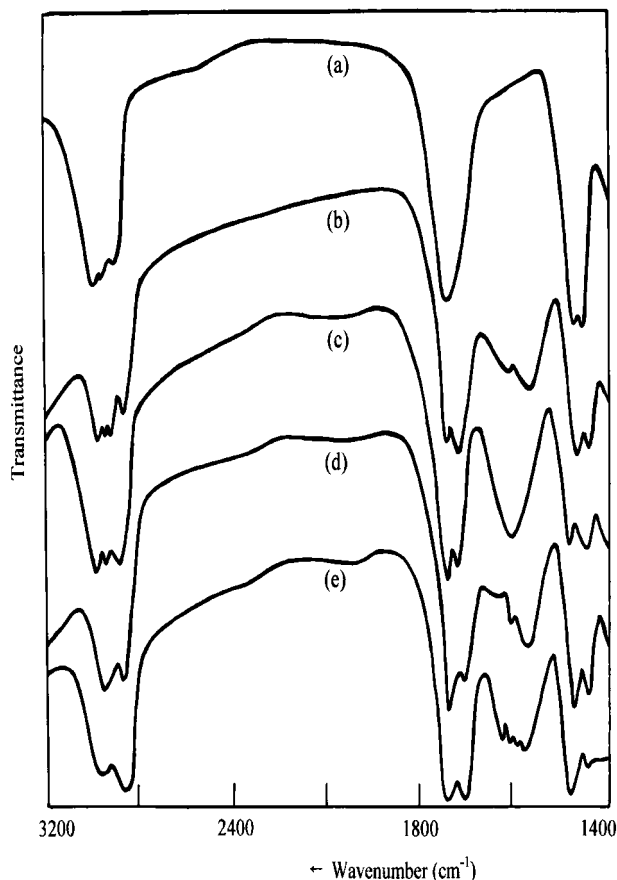


Figure 6 IR spectra for polyacrylate films with different $\text{M}(\text{NH}_3)_4^{2+}$ as coordination-crosslinking agents: (a) no $\text{M}(\text{NH}_3)_4^{2+}$, (b) with $\text{Cu}(\text{NH}_3)_4^{2+}$, (c) with $\text{Zn}(\text{NH}_3)_4^{2+}$, (d) $\text{Co}(\text{NH}_3)_4^{2+}$, (e) with $\text{Ni}(\text{NH}_3)_4^{2+}$.

in Figure 5. Two absorption peaks appear for (P—COO⁻)_nCo²⁺ (ca. 500 nm and 860 nm, curve a) and for (P—COO⁻)_nNi²⁺ (ca. 380 nm and 650 nm, curve b). These facts reflect that the coordination-crosslinking in the form of (P—COO⁻)_nCo²⁺ or (P—COO⁻)_nNi²⁺ also exists in the coating film.

IR Spectrographic Analysis

Figure 6 shows the IR spectra for polyacrylate films without and with different M(NH₃)₄²⁺ as coordination-crosslinking agents. The characteristic absorption peak (ca. 1600 cm⁻¹) of (P—COO⁻)_nM²⁺ does not appear in curve (a) but appears in curves (b–e). And the presence of (P—COO⁻)_nM²⁺ has also affected the conformation of —COOH: the peak of ~ 1743 cm⁻¹ due to C=O vibration of free —COOH is common to all samples (curves a–e), but the other small peak of ~ 1728 cm⁻¹ due to C=O vibration of dimer (—COO⁻)₂M²⁺ is present only for the samples containing the crosslinking agent M(NH₃)₄²⁺ (curves b–e). These facts show the presence of (P—COO⁻)_nM²⁺ coordination-crosslinking structure in the coating film.

CONCLUSION

Our investigations clearly demonstrate that M²⁺ in M(NH₃)₄²⁺ form does not react with P—COO⁻ without heating, but M²⁺ can set free from the

NH₃ ligand by heating and can join the coordination-crosslinking reaction with P—COO⁻ to form the coordination polymer (P—COO⁻)_nM²⁺. The TEM analysis revealed the crosslinking process of P—COO⁻ with metal ions, and the existence of coordination polymer (P—COO⁻)_nM²⁺ was proved by the linear sweep voltammetry polarographic analysis, ultraviolet-visible spectrographic analysis, and IR spectrographic analysis.

The authors express their thanks to Mr. Canan Ma for his encouragement and support.

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