

# Solution Spinning of the High $T_c$ Oxide Superconductor. II. Effect of Organic Acid on the Complex Formation of PVA with the Copper(II) Ion

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## SYNOPSIS

As basic research for the solution spinning of the high  $T_c$  oxide superconductor, the effect of organic acid on the complex formation of poly(vinyl alcohol) (PVA) with the copper [Cu(II)] ion was explored with various carboxylic acids, such as formic acid, acetic acid, *n*-butyric acid, and lactic acid. The effects of these acids on the interaction between PVA and Cu(II) acetate in aqueous solution were nonexistent, while a chelation of the Cu(II) ion and lactic acid was detected. In the solid state, a linear complex of PVA with the Cu(II) ion was formed by adding organic acid. The ligand of the linear complex was highly dependent on the kind of acid used. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

The polymer-metal complex has been studied in the field of functional polymeric material and in the textile industry as the antimicrobial fibers for medical use. It is clear that the reactivity of a polymer-metal complex is sometimes strongly affected by the polymer ligand that exists outside the coordination sphere and surrounds the metal complex.<sup>1</sup>

We have studied the preparation of a high  $T_c$  oxide superconducting long filament using a textile fiber spinning technology for the precursor of the oxide. The Ba-Y-Cu oxide filament is prepared by dry-spinning with a starting homogeneous aqueous solution containing acetates of Ba, Y, and Cu, PVA, and propionic acid.<sup>2-4</sup> The superconducting properties of the heated filament depend on the spinning dope as well as on the spinning conditions and heat treatment. In particular, the addition of propionic acid is a key to obtaining a stable viscous homogeneous spinning dope. The copper [Cu(II)] complex of PVA at pH > 7 has been studied by many investigators.<sup>5-9</sup> However, the influence of the complex formation of PVA with the Cu(II) ion on the spin-

ning dope has not been revealed. In a previous article, the effect of propionic acid on the interaction between PVA and Cu(II) acetate was studied, and the linear complex of PVA with the Cu(II) ion in the solid state, which should be beneficial for the formation of the precursor high  $T_c$  filament, was studied.<sup>10</sup>

The purpose of this article was to study the effects of formic acid, acetic acid, *n*-butyric acid, and lactic acid on the complex formation of PVA with Cu(II) acetate.

## EXPERIMENTAL

PVA (DP = 1700) was supplied from Nitivy Co. and had a degree of saponification of 85 mol % as determined by <sup>1</sup>H-NMR. Formic acid, acetic acid, propionic acid, *n*-butyric acid, and lactic acid were of analytical grade and were used without further purification. Other reagents were of analytical grade and were used without further purification.

Aqueous solutions for ultraviolet/visible (UV/vis) spectra measurement were contained 0–1.0 mol/L PVA, 0–0.1 mol/L Cu(II) acetate, and 0–0.8 mL/L organic acid. UV/vis spectra were recorded on a Shimadzu UV-1200 in the region of 200–

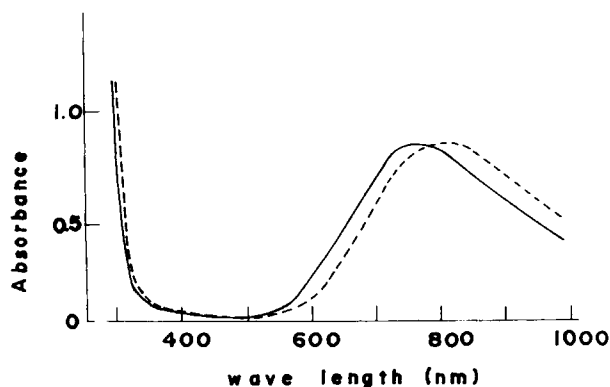
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1000 nm. The sample films were cast at 80°C on a polyethylene substrate after deaerating the solution. A Hitachi 285 was used for infrared (IR) spectroscopy. X-ray diffraction and differential scanning calorimetry (DSC) (Rigaku Denki Co. Ltd.) were used to investigate the structure of the films.  $^1\text{H-NMR}$  spectra were recorded on a Varian XL-200 (200 MHz).

## RESULTS AND DISCUSSION

### Effect of Organic Acids on the Interaction Between PVA and the Cu(II) Ion in Aqueous Solution

It was reported that an interaction between PVA and the Cu(II) ion was extremely weak or nonexistent in aqueous solution at  $\text{pH} < 5.8$ , and the effect of propionic acid on the interaction was also nonexistent.<sup>10</sup> At first, the effect of organic acid on the interaction between PVA and the Cu(II) ion in aqueous solution was examined by spectroscopy. Figure 1 shows the UV/vis absorption spectra of mixed solutions of Cu(II) acetate and PVA with *n*-butylic acid and lactic acid. The maximum absorption band for the solution with *n*-butylic acid is observed at 770 nm, due to the aqueous Cu(II) ion, whereas the solution with lactic acid has the maximum absorption band at 800 nm. The spectra of aqueous Cu(II) acetate solutions and mixed solutions of Cu(II) acetate and PVA with and without other acids are almost identical, indicating that the effect of these acids on the interaction between PVA and the Cu(II) ion in aqueous solution is nonexistent.



**Figure 1** UV/vis spectra of an aqueous solution of PVA and Cu(II) acetate of  $[\text{Cu}]/[\text{OH}] = 0.11$  with organic acid at room temperature: (—) *n*-butylic acid; (---) lactic acid.

**Table I** Molar Absorption Coefficient ( $\epsilon$ ) at  $\lambda_{\text{max}}$  of Various Cu(II) Acetate Solutions

Solution	Carboxylic Acid	pH	$\lambda_{\text{max}}$ (nm)	$\epsilon$ (L/mol cm)
Cu(II)	None	5.8	770	25
Cu(II)	Formic acid	4.3	770	24
Cu(II)	Acetic acid	4.3	770	24
Cu(II)	Propionic acid	4.3	770	24
Cu(II)	Butylic acid	4.3	770	24
Cu(II)	Lactic acid	4.3	800	24
PVA <sup>a</sup> + Cu(II)	None	5.5	770	25
PVA <sup>a</sup> + Cu(II)	Formic acid	4.3	770	24
PVA <sup>a</sup> + Cu(II)	Acetic acid	4.3	770	25
PVA <sup>a</sup> + Cu(II)	Propionic acid	4.3	770	26
PVA <sup>a</sup> + Cu(II)	Butylic acid	4.3	770	26
PVA <sup>a</sup> + Cu(II)	Lactic acid	4.3	800	25

<sup>a</sup> PVA 1 mol/L.

tent. The mixed solutions of Cu(II) acetate and lactic acid with and without PVA show same spectra shifted to 800 nm.

To clarify the interaction between the Cu(II) ion and lactic acid in aqueous solution, UV/vis spectra for aqueous solutions of Cu(II) acetate with a mixture of *n*-butylic alcohol and propionic acid instead of lactic acid were measured. The solution with the mixture had a maximum absorption band at 770 nm, and the interaction between the Cu(II) ion and the mixture was minor. Then, the shift to 800 nm by adding lactic acid is attributed to a chelation of lactic acid with the Cu(II) ion. The molar absorption coefficient ( $\epsilon$ ) was calculated from the linear slope of the absorbance at  $\lambda_{\text{max}}$  and the concentration of Cu(II) acetate and is listed in Table I. The  $\epsilon$  values of the aqueous Cu(II)-PVA solution with and without the acid are almost similar to those of the corresponding Cu(II) acetate solution.

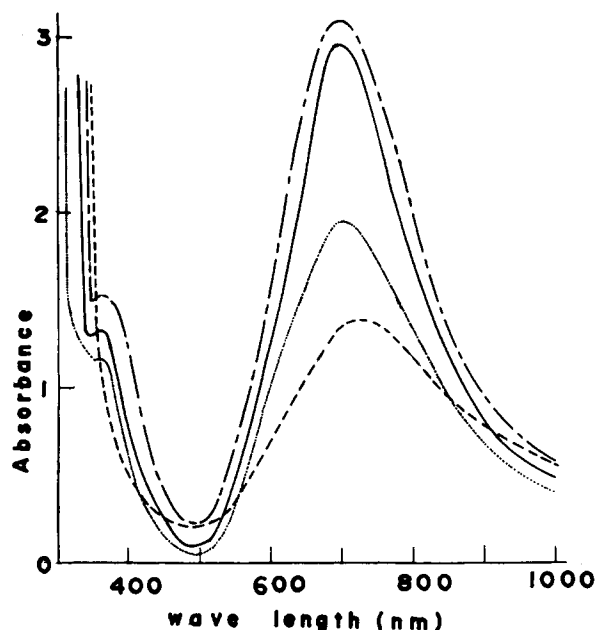
### Effect of Organic Acids on the Complex Formation of PVA with the Cu(II) Ion in the Solid State

The films made from aqueous solutions containing PVA and Cu(II) acetate with acids became bluish and soluble in water, whereas the film from the solution without acid was greenish and insoluble in water. The film from the solution with acetic acid tended to precipitate Cu(II) acetate, and the complex formation of PVA with the Cu(II) ion was minor by adding acetic acid as compared with other acids.

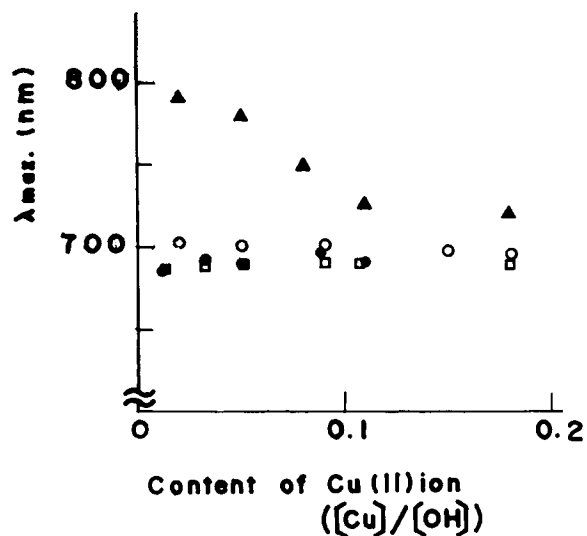
UV/vis spectra of the films with the acids were measured and the representative absorption spectra are shown in Figure 2. The maximum absorption bands at 670–690 nm and a smaller shoulderlike band at 370 nm are observed for the films with the acids except for lactic acid. This shows that formic acid and *n*-butyric acid could have some effect on the complex formation of PVA with the Cu(II) ion. However, the spectrum of the film with lactic acid has one maximum peak at 720 nm.

Figure 3 shows the relation between  $\lambda_{\max}$  and a content of the Cu(II) ion, showing a mol ratio of the Cu(II) ion to PVA ( $[Cu]/[OH]$ ). For the film with lactic acid, the  $\lambda_{\max}$  decreases from 790 nm to 720 nm with increasing amount of the Cu(II) ion. The  $\lambda_{\max}$  value for the film containing a small content of the Cu(II) ion corresponds to that of the aqueous solution, so the Cu(II) chelate with lactic acid is suggested to be formed for the film. As the amount of the Cu(II) ion increased, another complex would be formed. On the other hand, the films with other acids have a specific  $\lambda_{\max}$  value, which is independent of the concentration of the Cu(II) ion. The  $\lambda_{\max}$  for the film with formic acid of 690 nm is slightly long, depending on the ligand of the complex.

Figure 4 presents the relationship between the intensity of the maximum absorption and the content of the Cu(II) ion. The intensity for the film

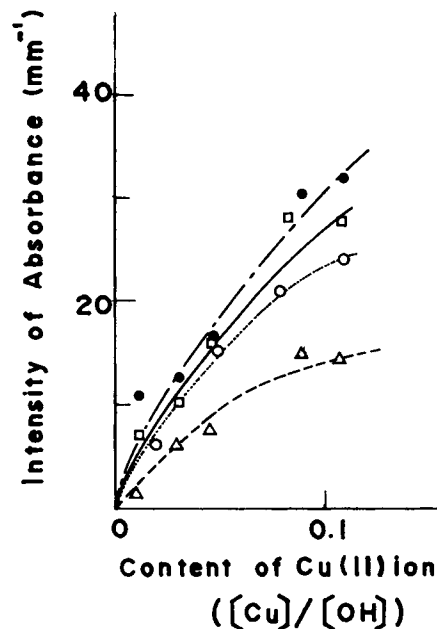


**Figure 2** UV/vis spectra of the film cast from an aqueous solution of PVA and Cu(II) acetate of  $[Cu]/[OH] = 0.11$  with organic acid: (·····) formic acid; (---) propionic acid; (—) *n*-butylic acid; (- - -) lactic acid.



**Figure 3**  $\lambda_{\max}$  for the film cast from an aqueous solution of PVA and Cu(II) acetate with organic acid: (O) formic acid; (●) propionic acid; (□) *n*-butylic acid; (▲) lactic acid.

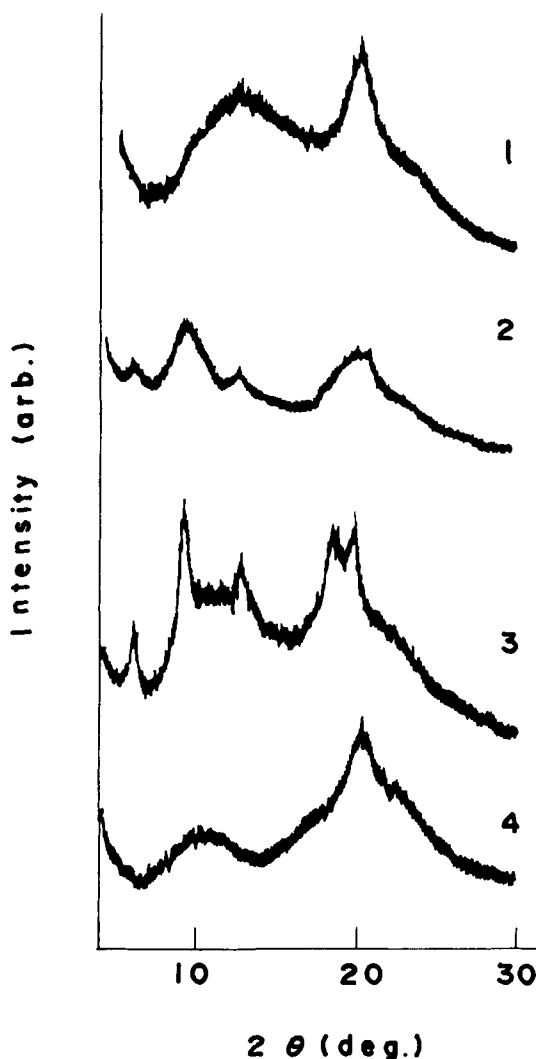
without acid becomes a plateau at more than  $[Cu]/[OH] = 0.05$ , and by adding the acids, the intensity increases with increasing the concentration of the Cu(II) ion.



**Figure 4** The relationship between intensity of maximum absorption and mol ratio of the Cu(II) ion of the film cast from an aqueous solution PVA and Cu(II) acetate with organic acid. (---Δ---) without acid; (·····O·····) formic acid; (- - -●- - -) propionic acid; (—□—) *n*-butylic acid.

X-ray diffraction patterns of these films were measured. Figure 5 shows the representative patterns for the films with various carboxylic acids. The PVA film had a sharp peak at  $2\theta = 20^\circ$ , and by adding the Cu(II) ion, the peak at  $2\theta = 20^\circ$  decreased and became broader. Moreover, a broad peak at  $2\theta = 10^\circ$  was observed.

It is well known that PVA is easily crystallized by casting because of the formation of hydrogen bonds by the hydroxy groups, and the peak at  $2\theta = 20^\circ$  was due to a reflection [101] of the crystal structure of PVA.<sup>11</sup> The addition of the Cu(II) ion broke the hydrogen bonding of PVA and made the



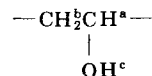
**Figure 5** X-ray diffraction patterns of the film cast from an aqueous solution PVA and Cu(II) acetate of  $[Cu]/[OH] = 0.11$  with organic acid by using  $CuK\alpha$  radiation: (1) formic acid; (2) propionic acid; (3) *n*-butylic acid; (4) lactic acid.

structure amorphous; the broad peak at  $2\theta = 10^\circ$  suggested the complex formation of PVA with the Cu(II) ion.

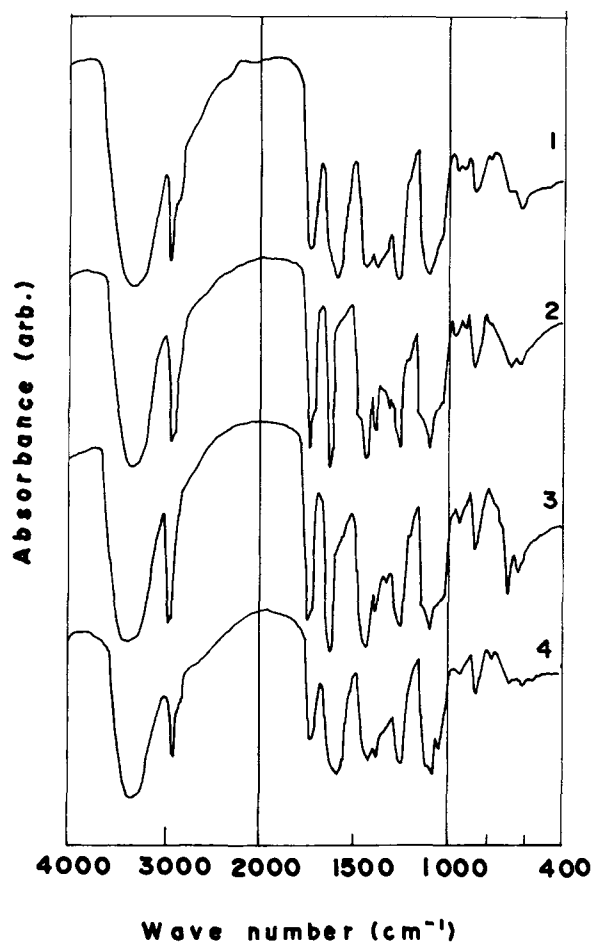
The films with formic acid and lactic acid have only one broad peak ranging from  $2\theta = 10^\circ$ – $12^\circ$ , whereas the films with propionic acid and *n*-butylic acid have new two peaks at  $2\theta = 7^\circ$  and  $14^\circ$  in addition to the peak at  $2\theta = 10^\circ$ . The acetate complex of the Cu(II) ion is usually a binuclear complex from two Cu(II) ions, four acetate ions, and two coordinate waters, and the structure of the complex is a monoclinic system with  $a = 13.10 \text{ \AA}$ ,  $b = 8.56 \text{ \AA}$ ,  $c = 13.88 \text{ \AA}$ , and  $\beta = 116^\circ 26'$ .<sup>12</sup> The peaks at  $2\theta = 7^\circ$ ,  $10^\circ$ , and  $14^\circ$  for the present films did not consist of the structure of the acetate complex of the Cu(II) ion. The peaks that appeared at  $2\theta = 14^\circ$  and  $7^\circ$  could indicate that other complex structures were formed by adding propionic acid or *n*-butylic acids. The complex in the films with these acids was different from that with formic acid and lactic acid.

IR spectra of these films are shown in Figure 6. These films have absorption bands at 1610, 1420, and  $680 \text{ cm}^{-1}$  as the characteristic bands of the carboxylate ion. The intensity of absorbance of these bands increases with increasing number of methylene groups in the primary alkyl group. The spectrum for the film with lactic acid has the special absorption band at  $1050 \text{ cm}^{-1}$ , and this absorption is caused by hydroxy groups in alcohol.

The  $^1H$ -NMR study of PVA-Cu(II) films with the acids was carried out in order to clarify the coordinated ligand with the Cu(II) ion formed by various acids. As the complex for the film with lactic acid is dependent on the content of the Cu(II) ion, the  $^1H$ -NMR study of two films of (A)  $[Cu]/[OH] = 0.02$  and (B)  $[Cu]/[OH] = 0.11$  was also investigated. The  $^1H$  NMR spectra of the  $D_2O$  solutions of the films are illustrated in Figure 7. There are four significant peaks at 4.9, 4.0, 2.1, and 1.7 ppm for the films. In addition to the four peaks, a smaller peak at 0.6 ppm for the film with formic acid, a small peak at 1.0 ppm for the film with *n*-butylic acid, and three smaller peaks at 4.5, 2.2, and 1.5 ppm for the film (A) are observed. The structure of PVA is shown as follows:



The peaks at 4.8, 4.0, and 1.7 ppm are based on the protons denoted by c, a, and b in PVA, respectively,<sup>13</sup> although the peak at 4.8 ppm contains a signal of HOD. The peak at 2.1 ppm shows methyl protons (d) in an acetate group ( $\text{CH}_3\text{COO---}$ ) and



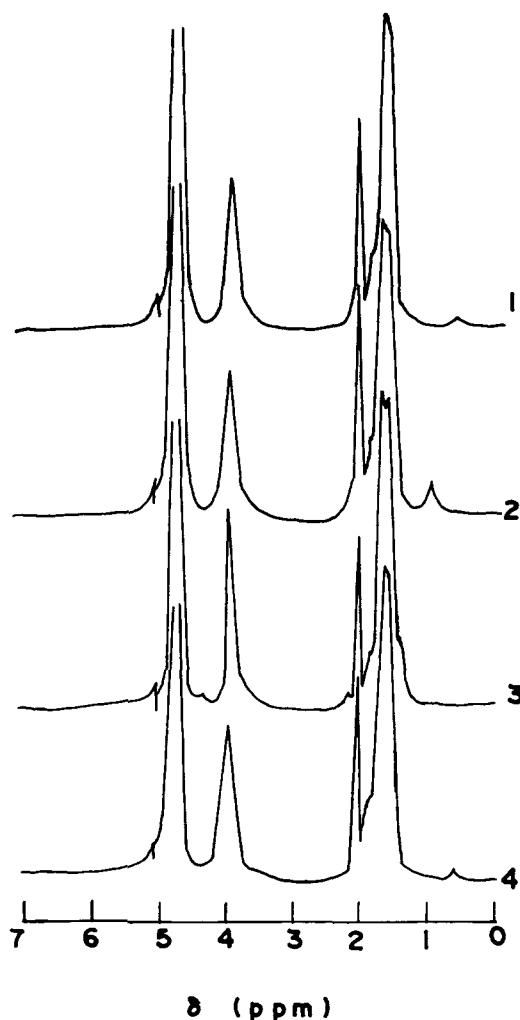
**Figure 6** IR spectra of the film cast from an aqueous solution of PVA and Cu(II) acetate of  $[Cu]/[OH] = 0.11$  with organic acid: (1) formic acid; (2) propionic acid; (3) *n*-butylic acid; (4) lactic acid.

an unsaponified vinyl acetate unit. The peak at 0.62 ppm in Figure 7(1) shows a proton (e) in the formate group ( $H^{\circ}COO-$ ). The peak at 1.0 ppm in Figure 7(2) is based on methyl protons (f) as an end group in the *n*-butylate group ( $CH_3^fCH_2^gCH_2COO-$ ), and the peak at 1.7 ppm contains the signal of methylene protons (g). The peaks at 1.5 and 4.5 ppm in Figure 7(3) show the protons (h) and (i) in lactic acid ( $CH_3^hCH^iOHCOOH$ ), respectively.

The integrated intensity of these peaks are summarized in Table II. The  $^1H$ -NMR spectrum of raw PVA indicated that the mol fraction of the unsaponified vinyl acetate unit in PVA was 0.15. The number of the ligands against the Cu(II) ion is estimated by considering the amount of the residual vinyl acetate unit and is also shown in Table II. Although ESR and NMR measurements in solution

and in the solid state would be required for a detailed structure of the complex, the ligand of the Cu(II) complex was affected by the kind of acid used.

Measurements of DSC were performed and the curves are shown in Figure 8. For PVA film, the endothermic peak below 200°C and the exothermic peak above 300°C due to the melting and decomposition of PVA, respectively, were observed. By adding the Cu(II) ion, the temperatures of these peaks decreased because of the formation of the PVA-Cu(II) complex, and a new broad exothermic peak over 200–250°C appeared for a decomposition of the polymer-metal complex and an oxidation of



**Figure 7** NMR spectra of the  $D_2O$  solution dissolved of the film cast from various aqueous solutions of PVA and Cu(II) acetate with organic acid: (1)  $[Cu]/[OH] = 0.11$  with formic acid; (2)  $[Cu]/[OH] = 0.11$  with *n*-butylic acid; (3)  $[Cu]/[OH] = 0.02$  with lactic acid; (4)  $[Cu]/[OH] = 0.11$  with lactic acid.

**Table II** Integrated Intensity of the Peaks from the NMR Spectra for the Films with Various Acids of  $[Cu]/[OH] = 0.11$ 

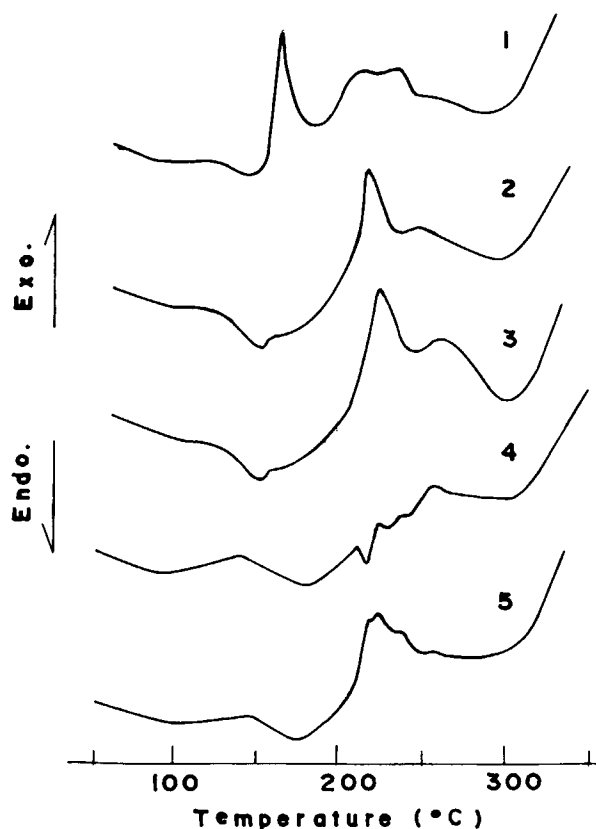
Film with Various Acids	Integrated Intensity								[ligand] [Cu]
	4.0	1.7	2.1	4.5	2.2	1.5	1.0	0.6 (ppm)	
Control <sup>a</sup>	7.0	14.0	3.3	—	—	—	—	—	—
Formic acid	5.7	13.5	3.2	—	—	—	—	0.1	0.5 <sup>b</sup>
Propionic acid	4.3	8.5	4.5	—	—	—	—	—	1 <sup>c</sup>
<i>n</i> -Butylic acid	5.0	12.0	3.3	—	—	—	1.0	—	2 <sup>b</sup>
Lactic acid (B)	5.6	11.2	3.0	—	—	—	—	0.1	0.5 <sup>b</sup>
Lactic acid (A)	5.5	13.0	2.6	<sup>e</sup>	0.2	1.1	—	—	3 <sup>f</sup>

(A)  $[Cu]/[OH] = 0.02$ ; (B)  $[Cu]/[OH] = 0.11$ .<sup>a</sup> PVA film.  $[Cu]/[OH] = 0$ .<sup>b</sup> Acetate group.<sup>c</sup> Formate group.<sup>d</sup> Butylate group.<sup>e</sup> Not calculated.<sup>f</sup> Lactic acid.

the Cu(II) ion.<sup>10</sup> The additional endothermic peak near 150°C and the exothermic peak near 220°C are shown for the films with propionic acid and *n*-butylic acid. This endothermic peak near 150°C arose from the melting of a new crystal structure formed by the complex containing the ligand groups, and another exothermic peak near 220°C showed a thermal decomposition and elimination of the ligand groups.

There is a new exothermic peak at 166°C for the film with formic acid as shown in Figure 8(1). The structure of the anhydrous Cu(II) formate type, such as  $Cu^{2+} - O - Cu^{2+}$ , was reported by Yamachi.<sup>14</sup> The exothermic peak at 166°C could be due to a thermal decomposition of the anhydrous Cu(II) formate type of complex. An endothermic peak at 218°C for the film (A) as shown in Figure 8(4) was due to melting of the complex containing lactic acid. The new exothermic peaks ranging from 200 to 250°C, as shown in Figure 8(1), 8(4), and 8(5), could arise from thermal decomposition and elimination of carboxylate groups.

In summary of these data, the effect of carboxylic acid in the solid state is to make the liner complex containing various carboxylate ions. On the solution spinning of a Y-Ba-Cu-O superconductor, the addition of organic acid enhanced the solubility of the Y, Ba, and Cu(II) acetates and enabled fiber formation to take place. It is generally accepted that the configuration of the polymer molecules in the crystalline or linear ordered regions of fibers can be linear or helical. The linear complexing should be beneficial for the formation of the precursor filament.



**Figure 8** DSC curves of the film cast from various aqueous solutions of PVA and Cu(II) acetate with organic acid, heating rate of 20°C/min: (1)  $[Cu]/[OH] = 0.11$  with formic acid; (2)  $[Cu]/[OH] = 0.11$  with propionic acid; (3)  $[Cu]/[OH] = 0.11$  with *n*-butylic acid; (4)  $[Cu]/[OH] = 0.02$  with lactic acid; (5)  $[Cu]/[OH] = 0.11$  with lactic acid.

## CONCLUSIONS

As basic research for the solution spinning of an oxide superconductor, the effect of various carboxylic acids on the interaction between PVA and the Cu(II) ion in aqueous solution and in the solid state was studied using UV/vis and IR spectroscopy, X-ray diffraction, DSC, and  $^1\text{H-NMR}$ . The effect of the acids on the interaction between PVA and the Cu(II) ion in aqueous solution was nonexistent, whereas a chelation of lactic acid with the Cu(II) ion was detected. In the solid state, the linear complexes were formed by adding the acids, and the ligand of the complexes depended on the kind of acid used. The type of ligand for the complex with lactic acid is changed with the concentration of the Cu(II) ion.

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