

Study of Complexes of Poly(vinyl pyrrolidone) with Copper and Cobalt on Solid State

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Received 12 June 2003; accepted 18 February 2004

DOI 10.1002/app.20620

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A polymer–metal complex is a metal complex containing a polymer ligand, showing a remarkably specific structure in which central metal ions are surrounded by a colossal polymer chain. Based on this polymeric ligand, the polymer–metal complex has interesting and important characteristics, especially catalytic activities. This activity is different from that of the corresponding ordinary metal complex of low molecular weight. In this work we studied the synthesis and characterization, in the solid state, of dif-

ferent poly(vinyl pyrrolidone)–cobalt (PVP/Co) and –copper (PVP/Cu) complexes. We used differential thermal analysis and FTIR as the experimental techniques. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1512–1518, 2004

Key words: metal–polymer complexes; solid-state structure; differential thermal analysis; infrared spectroscopy; catalysts

INTRODUCTION

In recent years, the study of polymer–metal complexes has been of great interest to many chemists^{1–10} because they have understood that it is not only an excellent model for metalloenzymes^{4,5} but also leads to developments of highly efficient catalysts.^{9,10} Some reviews on polymer–metal complexes have also been published in recent years.

Metal complexes are usually divided into the Werner-type and non-Werner-type, the latter of which is also called organometallic compounds, that contain carbon–metal bonding. Although most of the polymer–metal complexes studied so far belong to the Werner-type, those of the non-Werner-type are attractive because of their specific catalytic activities. This type of polymer–metal complex is synthesized by reaction of a polymer containing donating groups such as amine, heterocyclic nitrogen, carboxylic acid, ketone, phosphoric acid, or thiol with metal ion. The complex formation is often achieved very easily by mixing each of the solutions. The reaction of polymer ligand with metal ion or metal complex usually results in various coordination structures, which are divided chiefly into pendant and inter- and/or intramolecular bridged complexes.

EXPERIMENTAL

Materials

The samples of polyvinyl pyrrolidone (PVP) used in this work were provided by Janssen Chimica (Geel,

Belgium), Serva (Heidelberg, Germany), and Fluka Chemie (Buchs, Switzerland), respectively (see Table I). The sample provided by Fluka Chemie was in emulsion form and to obtain it in solid form, the sample first had to be freeze-dried.

Determination of the molecular weights by SEC was not possible because of solubility reasons, and thus it was necessary to characterize the different PVP samples by viscometry.

The intrinsic viscosity of the different PVP samples was obtained at 298 K using distilled water as solvent. The MHS (Mark–Houwink–Sakurada) constants used were $a = 0.55$ and $k = 67.6 \times 10^3 \text{ dL g}^{-1}$.^{11,12} The experimental measurements were carried out using an automatic viscometer (Viscobot 2, Lauda, Königshofen, Germany) by use of a Lauda thermostatic system. We also used different metallic transition element salts such as hexahydrated cobalt II, provided by Panreac Química SA (Barcelona, Spain).

Preparation of the complexes

The solutions were prepared by very slowly pouring the aqueous solution of the metallic salt onto the polymer in the solid state and allowing the mixture to remain for a minimum of 24 h before later use.¹³

The experimental measures were carried out in a differential thermal analyzer system (TA 2000, Mettler, Greifensee, Switzerland) and by FTIR spectroscopy (Nicolet Analytical Instruments, Madison, WI).

All the polymer/metal complexes were prepared in solution so that it was necessary to obtain them in the solid state. To achieve this we used several techniques: lyophilization, evaporation, and precipitation. The precipitation technique required more repetitive re-

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TABLE I
Molar Masses for PVP Samples Determined by
Viscometry

Polymer	Molar mass (g mol ⁻¹)	Supplier
PVP-1	154,000	Janssen Chimica
PVP-2	222,000	Janssen Chimica
PVP-3	625,000	Serva
PVP-4	3,070,000	Fluka Chemie

sults because with the lyophilization and evaporation we could not eliminate the excess salt. The precipitators used in our polymer/metal complexes were isopropylitic alcohol in the case of copper complexes and an acetone/isopropylitic alcohol mixture for the cobalt ones. Both are very good solvents for the polymer and the used inorganic salts (Cl₂Cu·2H₂O and Cl₂Co·6H₂O), respectively, which facilitated obtaining them (but not of the formed complex).

The solid compounds obtained in this way were characterized by a very low solubility in water and insolubility in common organic solvents. This behavior, turned to advantage to carry out tests of atomic absorption, confirmed the presence of the metal in the compound. The insolubility of the complexes appears because the metal can interact simultaneously with two chains, acting like a kind of bridge, as previously proposed by some authors.¹⁴

All the complexes obtained by precipitation presented different characteristic colors (given that each used metallic salts, totally different from the polymer, which is white in the solid state) that were revealed during breakup in aqueous solution. The observed colors varied from yellow to brown, with increasing concentration of added copper, for copper complexes, and from blue to violet for the polymer/cobalt complexes.^{3,15}

They also presented properties such as cohesion, mechanical strength, and in some cases a slight plasticity, which was the last property observed in several of the PVP/copper complexes. This behavior is similar to that presented by some copper salts that did not form a rigid complex because of the particular electronic configuration of the central atom, thus allowing the existence of several stable configurations (and even an infinite number of them) that differ in the metal/ligand distances.

These plasticity properties seem to be attributed to the Jahn-Teller effect. These two terms provide evidence of fluxional behavior and coordination, usually defined for the copper complexes (II), and they are frequent phenomena in the penta- and hexacoordinated compounds.

RESULTS AND DISCUSSION

Thermal analysis

Before testing the samples were warmed for 10 min at 130°C to eliminate the water and moisture absorbed.

Table II shows the glass-transition temperatures (T_g) of four PVP samples, where one may observe the T_g increasing with molar mass in the different PVP samples, as expected.

The thermal behavior of the PVP/Cu (3.37 wt % Cu, PVP-1) and PVP/Co (3.37 wt % Co, PVP-2) systems as a function of temperature is shown in Figures 1 and 2, respectively. In all samples of PVP/Cu and PVP/Co metal complexes exothermal transformations were observed.³ These transformations, which do not correspond to the thermal degradation of the polyvinyl pyrrolidone, are known to take place at temperatures oscillating between 230 and 250°C (depending on the molar mass of the PVP), and the initiation temperature of our transformations was substantially less than the first one (e.g., in some samples it began between 180 and 190°C).¹⁶

In the thermograms shown in Figures 3 and 4 we can observe the intensities of the transformations (given by the height of the peak). They will be different according to the concentration of metal, although the transformation speed and quantity of samples were constant in all the experimental measures. It is also observed that the specific heat before and after each transformation undergoes an increase, shown by the different levels of base lines after the transformation.^{17,18}

The peaks corresponding to copper complexes were sharper and narrower than those corresponding to the cobalt complexes (see Figs. 1 and 2), which can give us an estimate of transformation speed. Sharp and narrow peaks denote a reaction or quick transition, whereas wide and rounded peaks denote slow transformations. Any metal may be characterized by similar behavior if we modify its composition.¹⁵ In general we obtained more rounded peaks at lesser concentrations of metallic salt.

The glass-transition temperature of PVP (~170°C) does not appear in the thermograms of the PVP/metal complexes.³ However, as we have mentioned above, we observe one and, in some cases,

TABLE II
Glass-Transition Temperature for PVP Samples
Obtained by Differential Thermal Analysis^a

Polymer	T_g (°C)
PVP-1	162
PVP-2	173
PVP-3	176
PVP-4	178

^a Heating rate: 10°C/min.

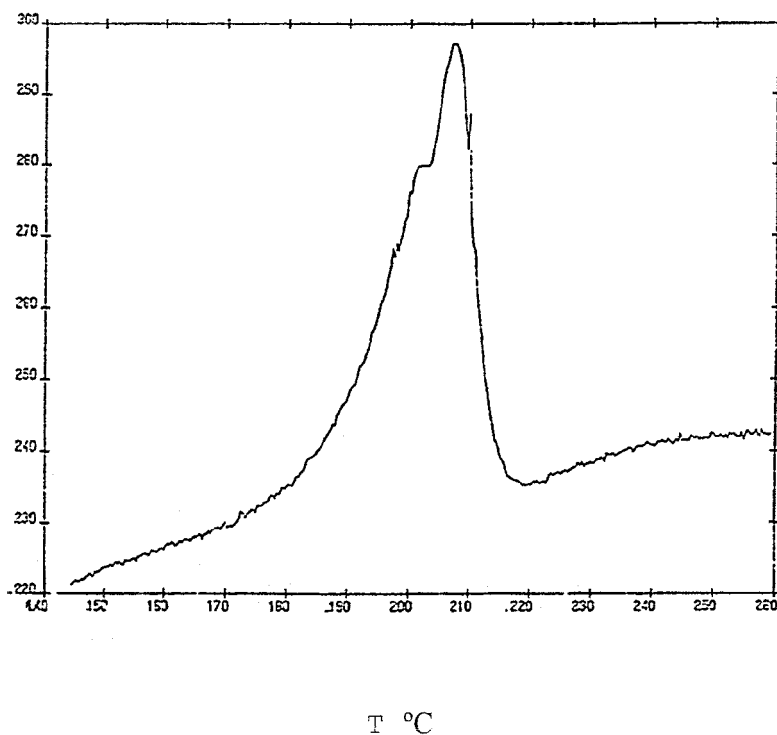


Figure 1 Thermogram of PVP-1 ($154,000 \text{ g mol}^{-1}$)/3.73 wt % of copper concentration. Heating rate: $10^\circ\text{C}/\text{min}$; sensitivity: $50 \mu\text{v}$.

two (for the copper complexes) exothermic transformations. We suppose that this phenomenon is attributable to the tendency of the polymer/metal complex to acquire a certain structural arrangement

or arrangements.¹⁹ These behaviors are always observed at temperatures higher than the glass transition, when the polymer chains possess greater mobility.

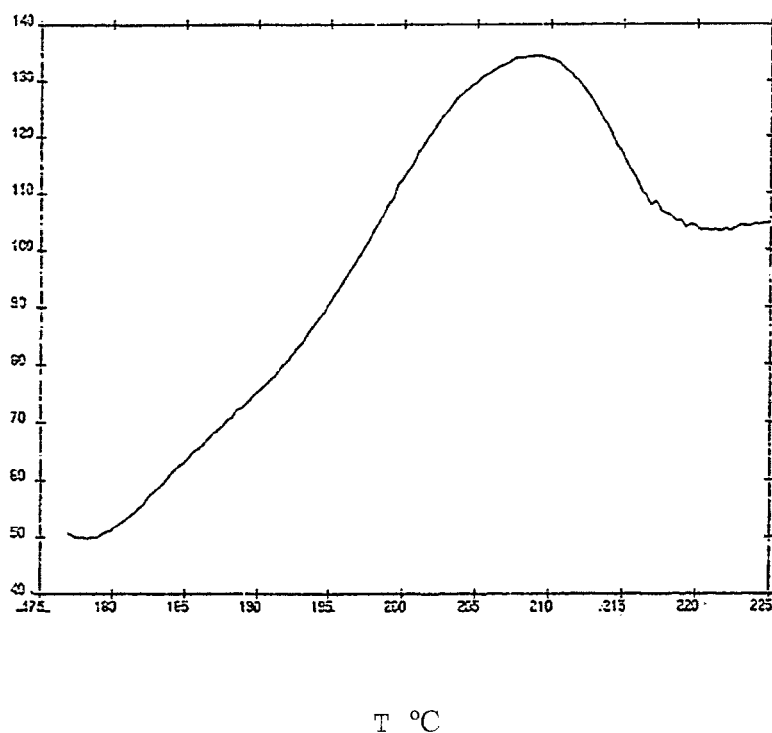


Figure 2 Thermogram of PVP-2 ($222,000 \text{ g mol}^{-1}$)/3.73 wt % of cobalt concentration. Heating rate: $10^\circ\text{C}/\text{min}$; sensitivity: $50 \mu\text{v}$.

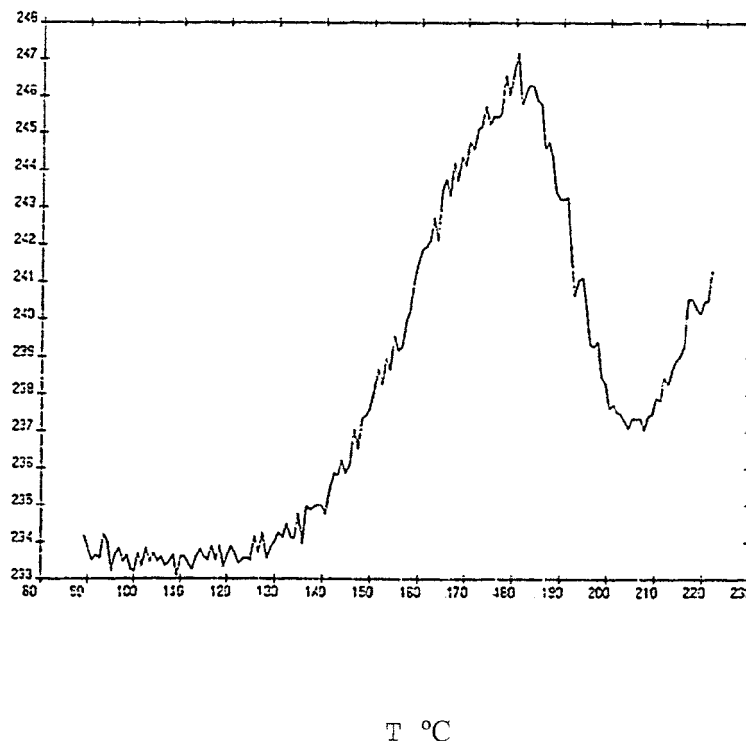


Figure 3 Thermogram of PVP-4 ($3.07 \times 10^6 \text{ g mol}^{-1}$)/0.37 wt % of copper concentration. Heating rate: $10^\circ\text{C}/\text{min}$; sensitivity: $50 \mu\text{v}$.

FTIR spectra

To carry out the infrared spectra all the samples were prepared as films after evaporation of the solvent on

KBr disks. The concentration of the polymer was maintained at a constant 1 wt %. For the films a drop from the solution was deposited onto the disk and

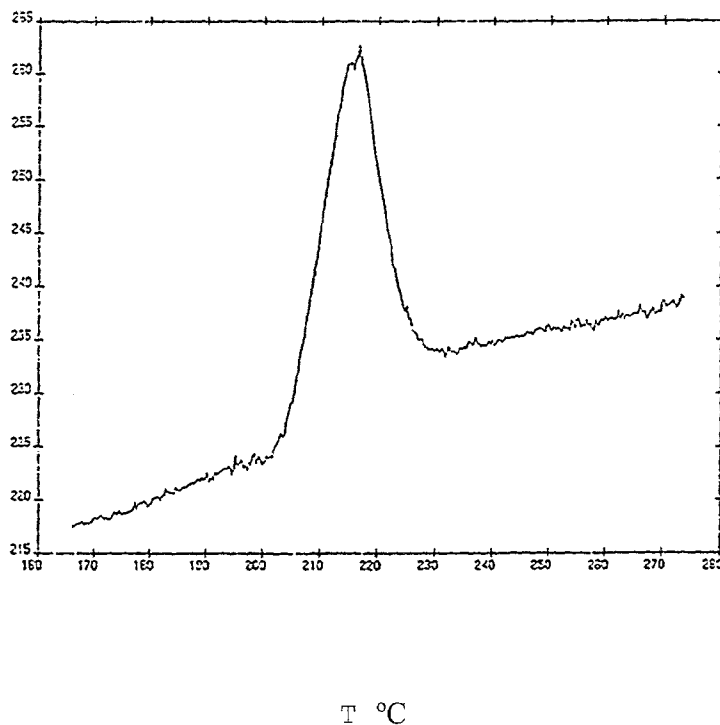


Figure 4 Thermogram of PVP-4 ($3.07 \times 10^6 \text{ g mol}^{-1}$)/3.73 wt % of copper concentration. Heating rate: $10^\circ\text{C}/\text{min}$; sensitivity: $50 \mu\text{v}$.

TABLE III
Infrared Bands for PVP and Its Complexes with Copper

Polymer and complex	$\nu_{\text{C=O}}$ (cm^{-1})	$\Delta\nu_{\text{C=O}}$ (cm^{-1})
PVP-1	1680	
PVP-2	1680	
PVP-3	1680	
PVP-4	1680	
1a	1673, 1616	7, 64
1b	1666, 1609	14, 71
2a	1673, 1616	7, 64
2b	1673, 1609	7, 71
3a	1673, 1616	7, 64
3b	1673, 1609	7, 71
4a	1673, 1609	7, 71
4b	1673, 1609	7, 71

then dried, first in the air until most of the solvent disappeared and then dried under vacuum at a temperature of 130°C to eliminate the remaining water present in the sample.

To execute the infrared spectra, we had to take particular care because the samples of PVP, like those of the synthesized polymer/metal complex, very easily absorb moisture from the environment. Thus, during the procedure we obtained the spectra of the water instead of obtaining the bands corresponding to the characteristic groups.

The polymer/metal complexes were also characterized by FTIR spectroscopy. This technique has been used by numerous investigators^{20–23} for the characterization of polymer/metal complexes, based on the fact that the frequency at which it absorbs a characteristic group of a polymer is modified when it is in complex form with metallic ions.

Tables III and IV show the absorption frequencies of the carbonyl group for the pure polymers and for the different polymer complexes with copper and cobalt.

The numbers 1–4 in Tables III and IV correspond to the samples of complexes that were synthesized with polyvinyl pyrrolidone, PVP-1, PVP-2, PVP-3, and PVP-4, and the letters a and b are related to the weight percentage of metal, 0.37 and 3.73, respectively.

Figure 5 shows the IR spectra of the PVP samples with different molecular masses. The spectra of the samples of pure PVP are similar, as expected, because the molecular masses should not affect the vibration mode frequencies of the characteristic groups of polymer.

Above 3500 cm^{-1} , the spectra of the polymer show an intense band in the area of tension of the O—H group. This band indicates the presence of coordination water. When we carry out the thermal treatment we eliminate residual water (there is a loss of 12 wt %) but we are not able to eliminate it completely, which prompts us to suppose that the water is a part of the chemical structure of the studied polymer.

Near 3340 cm^{-1} there is a very small band or shoulder that is impossible to be completely eliminated. It is probably not attributable to the residual hydration of the sample because it appears as a band separated from the maximum in the PVP. In view of the significant relative intensity of the C=O band in this spectra, this small peak could be its first harmonic or a combination band (it appears to double the frequency of the carbonyl).

The spectra of the different samples of pure PVP also present a very strong absorption, characterized by a very marked band in 1680 cm^{-1} , classically ascribed to the tension of the group carbonyl.^{15,24} However, the relatively low frequency at which it appears, compared with that of the carbonyl band in acetate or ester, has led some authors²⁵ to consider it as the total of the contributions of C=O and C—N groups. A narrow and half-intensity C—N tension band appears at a frequency of 1286 cm^{-1} .

Figures 6 and 7 show the FTIR spectra of PVP and PVC/Cu and PVC/Co complexes, respectively, at different concentration levels of copper and cobalt. We can observe (see Tables III and IV) a significant decrease in the intensity of the carbonyl band. New peaks are observed at minor frequencies upon addition of cobalt or copper salts, which suggests that the coordination occurs through the carbonyl group.¹⁵ These results verify the great importance of the resonance structure of the PVP and are also consistent with the results obtained by thermal analysis.

The maximum band corresponding to the carbonyl group is displaced for the different PVP/metal complexes obtained from the metal composition used for its formation.

By evidence of the shift to minor frequencies of the carbonyl group from 1680 to 1673 and 1666 and 1617 cm^{-1} , and taking into account the importance of the PVP resonance, we conclude that the coordination takes place through the PVP carbonyl group.²⁶ The structures of polymer/metal complexes are different perhaps because the copper and cobalt, together with the molecules of water and chlorine, impose different structures or because intra- and intermolecular complexes are formed between the repetitive units of the polymer or the nearest macromolecular chains.

TABLE IV
Infrared Bands for PVP/Co Complexes

Complex	$\nu_{\text{C=O}}$ (cm^{-1})	$\Delta\nu_{\text{C=O}}$ (cm^{-1})
1a	1673, 1623	7, 57
1b	1609	71
2a	1673, 1616	7, 64
2b	1609	71
3b	1673, 1609	7, 71
4a	1673, 1616	7, 64
4b	1609	71

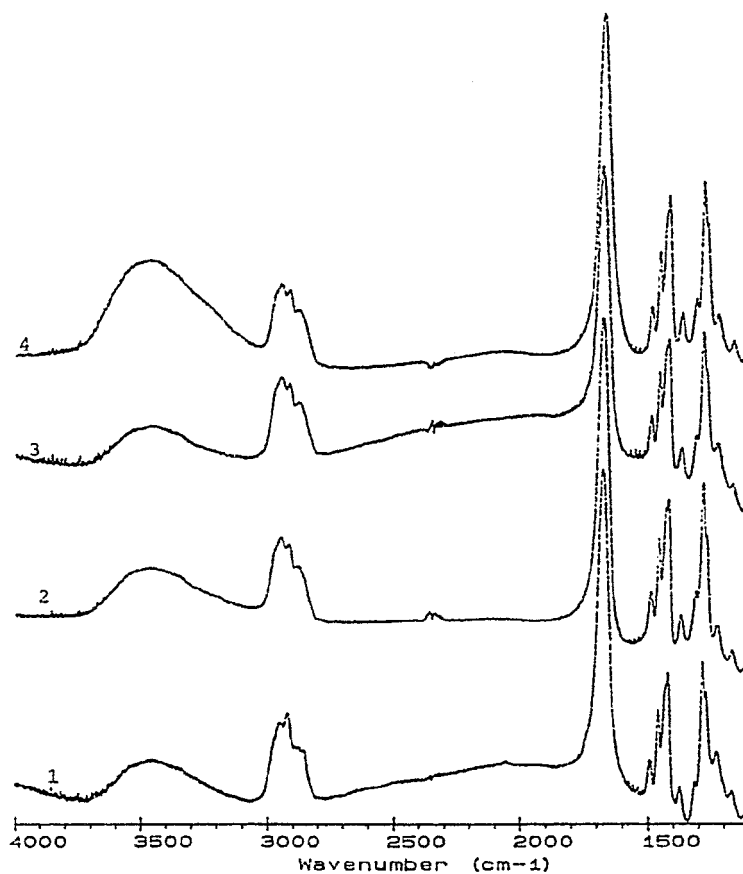


Figure 5 FTIR spectra of PVP samples: (1) $154,000 \text{ g mol}^{-1}$; (2) $222,000 \text{ g mol}^{-1}$; (3) $625,000 \text{ g mol}^{-1}$; (4) $3070,000 \text{ g mol}^{-1}$.

If we compare the results obtained for both metals we see that the copper spreads easily to form more than one type of structures. When the amount of co-

balt is in excess, the carbonyl band displaced to a higher wavelength indicates that the links are weakened, signifying the presence of a single-structure

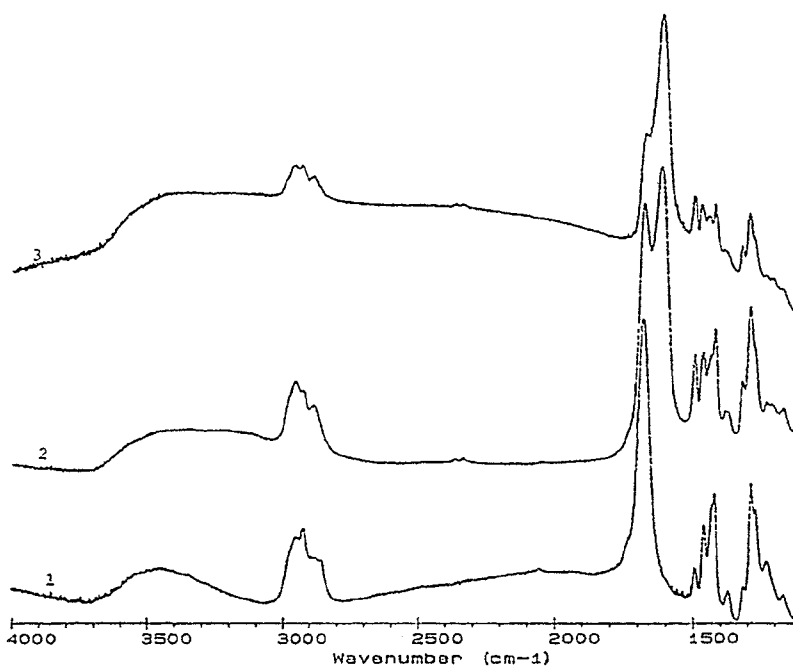


Figure 6 FTIR spectra for PVP ($154,000 \text{ g mol}^{-1}$) and various polymer complexes with copper: (1) PVP-1; (2) PVP-1/0.37 wt % of copper; (3) PVP-1/3.73 wt % of copper.

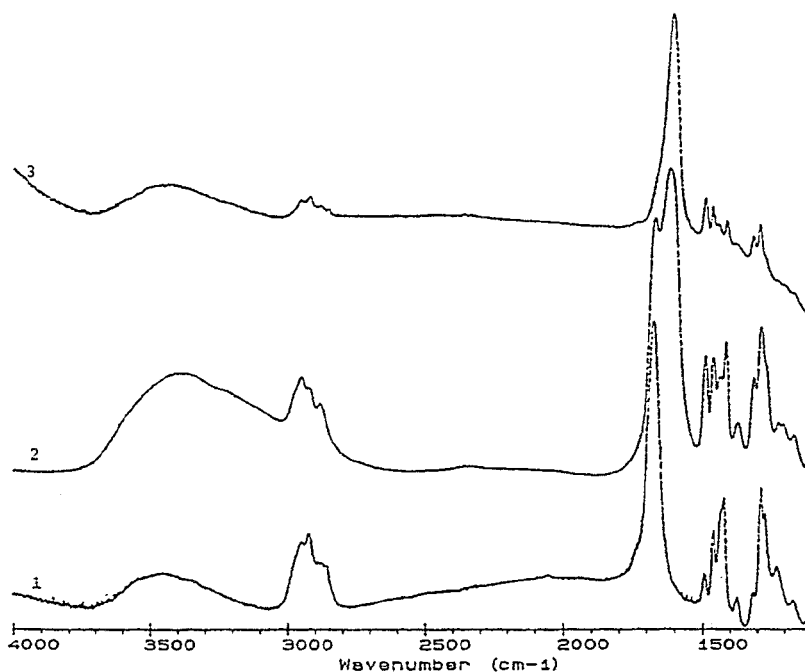


Figure 7 FTIR spectra for PVP ($154,000 \text{ g mol}^{-1}$) and various polymer complexes with cobalt: (1) PVP-1; (2) PVP-1/0.37 wt % of cobalt; (3) PVP-1/3.73 wt % of cobalt.

type. The presence of more types of structures is confirmed by the appearance of other bands at lower frequencies.

CONCLUSIONS

From these results, we can conclude that the coordination takes place through the PVP carbonyl group. Analysis of the behavior of these complexes shows that PVP/copper and PVP/cobalt do not depend on molar masses of polymer. The band (in the polymer-metal complex) corresponding to the carbonyl group is a function of the metal concentration.

References

- Díaz, E.; Valenciano, R.; Landa, P.; Arana, J. L.; González, J. *Polym Test* 2002, 21, 247.
- Díaz, E.; Valenciano, R.; Katime, I. *Anal Uímica Soc Española Uímica* 1995, 91, 5.
- Katime, I.; Ochoa, J. R. *J Appl Polym Sci* 1987, 34, 1953.
- Kaneko, M.; Tsuchida, E. T. *J Polym Sci Macromol Rev* 1987, 16, 397.
- Tsuchida, E. T.; Nishide, H. *Adv Polym Sci* 1977, 24, 1.
- Samuels, G. J.; Meyer, T. J. *J Am Chem Soc* 1981, 103, 307.
- Tsuchida, E.; Kaneko, M.; Nishide, N. *Macromol Chem* 1973, 164, 203.
- Meyer, C. T.; Pineri, M. J. *J Polym Sci* 1975, 13, 1057.
- Clear, J. M.; Kelly, J. M.; O'Connell, C. M.; Vos, J. G. *J. Chem Res* 1981, M, 3039; S, 260.
- Clear, J. M.; Kelly, J. M.; Vos, J. G. *Macromol Chem* 1983, 184, 613.
- Levy, G. B.; Frank, H. P. *J Polym Sci* 1953, 10, 371.
- Levy, G. B.; Frank, H. P. *J Polym Sci* 1955, 17, 247.
- Kurimura, Y.; Yamada, K.; Tsuchida, E.; Kaneko, M. *J Polym Sci* 1971, A1, 3521.
- Bedetti, R.; Carunchio, V.; Cernia, E. *Polym Lett Ed* 1975, 13, 329.
- Lehtinen, A.; Purokoski, S.; Lindberg, J. J. *Makromol Chem* 1975, 176, 1553.
- Tamareselvy, K.; Venkatarao, K.; Kothandaraman, H. *J Polym Sci* 1990, A28, 2679.
- Allan, J. R.; Bain, D. R.; Carson, B. R. *Thermochim Acta* 1990, 165.
- Gal, A.; Cais, M.; Kohn, D. M. *J Polym Sci* 1977, 15, 461.
- Lyons, A. M.; Vasile, M. J. *Macromolecules* 1988, 21, 3125.
- Biedermann, M. G.; Griessl, E. *Makromol Chem* 1973, 172, 49.
- Roda, J. *Makromol Chem* 1977, 178, 203.
- Coleman, M. M.; Skrovanek, D.; Painter, P. *Macromolecules* 1988, 21, 59.
- Lee, J. Y.; Painter, P. C.; Coleman, M. M. *Macromolecules* 1988, 21, 346.
- Barbucci, R.; Casolaro, M.; Maguari, A. *Makromol Chem* 1989, 190, 2627.
- Moskala, E. J.; Varnell, D. F.; Coleman, M. M. *Polymer* 1985, February, 26.
- Spindler, R.; Shriver, D. F. *Macromolecules* 1986, 19, 347.