Study of complexes of Poly(9-vinylcarbazole) with copper, cobalt and chromium on solid state

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Estudio en estado sólido de los complejos de poli-9-vinilcarbazol con cobre, cobalto y cromo

Estudi en estat sòlid dels complexos de poli-9-vinilcarbazol amb coure, cobalt i crom

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RESUMEN

En este trabajo hemos estudiado la síntesis y caracterización en estado líquido y sólido de diferentes complejos de poli-9-vinilcarbazol con metales de transición como son el $CuCl_2 \cdot 2H_2O$, $CoCl_2 \cdot 6H_2O$ y $CrCl_3 \cdot 6H_2O$. Los complejos poliméricos fueron caracterizados mediante FTIR. Los ensayos espectroscópicos mostraban que la unión entre el metal y el grupo metálico tenía lugar a través del nitrógeno terciario del grupo carbazol. Los ensayos térmicos demostraban que estos complejos poseían una estabilidad térmica y una temperatura de transición vítrea mayor que las del polímero. Las estructuras de los complejos polímero-metal presentaban porosidades ocupadas por el catión metálico.

Palabras clave: Complejos polímero-metal, estructura del estado sólido, análisis térmico diferencial, espectroscopia de infrarrojo, SEM.

SUMMARY

In this paper we have studied the synthesis and characterization in solution and on solid state of different poly(9-vinylcarbazole) with some transition metal chlorides such as $CuCl_2 \cdot 2H_2O$, $CoCl_2 \cdot 6H_2O$ and $CrCl_3 \cdot 6H_2O$. The polymer-metal complexes were characterized by FTIR and the result revealed that the infrared spectra of the complexes show significant shift with respect to that of PNVC, indicating that linking between the polymer and metal may be tacking place only through the tertiary nitrogen of the carbazole side group. The thermal stability and glass transition temperature of the polymer-metal complexes were found to be higher than that of the polymer. The pores of the polymer are filled after interaction with cation with polymeric ligand.

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

RESUM

En aquest treball hem estudiat la síntesi i caracterització en estat líquid i sòlid de diferents complexos de poli-9-vinilcarbazol amb metalls de transició com són el $CuCl_2 \cdot 2H_2O$, $COCl_2 \cdot 6H_2O$ i $CrCl_3 \cdot 6H_2O$. Els complexos polimèrics van ser caracteritzats mitjançant FTIR. Els assajos espectroscòpics mostraven que la unió entre el metall i el grup metàl·lic tenia lloc a través del nitrogen terciari del grup carbazol. Els assaigs tèrmics demostraven que aquests complexos posseïen una estabilitat tèrmica i una temperatura de transició vítria més grans que les del polímer. Les estructures dels complexos polímer-metall presentaven porus ocupats pel catió metàl·lic.

Paraules clau: Complexos polímer-metall, estructura de l'estat sòlid, anàlisi tèrmica diferencial, espectroscòpia d'infraroig, SEM.

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INTRODUCTION

The preparation of functional polymers by chemical modification is an important technique, which has been used extensively both industrially to modify the properties of the polymers for various technological applications and in the area of polymer-supported chemistry to prepare chemically reactive polymers(1,2). In principle, the functional groups may be part of the polymer backbone or linked to a side chain as a pendant group. A required active functional group can be introduced onto a polymeric chain (a) by incorporation during the synthesis of the polymer itself through polymerization of monomers containing the desired functional groups, and (b) chemical modification of a suitably non-functionalized polymer(3) . A polymer-metal complex is a metal complex containing a polymer ligand, presenting a remarkably specific structure in which central metal ions are surrounded by an enormous polymer chain. Based on this polymeric ligand, the polymer-metal complex shows interesting and important characteristics, especially catalytic activities different from the corresponding ordinary metal complex of low molecular weight.

Usually the metal complex is divided into the Werner-type and non-Werner-type complexes, the latter of which are so called organometallic compounds which 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 attracting much attention because of their specific catalytic activities. The formation through complexation of polymeric ligand with metal ion is syntethized by reaction of a polymer containing donating groups such as amine, heterocyclic nitrogen, carboxylic acid, ketone, phosphonic acid, or thiol with metal ion. The complex formation is often achieved very easily by mixing each of the solutions(4,5).

EXPERIMENTAL

Materials

The samples of poly(9-vinylcarbazole)(PNVC) used in this work were provided by Aldrich. The intrinsic viscosity of PNVC was obtained at 298 K using tetrahydrofurane (THF, Panreac p.a., Barcelona, Spain) as solvent. The MHS (Mark-Houwink-Sakurada) constants used were a=0.65 and K=14.4x10^{-5} dl g^{-1} (6). The molar mass obtained was 50.000 g mol^{-1}.

We have also used different metallic transition element salts, were provided by Panreac Química S.A. (Barcelona, Spain) (PRS), such as cobalt (II) chloride 6-hydrate, copper (II) chloride 2-hydrate and chromium (III) chloride 6-hydrate. The viscometric measurements were carried out using a suspend-level dilution modified Ubbelohde viscometer at 298 K using to it Lauda thermostatic system.

Synthesis of polymer-metal complexes

Polymer-metal complexes of PNVC were synthethized by very slowly pouring the solution of PNVC-THF onto the metallic salt in the solid state. The mixture in different concentrations (see Table I, II and III) was heated under reflux with stirring at 50 °C for 1 hour. The experimental measurements were carried out in a differential scanning calorimeter (DSC) and by FTIR spectroscopy.

PNVC-Copper complexes: The initial green colour of these solutions (that was more intense with the concentration) changed gradually to gold. After 10 minutes of beginning the reaction the solutions sharply changed their colour to dark green.

Table 1. *Composition of reaction mixtures for the complexes with copper.*

PNVC-Copper complexes		
Sample	Mole ratio salt: PNVC	THF (ml)
1	0.090	50
2	0.999	50
3	1.698	50
4	2.004	50
5	3.001	50
6	4.913	75
7	5.48	75
8	5.95	75

Table 2. *Composition of reaction mixtures for the complexes with cobalt.*

PNVC-Cobalt complexes		
Sample	Mole ratio salt: PNVC	THF (ml)
9	0.083	50
10	1.005	50
11	1.72	50
12	2.003	50
13	3.028	50
14	4.96	75
15	5.93	75

Table 3. *Composition of reaction mixtures for the complexes with chromium.*

PNVC-Chromium complexes		
Sample	Mole ratio salt: PNVC	THF (ml)
16	0.090	50
17	0.997	50
18	1.698	50
19	2.012	50
20	2.999	50
21	4.996	75
22	6.036	75

PNVC-Cobalt complexes: Initially the solutions were blue colour (increasing the colour intensity with the concentration). These solutions sharply changed their colour to very dark blue at 3 minutes.

PNVC-Chromium: The observed initial colours varied from green to violet with increasing concentration of added chromium.

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 results because with the lyophilization and evaporation we could not eliminate the excess salt. The precipitators used in our polymer-metal complexes were methanol. Tetrahydrofurane and methanol (Panreac p.a., Barcelona, Spain) are very good solvents for the used metallic salts ($CuCl_2 \cdot 2H_2O$, $CoCl_2 \cdot 6H_2O$ and $CrCl_3 \cdot 6H_2O$). But methanol is not a solvent for the polymer. Some common organic solvents such as tetrachloroethane, tetrahydrofurane, etc., are good solvents for the polymer-metal complexes studied. The solubility of complexes appears because the metal can interact with only one chain. The insolubility appears because the metal can interact simultaneously with two chains, acting like a kind of bridge, as previously proposed by some authors(4-7). The polymer-complexes obtained by precipitation presented different characteristic colours, given that each of the metallic salts is totally different from the white coloured polymer in the solid state.

RESULTS AND DISCUSSION

FTIR spectra

Fourier transform infrared spectra were recorded using KBr pellets by an Avatar 370 (Thermonicolet) FTIR spectrometer. The pellets were dried under vacuum at a temperature of 70ºC to eliminate the remaining water present in the sample. This technique has been used by numerous investigators(8-10) 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 salts. Spectral analysis was performed in order to determine the chemical structure of the complexes.

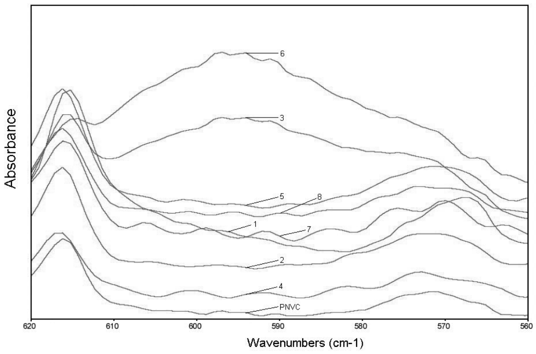

***Figure 1**. FTIR spectra of PNVC and various polymer complexes with copper: samples 1, 2, 3, 4, 5, 6, 7 and 8.*

PNVC-Copper complexes

Figure 1 shows that the infrared spectra of the polymer-Copper complexes present some significant shifts with respect to that of PNVC. Spectral inspection shows the presence of a band at 595 cm^{-1} wave numbers for the samples 3 and 6. These samples present different behaviour like we can observe in the Figure 2. The spectra of the different samples present a very marked band in 810 cm^{-1}.

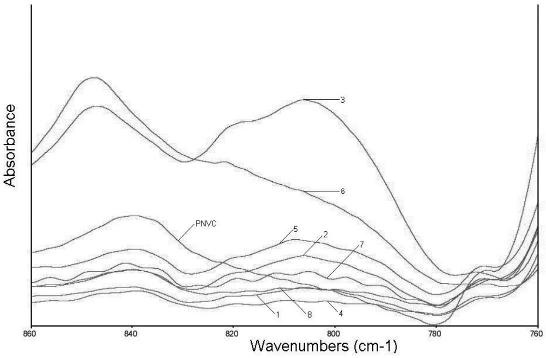

***Figure 2.** FTIR spectra of PNVC and various polymer complexes with copper: samples 1, 2, 3, 4, 5, 6, 7 and 8.*

This band can be assigned to the formation of complexes with copper. This band is present in all the studied polymer-metal complexes.In this picture we can observe like for the samples 3 and 6 some bands are displaced to different frecuencies compared with the other sample(11, 12); for example the present bands at 840, 900, 920 and 960 cm^{-1}.We can see also at 985 cm^{-1} a band appears in the spectra of the polymer-metal complexes with copper for the samples 3 and 6. This is a characteristic band of tetrahydrofurane. The tetrahydrofurane is the solvent used in the formation of the complexes. That which suggest us that the solvent participates in the coordination of the complexes.

Above 1260 cm^{-1} a new band appear for all studied samples and can be also assigned to the formation of complexes with copper and this band is present in all the studied polymer-metal complexes (see Figure 3).

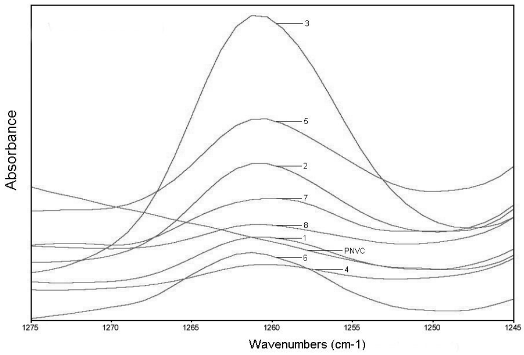

***Figure 3.** FTIR spectra of PNVC and various polymer complexes with copper: samples 1, 2, 3, 4, 5, 6, 7 and 8.*

Spectral inspection in Figure 4 shows the presence of a new band at 1725 cm^{-1} the samples 1, 3 and 6. In this Figure we can see a very strong absorption above 1775 cm^{-1} in the spectra of the metallic complexes of cupper. These bands are very difficult to assign.

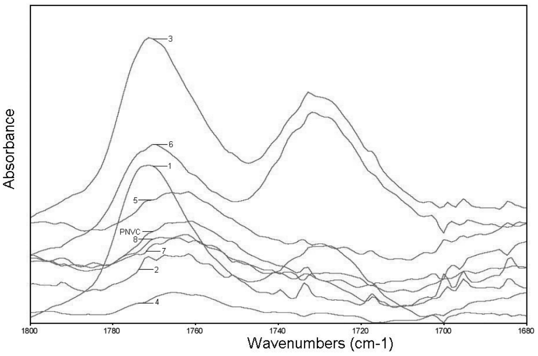

***Figure 4.** FTIR spectra of PNVC and various polymer complexes with copper: samples 1, 2, 3, 4, 5, 6, 7 and 8.*

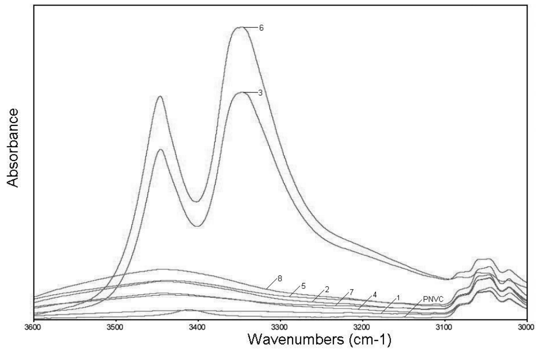

***Figure 5**. FTIR spectra of PNVC and various polymer complexes with copper: samples 1, 2, 3, 4, 5, 6, 7 and 8.*

As can be seen in Figure 5 above 3500 cm^{-1}, the spectra of the polymer show an intense band in the area of tension of the O-H group for the samples 3 and 6. This band indicates the presence of coordination water. When we carry out the thermal treatment we eliminate residual water but we are not able to eliminate it completely. These results suggest that the water is a part of the polymer-copper complexes in these samples.

PNVC-Cobalt complexes

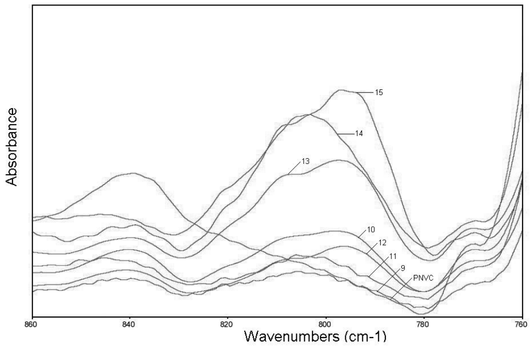

***Figure 6**. FTIR spectra of PNVC and various polymer complexes with cobalt: samples 9, 10, 11, 12, 13, 14 and 15*.

We can see in Figure 6 and 7 at 800 and 1250 cm^{-1}respectively two new bands arise in the spectra of polymer-Cobalt complexes. These peaks do not appear in the polymer spectra, neither in that of the solvent. These bands are also independently in all the carried out spectra of the polymer-metal complexes of the metallic salts used for their formation. In the Figure 8 we can observe that at 1650 cm^{-1} most of the samples of complexes presents a new band that does not appear in that of the polymer. As can be observed in Figure 8 for the samples 9, 11 and 14 appears a new band very intense at 1725 cm^{-1}. In the spectra of all the samples of complexes formed with cobalt we do not find coordination water, neither peaks of absorption corresponding to the solvent as it happens with the complexes of cupper.

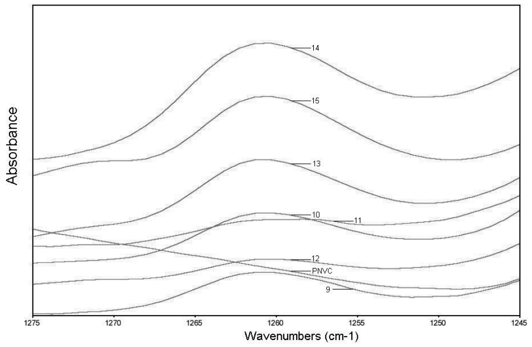

***Figure 7.** FTIR spectra of PNVC and various polymer complexes with cobalt: samples 9, 10, 11, 12, 13, 14 and 15.*

PNVC-Chromium Complexes

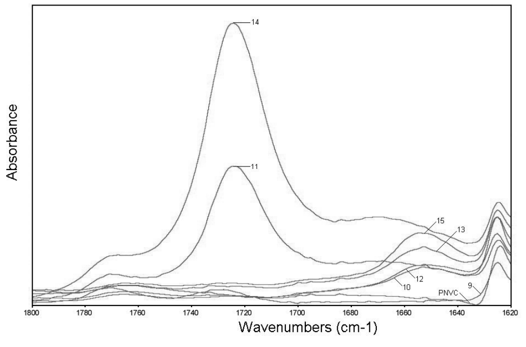

***Figure 8.** FTIR spectra of PNVC and various polymer complexes with cobalt: samples 9, 10, 11, 12, 13, 14 and 15.*

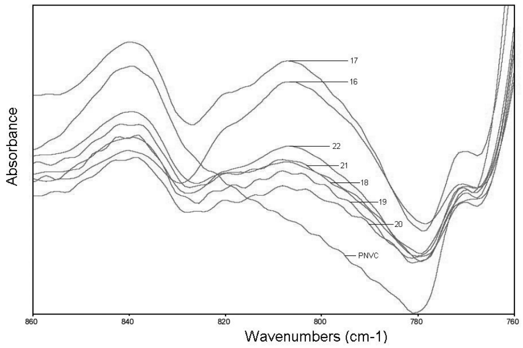

***Figure 9.** FTIR spectra of PNVC and various polymer complexes with chromium: samples 16, 17, 18, 19, 20, 21 and 22.*

In the study spectrometer carried out to the complexes formed with the metallic salts of chromium, we have found two bands, one at 800 cm^{-1} (Figure 9) and another at 1250 cm^{-1}, see Figure 10, that also present the complexes formed by the metallic salts of copper and cobalt. These bands are not characteristic of the polymer neither of the solvent. They are characteristic of the polymer-metal complexes. Neither coordination water is observed which it would indicate the presence of a band of absorption among 3100-3500 cm^{-1}.

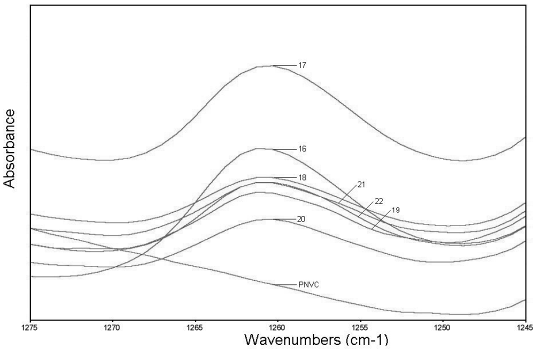

***Figure 10.** FTIR spectra of PNVC and various polymer complexes with chromium: samples 16, 17, 18, 19, 20, 21 and 22.*

The results obtained by FTIR make us think that in the union of poly(9-vinylcarbazole) with the metallic salts, the solvent and the coordination water alone participate in the samples 3 and 6. This union also takes place through the tertiary nitrogen of the group carbazole of the polymer.

SEM

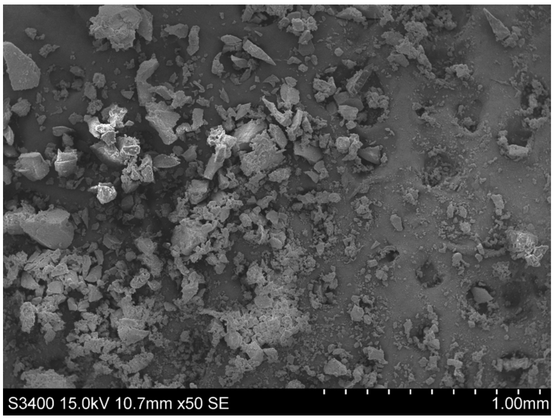

***Figure 11.** SEM of PNVC*

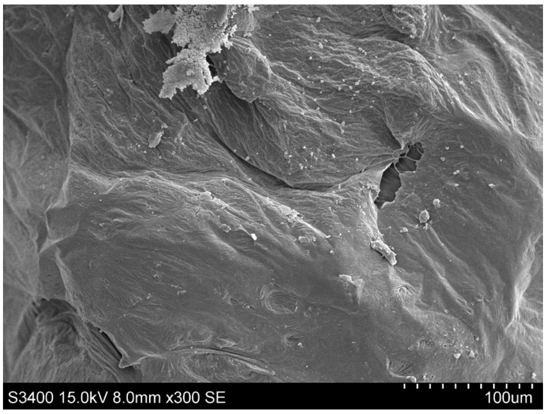

***Figure 12**. SEM of PNVC-copper complex: sample 1*

Scanning electron microscope of polymer and polymer – metal complexes was carried out to understand the structure. It is clear from the SEM (Hitachi S 3400N, Japan) the polymer is porous and has amorphous structure (Fig. 11). The pores of the polymer are filled after interaction with cation with polymeric ligand (Fig. 12). The nature of the polymer and polymer-metal complexes is quite different due to quelation of metal in polymeric backbone. This complexation significantly enhances the cristallinity of the polymers(13, 14) and changes consequently its chemical and physical properties.

Thermal analysis

The differential thermal analysis(DSC) were performed with a differential scanning calorimeter 2920 (TA Instruments). About 10 mg of each sample was heated in argon from 25 to 300 ºC with a heating rate of 10 ºC/min.

Thermal studies have been carried out on the polymer and polymer-metal complexes.

Typical DSC heating curves for PNVC and its metal complexes with copper are shown Figure 13. The glass transition temperature (Tg) for poly(9-vinylcarbazole) is found to be 171 ºC and for their complexes with copper are bigger and nearer to 225 ºC. The higher Tg values for polymer-metal complexes with copper than poly(9-vinylcarbazole) is due to the decrease in segmental mobility of the polymer-metal complexes as the result of anchosing of the metal ions in between in the chains and also can be due to the crystallinity of the polymer-metal complexes as they have revealed the studies carried out by others authors(13). In this picture we can see as the samples 3 and 6 have different thermograms, that which agrees with the result obtained by FTIR. These samples are those that in the formation of the complexes coordination water exists.

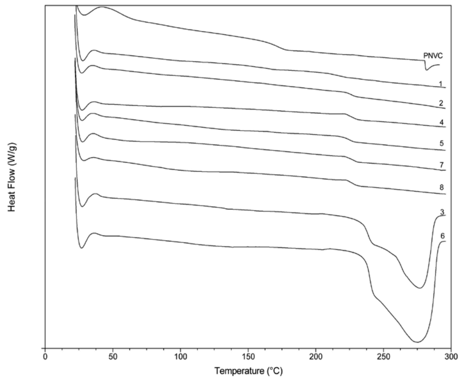

***Figure 13.** DSC curves of PNVC and PNVC-copper complexes: samples 1, 2, 3, 4, 5, 6, 7 and 8.*

The thermograms for poly(9-vinylcarbazole) and cobalt complexes are shown in Figure 14. In all the samples of PNVC-Cobalt metal complexes endothermal transformations were observed(9). These transformations, which do not correspond to the thermal degradation of the poly(9-vinylcarbazole), are known to take place to higher temperatures. They will be different according to the concentration of the metal. We suppose that this phenomenon is attributable to the tendency of the polymer-metal complex to acquire a certain structural arrangement or arrangements(9,14). These behaviours are always observed at temperatures smaller than the glass transition, when the polymer chains possess less mobility. The glass transition temperature of PNVC does not appear in the thermograms of the PNVC-Cobalt complexes for all the studied samples excepting the sample 9 that is the sample with less concentration of salt metallic. These results are similar to those obtained by FTIR.

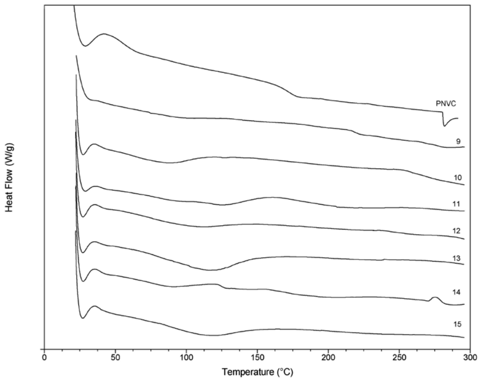

***Figure 14.** DSC curves of PNVC and PNVC-cobalt complexes: samples 9, 10, 11, 12, 13, 14 and 15.*

The thermal behaviour of the PNVC and PNVC-Chromium complexes as a function of temperature is shown in Figure 15. We can observe the glass transition temperature of the complexes is bigger than that of the polymer (near to the 220 ºC) for all the studied samples. These complexes have some similar thermograms to those of the copper although with lightly smaller glass transition temperatures. However in these complexes as we have been able to observe in the FTIR spectra there is not coordination water and the solvent does not participate in the union with the metal.

Thermogravimetry analysis of the polymer-metal complexes reveals the variation of thermal stability by complexation with metal ions. The thermal decomposition behaviour of a polymer-metal complex depends on the macromolecular characteristics of the polymer support and the type of coordination geometry. The order of stability observed in all of them can be described as that the polymer presents a smaller thermal stability than its complexes(9,13).

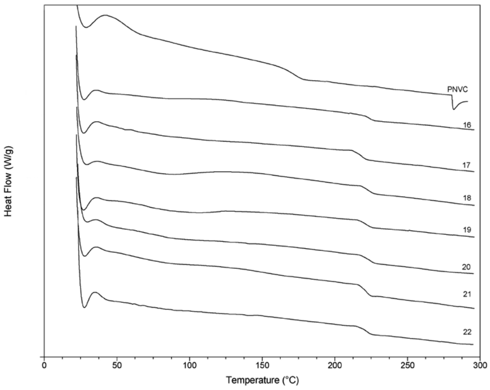

Figure 15. DSC curves of PNVC and PNVC-chromium complexes: samples 16, 17, 18, 19, 20, 21 and 22.

CONCLUSIONS

From these results, we can conclude that the coordination takes place only through the tertiary nitrogen of the carbazole side group. The polymer-complexes obtained by precipitation presented different characteristic colours, given that each of the metallic salts is totally different from the white coloured polymer in the solid state. For the samples 3 and 6 the solvent and the coordination water participate in the polymer-metal complexes. The glass transition temperatures of the polymer-metal complexes are higher than that of the polymer. The complexation enhances the cristallinity of the polymers and changes consequently its chemical and physical properties.

ACKNOWLEDGEMENTS

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