Characterization and Magnetic Behavior of Cobalt(II) and Gadolinium(III) Polyacrylates

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SYNOPSIS

The characterization and magnetic behavior of Co(II) and Gd(III) polyacrylates prepared by organic gelation synthesis have been studied. Gd(III)-polyacrylate shows a higher thermal stability due to stronger ionic interactions. IR spectra of both compounds reveal that carboxylate groups and water molecules exist in the coordination sphere with various forms of complexation. The samples are x-ray amorphous and have complex structures with the randomly distributing metal atoms along the PAA chain. The a.c. susceptibility measurements between 4.2 K and 250 K indicated a low temperature magnetic ordering. Annealing the samples at 160°C for 48 h result in the appearance of a spin-glass behavior in the in-phase and out-of-phase susceptibility curves. The presence of different sizes and shapes of clusters, however, precludes the determination of effective magnetic moments and Curie temperatures. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Investigations on the properties of synthetic polymers containing metal ions have been stimulated in recent years. The potentially important applications of these molecular systems as precursors to ceramics,[1-2] fluorescent probes,[3-5] and magnetic materials[6] are in intensive progress. Polymers are generally used as a matrix for these complexes. There is not much literature, however, on the polymeric systems in which the metals are directly bonded to the chain. The rare earth and transition metal complexes of poly(acrylic acid) (PAA),[3-7] poly(methacrylic acid) (PMA),[3] and copolymers of PAA and PMA[3,4] have been reported with some infrared spectral and fluorescent data, while their magnetic behavior have not yet been investigated. Only a few systems involving metal complexes that order magnetically at low temperatures[8-10] and a polymeric Schiff base complex ordering at room temperature[11] have been studied.

Considering that molecular lattices are able to perform several functions of metallic lattices, we have undertaken a series of experiments of PAA with various first raw transition metal ions and rare earth ions. We have carried out magnetic measurements in the temperature range of 4.2 to 250 K. In order to add some structural insight, we have also recorded the IR spectra and x-ray diffraction patterns. We present here the noticeable results obtained with Co(II) and Gd(III). The magnetic behavior of the Fe(III)-PAA system has been excluded regarding the possible contribution of any ferromagnetic iron oxide particle present in the sample.

EXPERIMENTAL

Metal polyacrylates were obtained by organic gelation synthesis. In all the preparations, the equivalent ratio of the metal to carbonyl groups was 1:1. In a beaker, a quantity of PAA (BDH, $M_w \sim 230{,}000$ g mol^{-1}, 25% solution, d = 1.09 g mL^{-1}, pH = 1.00–2.00) was diluted with distilled water. Concentrated ammonia was dropwise added upon stirring until pH = 8. A solution containing the related metal nitrate in distilled water was then added into the polymer solution. The gelatinious precipitates formed (I) were filtered through a small porosity funnel, washed with cold water, and then dried in oven at

100°C for 24 h. A second set of samples (II) were obtained by annealing the first samples (I) at 160°C for 48 h. I and II were used in chemical analysis and physical measurements.

Organic elemental analyses of the samples were performed on a Hewlett-Packard Model 185 analyzer, and determinations of cobalt content were done by using a Perkin-Elmer Model 370 Atomic Absorption Spectrophotometry. Gadolinium content was determined thermogravimetrically by ignition to the oxide under flowing air.

Thermogravimetric data were recorded by using a Setaram TGA 92 instrument under the following conditions; sample weight approx. 12 mg, dynamic argon atmosphere, platinum crucibles (130 mL), heating program 25 to 350°C with 7°C min^{-1}, 350 to 550°C with 2°C min^{-1}, 550 to 600°C with 10°C min^{-1}.

FTIR spectra were obtained with a Shimadzu FTIR 8101 Spectrophotometer at a resolution of 4 cm^{-1} employing the KBr disk method.

X-Ray diffraction patterns were collected by a Phillips PW 1140/00 Dy 687 diffractometer using CuKa radiation with Ni filter.

Magnetic a.c. susceptibility measurements were done between 4.2 K and 250 K, using a LR 400 mutual inductance bridge with a precision of 10^{-7} e.m.u. The amplitude of the excitation field was 1.8 Oe, and the frequency of the field was 16 Hz.

RESULTS AND DISCUSSION

The results of the chemical analyses and TG measurements are given in Table I. The TG curves indicated a two-stage breakdown corresponding to dehydration followed by degradation. However, the second step also involves the removal of water molecules at higher temperatures, captivated between the contracted polymer chains under the preparative conditions. The DTG peak temperatures showed an earlier onset of both steps for the cobalt polyacrylate. The nature of the metal ion is known to have a great

influence on the stability of the PAA salts.[12] In this case, the stronger ionic interactions with the Gd^{3+} ions seem to reduce the mobility of the chains for intermolecular and intramolecular degradation. The decomposition resulted in the formation of a mixed residue consisting of the metal oxide with some metal containing organic derivative of the polymer, mostly the carbide, after dehydration and decarboxylation of the PAA backbone. Annealing the samples at 160°C for 48 h only lowered the water content upon the further loss of surface water and uncoordinated water but not altered the thermal stability of the materials.

The structural configurations of the samples were analyzed by IR spectroscopy and x-ray diffraction techniques. The powders were all x-ray amorphous. FTIR spectra showed the characteristics of the carboxylate coordination and water molecules in the coordination sphere (Table II). For polymer materials with phosphorylic and carboxylic acid groups, ion uptake from solution takes place only under formation of coordination bonds.[13] The characteristic frequency corresponding to the protonated carboxylate group at 1710 cm^{-1} completely disappeared in all the samples. However, a shoulder remained, because complete chelation is not achievable based on the length of the polymer chain and steric effects. The symmetrical (v_s, 1413 cm^{-1}) and antisymmetrical (v_a, 1556 cm^{-1}) stretching frequencies of the ionized carboxylate groups in aqueous solution shift when complexed with metal ions.[14] Analysis of the spectra showed that both v_a and v_s shifted to higher and lower wave numbers in a split pattern, indicating more than one type of complexation such as bidentate, bridging, and even monodentate. The only significant change is the sharp peak observed at 1393 cm^{-1} in the spectrum of Gd(III)-PAA, which probably reflects a difference in the complexation of Gd^{3+} due to its larger ionic radius relative to that of Co(II). The bands in the region of 600 cm^{-1} to 900 cm^{-1} are indicative of the formation of aquo complexes.[15] This region was quite unresolved for the gadolinium samples but more intensive. This is not surprising

Table I   Chemical Composition, TG, and DTG Data of Co(II) and Gd(III) Polyacrylates

				DTG Peak Temperatures (°C)	
Sample	Metal (%)	H$_2$O (%)	Metal : Carbon (mol : mol)	Dehydration	Degradation
Co(II)-PAA (I)	20.5	16.7	1 : 8	300	450
Co(II)-PAA (II)	24.2	11.8	1 : 8	300	450
Gd(III)-PAA (I)	57.9	13.3	1 : 3	330	480
Gd(III)-PAA (II)	64.3	8.52	1 : 3	330	480

Table II   Infrared Data for Co(II) and Gd(III) Polyacrylates

Sample	O—H str. (cm^{-1})	C—H str. (cm^{-1})	v_s (COO$^-$) (cm^{-1})	v_a (COO$^-$) (cm^{-1})	M—OH$_2$ (cm^{-1})
Co-PAA	3389, 3239	2961	1564, 1546	1465, 1427, 1406, 1346, 1324	867, 777 645
Gd-PAA	3389, 3196	2940	1564, 1546	1465, 1423, 1393(sh), 1346, 1324	unresolved

when one considers the large hydration enthalpy and high coordination numbers of the gadolinium ion[16] as well as its complex microscopic environment. The O—H stretching vibration appeared as a strong band between 3200 cm^{-1} to 3400 cm^{-1}, split slightly to a doublet because of the various symmetries of the coordinated water. Annealing the samples created almost no effect in the spectra except that some more water was removed. Consequently, the C—H str. vibrations at around 2950 cm^{-1}, which was overlapped by the O—H str. bands became more noticeable.

Scheme 1 shows some of the possible ways of formation of coordination bonds. There are contradictory reports[14] regarding the nature of carboxylate coordination, because of the uncertainties particularly in locating the v_s. Nevertheless, the octahedral coordination of Co^{2+} appears reasonable to assume in the light of elemental analysis and IR data. On the other hand, the range of coordination numbers adopted by the lanthanides makes it more difficult to assign a structure. The bidentate complexation seems, however, to be more stable among the various

forms due to the low strain energy of the chelate with the larger Gd^{3+} ion.[7]

The results of the a.c. susceptibility measurements of the samples are shown in Figures 1 and 2. The behavior of the a.c. susceptibility markedly depended on the past thermal history of the samples. As seen in the figures, thermal annealing strongly influences the magnetic properties by exhibiting a peak at low temperatures. Fitting the susceptibility data to the Curie-Weiss law between 100 K and 250 K reflects the paramagnetic nature of the samples in this temperature range. Deviations from Curie type behavior tend to be noticeable at low temperatures for low symmetry systems.[16] In the low temperature region, cusp-like peaks in the in-phase susceptibility X', and out-of phase susceptibility X", were observed. This "spin-glass" behavior can be clearly seen for the annealed samples. The characteristic features such as the freezing temperature and shape of the cusp change with the annealing process. This implies that the environment of the magnetic ion or clusters may play an important role for the freez-
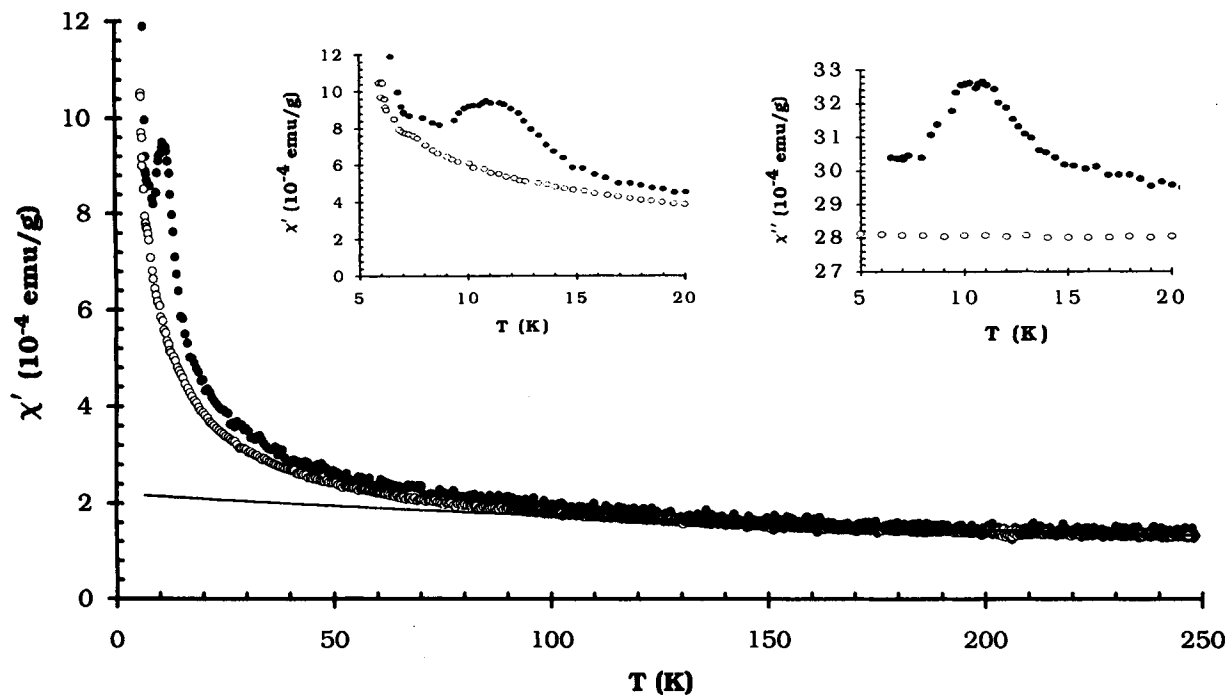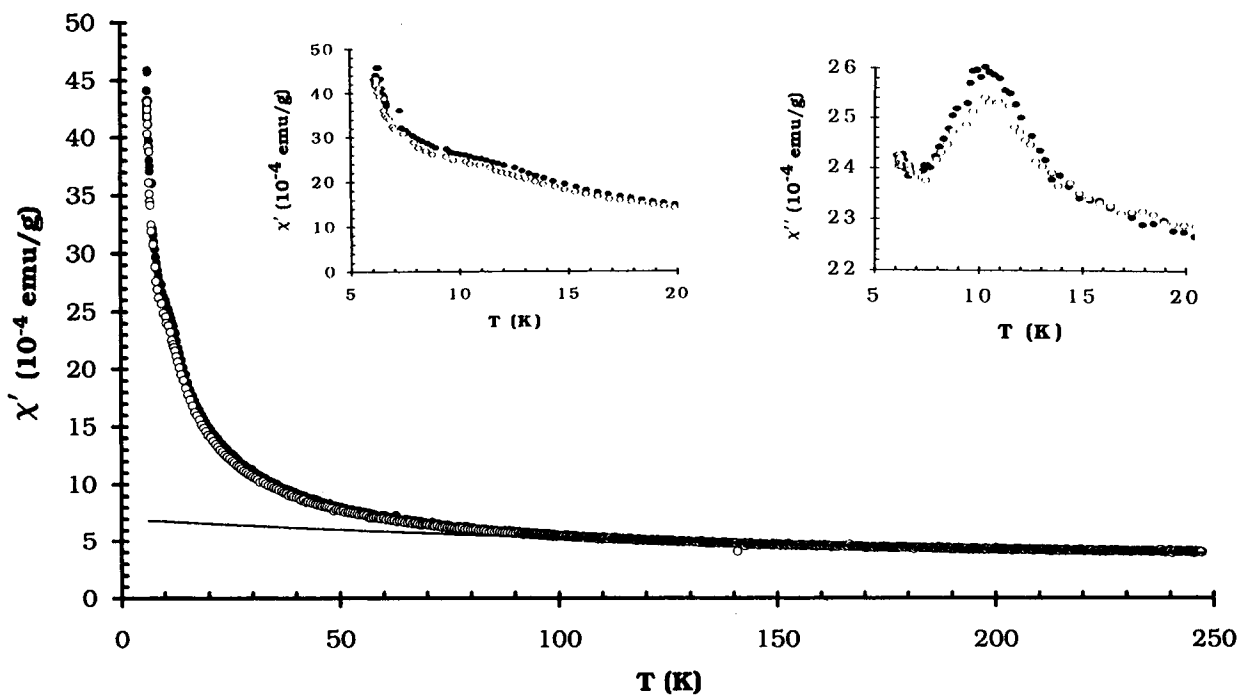

Scheme 1
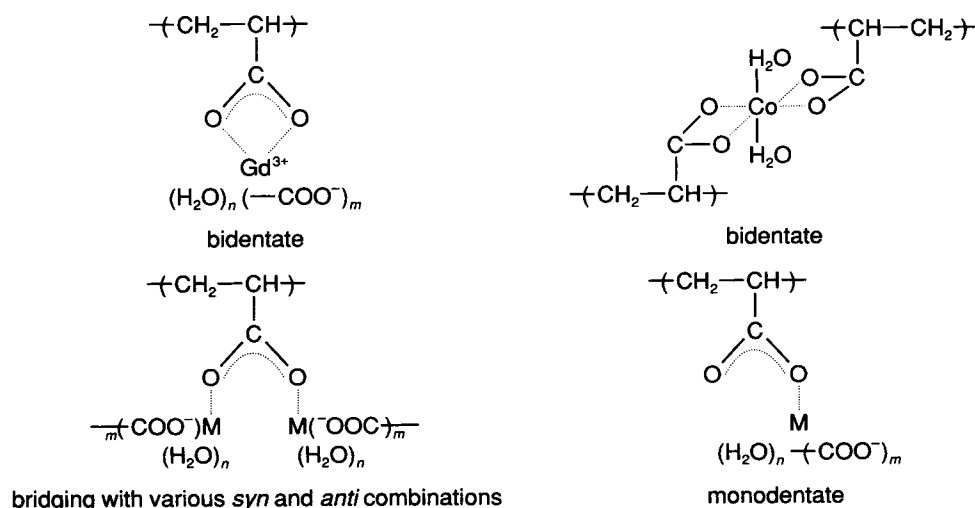
Figure 1   Temperature dependence of the a.c. susceptibility for the Co(II) polyacrylate. The solid line is the Curie-Weiss curve calculated from the fitted parameters at temperatures higher than 100 K. ○ sample I, ● sample II.

Figure 2   Temperature dependence of the a.c. susceptibility for the Gd(III) polyacrylate. The solid line is the Curie-Weiss curve calculated from the fitted parameters at temperatures higher than 100 K. ○ sample I, ● sample II.

ing at low temperatures. The changes in the magnetic properties are probably due to the formation of more ordered structural phases by heat treatment. The complex formation makes the macromolecules to coil tighter. Marked contraction of the polymer having a random distribution of the metal ions by intrapolymer chelation may lead to formation of weakly interacting clusters. At temperatures well below the peaks, the susceptibilities increase again, which probably originates from contributions of finite clusters, e.g., single ions, pairs, etc.

Correlation of the magnetic behavior with the structural arrangement would provide a useful information. However, it is difficult to derive the effective magnetic moments and Curie temperatures from magnetic data. Because the number of water molecules may vary rather easily and the metal ions distribute irregularly along the chain, the actual molecular weight of each of the samples could not be determined. There are different sizes and shapes of clusters in these polymeric systems.

CONCLUSION

Our results indicate that Co(II) and Gd(III) polyacrylates have promising magnetic properties. The observed low-temperature ordering needs further investigation in order to understand the magnetic behavior. The frequency dependence of the a.c. susceptibility measurements, optimization of the synthetic conditions, and annealing procedure are in progress.

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