

Effect of Chromium Aging on the Structural and Thermal Properties of Chromium Polyacrylate

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ABSTRACT: The effects of aging time of Cr(III) solutions on the structural, thermal, magnetic, and morphological properties of chromium polyacrylate complexes were studied. Chromium retention was found to increase with longer aging periods. IR spectra revealed the formation of polychelate structures with noticeable changes on aging. The interaction of multivalent, polynuclear Cr(III) species with the

polymer backbone resulted in a decrease in thermal stability for the complexes prepared from olated chromium solutions. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 490–493, 2005

Key words: metal–polymer complexes; structure–property relationships; polyelectrolytes; transition metal chemistry

INTRODUCTION

Polymer–metal complexes are attractive materials with miscellaneous uses in catalytic,¹ environmental,² and biochemical^{3–6} applications. One of the most versatile and studied polymers is poly(acrylic acid) (PAA). Complexes formed by reactions of PAA with transition-metal and rare-earth ions have been investigated intensely by many authors. Particular interest has been focused on the complexes of first row transition-metal ions toward the determination of stability constants,^{7,8} structural features, and thermal properties.^{9,10} PAA–metal complexes have also received attention as precursors to ceramics and ceramic superconductors.^{11,12} Co(II)–PAA and Gd(III)–PAA have been shown to possess promising magnetic properties, such as magnetic ordering at low temperatures and spin-glass behavior on annealing.¹³ The development of these materials requires a precise knowledge of their thermal and magnetic properties.

The swelling and deswelling of crosslinked polyelectrolytes in the presence of complexing ions has been the subject of several research studies in view of environmental chemistry. Interactions of small particles of PAA gels with chromium ions in aqueous solutions have been studied, and the effects of pH and aging time on the retention of multivalent species have been demonstrated.¹⁴ At pH values above the

solubility limit, ion fixation and release has been established as a fast and complete process occurring probably over the surface, whereas the aging time of the chromium solutions has a relatively small influence on the results. Here, we report the effects of chromium aging on the structural features and thermal properties of chromium polyacrylates prepared by organic gelation synthesis. The characterization of the complexes by IR spectral, thermal, crystallographic, magnetic, and optical methods are presented.

EXPERIMENTAL

Materials

CrCl₃ · 6H₂O was purchased from BDH (BDH, Poole, UK) and was used as received. PAA was a commercial sample from Aldrich (weight-average molecular weight ≈ 250,000 g/mol, 35% solution, density = 1.150 g/mL, refractive index = 1.3950; Aldrich, Milwaukee, WI).

Preparations

Four different products were prepared: a product prepared from fresh Cr(III) solution (1) and products prepared with Cr(III) solutions aged for 1 week (2), 3 weeks (3), and 5 weeks (4). The reactions were started by the addition of Cr(III) solution (15 mL, 2.5M) to PAA solution (20 mL, 2.5M) with the medium pH kept around 8 by the dropping of concentrated ammonia. The reaction mixture was agitated for complete mixing during the reaction course. The gelatinous precipitates formed (1–4) were removed by filtration and dried at room temperature for 24 h. The complexes

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were then washed with distilled water and ethanol and dried again.

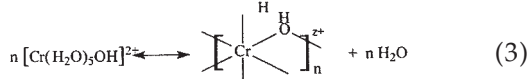
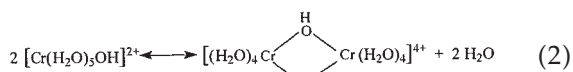
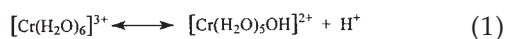
Characterizations

Fourier transform infrared (FTIR) spectra were obtained with a Mattson 1000 spectrophotometer (Mattson, Waltham, MA) in the 4000–400-cm⁻¹ range with the KBr disk method. Thermogravimetric analysis (TGA), differential thermogravimetry (DTG), and differential thermal analysis (DTA) data were recorded with a Shimadzu DTG-60H thermal analyzer (Shimadzu, Kyoto, Japan) with a sample weight of approximately 3 mg, a dynamic nitrogen atmosphere (15 mL/min), and heating to 900°C at 20°C/min in alumina crucibles. The chromium content was determined thermogravimetrically by ignition to the oxide (Cr₂O₃). The powder diffraction patterns were recorded with a Rigaku DMAX 2200 XRD instrument (Cu lamp, λ_{Kα} = 1.5418; Rigaku, Tokyo, Japan). Magnetic susceptibilities were determined by the Gouy method. A Cameca SU-30 model Semprobe scanning electron microscope (CAMECA, Paris, France) was used for optical analyses.

RESULTS AND DISCUSSION

Complexation studies with Cr(III) solutions

One of the important aspects of chromium chemistry is the slow, stepwise hydrolysis of Cr(III) ions in aqueous solutions [eqs. (1)–(3)]. This specific reaction is called *olation*, where linear or cyclic polynuclear species bridged by hydroxo groups are formed.¹⁵ The degree of polymerization is known to increase with the aging time of the solution, ranging from dimers to polymers of colloidal dimensions to precipitated Cr(III) hydroxide. Although it is difficult to define the exact distribution of species; dimeric, trimeric, and tetrameric species have been successfully isolated and characterized:¹⁶



The Cr–PAA complexes studied in this work were prepared with fresh and aged Cr(III) solutions. The compounds listed in Table I were green powders. The Cr content of the samples increased with the aging time because of the interaction of highly charged, polymetallic ions with the polymer backbone. The powder samples were almost X-ray amorphous, and

TABLE I
Chromium Contents, Magnetic Measurements, and Crystallinities of the Complexes

Sample	Aging time	Cr (%)	χ _g	χ _c (%)
PAA	—	—	—	6.4
1	Fresh	7.3	8.38 × 10 ⁻⁷	7.7
2	1 week	8.5	1.01 × 10 ⁻⁶	6.7
3	3 weeks	9.7	1.16 × 10 ⁻⁶	NR
4	5 weeks	15.5	1.36 × 10 ⁻⁶	6.5

χ_g = gram-magnetic susceptibility; χ_c = percentage crystallinity; NR = not recorded.

the aging time of the Cr(III) solution apparently had no significant effect on the crystallinity of the complexes with PAA, which had inherently low crystallinity. Magnetic measurements indicated a very slight decrease in the gram-magnetic susceptibility values. This might be explained by possible magnetic spin-coupling interactions between the Cr(III) centers in the complexed polynuclear species. However, magnetic data has not been exhaustively studied as they have for the Co(II) and Gd(III) analogues.¹³ A completely different magnetic ordering may be expected from low-temperature measurements.

FTIR spectra

The FTIR spectra showed the characteristics of carboxylate coordination¹⁷ and water molecules in the coordination sphere (Fig. 1). The spectra showed strong, broad bands in the region 3800–2800 cm⁻¹ due to O–H stretching vibrations of the nonionized acid groups and coordinated water. On complexation, the hydrogen-bonding interactions between the carboxylic acid groups of the polymer chains were broken, and the C–H stretching vibrations around 2950 cm⁻¹ became more noticeable. The frequencies corresponding to the protonated carboxylate group at 1710 cm⁻¹ (s) and 1651 cm⁻¹ (sh) underwent intensity reductions in the complexes. Because no complete chelation was achievable on the basis of the length of the polymer chain and steric effects, the 1710-cm⁻¹ peak remained a weak band, whereas the 1651-cm⁻¹ peak disappeared through complexation. A new band appeared at about 1547 cm⁻¹, which may be attributed to the ν_a(COO⁻). For the complexes prepared from aged Cr(III) solutions, the intensities of the symmetric (1408 cm⁻¹) and asymmetric (~1547 cm⁻¹) stretching frequencies of the ionized carboxylate group of PAA became stronger, although no shifting was observed. The difference in the energies (Δ) between these symmetric and asymmetric stretches of carboxylate ligands may be used to provide information on the coordination mode of carboxylates.¹⁸ For unidentate coordinations, Δ was quite large, but it was relatively small in chelated complexes. The presence of more

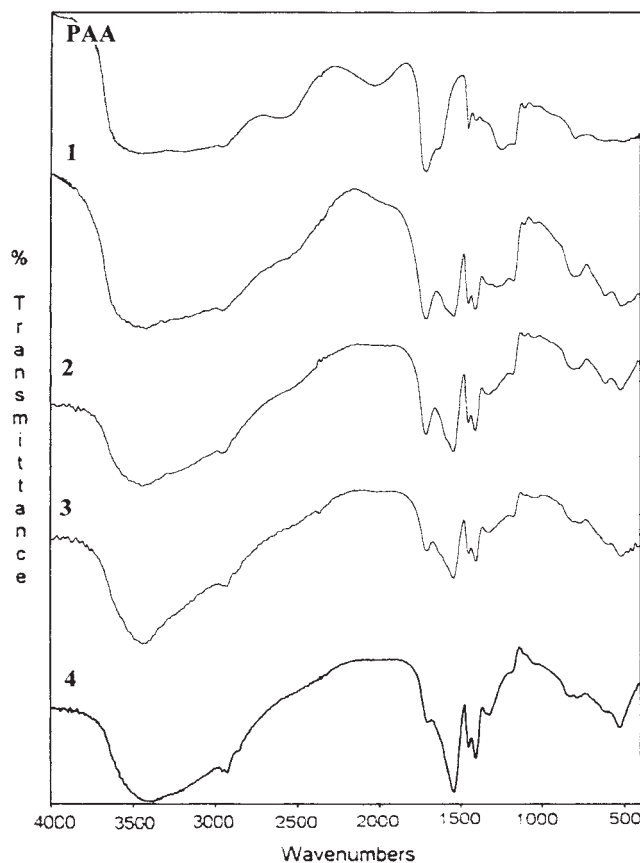


Figure 1 FTIR spectra of PAA and 1–4.

than one type of Cr(III) oligomer in solution and random binding with the polymer through interchain or intrachain mechanisms led to the presence of more than one type of complex in the solid state. Nevertheless, we assumed bidentate chelating in the complexes for which $\Delta \approx 140 \text{ cm}^{-1}$. According to these results, the structural configurations in Scheme 1 are suggested for the complexes with the consideration of octahedral coordination around Cr(III) completed by water molecules.

Thermal studies

The DTG and DTA curves of PAA and the complexes are shown in Figures 2 and 3, respectively. The thermogravimetric decomposition curve of PAA showed a three-stage breakdown in the tem-

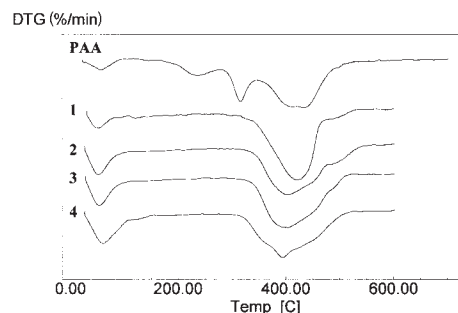
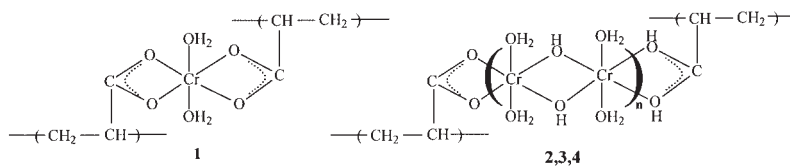


Figure 2 DTG curves of PAA and 1–4.

perature range 150–550°C after the removal of surface water at 58°C. Dehydration of the hydrogen-bonded groups took place in the first stage with a DTG peak temperature of 235°C, which matched an endothermic peak in the DTA curve. The second stage was the decomposition of the carboxyl groups at 316°C, and the third stage was the rupture of the polymer chain at 414–433°C. The decompositions of the complexes, on the other hand, proceeded in one major step with the removal of trapped water and coordinated water and contiguous further dehydration and decarboxylation processes. DTG and DTA traces showed broad, nonsymmetrical peaks with shoulders on both sides that arose from the overlap of a bench of such transformations.

The thermal stabilities of polymer–metal complexes are mainly determined by two oppositely competing processes: (1) complexation with a metal ion reduces the mobility of the chains for intermolecular and intramolecular degradation, and (2) the rupture of the intermolecular hydrogen-bonding network between the carboxyl groups of the polymer chain by complex formation enhances the mobility of the chains for thermal degradation. The complexes prepared in this study displayed an earlier onset of thermal decomposition with respect to intact PAA, as shown by the thermal data summarized in Table II. Apparently, the stability loss by intermolecular H-bond breakage was more effective than the stability gain by complexation with Cr^{+3} . Similar behavior was previously observed and well explained by a kinetic study, which verified that PAA had a higher activation energy for thermal decomposition than its metal salts and complexes.¹⁰ The stability decrease observed for the complexes prepared from aged



Scheme 1

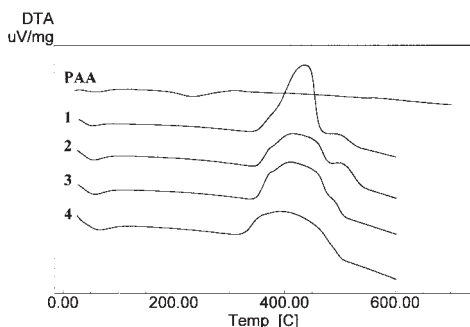
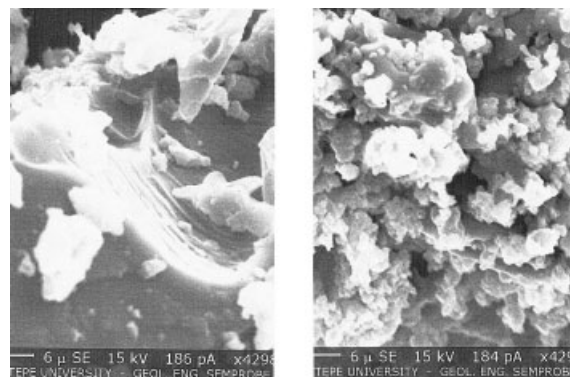


Figure 3 DTA curves of PAA and 1-4.



(a) (b)

Figure 4 SEM images of 1 and 4.

chromium solutions was due to the changing nature of the complexing ions with the aging time.

Olated species with greater average positive charges and number of Cr atoms were formed upon aging. Although the increase in charge favored stronger interactions, the increase in nuclearity resulted in relatively unstable coordination geometries, as proposed in Scheme 1, and consequently, the thermal decomposition temperatures of the samples prepared from aged Cr(III) solutions shifted to lower values parallel to the aging period.

Morphology

Figure 4 shows the scanning electron microscopy (SEM) images of complexes prepared with fresh and aged Cr(III) solutions. The surface of 4 [Fig. 4(b)] exhibited a sponge-like morphology, displaying the interaction of active carboxylate sites on the polymer chain with polynuclear metallic species.

CONCLUSIONS

On aging, the olation of Cr (III) ions in aqueous solutions led to the formation of multivalent, polynuclear species. The binding of these polycations with PAA resulted in the formation of complexes with different characteristics, which depended on the aging time of the chromium solutions. The chromium content in the

complexes increased with increasing aging period due to the complexation of a number of metal ions per carboxylate site. This interaction introduced different geometrical arrangements as shown by the IR spectra. Thermal studies revealed the variation of thermal stability with aging time. As an important conclusion, we can state that the complexes prepared from aged chromium solutions were thermally less stable. The stability loss might be explained on the basis of thermodynamically unfavorable coordination geometries established by the polynuclear Cr(III) ions. Aging had no significant effect on the crystallinity of the samples.

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TABLE II
Thermal Decomposition Temperatures of PAA and Its Cr³⁺ Complexes

Sample	TGA (°C) ^a	DTA (°C) ^b
PAA	150–550	235 (endo), 316 (exo), 414 (exo), 433 (exo)
1	≈60–500 (422)	422 (exo)
2	≈60–510 (401)	401 (exo)
3	≈60–500 (401)	401 (exo)
4	≈60–500 (393)	393 (exo)

^a The numbers in parentheses refer to the most intense DTG peak temperatures.

^b Peak temperatures of the most intense transformations.