4872 Macromolecules 1990, 23, 4872-4873

Notes

Oxygen Molecule Adsorption in Cobalt(II) Salts of Ethylene–Methacrylic Acid Copolymer

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Received January 30, 1990;
Revised Manuscript Received April 18, 1990

Recently we found the existence of a selective oxygen molecule adsorption in Mn(II) complex salts with 1,3-bis(aminomethyl)cyclohexane (BAC) of ethylene–methacrylic acid copolymer.[1] In this system, the sorption and desorption of a O_2 molecule was closely connected with the order–disorder transition of ionic clusters proposed by our previous paper.[2,3] The O_2 molecules adsorbed in the complex salts are released on aging in vacuo above the transition temperature (T_i). Moreover, the color of the sample changed to dark brown by the adsorption of O_2, and the dark brown sample was decolorized by the desorption of O_2. It is worthwhile to examine functional properties of ionomers containing various transition-metal salts and/or their complex salts with organic amines.

This paper reports an existence of oxygen molecule adsorption in Co(II) salts of ethylene–methacrylic acid copolymer (EMAA). This adsorption was discussed in terms of UV–visible spectral and electron spin resonance (ESR) studies. The Co(II) salts are denoted hereafter as EMAA-xCo, where x is the degree of neutralization by Co^{2+}.

EMAA was obtained from Du Pont–Mitsui Polychemicals Co., Ltd., ACR-1560, whose MAA content was 5.4 mol %. The Co(II) salts were prepared by a melt reaction of EMAA and cobaltous acetate in an extruder at 137–217 °C. Pellet samples obtained in this reaction were reformed into sheets by compression molding at about 157 °C and then cooled to room temperature at a rate of 30 °C/min by circulating cold water in the mold jacket. The formation of the Co(II) salts was confirmed by IR spectroscopy.[4,5] As the Co(II) content increased, the absorption at 1700 cm^{-1}, which is attributed to a stretching vibration of COOH, was depressed, while the absorption at 1580 cm^{-1}, which is consistent with the asymmetric stretching vibration of the COO^- in cobaltous acetate,[4] newly appeared and then increased. ESR spectra described later also support the formation of the Co(II) salts.

UV–visible spectra were recorded in films of 0.3–0.6 mm thick by using a Shimadzu double-beam spectrophotometer (UV-210A). The films were held in a box equipped with two quartz windows for the light path. When temperature-controlled water was circulated around the box, the spectra were measured at temperatures between 24 and 91 °C under 1 atm of O_2. ESR spectra were recorded by using an X-band spectrometer (JES-ME-3X, JEOL Co., Ltd.) under the following conditions: a 100-kHz field modulation and a modulation width of 1 mT were employed, the sample was sealed in a quartz tube under an oxygen-free atmosphere, and temperature was controlled by heating an air-flow just before the inlet of the cavity. The magnetic field was calibrated with Mn^{2+} in MgO as standard and an X-band frequency counter.

As reported previously,[5,6] the EMAA–Co(II) system shows thermochromism due to a transformation in cobaltous carboxylate from an octahedral coordination at room temperature to a tetrahedral coordination at high temperatures above 50 °C; in the visible spectra, there were observed doublet peaks at 490 and 520 nm and one peak at 570 nm at room temperature, which are assigned to ${}^4T_{1g}(F)$–${}^4T_{1g}(P)$ and ${}^4T_{1g}(F)$–${}^4A_{2g}$ transitions in an octahedral coordination, respectively. With increasing temperature above 50 °C, one peak at 580 nm, assigned to a ${}^4T_{1g}(F)$–${}^2A_{2g}$ transition in the tetrahedral coordination, appeared and gradually increased in intensity.

Figure 1a shows a UV–visible spectral change of EMAA–0.60Co by aging at 24 °C under 1 atm of O_2. In the original sample, doublet peaks at 490 and 520 nm and one peak at 570 nm in the octahedral coordination are observed, and one big peak appears at 250 nm. The 250-nm peak may be attributed to a charge-transfer transition associated with COO^- groups. As the sample is aged under 1 atm of O_2, four main peaks appear near 345 (I), 367 (II), 383–408 (III) and 620 nm (IV) and gradually increase. In addition, the III peak shifts to higher wavelengths and becomes predominant after aging long enough. On the other hand, the peak at 250 nm remains constant regardless of aging time. A UV–visible spectral change of EMAA–0.60Co by aging at 91 °C under 1 atm of O_2 is shown in Figure 1b. In the original samples, there is observed one peak at 580 nm, which is assigned to a ${}^4T_{1g}(F)$–${}^2A_{2g}$ transition in the tetrahedral coordination. As the sample is aged under 1 atm of O_2 at 91 °C, I and II peaks are seen at the initial stage of aging (up to 8 min), but with more aging, the III peak appears and shoots out. Here, the III peak shifts from 380 to 450 nm at 80 min on aging. The IV peak seen as a shoulder of the III peak becomes bigger by aging as well as that at 24 °C. These spectral changes may indicate an existence of an O_2 molecule adsorption in the present system: Actually similar UV spectral change due to O_2 molecule adsorption has been found in several polymers containing Co(II) complex salts.[7,8]

As seen in Figure 1, the rate of O_2 adsorption apparently increased with increasing temperature. On the other hand, the desorption of O_2 molecules was seen in vacuo in the higher temperature range above 110 °C.

Figure 2 shows ESR spectra of EMAA–0.60Co at several temperatures. The ESR spectra show almost axial

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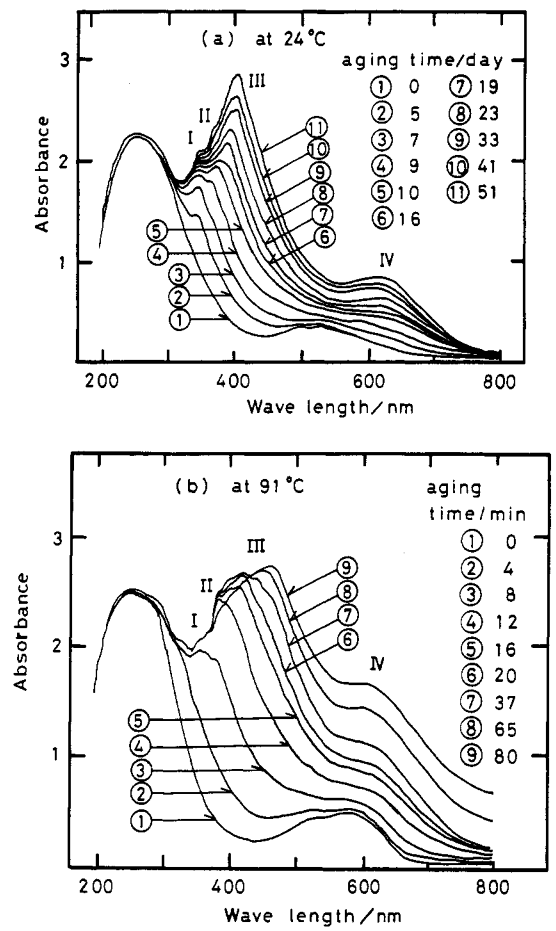

Figure 1. UV-visible spectral change of EMAA-0.60Co by aging under 1 atm of O_2 at (a) 24 °C and (b) 91 °C.

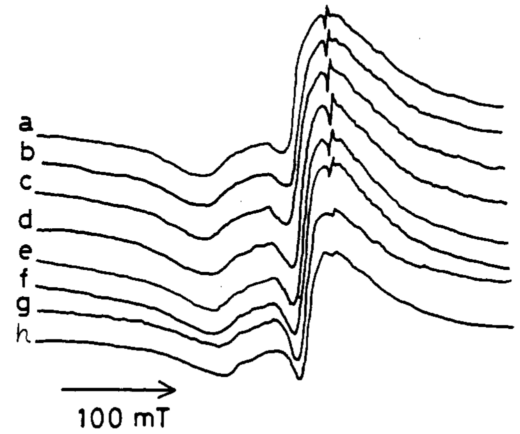

Figure 2. Temperature-dependent ESR spectra of EMAA-0.60Co in the magnetic field 0 up to about 500 mT with a 100-kHz magnetic field modulation of 1 mT. Recorded temperature is 20 °C (a), 29 °C (b), 40 °C (c), 50 °C (d), 55 °C (e), 60 °C (f), 68 °C (g), and 80 °C (h). The sharp signals are observed at ca. 330 mT, $g = 2.004$ (see text).

symmetric g-values, for instance, $g_{\parallel} = 2.969$ and $g_{\perp} = 2.274$ at room temperature. With increasing temperature, the line shape gradually changes, exhibiting smaller g-anisotropy. Finally the spectrum of nonaxial g-anisotropy was obtained, for instance, $g_x = 2.771$, $g_y = 2.149$, $g_z = 1.980$ at 80 °C. This variation of ESR spectra by temperature can be understood by assuming the transformation from the octahedral to the tetrahedral coordination in the Co(II) salts as indicated in the UV and visible absorptions.

In addition to these main absorptions, the sharp, but weak in intensity, absorption at $g = 2.004$ is observed in Figure 2. With increasing temperature, this line gradually grows up toward 50 °C but inversely declines above 50 °C and is considerably depressed at 80 °C. Since the order-disorder transition of the ionic clusters was estimated as about 50 °C in EMAA-0.60Co,[2] the depression of the line above 50 °C might be associated with the order-disorder transition. These ESR results are also compatible with the UV-visible ones described already, if one assumes that this sharp line is attributed to the O_2 adsorption effect. Actually the rate of O_2 adsorption apparently increased with increasing temperature. Therefore, we can assign, at present, this absorption as a Co(II)-O_2 complex, probably Co(III)-O_2^-; that is, a O_2^- species, in which an unpaired electron was transferred in part from Co(II), may give this paramagnetic absorption with a g-value quite similar to the free electron one ($g = 2.0023$). At the higher temperature range above 50 °C, this complexation is destroyed, leading to the desorption of O_2 molecules.

In concluding the ESR results, the temperature dependence of the ESR spectra of a EMAA-Co(II) system corresponds well to the change of the energy of Co(II) d-orbitals and accordingly the change of the g-value of the Co(II) ESR absorption. The g-value change suggests the deformational change of the Co(II) environment from the octahedral symmetry. Moreover, the signal at $g = 2.004$ characteristic of the O_2 adduct on the Co(II) ions was demonstrated.

An existence of O_2 adsorption was pursued for cobaltous acetate and Co(II) complex salts with 1,3-bis(aminomethyl)cyclohexane of EMAA, but both systems, noteworthily, were inactive for the O_2 adsorption. This result indicates that a characteristic structure of Co(II) salts functionalized by a polymeric environment may be responsible for the O_2 adsorption; it is postulated that the characteristic structure results from the formation of ionic aggregations such as ionic clusters in the ionomers.

The present work indicates an existence of O_2 molecule adsorption in a EMAA-Co system. Quantitative experiments for the O_2 adsorption are in progress for the present system.

References and Notes

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Registry No. ACR-1560, 25053-53-6; O_2, 7782-44-7; cobaltous acetate, 71-48-7; (ethylene)(methyl methacrylate)·cobalt(2+) (copolymer), 76522-78-6.