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Communications to the Editor

ESR Studies of Structure in Ethylene–Acrylic Acid Copolymers Neutralized with Manganese(II) Acetate

One of the most interesting aspects of polymers containing ionic bonds is the formation of ion clusters. Small-angle X-ray scattering, mechanical and dielectrical properties, and electron microscopy as well as other techniques have yielded much evidence for the existence of ion clusters, mainly for alkali metal and alkaline earth salts of ethylene–methacrylic acid and styrene–methacrylic acid copolymers.[1] In ionomers containing transition-metal salts, some paramagnetic properties of the transition-metal salts permit us to study the structure and molecular motion of the ionomers by means of various magnetic measurements. Pineri et al.[2] and we[3] reported electron spin resonance (ESR) studies of Cu(II) salts of a few copolymers containing carboxylic acid[5] and determined the structures of the complexes. However, there has been little ESR study of ionomers containing Mn(II) salts. It is reported that the ESR spectra for various Mn(II) salts usually undergo a marked change with ion concentration depending on whether Mn^{2+}–Mn^{2+} exchange interaction exists or not.[4] This aroused our interest in ESR studies of ionomers containing Mn^{2+} ions in different concentrations. The purpose of this work is to clarify by ESR studies the structure of ethylene–acrylic acid copolymers (E–AA) neutralized with manganese acetate.

The E–AA copolymer was EAA9300 of Union Carbide Co., the AA content of which was determined to be 9.3 mol % by titration. Manganese(II) salts of the E–AA copolymer were prepared by adding saturated manganese acetate in 2:1 tetrahydrofuran (THF)–methanol to 1 wt % E–AA copolymer in 4:1 THF–methanol dropwise at 64 °C under a nitrogen atmosphere. The Mn(II) salt samples were recovered by adding methanol to the salts in THF–methanol at about 5 °C. The degree of neutralization, x, was determined by quantitative analysis of Mn in the copolymer using the method developed by Yamada et al.[5]

The ESR spectra were obtained with an X-band ESR spectrometer (Japan Electron and Optics Laboratory Co. Ltd., Type JES-ME-3X) equipped with 100-kHz field modulation. The magnetic field was calibrated with 1/2000 mol % Mn^{2+} in MgO[6] and an X-band frequency counter.

Figure 1 shows the ESR spectra of E–AA copolymers neutralized with manganese acetate. The ESR spectra undergo a definite change with x. The ESR spectra exhibit six peaks for $x = 14\%$, whereas they become only one peak for $x = 62\%$. The ESR spectrum for Mn^{2+} (for example, manganese(II) acetate) is known to split into six peaks in the isolated state, which are ascribed to the hyperfine interaction of the manganese nucleus, $I = {}^5/_2$, with an unpaired electron. However, it coalesces into one peak when Mn^{2+}–Mn^{2+} exchange interaction exists.[4] Therefore, the ESR spectra suggest that the Mn(II) salts exist as the isolated complex in the copolymers with $x = 14\%$. On the other hand, in the copolymers with $x = 62\%$, appreciable Mn^{2+}–Mn^{2+} exchange interaction may be expected.

Infrared spectra for the E–AA copolymers neutralized by manganese acetate were measured with a differential grating infrared spectrometer (Japan Spectroscopic Co. Ltd., Type IRA-2). The symmetric and asymmetric stretching vibrations for the COO groups in the manganese carboxylates were observed at 1408 and 1585 cm^{-1}, respectively. This indicates that the structure of the Mn(II) salts may be a bridging structure similar to the bridging structure of anhydrous manganese acetate.[7] Furthermore, this bridging structure may be retained in copolymers with values of x from 14 to 62%, since the IR spectra showed no dependence upon x, except for intensities. Therefore, the change of the ESR spectra with x in Figure 1 may not originate in the structure of the complex itself but may be caused by a Mn^{2+}–Mn^{2+} exchange interaction between the Mn(II) complexes. This existence of the Mn^{2+}–Mn^{2+} interaction suggests that the distance between Mn^{2+} ions may be about 5.6 Å.[4] Although we cannot exclude the possibility that the copolymer itself may be blocky in nature, the ESR spectra indicate a structural change as x increases from 14 to 62%. At present, we cannot clarify the cause of this structural change unambiguously.

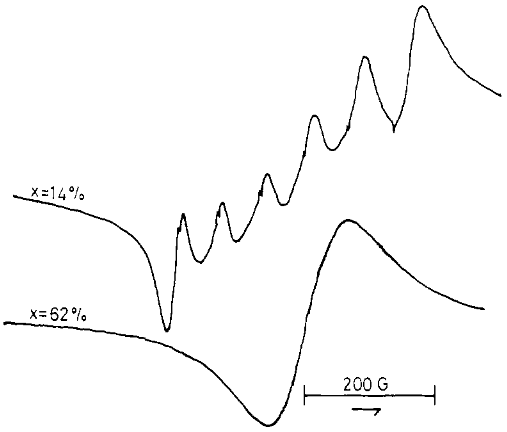

Figure 1. ESR spectra of ethylene–acrylic acid copolymers neutralized with manganese acetate. The six small absorptions overlapping in the $x = 14\%$ spectrum come from the 1/2000 Mn^{2+} in MgO reference. x is the degree of neutralization.

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References and Notes

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