

Oxygen gas sorption of Mn(II) complex salts of ethylene ionomer with various organic amines

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Manganese(II) (Mn(II)) complex salts of poly(ethylene-*co*-methacrylic acid) (EMAA) were produced from a precursor Mn(II) salt of EMAA and eight different kinds of organic amines, and their oxygen-gas (O₂) sorption behavior was investigated using visible absorption and infrared spectroscopies. It was found that the Mn(II) complex salts exhibit a selective O₂ sorption during ageing at room temperature in air and release sorbed O₂ molecules from ionic aggregates of the Mn(II) complex ions above 343 K *in vacuo*. From these results, the relationship between the O₂ sorption behaviour and the chemical structure of amines is discussed.

1. Introduction

Ionomers are today defined as polymers containing hydrophobic polymer backbones with a small amount of metal or ammonium salts at terminals of short chain branches or polymer backbones. Ionic aggregates, which are formed by the aggregation of hydrophilic ionic groups in the polymer matrix, act as rigid cross-links and impart dramatic increases in mechanical, melt, and chemical properties [1–4]. For such unique characteristics, tremendous studies have been brought into practice to elucidate the relationship between the morphology and physicochemical properties of many ionomer systems [5–7].

Recently we have found that the manganese(II) (Mn(II)) complex salts of poly(ethylene-*co*-methacrylic acid) (EMAA) with 1,3-*bis*(aminomethyl) cyclohexane (BAC) exhibits a selective oxygen-gas (O₂) sorption during ageing at room temperature in air [8]. The Mn(II) salts of EMAA are transparent light brown and maintain their transparency during ageing at room temperature in air for several weeks. On the other hand, the colour of the Mn(II) complex salts of EMAA with BAC changes from transparent light brown to dark brown within a few days. When the dark brown samples are heated at a temperature above 343 K, the colour returns to the original one. We concluded that these changes are attributed to the sorption and desorption of O₂ at the site of ionic aggregates formed by the Mn(II) complexes with BAC from the following observations. The dark brown samples showed the development of new peaks near 469, 500, 650 nm as shoulders in the visible spectra on

a large absorption band centred at about 200 nm. The intensity of the 469 nm peak increased remarkably under an O₂ atmosphere, while it remained unchanged under argon or nitrogen atmospheres. Moreover, sorption of O₂ molecules was gravimetrically detected during the pressurization and depressurization processes under an O₂ atmosphere using an electromicrobalance, where the residual amount of O₂ sorbed at $p = 0$ (p = pressure of O₂ gas in cm Hg) was determined to be about $(2-5) \times 10^{-5}$ g cm⁻³ (polymer). As expected, however, a similar experiment under a nitrogen (N₂) atmosphere revealed no observable sorption of N₂.

In this study, we investigated the effect of organic amines upon the O₂ sorption behaviour of the Mn(II) complex salts of ethylene ionomers. Samples were Mn(II) complex salts of EMAA made from eight different kinds of organic amines. Changes of the intensity of the 469 nm peak on the visible spectra were examined by assuming that the development of this peak closely correlates with the amount of sorbed O₂ and an attempt has been made to elucidate the relationship between the O₂ sorption behaviour and the chemical structure of amines.

2. Experimental procedure

2.1. Materials

The starting EMAA is a random ethylene copolymer made on a high-pressure autoclave of Du Pont-Mitsui Polychemicals Co. Ltd, and contains 5.4 mol % methacrylic acid unit. The 60% neutralized Mn(II) salt of

EMAA (EMAA-0.6Mn) was prepared by a melt reaction of EMMA with Mn(II) acetate tetrahydrate in an extruder at 473–513 K [4]. The formation of Mn(II) carboxylates was confirmed by the infrared spectra: the 1698 cm^{-1} peak of the carbonyl stretching band for COOH dimers was depressed and the 1589 cm^{-1} peak of the carboxylate asymmetric stretching band for $(\text{COO}^-)_2\text{Mn}^{2+}$ was developed. The complex formation of EMMA-0.6Mn with organic amines was accomplished by a melt reaction using a Toyoseiki Laboplastmill at 433–463 K with the rotor turning at

60 rev min^{-1} for 10–30 min under a constant flow of dry nitrogen. A typical reaction of the complex formation is illustrated in Fig. 1. At the end of reaction, the mixtures were immediately removed, compression moulded into 200–300 or 30–60 μm thick films at 10 MPa and $\sim 420\text{ K}$, and stored in a vacuum desiccator for subsequent property measurements.

The complex ionomers used in this study are denoted as EMMA-0.6Mn- y AMINE, where y is the equivalent ratio of amino group to carboxylic acid group (5.4 mol%) and AMINE is the type of organic amines as listed in Table I. Table I also includes the chemical structure and boiling point data.

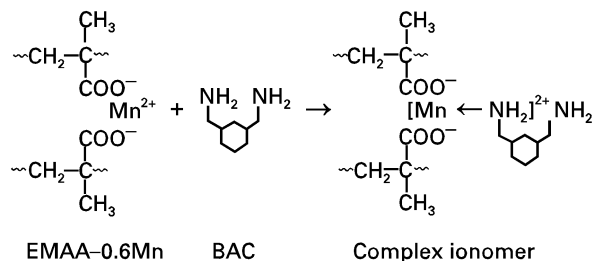


Figure 1 A typical reaction of the complex formation between the Mn(II) salt of EMMA and 1,3-bis(aminomethyl)cyclohexane.

2.2. Measurements

The elemental analysis data for the complex ionomers aged in the vacuum desiccator for about 80 days were obtained in the Laboratory for Organic Elemental Microanalysis of Kyoto University. Infrared spectra were measured on the 30–60 μm thick films using a Perkin-Elmer 1640 Fourier Transform-infrared (FT-IR) spectrometer at room temperature, where 64 scans at a resolution of 4 cm^{-1} were signal averaged.

TABLE I Chemical structure and boiling point of organic amines used to make complex Mn(II) salt of EMMA

Amine	Abbreviation	Chemical structure	Boiling point (K)
1,3-Bis(aminomethyl)cyclohexane	BAC		518–521
Aminomethylcyclohexane	AMC		437
1,8-Diaminooctane	DAO	$\text{H}_2\text{N}-(\text{CH}_2)_8-\text{NH}_2$	513–514
<i>n</i> -Dodecylamine	DDA	$\text{C}_{12}\text{H}_{25}\text{NH}_2$	520–522
Isophoronediamine	IDA		503
<i>meta</i> -Xylenediamine	MXDA		518–521
<i>cis</i> -Myrtanylamine	MA		473
Poly(oxypropylene)diamine	PODA	$\text{H}_2\text{N}-(\text{CH}_2\text{CHO})_n-\text{NH}_2$ ($n = 5,6$)	–

Visible absorption spectra were measured on the 200–300 μm thick films using a Hitachi spectrophotometer model 330 or a Shimadzu recording spectrophotometer model UV-2100 PCS at room temperature. Differential scanning calorimetric (DSC) data were obtained using a Seiko Denshi DSC-210 (SSC-5000 system) at a heating/cooling rate of 10 K min^{-1} under a dry nitrogen flow of 30 ml min^{-1} over a temperature range 273–423 K. A 10 mg specimen was sampled from the compression-moulded films which were aged in the vacuum desiccator for a few months.

3. Results and discussion

3.1. Elemental analysis

Table II summarizes elemental analysis data for the mixtures of EMAA–0.6Mn with various amines aged in the vacuum desiccator for about 80 days, where y_{ad} and y_{ob} are the equivalent ratios of amino group to carboxylic acid calculated from the amount of amines added and from nitrogen, carbon, and hydrogen analysis data, respectively. Comparing y_{ad} with y_{ob} clearly shows that y_{ob} is always smaller than y_{ad} and the discrepancy becomes larger with increasing y_{ad} in the case of BAC. The results indicate that about half of the amines may evaporate during the melt reaction at high temperatures or during the ageing in the vacuum desiccator, and this tendency is more obvious for amines that have a lower boiling point. Although y_{ad} is different from y_{ob} , y_{ad} is adopted as y in the rest of the text in order to denote the samples.

3.2. Fourier transform–infrared spectroscopy

Fig. 2 shows infrared spectra for the mixtures of EMAA–0.6Mn with various amines ($y = 1.0$) in the range 1100–1800 cm^{-1} , where the spectra were obtained immediately after thin films were made by compression moulding. EMAA–0.6Mn exhibits the carbonyl stretching band of COOH dimers at 1698 and 1670 cm^{-1} , but these peaks are scarcely seen for the spectra of the amine mixtures. Probably, a part of the amines added reacts with unneutralized carboxylic acids and form ammonium salts. By the reaction of EMAA–0.6Mn with amines, a peak at 1589 cm^{-1} , assigned to the asymmetric stretching band for COO^- ($\nu_{\text{as}}(\text{COO}^-)$) of the Mn(II) carboxylates, is depressed into a shoulder peak and another peak develops around 1540–1555 cm^{-1} . At the same time, a peak at 1395 cm^{-1} , assigned to the symmetric stretching band for COO^- ($\nu_{\text{s}}(\text{COO}^-)$) of the Mn(II) carboxylates, shifts to a higher frequency around 1405–1410 cm^{-1} . These results indicate that changes occur in the local environment of ion pairs and therefore, strongly support the complex formation between Mn(II) carboxylates and amino groups of amines. Thus, amino groups of the amines appear to form Mn(II) complex salts as well as ammonium salts. However, a close examination of the $\nu_{\text{as}}(\text{COO}^-)$ band of the Mn(II) complex salts shows that in the

TABLE II Elemental analysis data for the mixtures of EMAA–0.6Mn with various amines

Ionomer mixtures	y_{ad}^{a}	Elemental analysis results			
		N(%)	C(%)	H(%)	y_{ob}^{a}
EMAA–0.6Mn	0	0	79.35	13.18	0
EMAA–0.6Mn–0.6BAC	0.6	1.12	78.47	12.95	0.50
EMAA–0.6Mn–1.0BAC	1.0	1.47	78.34	13.07	0.67
EMAA–0.6Mn–1.6BAC	1.6	2.20	77.41	13.03	0.95
EMAA–0.6Mn–1.0AMC	1.0	0.92	78.10	12.81	0.42
EMAA–0.6Mn–1.0DAO	1.0	1.39	76.82	12.72	0.63
EMAA–0.6Mn–1.0DDA	1.0	1.00	78.29	13.02	0.49
EMAA–0.6Mn–1.0IDA	1.0	1.12	76.84	12.64	0.51
EMAA–0.6Mn–1.0MXDA	1.0	1.12	77.46	12.68	0.50
EMAA–0.6Mn–1.0MA	1.0	0.83	77.82	12.57	0.38

^a y_{ad} and y_{ob} are the equivalent ratios of amino group to carboxylic acid group calculated from the amount of amines added and from the N(%), C(%), H(%) values obtained from elemental analysis, respectively.

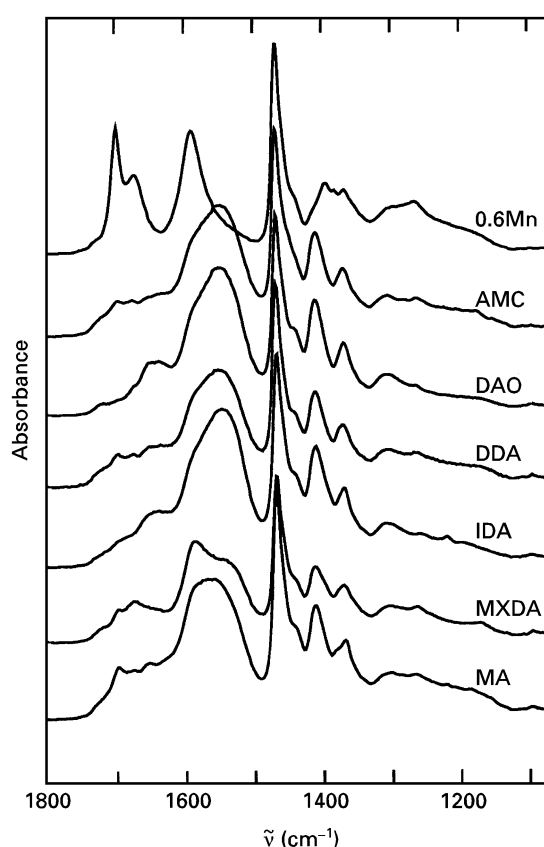


Figure 2 FT–IR spectra for the Mn(II) complex salts of EMAA with various amines ($y = 1.0$) in the range 1100–1800 cm^{-1} . The spectra were obtained immediately after thin films were made by compression moulding at 423 K.

Mn(II)–MXDA complex, the intensity of the 1550 cm^{-1} band is lower than and in the Mn(II)–MA complex is almost equal to that of the 1589 cm^{-1} band, suggesting low reactivity of MXDA and MA to EMAA–0.6Mn. These are probably due to weaker basicity of MXDA [9] and larger steric hindrance of MA compared with the others. These complex salts exhibited poor O_2 sorption as described in the following section.

3.3. Visible absorption spectroscopy

In our previous paper [8], we reported that visible absorption intensity at 469 nm for EMAA–0.6Mn–1.25BAC increased during ageing at room temperature under an O₂ atmosphere. From the result of sorption and desorption isotherms of O₂, we attributed this change to a selective adsorption of O₂ at the vicinity of Mn(II) cations. Fig. 3 shows changes of visible absorption intensity at 469 nm for the Mn(II) complex salts with various amines ($y = 1.0$) during ageing at room temperature under a dry air. The absorption intensity is normalized to the same film thickness of 1 mm and calculated by assuming that the intensity is zero at an ageing time of zero. The results clearly demonstrate that an increase of the peak intensity at 469 nm is strongly dependent on the type of amines. Assuming that this increase closely correlates with the amount of sorbed O₂, the amine dependence on an O₂ sorption rate is in the order of PODA > DDA > DAO > BAC > AMC, IDA, MA, MXDA. The results can point out a few distinct features of the chemical structure of amines.

1. Aliphatic, primary amines with a straight chain (PODA, DDA, DAO) tend to exhibit a large O₂ sorption rate.

2. Amines having bulky groups (IDA, MA) tend to prevent O₂ from being adsorbed at the site of ionic aggregates.

3. Ether group in the main chain of PODA probably plasticizes ionic aggregate regions and enhances O₂ diffusion.

4. No definitive reasons are given at this stage about the difference caused by BAC and AMC. A plausible explanation is that two amino groups of BAC are coordinated with one Mn(II) cation, resulting in the formation of a more compact complex structure, and also stabilizing O₂-adsorbed Mn(II) complexes.

From these features, it is concluded that the chemical structure of amines appears to be a dominant factor determining the O₂ sorption behaviour of the Mn(II) complex salts, and that the O₂ diffusion rate into the bulk polymer may influence their O₂ sorption behaviour. We are currently conducting quantitative analysis to measure gravimetrically the amount of O₂ sorbed. This will, hopefully, provide more information on the relationship between the changes in the visible spectra and the amount of O₂ sorbed.

Regarding the plasticizing effect, DSC measurements provide supporting evidence for our hypothesis. Table III summarizes DSC data for EMAA–0.6Mn, EMAA–0.6Mn–1.0BAC, and EMAA–0.6Mn–1.0PODA, where the samples were aged at room temperature in the vacuum desiccator for a few months. In general, ethylene ionomers exhibit two endothermic peaks near 330 and 363 K in the first heating when the samples are aged for more than several days at room temperature. The high-temperature peak is assigned to a melting of polyethylene crystallites, T_m , and the low-temperature peak is assigned to a transition associated with ionic aggregate regions (T_i) [10, 11]. The enthalpy changes at T_i (ΔH_i) and T_m (ΔH_m) are calculated from the peak area of each endothermic peak. As shown in Table III, all the three have T_m at

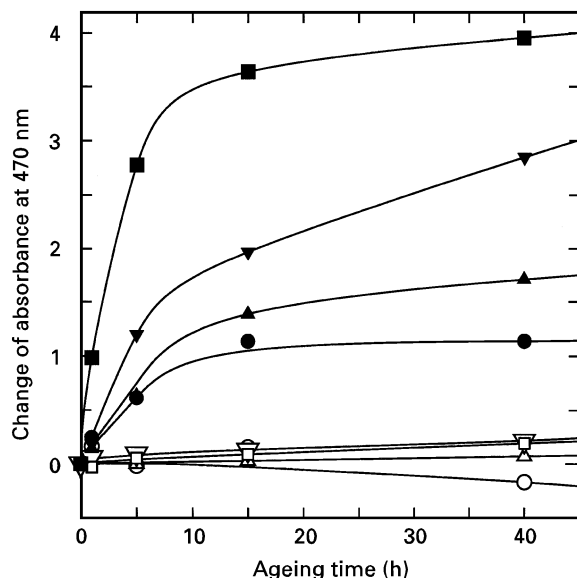


Figure 3 Changes of visible absorption intensity at 469 nm for the Mn(II) complex salts of EMAA with various amines ($y = 1.0$) during ageing at room temperature under a dry air: (○) MXDA; (△) MA; (□) IDA; (▽) AMC; (●) BAC; (▲) DAO; (▼) DDA; (■) PODA. In each sample, the absorption intensity is normalized to the same thickness of 1 mm.

TABLE III DSC data for EMAA–0.6Mn, EMAA–0.6Mn–1.0BAC and EMAA–0.6Mn–1.0PODA

Complex ionomer	T_i^a (K)	ΔH_i^b (J g ⁻¹)	T_m^c (K)	ΔH_m^d (J g ⁻¹)
EMAA–0.6Mn	332	17.0	364	46.0
EMAA–0.6Mn–1.0BAC	339	16.0	362	21.2
EMAA–0.6Mn–1.0PODA	327	8.0	363	36.1

^a T_i is a transition temperature associated with ionic aggregate regions.

^b ΔH_i is the enthalpy change at T_i .

^c T_m is the melting temperature of polyethylene crystallites.

^d ΔH_m is the enthalpy change at T_m .

the same temperature around 363 K. However, EMAA–0.6Mn–1.0PODA presents a lower T_i by 5–12°C and a smaller ΔH_i than those of the other two. This indicates that PODA preferentially plasticizes ionic aggregate regions by the interaction between ether groups and ion pairs. The plasticizing effect is very attractive for us because it possibly allows new materials to develop new materials which quickly sorb O₂. From this point of view, a further study is underway to prove this hypothesis, and the results will be reported elsewhere in the near future.

3.4. Changes of infrared spectra caused by O₂ adsorption

Fig. 4 shows changes of infrared spectra for EMAA–0.6Mn–1.0PODA during ageing under dry air and by subsequent thermal treatments. Spectrum A, measured immediately after compression moulding at 423 K, exhibits $\nu_{as}(\text{COO}^-)$ at 1553 cm⁻¹. Ageing the sample for 2 h at room temperature under dry air resulted in almost no changes, as shown in Spectrum B, but dramatic changes are seen in the $\nu_{as}(\text{COO}^-)$ peak of Spectrum C after ageing for 20 h, where the $\nu_{as}(\text{COO}^-)$ peak shifts to a higher frequency by 7 cm⁻¹ and a new peak appears at 1616 cm⁻¹. Both

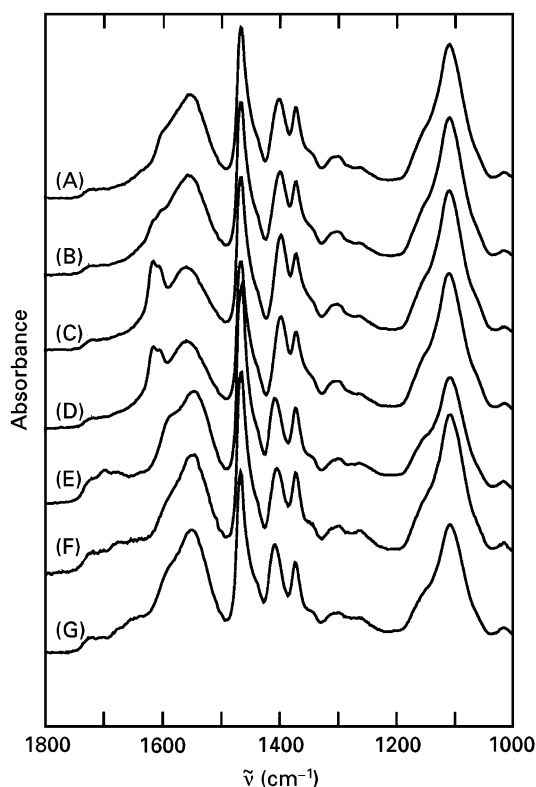


Figure 4 Changes of FT-IR spectra for EMAA-0.6Mn-1.0PODA during ageing under dry air and by subsequent thermal treatments: (A) The original sample immediately after compression moulding at 423 K; (B, C) the samples aged for 2 and 20 h under a dry air, respectively; (D) obtained after storing the sample C for 6 h at room temperature under vacuum; (E) obtained by heating sample C at 423 K for 1 h under vacuum; (F) the sample made by pressing sample C at 423 K for 30 min; (G) the sample aged for 24 h at room temperature under vacuum.

the $\nu_{\text{as}}(\text{COO}^-)$ and new peaks maintain their peak positions and intensities when a 20 h aged sample was stored for 6 h at room temperature under vacuum (Spectrum D). However, the $\nu_{\text{as}}(\text{COO}^-)$ peak almost returns to the original wave number and the new peak disappears when the 20 h aged sample was heated for 1 h at about 419 K under vacuum and then cooled to room temperature at about 30°C h^{-1} (Spectrum E), or else compression moulded at 423 K (Spectrum F). To investigate causes of the peak shifting and the development of the 1616 cm^{-1} peak, a thin film was aged for 24 h at room temperature under vacuum and then the infrared measurement was carried out (Spectrum G). In contrast to the ageing under air (Spectrum C), no changes are obvious in Spectrum G, which implies that the peak shifting and the 1616 cm^{-1} peak should originate from O_2 adsorption at the vicinity of Mn(II) cations. The origin of the distinctive 1616 cm^{-1} peak is probably attributed to $\nu_{\text{as}}(\text{COO}^-)$ vibrations of EMAA-0.6Mn-1.0PODA whose local environment is influenced by adsorbed O_2 molecules. Another assignment might be the stretching band of O-O for O_2 molecules adsorbed at the vicinity of Mn(II) cations. The shifting of the $\nu_{\text{as}}(\text{COO}^-)$ peak near 1550 cm^{-1} and the appearance of a new peak near 1610 cm^{-1} , were commonly observed in other Mn(II) complex ionomers aged in air. Regarding the effect of thermal treatments, the desorption of O_2 molecules from ionic aggregates of the Mn(II) complex ions

appears to begin at a temperature of about 343 K [8]. As shown in Table III, the DSC thermogram of EMAA-0.6Mn-1.0PODA exhibits two endothermic peaks at 327 and 363 K, which are assigned to a transition associated with the ionic aggregate regions, T_i , and a melting of polyethylene crystallites, T_m , respectively. Above T_i , molecular motions inside the ionic aggregate regions begin and become more vigorous with increasing temperature. Therefore, these motions are probably responsible for releasing O_2 molecules from the adsorption sites.

4. Conclusions

1. Mn(II) complex salts made from EMAA-0.6Mn and various organic amines demonstrate a selective O_2 sorption during ageing at room temperature and the O_2 sorption rate is strongly dependent on the chemical structure of coordinating amines in the order of $\text{PODA} > \text{DDA} > \text{DAO} > \text{BAC} > \text{AMC, IDA, MA, MXDA}$.

2. The O_2 adsorption at the vicinity of Mn(II) cations causes (a) an increase in the intensity of the 469 nm peak in the visible spectrum and (b) peak shifting of $\nu_{\text{as}}(\text{COO}^-)$ band and development of a new peak near 1610 cm^{-1} in the IR spectra.

3. The IR spectra show that with increasing temperature under vacuum, the O_2 molecules adsorbed begin to be released from ionic aggregates of the Mn(II) complex ions at a temperature near $\sim 343\text{ K}$.

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