h at 35 °C. After it was cooled, the reaction mixture was washed with 5% Na_2CO_3, 2% HCl, and water. After the chloroform layer was dried with $MgSO_4$, the chloroform was removed and the residual solid was recrystallized from a mixture of toluene–heptane (1:1 v/v): yield 44.4%; mp 95–96 °C. 1 has the following properties: ^1H NMR ($CDCl_3$) δ 6.7–7.5 (m, 3 H, aryl), 5.6–6.2 (m, 2 H, $=CH_2$), 3.7–4.2 (m, 16 H, CH_2), 2.4 (s, 3 H, CH_3), 2.0 (s, 3 H, CH_3); IR (KBr) ν 1740, 1640, 1600, 1190 cm^{-1}. Anal. Calcd for $C_{20}H_{27}NO_3$: C, 61.06; H, 6.92; N, 3.56. Found: C, 61.20; H, 7.13; N, 3.48.

4′-[1-[[(1-Propen-2-ylcarbonyl)oxy]imino]ethyl]-2,3-benzo-1,4,7,10,13,16-hexaoxa-2-cyclooctadecene (2). 2 was prepared from the oxime of 4′-acetobenzo-18-crown-6[10] and methacryloyl chloride by a procedure similar to that described for 1: yield 20.7%; mp 55–56 °C; ^1H NMR ($CDCl_3$) δ 6.7–7.5 (m, 3 H, aryl), 5.6–6.2 (m, 2 H, $=CH_2$), 3.5–4.4 (m, 20 H, CH_2), 2.4 (s, 3 H, CH_3), 2.1 (s, 3 H, CH_3); IR (KBr) ν 1740, 1640, 1600, 1180 cm^{-1}. Anal. Calcd for $C_{22}H_{31}NO_8\cdot{}^3/_2H_2O$: C, 56.89; H, 7.38; N, 3.02. Found: C, 56.81; H, 7.06; N, 2.96.

The polymers were prepared by copolymerization of corresponding monomers with AIBN as an initiator at 55 °C in vacuo. *N*,*N*-Dimethylformamide and dioxane were used as solvents for P15 and P18, respectively. The polymers were purified by dissolving in chloroform and precipitating with methanol. The fractions of 1 in P15 and 2 in P18 determined from their absorbance at 298 nm in CH_2Cl_2 ($\epsilon = 9.63 \times 10^3$ L/mol·cm) were 0.21 and 0.18, respectively. The weight-average molecular weight of P15 determined by GPC with polystyrene standards was 18000. The viscosity-average molecular weight of P18, determined by the viscosity–molecular weight relationship for polystyrene, was 164000. Alkali-metal picrates were prepared and purified according to the procedure described in ref 11.

The polymer film was photolyzed with 313-nm light isolated from a 75-W high-pressure mercury lamp using a glass filter (Toshiba UV-D33S) and a solution filter of K_2CrO_4 (1-cm thickness).[12] The half-width of the light was 22 nm, and the intensity was 3.0×10^{-9} einstein/s·cm^2. Sample films (~0.5 μm) were prepared on quartz plates (1 × 4 × 0.9 cm) by casting THF–methanol (1:1 v/v) solutions containing the polymer and alkali-metal picrates. The quantum yield (Φ) of photolysis of the oxyimino moieties of the polymers in the solid state was determined in air by measuring the decrease in the absorbance at 1740 cm^{-1}. A quartz plate coated with the polymer film was immersed in 10 mL of a mixed solvent of *n*-heptane and 1,2-dichloroethane (3:2 v/v) for 1 h at 25 °C, until the releasing equilibrium was accomplished. The released amounts of picrate salt and crown ether in the solvent were measured by HPLC.

References and Notes

(1) Vögtle, F. *Host Guest Complex Chemistry*; Springer-Verlag: Berlin, 1984.
(2) Tsunooka, M.; Cha, Y. S.; Tanaka, M. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 739.
(3) Ohta, H.; Tokumaru, K. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2393.
(4) Sakuragi, H.; Iskikawa, S.; Nishimura, T.; Yoshida, M.; Inamoto, N.; Tokumaru, K. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1949.
(5) Tsunooka, M.; Imono, S.; Nakayama, K.; Kuwabara, H.; Tanaka, M. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 317.
(6) Bourgoin, M.; Wong, K. H.; Hui, J. Y.; Smid, J. *J. Am. Chem. Soc.* **1975**, *97*, 3462.
(7) Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J. *Chem. Rev.* **1985**, *85*, 271.
(8) Xu, W. Y.; Smid, J. *J. Am. Chem. Soc.* **1984**, *106*, 3790.
(9) Xu, W. Y.; Roland, B.; Smid, J. *Macrmolecules* **1985**, *18*, 2061.
(10) Kopolow, S.; Hogen Esch, T. E.; Smid, J. *Macromolecules* **1973**, *6*, 133.
(11) Coplan, M. A.; Fuoss, R. M. *J. Phys. Chem.* **1964**, *68*, 1177.
(12) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.

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Selective Oxygen Gas Sorption of Complex Mn(II) Salts of Ethylene–Methacrylic Acid Copolymer with 1,3-Bis(aminomethyl)cyclohexane

Recently we have studied the development and physical properties of various complex transition-metal salts with organic amines.[1-4] In the course of work on various functional properties of ionomers containing complex transition-metal salts with organic amines, we find a selective O_2 sorption of the complex Mn(II) salts of ethylene–methacrylic acid copolymer (EMAA) with 1,3-bis(aminomethyl)cyclohexane [$1,3\text{-}(H_2NCH_2)_2C_6H_{10}$] (BAC), which are hereafter denoted as EMAA–*x*Mn–*y*BAC, where *x* is the degree of neutralization by Mn and *y* is the equivalent ratio of BAC as divalent base to COOH. This paper reports the selective O_2 sorption and desorption of EMAA-xMn-yBAC.

EMAA is ACR-1560 from Du Pont–Mitsui Polychemicals Co., Ltd., whose MAA content is 5.4 mol %. The Mn(II) salts and their complex salts with BAC were prepared by a melt reaction of EMAA and manganese acetate and that of the Mn(II) salts and BAC, respectively, in an extruder at 137–217 °C. The formation of the Mn(II) salts and the complex Mn(II) salts with BAC was confirmed by IR[5] as shown in Figure 1: in the Mn(II) salts, the 1700-cm^{-1} peak of COOH was depressed and the absorption peak at 1580 cm^{-1}, which is attributed to the asymmetric vibration of the COO group in the manganese carboxylate, appeared and increased with increasing Mn content. With the addition of BAC to the Mn(II) salts, the peak at 1580 cm^{-1} was replaced by the peak at 1530 cm^{-1}, which indicates the formation of the complex Mn(II) salts with BAC.

Visible absorption spectra were measured in films about 0.3–0.6 mm thick by use of a doulbe-beam spectrophotometer (Shimadzu, UV-210A). The sorption isotherms were determined gravimetrically on a Cahn 2000 electromicrobalance, as described previously.[6] Here, a buoyancy compensator method was used to increase the precision of the data. Electron spin resonance (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 and an X-band frequency counter.

Figure 2a shows visible spectra for EMAA–0.60Mn–*y*BAC at room temperature. In the Mn(II) salts (EMAA–0.60Mn), no absorption peak is observed in the wavelength range from 400 to 800 nm, which is consistent with the visible spectra of manganese acetate; the latter has only low-intensity spin-forbidden bands in the visible region.[5] In EMAA–0.60Mn–*y*BAC, the intensity of absorption clearly increases with increasing BAC content, and three small peaks are seen near 469, 500, and 650 nm as shoulders on a large absorption band. As the result, the color of these samples was a dark brown. Figure 2b shows the temperature dependence of the absorption intensity

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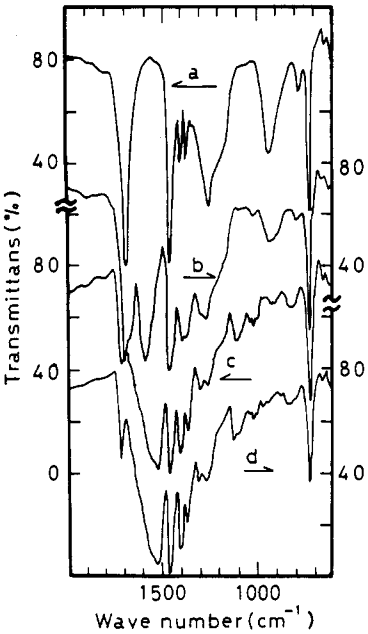

Figure 1. IR spectra for EMAA (a), EMAA–0.60Mn (b), EMAA–0.60Mn–0.40BAC (c), and EMAA–0.60Mn–1.25BAC (d).

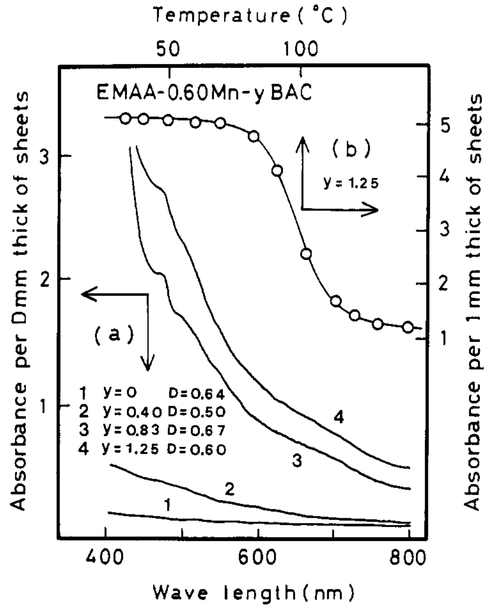

Figure 2. (a) Visible spectra of EMAA–0.60Mn–yBAC at room temperature. (b) Temperature dependence of absorbance at 469 nm. Each datum was obtained after keeping the sample at each temperature for about 10 min.

at 469 nm for EMAA–0.60Mn–1.25BAC. The intensity remains almost constant below 70 °C and decreases with increasing temperature above ca. 70 °C. The dark brown color disappeared on annealing above 70 °C. The decolorized sheets gradually became brown again on storage in air at room temperature. To determine what causes this thermochromism, visible spectra were measured for the decolorized films exposed to several gases at 1 atm at room temperature. Figure 3 shows changes in absorption intensity at 469 nm of the decolorized films with aging time at room temperature under 1 atm. Apparently the intensity increases only under an O_2 atmosphere. These results suggest that O_2 gas is selectively absorbed in the sample, accompanying the change of color to brown.

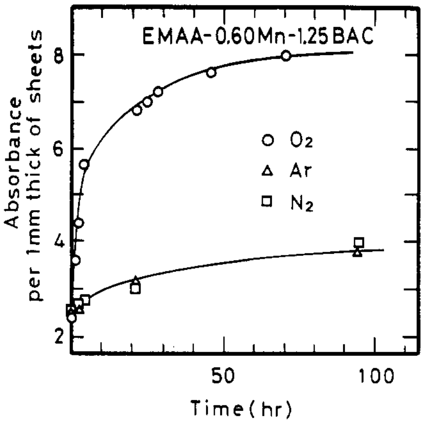

Figure 3. Change of visible absorption intensity at 469 nm with aging time under O_2, Ar, and N_2 gas atmospheres of about 1 atm at room temperature.

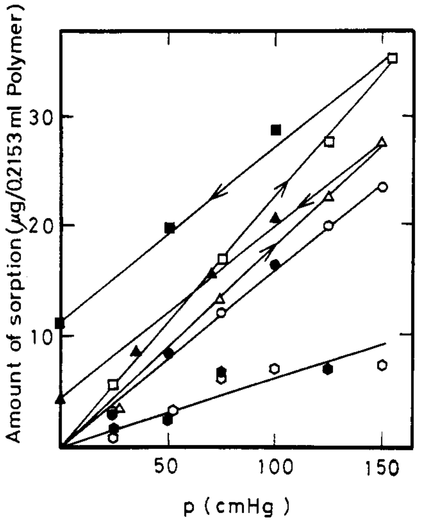

Figure 4. Sorption and desorption isotherms of O_2 and N_2 for EMAA–0.60Mn–0.83BAC at 25 °C. Open symbols, sorption data; closed symbols, desorption data. Data of O_2 (○) and N_2 (○) for unannealed (dark brown) samples; data of O_2 for annealed (decolorized) samples (obtained by cooling to 25 °C after annealing in 1.5 × 10^{-2} Torr at 110 °C for 10 h) stored in 1.5 × 10^{-2} Torr at 25 °C for 10 h (△) and 11 days (□).

Figure 4 shows sorption and desorption isotherms of O_2 and N_2 in EMAA–0.60Mn–0.83BAC at 25 °C. The isotherms under N_2 show a single straight line, which indicates that N_2 gas is dissolved in the polymer matrix according to Henry's law. The isotherms under O_2 are complicated. The sorption and desorption isotherms under O_2 for the unannealed sample (dark brown) also obey Henry's law. Absorption coefficients were estimated as 5.2 × 10^{-4} cm^3(STP)/cm^3(polymer)·cmHg for O_2 and 2.2 × 10^{-4} cm^3(STP)/cm^3(polymer)·cmHg for N_2, which are fairly consistent with those for low-density polyethylene with 50% crystallinity.[7] However, it is emphasized that the amount of sorption became larger on storing the annealed samples (decolorized sample) at 25 °C and that the isotherms have a hysteresis between sorption and desorption. Sorption coefficients were estimated as 6.0 × 10^{-4} and 7.2 × 10^{-4} cm^3(STP)/cm^3(polymer)·cmHg for 10 h and 11 days of storage duration, respectively. The desorption isotherms deviate considerably from the sorption isotherms, indicating the presence of O_2 adsorbed chemically in the polymer. The residual amounts of O_2 adsorbed at $p = 0$ are about 2.0 × 10^{-5} and 5.2 × 10^{-5} g/cm^3(polymer) for 10 h and 11 days of aging time, respectively, which indicates that the O_2 adsorption increases with aging at room temperature.

In previous work[3,4] on the complex Zn(II) salts of EMAA with BAC, we found that the ionic clusters undergo an

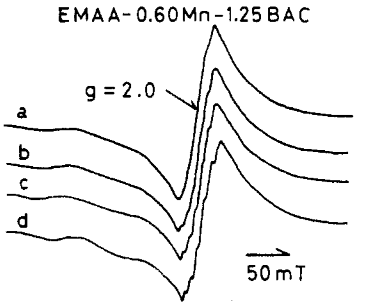

Figure 5. ESR spectral changes of the decolorized EMAA-0.60Mn-1.25BAC with exposure to air. The decolorized sample after heat treatment at 130 °C in vacuo gave spectrum a at room temperature. Its vacuum was then broken and after some aging times spectra b (6-h aging), c (78-h aging), and d (416-h aging) were obtained.

order-disorder transition near 57 °C (T_i). The ordered structure inside the ionic clusters is transformed into a disordered state above T_i. When the sample is cooled from a temperature above T_i to room temperature, the ionic clusters are in the disordered state inside but gradually reconstruct the ordered structure with a long relaxation time of about 32 days at 28 °C. In EMAA-0.60Mn-0.83BAC, T_i was about 51 °C, obtained by DSC and thermal expansion measurements. The ionic clusters are of course assemblies of the complex Mn(II) salts with BAC. It is the ordered ionic clusters but not the disordered ones that adsorb O_2 molecules selectively; this conclusion is drawn from the following facts: (1) The decolorizing of dark brown samples occurs above 70 °C, which may correspond to T_i (51 °C), as inferred from the effect of heating speed on the visible absorption measurements (see Figure 2b). (2) The amount of O_2 adsorbed chemically increases upon aging the decolorized samples at room temperature under O_2, but the dissolution of O_2 in the polymer matrix occurs only in the dark brown sample (see Figure 4). (3) We are carrying out ESR work on EMAA-xMn-yBAC. Preliminary data indicate that O_2 molecules are adsorbed at the vicinity of Mn^{2+} inside the ionic clusters.[8] Figure 5 shows ESR spectra of EMAA-0.60Mn-1.25BAC (decolorized sample) taken at room temperature after the heat treatment above 130 °C in vacuo. When the decolorized sample annealed at 130 °C in vacuo was stored at room temperature under air (O_2) atmosphere, several broad peaks, which may be ascribed to the Mn^{2+}-Mn^{2+} fine structure in the ionic aggregations,[9] became sharper and stronger, whereas the Mn^{2+}-Mn^{2+} interaction gradually decreased in magnitude. In addition, the six hyperfine line absorptions of isolated Mn^{2+} ($I = {}^5/_2$)[9] appeared. These results suggest that ordered ionic clusters are formed on storing at room temperature and that adsorption of O_2 to Mn^{2+} weakens the Mn^{2+}-Mn^{2+} interaction. Thus ESR results are fully compatible with the visible spectral variation by temperature as well as by absorbing O_2 gas.

In conclusion, this work indicates that the EMAA-Mn-BAC system selectively adsorbs O_2 gas and the adsorption site is the ordered ionic clusters formed by the complex Mn(II) ions with BAC.

Registry No. EMAA-xMn-yBAC (complex), 121231-23-0; O_2, 7782-44-7; N_2, 7727-37-9.

References and Notes

(1) Yano, S.; Tadano, K.; Sugiura, T.; Hirasawa, E. *Structure and Properties of Ionomers*; NATO ASI Series; Pineri, M., Eisenberg, A., Eds.; D. Reidel Co.: Dordrecht, 1987; p 481.
(2) Yano, S.; Yamamoto, H.; Tadano, K.; Yamamoto, Y.; Hirasawa, H. *Polymer* **1987**, *28*, 1965.
(3) Tadano, K.; Hirasawa, E.; Yamamoto, Y.; Yamamoto, H.; Yano, S. *Jpn. J. Appl. Phys.* **1987**, *26*, L1440.
(4) Tadano, K.; Hirasawa, E.; Yamamoto, H.; Yano, S. *Macromolecules* **1989**, *22*, 226.
(5) Edward, D. A.; Hayward, R. N. *Can. J. Chem.* **1958**, *46*, 289.
(6) Kamiya, Y.; Mizoguchi, K.; Naito, Y.; Hirose, T. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 535.
(7) Michaels, A. S.; Hixler, H. J. *J. Polym. Sci.* **1961**, *50*, 393.
(8) The detailed analysis will be published elsewhere by J. Yamauchi, S. Yano, and E. Hirasawa.
(9) Yamauchi, J.; Yano, S. *Macromolecules* **1982**, *15*, 210. Toriumi, H.; Weiss, R. A.; Frank, H. A. *Macromolecules* **1984**, *17*, 2104.

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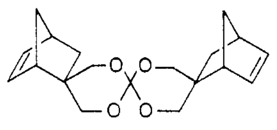
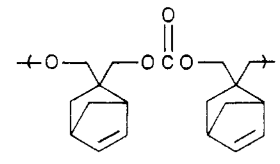
Unusual Ring-Opening Polymerization of a Spiro Orthocarbonate Containing Norbornene Moiety

Cationic polymerization of norbornene spiro orthocarbonate (NSOC) is believed to proceed according to the general polymerization mode accepted for all other six-membered spiro orthocarbonates (SOCs) (Scheme I[1]), to give poly(ether-carbonate), poly(NSOC).[2] NSOC is an important monomer among many SOCs which show expansion in volume on polymerization[1c,3] since it has been actually used for carbon fibre composites and epoxy coatings with improved toughness and stability by reducing shrinkage stress of epoxy resin matrix.[2,4] Recently we have found, however, that NSOC polymerizes cationically along a different mechanism from Scheme 1 to afford a structurally different polymer from [poly(NSOC)], which is described in this paper.


NSOC


poly(NSOC)

NSOC (mp 270 °C) was treated with BF_3OEt_2 at 100 °C in chlorobenzene (100 wt %) for 24 h.[5] The polymer obtained as the methanol-insoluble fraction (yield 50%, $\bar{M}_n$ 3100, $\bar{M}_w/\bar{M}_n$ 1.75)[6] did show very reduced olefinic proton signals (to 22% of the original NSOC) in ^{1}H NMR as illustrated in Figure 1A,B, although IR and elemental analysis data[7] did not deny the proposed poly(ether-carbonate) structure, poly(NSOC).[8] In more than 20 experiments under various conditions the reduction of the olefinic signals was always observed. Especially, the signals decreased to only 2% under drastic conditions (with 50

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