Table I
Polymerization of Hexafluoro-1,3-butadiene with Cesium Fluoride

initiator	solvent	temp, °C	time, days	yield, %
CsF	toluene	0	7	0
		20	7	20.8
		60	1	0
		60	7	58.9
		80	7	47.4
	THF	60	7	71.6

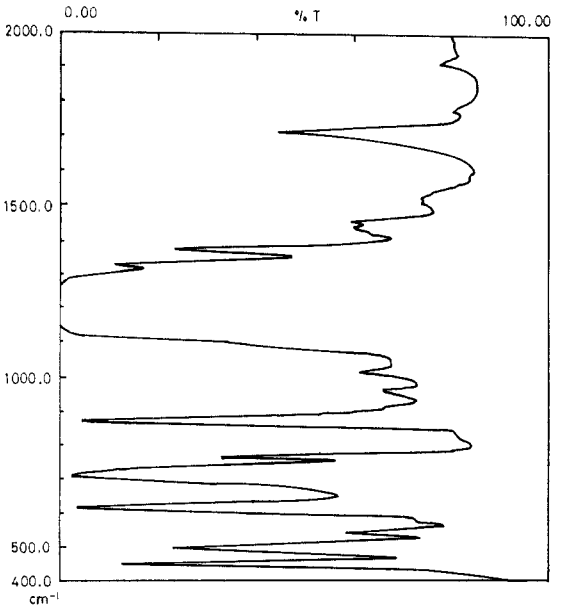

Figure 1. IR spectrum of poly(HFBD) obtained with cesium fluoride in toluene at 60 °C for 7 days (rolled film sample).

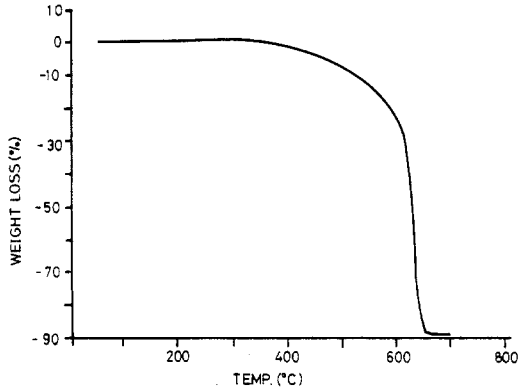

Figure 2. TGA of poly(HFBD) obtained with cesium fluoride in toluene at 60 °C for 7 days.

hexafluorobenzene, 2,2,2-trifluoro-1-(trifluoromethyl)-ethanol, and 1,1,2-trichloro-1,2,2-trifluoroethane. The polymer is, therefore, precipitated as the polymerization reaction proceeds and the GPC eluogram is not recorded.

Figure 1 shows the infrared spectrum of poly(HFBD) obtained with cesium fluoride in toluene at 60 °C for 7 days.[11] The spectrum shows a very strong broad band between 1100 and 1300 cm^{-1} for C-F absorption. Toy et al. have reported that two characteristic absorption peaks at 5.6 μm (1786 cm^{-1}) and 5.8 μm (1724 cm^{-1}) are assignable to a pendant perfluorovinyl group and a CF=CF group, respectively.[9c] In Figure 1 a very small peak at 1775 cm^{-1} and a strong absorption at 1715 cm^{-1} are observable, which means the 1,4-moiety is suggested as the predominant configuration in the polymer.

The thermal character of polymer obtained was analyzed by thermogravimetric analysis (TGA). Figure 2 shows that poly(HFBD) is highly stable against heat, and the polymer begins to decompose at 360 °C.

Poly(HFBD) obtained here shows very high heat resistance though it possesses CF=CF groups in the polymer main chain. Various modifications and variations may be made by the reaction of this functional group with many reagents. This polymer is a new material having application in several fields and industries.

Further investigation on anionic polymerization of HFBD and characterization of poly(HFBD) obtained are in progress.

Registry No. HFBD (homopolymer), 25036-06-0; CsF, 13400-13-0.

References and Notes

(1) Ito, H.; Miller, D. C.; Wilson, C. G. *Macromolecules* **1982**, *15*, 915.
(2) Ito, H.; Giese, B.; Engelbrecht, R. *Macromolecules* **1984**, *17*, 2204.
(3) Iwatsuki, S.; Kondo, A.; Harashima, H. *Macromolecules* **1984**, *17*, 2473.
(4) Narita, T.; Hagiwara, T.; Hamana, H.; Nara, T. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 301.
(5) Narita, T.; Hagiwara, T.; Hamana, H.; Nara, T. *Polym. J.* **1988**, *20*, 277.
(6) Narita, T.; Hagiwara, T.; Hamana, H.; Maesaka, S. *Polym. J.* **1988**, *20*, 519.
(7) Wall, L. A., Ed. *Fluoropolymers*; Wiley-Interscience: New York, 1972.
(8) (a) Toy, M. S.; Lawson, D. D. *J. Polym. Sci., Part B* **1968**, *6*, 639. (b) Toy, M. S.; Newman, J. M. *J. Polym. Sci., A-1* **1969**, *7*, 2333. (c) Toy, M. S.; Stringham, R. S. *J. Polym. Sci., Polym. Lett. Ed.* **1976**, *14*, 717.
(9) HFBD was purified by passing through a calcium sulfate and molecular sieve column in vapor phase and collected at dry ice temperature under reduced pressure. Polymerization was carried out in a sealed glass ampule under purified nitrogen atmosphere. The reaction was terminated with hydrochloric acid/methanol and the reaction mixture was poured into methanol.[10] The solid polymer was filtered off and dried to constant weight.
(10) The initiators used here were prepared according to the following literature: (a) Narita, T.; Hagiwara, T.; Hamana, H. *Nippon Kagaku Kaishi* **1985**, 1945. (b) Narita, T.; Hagiwara, T.; Hamana, H.; Goto, M. *Makromol. Chem.* **1986**, *187*, 731. (c) Ishimori, M.; Hagiwara, T.; Tsuruta, T.; Kai, Y.; Yasuoka, N.; Kasai, N. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1165. (d) Kageyama, H.; Kasai, Y.; Suzuki, C.; Yoshino, N.; Tsuruta, T. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 89. (e) Narita, T.; Hagiwara, T.; Hamana, H.; Irie, H.; Sugiyama, H. *Polym. J.* **1987**, *19*, 985. (f) Narita, T.; Hagiwara, T.; Hamana, H.; Miyasaka, T.; Wakayama, A.; Hotta, T. *Makromol. Chem.* **1987**, *188*, 273.
(11) IR spectrum of a rolled film of poly(HFBD) was recorded. The authors would like to express their grateful acknowledgment to Prof. Masamichi Kobayashi at Osaka University for IR measurements.

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Photoinduced Release of Alkali Picrates Using Photoreactive Poly(crown ether)s

Crown ethers are well-known to dissolve alkali-metal salts into low polarity media by binding cations.[1] In this paper we report both the synthesis of polymers that have photochemically labile crown ether units and the pho-

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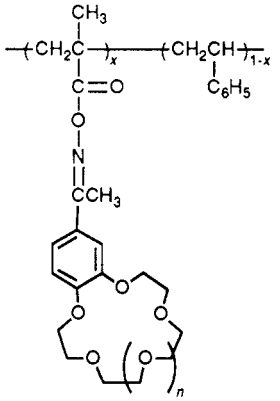
toinduced release of alkali-metal picrates from complexes of picrate and the polymer. The photoinduced selective release of picrate salts from the exposed polymer matrix into a solvent may have possible use as a photoimaging system. Most recording of images with light has been done by dyeing the photoreacted areas of polymer films.[2]



P15: $n = 1$, $x = 0.21$
P18: $n = 2$, $x = 0.18$

The polymers P15 and P18 showed λ_{max} at 270 nm and a shoulder peak at 300 nm. On irradiation with UV light the cleavage of pendant —ON= bonds in the polymer and the subsequent abstraction of hydrogen atoms from polymer molecules and/or residual solvent molecules led to the formation of a 4′-(1-iminoethyl)benzo crown, which can be hydrolyzed to a 4′-acetobenzo crown. The mechanism of photolysis of aromatic oxime esters has been studied in detail.[3,4] The formation of azines due to dimerization of imino radical intermediates was not observed for the present polymers. Acyloxy radicals generated on the polymer backbone by the photolysis have been known to decarboxylate, causing scission and cross-linking of the polymer chain.[5] The quantum yield (Φ) for photolysis of oxyimino moieties of the polymers in the solid state was 0.19 in air and was independent of the ring size of the crown ether units. In the presence of alkali metal picrates (PiM) the Φ values for P15 and P18 were 0.15–0.06 and 0.1–0.04, respectively, being dependent on the countercation of picrate anion. The photoreaction of the present polymers did not cause significant change in film properties.

Yellow clear films of the polymer containing PiM were prepared by forming ion-pair complexes between PiM and crown ether moieties immobilized on a polymer backbone. No clear films could be obtained at a PiM/crown ratio above 1/2, except the P15–PiNa, P18–PiNa, and P18–PiK systems, which gave clear films at a PiM/crown ratio of unity. The formation of free crown ethers in the polymer matrix on exposure with 313-nm light released PiM, as PiM–crown complexes, into a mixed solvent of *n*-heptane and 1,2-dichloroethane (3:2 v/v). No PiM was released from the unexposed polymer. Plots of the fraction of PiM released versus degree of photolysis of oxyimino units for P15 are shown in Figure 1a. A PiM/crown ratio was 1/2 before photolysis was started. The fraction of released PiM increased with increasing degree of photolysis of oxyimino units, although the efficiency of release was dependent on the countercation of the picrate anion. PiM was released from the polymer matrix into the mixed solvent as a 1:1 tight ion pair–crown complex, since a bathochromic shift of λ_{max} of picrate due to the formation of a 2:1 complex of crown with alkali picrate was not observed.[6] The quantities of PiM released from the polymer matrix were governed by the stability of PiM–liberated crown ether complexes in the solvent and the competition between

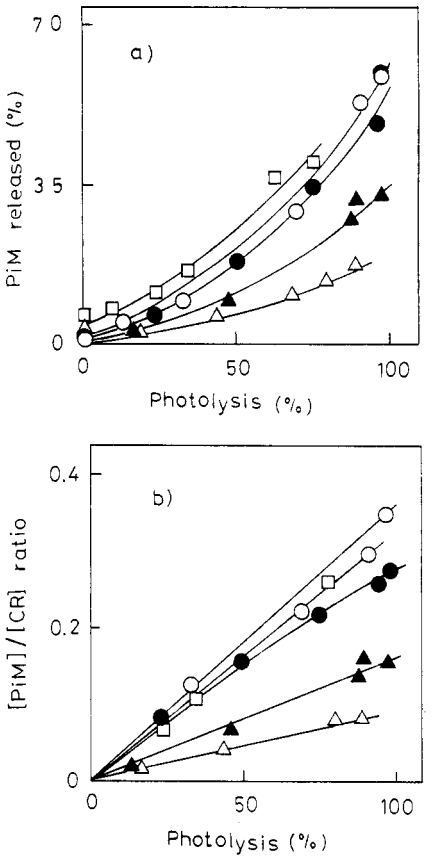


Figure 1. Relationships between degree of photolysis of P15 and (a) amount of PiM released and (b) ratio of released PiM to released crown ether ([PiM]/[CR]). Alkali-metal picrate: (●) PiNa; (○) PiK; (□) $PiNH_4$; (▲) PiRb; (△) PiCs. Initial PiM/crown ratio of polymer films was 0.5.

binding of PiM by crown units immobilized on the polymer and that of liberated crown ethers. When a blend of 4′-acetobenzo-15-crown-5 and PiM (PiM/crown = 1/2) was dissolved in the mixed solvent, the solubility of PiM, as a PiM–crown complex, decreased in the order PiNa > PiK > $PiNH_4$ > PiRb > PiCs, which except for $PiNH_4$, was consistent with the order of release efficiency of PiM from the exposed polymer film. It is well-known that the cation binding ability of crown ethers is strongly dependent on cation size and hole size of crown ethers.[7] As shown in Figure 1b the molar ratio of released PiM to released crown ether ([PiM]/[CR]) increased with increasing degree of P15 photolysis. The PiM binding to liberated crowns competes with that to crown units immobilized on polymer. Thus the amount of PiM released is a function of the amount of liberated crown ethers, i.e., degree of photolysis. A release mechanism of picrates bound to crown ether network polymers into solutions by an addition of soluble ligands, e.g., crown ethers, has been studied in detail.[8,9] An increase in temperature (10–40 °C) slightly increased the release efficiency of PiM. Similar results on the photoinduced release of PiM were obtained for P18, except that the efficiency of PiM release was higher than that for P15 and was less dependent on the countercation of picrate anion. When a proper solvent as a developer is chosen, the exposed regions of the polymer film are decolored, while the unexposed ones remain colored.

Experimental Section. 4′-[1-[[(1-Propen-2-ylcarbonyl)oxy]imino]ethyl]-2,3-benzo-1,4,7,10,13-pentaoxa-2-cyclopentadecene (1). Methacryloyl chloride (1.92 g) was added stepwise to a solution of oxime of 4′-acetobenzo-15-crown-5[10] (6.0 g) and triethylamine (1.87 g) in chloroform at 0 °C. The reaction was continued for 15

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 (ϵ = 9.63 × 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-$(H_2NCH_2)_2C_6H_{10}$] (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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