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Syntheses and radical ring-opening polymerizations of 1,1-bis(hydroxymethyl)-2-vinylcyclopropane and 1,1-bis(methoxymethyl)-2-vinylcyclopropane

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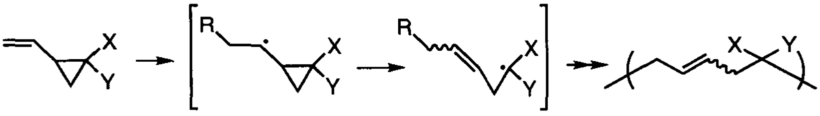
Summary

Syntheses and radical ring-opening polymerization of 1,1-bis(hydroxymethyl)-2-vinylcyclopropane (**1a**) and 1,1-bis(methoxymethyl)-2-vinylcyclopropane (**1b**) were examined. Novel polymers bearing hydroxyl and methyl ether moieties in the side chains as well as olefinic moieties in the main chain were obtained. The main structure of the polymers, obtained by radical polymerization, originated from the cleavage of the cyclopropane ring near the hydroxymethyl or methoxymethyl groups. The difference in the two-center energies and bond orders of the C-C bonds of the cyclopropane ring well explained the selectivity in the direction of the cleavage. The number-average molecular weights ($\overline{M}_n$) of poly(**1a**) and poly(**1b**) were 94200 and 11200 in the polymerization in bulk at 60 °C, respectively. The intermolecular hydrogen bonding of **1a** might increase the radical polymerizability. The oxygen permeability of poly(**1a**) was 6.19 $\mathrm{mL \cdot 20\ mm \cdot m^{-2} \cdot day^{-1} \cdot atm^{-1}}$ at 35 °C, demonstrating that poly(**1a**) could be a good oxygen barrier material.

Introduction

Polymers having hydroxyl groups in the side chains and their derivatives obtained by polymer reactions are useful as biocompatible materials,(1) reactive polymers,(2) and so on, like poly(vinyl alcohol), one of the industrially most important polymers having hydroxyl groups. Meanwhile, radical ring-opening polymerization of vinylcyclopropanes has been reported (Scheme 1).(3)

Scheme 1



X, Y ; Radical stabilizing group

Herein, we wish to report the syntheses and radical ring-opening polymerizations of vinylcyclopropanes having hydroxymethyl (**1a**) and methoxymethyl groups (**1b**). The novel polymers might be interesting functional polymers having hydroxyl groups in the side chain and double bonds in the main chain. In this paper, the influences of hydrogen bonding of the hydroxyl groups on polymerization,(4) mechanistic aspects of the selectivity of ring-cleavage of the cyclopropane ring by molecular orbital calculations, the volume

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change on polymerization, and the oxygen permeability of the obtained polymers are described.

Experimental

Measurements

^1H and ^{13}C-NMR spectra of monomers and polymers were recorded at 27 °C on JEOL JNM-EX-90 and JNM-EX-400 spectrometers, using tetramethylsilane (TMS) as an internal standard in chloroform-*d*. IR spectra were obtained with a JASCO FT/IR-5300 at 25 °C. Molecular weight and its distribution ($\overline{M}_w/\overline{M}_n$) were determined by gel permeation chromatography (GPC) on a TOSOH HLC-8020 system with a data processor equipped with four polystyrene columns (TSK gels G6000H, G5000H, G4000H, and G2500H), using LiBr solution in DMF (5.8 mM) as an eluent (flow rate 1.0 mL/min), polystyrene calibration, and refractive index and ultraviolet detectors. Thermal analyses were performed on Seiko Instruments DSC220C and TG/DTA220. The glass transition temperature was taken as an inflection point on a trace by differencial scanning calorimetry at a heating rate of 10 °C/min. The 10 % weight loss temperature was determined by thermo-gravimetric analysis at a heating rate of 10 °C/min under a nitrogen atmosphere. Densities of **1a** and poly(**1a**) were measured by the density gradient tube method with *n*-hexane/carbon tetrachloride as a density gradient liquid at 25 °C with a Shibayama Scientific Co. Ltd. Model A.

Materials

Chlorobenzene, DMF and methanol were dried and distilled by the usual methods and stored over molecular sieves (4A). Initiators 2,2'-azobis(isobutyronitrile) (AIBN, Tokyo Kasei Kogyo Co. Ltd.), benzoyl peroxide (BPO, Nacalai Tesque, Inc.), di-*tert*-butyl peroxide (DTBP, Nacalai Tesque, Inc.), and 2,2'-azobis(2-methylpropionamidine) dihydrochloride (V-50, Wako Pure Chemical Industries, Ltd.) were used as received.

1,1-Bis(hydroxymethyl)-2-vinylcyclopropane (1a)

1a was prepared according to the reported method.[3b)]

1,1-Bis(methoxymethyl)-2-vinylcyclopropane (1b)

To a suspension of sodium hydride (1.53 g, 63.6 mmol) in THF (60 mL) was added dropwise **1a** (3.40 g, 26.5 mmol) at 0 °C. Methyl iodide (8.28 g, 53.8 mmol) was added to the mixture at 0 °C, and the mixture was stirred at room temperature for 24 h. Precipitated sodium iodide was filtered off and the filtrate was concentrated. The residual liquid was distilled under a reduced pressure to obtain 3.24 g of **1b** (78 %) : bp 49 °C / 2.0 mmHg ; ^1H-NMR ($CDCl_3$) : δ 0.60-0.95 (m, 2H), 1.43-1.84 (m, 1H), 3.26 (s, 6H), 3.16-3.56 (m, 4H), 4.95-5.88 (m, 3H) ; ^{13}C-NMR ($CDCl_3$) : δ 14.84, 24.80, 27.03, 58.49, 58.56, 71.94, 76.39, 115.14, 136.12 ; IR (neat): 3080, 2982, 2878, 1635, 1452, 1400, 1267, 1194, 1107, 1037, 966, 902, 814, 773, 683 cm^{-1}. Anal. Calcd for $C_9H_{16}O_2$: C, 69.19 ; H, 10.32. Found : C, 68.92 ; H, 10.15.

Adduct of 1a and Benzyl Mercaptan (Adduct 1a-BM). To **1a** (0.385 g, 3 mmol) and benzyl mercaptan (0.373 g, 3 mmol) in a glass tube were introduced an AIBN (22.2 mg, 3 mol%) and a chlorobenzene (3 mL). The tube was cooled, degassed, sealed off, and heated at 60 °C for 20 h. Adduct **1a-BM** was isolated from the resulting mixture by silica gel column chromatography (eluent ; ethyl acetate), yield 0.746 mg (98 %), conversion of **1a** 100 %. ^1H-NMR ($CDCl_3$) : δ 1.97-2.02 (m, 2H), 2.98-3.00 (m, 2H x 6/7), 3.06 (d, *J* = 8.0 Hz, 2H x 1/7), 3.60-3.80 (m, 7H), 5.45-5.52 (m, 2H x 6/7), 5.53-5.60 (m, 2H x 1/7), 7.20-7.31 (m, 5H) ; ^{13}C-NMR ($CDCl_3$) : δ 30.80, 33.23, 35.41, 41.84, 64.90, 126.96, 128.11, 128.49, 128.89, 130.78, 138.27. ; IR (neat): 3358, 3027, 2917, 1601, 1493, 1453, 1225, 1200, 1071, 1030, 968, 922, 768, 700, 565, 473 cm^{-1} ; FAB-MS *m/z* 253 (M); high-resolution mass (FAB) calcd for $C_{14}H_{21}SO_2$ 253.1262, found 253.1256.

Adduct of 1b and Benzyl Mercaptan (Adduct 1b-BM). The title compound was prepared from **1b** and benzyl mercaptan similarly to adduct **1a-BM**. Eluent of silica gel column chromatography : ethyl acetate : *n*-hexane = 1/4 (volume ratio), Yield 97 %, conversion of **1b** 100 %. ^{1}H-NMR ($CDCl_3$) : δ 2.08-2.11 (m, 2H x 1/5), 2.12-2.15 (m, 2H x 4/5), 3.00 (d, *J* = 5.6 Hz, 2H x 4/5), 3.10 (d, *J* = 5.6 Hz, 2H x 1/5), 3.30 (s, 6H), 3.29-3.38 (m, 6H), 3.65 (s, 1H x 4/5), 3.68 (s, 1H x 1/5), 5.45-5.47 (m, 2H x 4/5), 5.48-5.50 (m, 2H x 1/5), 7.21-7.30 (m, 5H) ; ^{13}C-NMR ($CDCl_3$) : δ 31.55, 33.27, 35.04, 35.83, 39.39, 58.89, 73.01, 126.85, 127.71, 128.42, 128.88, 130.38, 131.44, 138.46. ; IR (neat): 3029, 2980, 2893, 2749, 1603, 1495, 1478, 1453, 1420, 1391, 1194, 1111, 1028, 968, 918, 768, 700, 565, 471 cm^{-1} ; FAB-MS *m/z* 281 (M); high-resolution mass (FAB) calcd for $C_{16}H_{25}SO_2$ 281.1675, found 281.1622.

Polymerizations of 1. General Procedure. To a monomer (3 mmol) in a polymerization tube was introduced an initiator and, if necessary, subsequently a solvent. The tube was cooled, degassed, sealed off, and heated at a set temperature for 20 h. Poly(**1a**) was isolated from the resulting mixture by reprecipitation with ether, and dried *in vacuo* at 50 °C. Poly(**1b**) was isolated from the polymerization mixture by separation with a preparative high performance liquid chromatography (HPLC) (Japan Analytical Industry LC-908) equipped with two polystyrene gel columns (JAIGEL-H1 and H2), using chloroform as an eluent.

Poly(1a). Yield 74 % (run 2 in Table 1). ^{1}H-NMR (DMSO-d_6) : δ 1.90 (br, s, 2H), 3.26 (br, s 4H), 5.44 (br, s, 2H).; ^{13}C-NMR (DMSO-d_6) : δ 34.36, 35.51, 42.39, 63.99, 66.26, 126.71, 128.31.; IR (cast) : 3376, 2930, 1655, 1439, 1279, 1024, 878 cm^{-1}.; Anal. Calcd for $(C_7H_{12}O_2)_n$: C, 65.60 ; H, 9.44. Found : C, 65.07 ; H, 9.69.

Poly(1b). Yield 63 % (run 1 in Table 2). ^{1}H-NMR ($CDCl_3$) : δ 1.90-2.01 (m, 4H), 3.07 (s, 4H), 3.22 (s, 6H), 5.36-5.48 (m, 2H).; ^{13}C-NMR ($CDCl_3$) : δ 30.03, 35.65, 35.91, 42.41, 42.58, 59.43, 77.12, 127.53, 128.85, 129.01, 129.19.; IR (cast) : 2951, 1653, 1443, 1280, 1261, 1030, 863 cm^{-1}.; Anal. Calcd for $(C_9H_{16}O_2)_n$: C, 69.19 ; H, 10.32. Found : C, 69.76 ; H, 10.46.

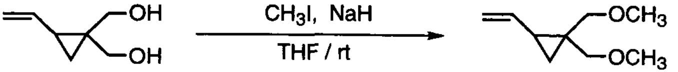
Molecular Orbital Calculations. All computations were done on an Apple Macintosh IIci equipped with a 21 MIPS coprocessor board with use of SONY Tektronix CAChe system version 3.02. Geometries were optimized first with Molecular Mechanics using the CAChe MM2 program and second with Molecular Dynamics using MM2 force field parameters and finally with MOPAC version 6.02 for the CAChe system, using a PM3 Hamiltonian. The calculations were carried out by the unrestricted Hartree-Fock (UHF) method. All calculations were done with full optimization of all geometrical variables (bond lengths, bond angles, and dihedral angles).

Results and Discussion

Monomer Syntheses

The monomer, 1,1-bis(hydroxymethyl)-2-vinylcyclopropane (**1a**), was prepared via reduction of 1,1-bis(ethoxycarbonyl)-2-vinylcyclopropane with lithium aluminum hydride according to the previously reported method.[3b)] **1b** was prepared by the methylation of **1a** with methyl iodide and sodium hydride as a base in tetrahydrofuran (THF) (Scheme 2).

Scheme 2

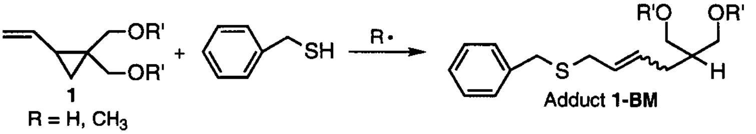


1a **1b** 78 %

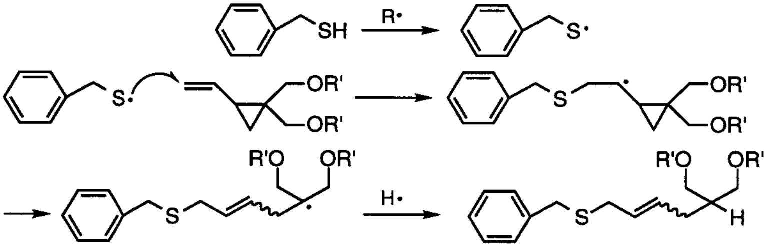
Model Reaction

Radical addition of benzyl mercaptan to **1** was carried out using AIBN as an initiator in chlorobenzene (1 M) at 60 °C for the analysis of polymer structure (Scheme 3). The reaction proceeded in quantitative conversion to afford the corresponding adduct (adduct **1-BM**) in nearly quantitative yield. The structures of the adducts were determined by ^{1}H-, ^{13}C-NMR and IR spectra besides high-resolution mass spectra. In the ^{1}H-NMR spectra, signals assignable to cis and trans isomers were observed for the olefinic and allylic protons. The ratios of the isomers of adducts **1a-BM** and **1b-BM** calculated by their integration ratios were 6:1 and 4:1, respectively. We have failed in separation and identification of the isomers by preparative HPLC and ^{1}H-NMR spectral analyses. The plausible mechanism of the radical addition of benzyl mercaptan to **1** is illustrated as Scheme 4.

Scheme 3



Scheme 4



Radical Polymerization of 1

Radical polymerizations of the monomers **1a** and **1b** were carried out using appropriate radical initiators such as AIBN, V-50, BPO, and DTBP at 60, 80, and 120 °C in bulk, chlorobenzene, DMF, methanol, and water. The conditions and results of the polymerizations of **1a** are summarized in Table 1.

A colorless transparent solid polymer was obtained as an ether-insoluble fraction. The conversion of **1a** was determined by the integration ratio of the olefinic proton signals of the monomer at 5.0~5.3 ppm and the signals of α-methylene protons of hydroxyl group at 3.2 ppm in the ^{1}H-NMR of the crude polymerization mixture. The conversion of the monomer corresponded almost to the yield of the polymer. Polymers with relatively high molecular weights ($\overline{M}_n$; ~94200) were obtained in bulk and in chlorobenzene, although the hydroxymethyl group should have less radical stabilizing effect than the electron-withdrawing ethoxycarbonyl group.[5] The obtained polymer was soluble in DMF, dimethyl sulfoxide (DMSO), and methanol, but insoluble in chloroform, THF, and *n*-hexane. The molecular weight of the polymer obtained in the polymerization in DMF was definitely small, presumably due to an intermolecular hydrogen bonding interaction between carbonyl groups of DMF and hydroxyl groups of **1a**. Precipitation of the polymer was observed during the polymerization in chlorobenzene (runs 4 ~ 6 in Table 1). In this case, the polymerization might proceed similarly to the polymerization in the bulk, resulting in relatively high molecular weight, since the polymer is almost insoluble in its monomer. Although the molecular weight of the polymer obtained by the polymerization in methanol (run 10 in Table 1) was higher than that of the polymer obtained in DMF (run 7 in Table 1), the yield of the former polymer was much lower than that of the latter. Formation of a low molecular weight polymer ($\overline{M}_n$ = 4500) was observed as an ether-soluble fraction in the polymerization in methanol. Since methanol is a poorer chain transfer agent than DMF, the molecular weights of the polymers might be affected by the intermolecular hydrogen bonding as well as by chain transfer. Consequently, the local concentration of the monomer might be reduced resulting in a decrease in the molecular weight of the polymer.

Table 1. Radical Polymerization of **1a**[a]

run	initiator	temp (°C)	solvent (M)	conv[b] (%)	yield[c] (%)	$\overline{M}_n$ ($\overline{M}_w$ / $\overline{M}_n$)[d]	polymer structure[b] (%)		olefin content (%)
							2	3	
1	AIBN	60	none	53	56	94200 (4.54)	100	0	82
2	BPO	80	none	90	74	35100 (1.80)	89	11	79
3	DTBP	120	none	63	60	-[e]	-	-	-
4	AIBN	60	chlorobenzene(1)	75	71	25600 (1.77)	100	0	83
5	BPO	80	chlorobenzene(1)	83	77	36700 (3.80)	93	7	80
6	DTBP	120	chlorobenzene(1)	3	3	-[f]	-	-	-
7	AIBN	60	DMF(1)	61	63	7900 (1.20)	100	0	85
8	BPO	80	DMF(1)	55	48	8200 (1.20)	91	9	82
9	DTBP	120	DMF(1)	0	0	-	-	-	-
10	AIBN	60	MeOH(1)	53	30	20400 (1.46)	100	0	80
11	V-50	60	H_2O(1)	87	84	18000 (2.09)	100	0	81

a) Conditions: **1a** 3 mmol ; initiator 3 mol% vs. **1a** ; 20 h.

b) Determined by ^{1}H-NMR.

c) Ether-insoluble part.

d) Estimated by GPC based on polystyrene standards, eluent LiBr solution in DMF (5.8 mM).

e) Crosslinked polymer was obtained.

f) Not determined.

Table 2. Radical Polymerization of **1b**[a]

run	initiator	temp (°C)	solvent (M)	conv[b] (%)	yield[c] (%)	$\overline{M}_n$ ($\overline{M}_w$ / $\overline{M}_n$)[d]	polymer structure[b] (%)		olefin content (%)
							2	3	
1	AIBN	60	none	71	63	11200 (1.74)	78	22	77
2	BPO	80	none	88	47	10700 (1.73)	64	36	50
3	DTBP	120	none	63	60	-[e]	-	-	-
4	AIBN	60	chlorobenzene(1)	65	59	5500 (1.51)	78	22	80
5	BPO	80	chlorobenzene(1)	47	46	2500 (1.38)	63	37	52
6	DTBP	120	chlorobenzene(1)	2	2	-[f]	-	-	-
7	AIBN	60	DMF(1)	71	65	2300 (1.23)	78	22	76
8	BPO	80	DMF(1)	56	51	3200 (1.05)[h] 1600 (1.07)	62	38	53
9	DTBP	120	DMF(1)	0	0	-[f]	-	-	-

a) Conditions: **1b** 3 mmol ; initiator 3 mol% vs. **1b** ; 20 h.

b) Determined by ^{1}H-NMR.

c) Preparated by HPLC.

d) Estimated by GPC based on polystyrene standards, eluent LiBr in DMF (5.8 mM).

e) Crosslinked polymer was obtained.

f) Not determined.

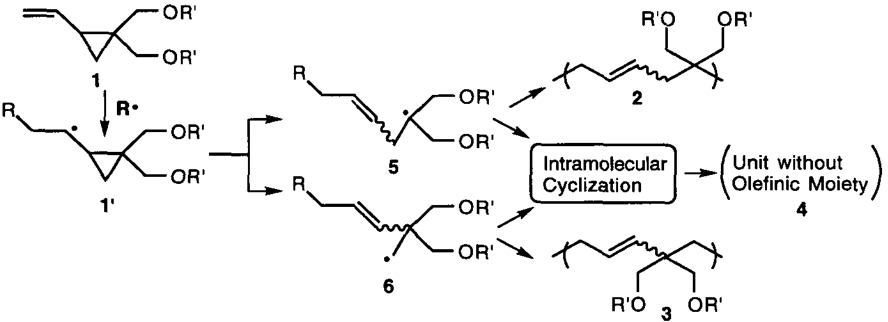
g) Bimodal peaks appeared by GPC.

Polymerizations of **1b** were carried out under the conditions similar to those of the polymerization of **1a**. The results are summarized in Table 2. A colorless viscous polymer was obtained from separation with preparative HPLC. The obtained polymer was soluble in common organic solvents such as chloroform, THF, *n*-hexane, ether, and methanol. The conversion of **1b** corresponded almost to the yield of the polymer. In the polymerization at 120 °C in the bulk, a crosslinked polymer was obtained (run 3 in Table 2). In the polymerization at 120 °C in solvents, the conversion of **1b** was nearly 0 % (runs 6 and 9 in Table 2). Rapid termination reaction might proceed at high temperature. The molecular weight of the polymer obtained by the polymerization of **1b** was much smaller than that of **1a**. It may be caused by the electron-donating effect of the methoxymethyl groups. The lower polymerizability of **1b** than that of **1a** may be also explained by the absence of hydroxyl groups in **1b**, which are effective to increase polymerizability by hydrogen bonding.

The structure of the polymer prepared from **1a** was examined by ^{1}H- and ^{13}C-NMR spectroscopies. The ^{1}H-NMR spectrum of poly(**1a**) obtained by the polymerization with BPO as an initiator at 80 °C in chlorobenzene is shown in Figure 1. The absence of the signals due to the cyclopropane ring protons (0.5~1.0 and 1.4~1.7 ppm) in the ^{1}H-NMR spectrum confirms that no cyclopropane ring structure is incorporated into the polymer. Because the integration ratio of signal *a* due to allylic methylene protons to signal *b* due to the olefinic protons is smaller than 4:2, **2a** cannot be the sole product. Unit **3a** is contained in the polymer in addition to **2a**, which is another polymer unit formed via 1,5-ring-opening polymerization. Moreover, the integration ratio of signal *b* to signal *c* due to the α-methylene protons of the hydroxyl groups is smaller than that expected for the polymer consisting only of **2a** and **3a**, a polymer unit without the olefinic moiety (**4a**) is also present (20 %) in poly(**1a**). The uni modal GPC curve of the polymer suggests that the consumption of the olefinic structure is not caused by an intermolecular reaction such as grafting or cross linking but by an intramolecular reaction as reported in the cases of several 1,1-disubstituted-2-vinylcyclopropanes.3a~c) The polymer structure was also confirmed by the ^{13}C-NMR spectrum (Figure 2). The structure of poly(**1b**) was determined similarly to poly(**1a**). The ^{1}H- and ^{13}C-NMR spectra of poly(**1b**) are shown in Figures 3 and 4, respectively. The signal of the α-methylene protons in the side chain of poly(**1b**) was observed at a higher field than that of the methyl protons of the methoxymethyl group (Figure 3), which is assumed to be originated from the conformation of the methoxymethyl groups.6)

The plausible mechanism of the radical ring-opening polymerization of **1a** and **1b** is illustrated in Scheme 5. The structure of the unit without the olefinic moiety (**4**) seems to be a cyclic one like cyclobutane or a larger cyclic containing unit, which is similar to that reported in the cationic polymerization of vinylcyclopropane.7) However, the detailed structure is not clear because of the difficult characterization of the cyclic structure by NMR.

Scheme 5



Beckwith et al. reported that the ring-opening of a cyclopropylmethyl radical proceeds in the direction which affords the more highly substituted radical.8) Molecular orbital calculations were carried out to examine the selectivity in the direction of the cleavage of the cyclopropane ring of **1a** and **1b**. The calculation results of two-center energies and bond orders of radical intermediate (**1'**), which is formed by the addition of methyl radical to **1a** or **1b**, are summarized in Table 3. The more positive the two-center energy is, the more easily the bond cleaves.3b~c) Therefore, bond C_1-C_2 of **1a'** should be more easily cleaved than bond C_1-C_3. The bond order of bond C_1-C_2 is smaller than that of C_1-C_3, which agrees well with the result of the two-center energy. Thus, bond C_1-C_2 of **1a** is likely to cleave more easily than C_1-C_3. From the comparison of Tables 1 and 2, the selectivity of the ring cleavage of vinylcyclopropane of **1b** is smaller than that of **1a**, which agrees with the calculation result. For this reason, the electron-donating effect of the methoxymethyl groups increases the electron density of bond C_1-C_2.

To examine the hydrogen bonding effect of **1a** in the polymerization, IR spectra of **1a** in dichloromethane were measured at various concentrations. Figure 5 shows O-H stretch IR data for 0.125~1 M **1a** in dichloromethane. The sharp absorption at 3600 cm^{-1}

and broad absorption around 3400 cm^{-1} are assigned to free and hydrogen-bonded O-H stretches, respectively. The ratio of the intensity of the absorption assignable to the hydrogen-bonded O-H stretch to that of the free O-H stretch increased with an increase in the concentration of **1a**. Therefore, intermolecular hydrogen bonding can be concluded to increase as the monomer concentration increases.[4c)] In chlorobenzene (1 M), the intermolecular hydrogen bonding of **1a** should be sufficiently large to accelerate the polymerization because of an increase in the local monomer concentration.

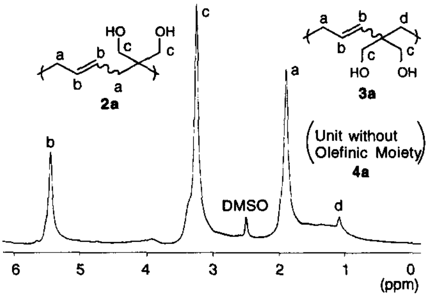


Figure 1. ^{1}H-NMR spectrum of poly(**1a**)
(solvent DMSO-d_6 / TFA = 100 / 1 (volume ratio), 400 MHz). The broad signal at 1~2 ppm contains the proton signals of unit **4a**. Polymerization conditions: in chlorobenzene (1 M), 3 mol % BPO, 80 °C, 20 h (run 5 in Table 1).

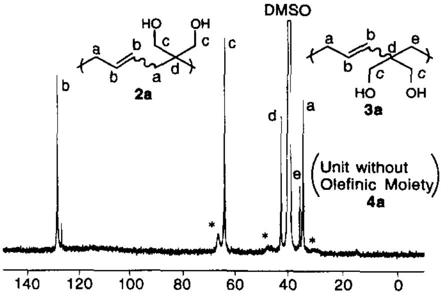


Figure 2. ^{13}C-NMR spectrum of poly(**1a**)
(solvent DMSO-d_6, 100 MHz). *: Signals assignable to unit **4a**. Polymerization conditions: inchlorobenzene (1 M), 3 mol % BPO, 80 °C, 20 h (run 5 in Table 1).

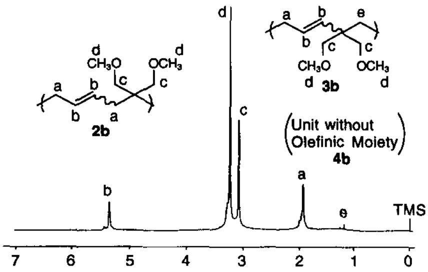


Figure 3. ^{1}H-NMR spectrum of poly(**1b**)
(solvent CDCl$_3$, 400 MHz). The broad signal at 1~2 ppm contains the proton signals of unit **4b**. Polymerization conditions: in chlorobenzene (1 M), 3 mol % BPO, 80 °C, 20 h (run 2 in Table 2).

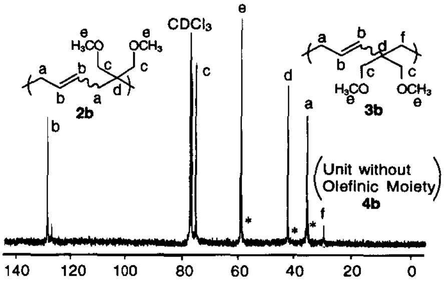
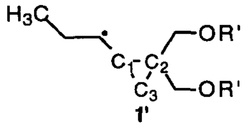


Figure 4. ^{13}C-NMR spectrum of poly(**1a**)
(solvent CDCl$_3$, 100 MHz). *: Signals assignable to unit **4b**. Polymerization conditions: in chlorobenzene (1 M), 3 mol % BPO, 80 °C, 20 h (run 2 in Table 2).



1'

Table 3. Calculated Two-Center Energy and Bond Order of **1'**

R'	bond	two-center energy (eV)	bond order
H	C_1-C_2	-11.435	0.943
	C_1-C_3	-12.099	0.984
CH_3	C_1-C_2	-10.555	0.867
	C_1-C_3	-10.144	0.829

The volume change associated with the polymerization of **1a** was determined by comparison of the densities of **1a** and poly(**1a**), which were measured by the density gradient tube method at 25 °C. The densities of **1a** and poly(**1a**) obtained by the polymerization in bulk at 60 °C (run 1 in Table 1) were 1.078 and 1.150, respectively. The volume shrinkage on the radical polymerization of **1a** is 6.7 %, which is almost the same as that of other usual ring-opening monomers.[3a~c)]

In general, polymers having hydroxyl groups are expected to function as oxygen barrier materials like an ethylene-vinylalcohol copolymer.[9)] The oxygen permeability of the cast film of poly(**1a**) was measured. Although the film was not elongated, the oxygen permeability was 6.19 mL·20 mm·m^{-2}·day^{-1}·atm^{-1} at 35 °C, which was as small as that of poly(vinylidenechloride). The logarithmic value of oxygen permeability of poly(**1a**) with those of other polymers are summarized in Table 4. At 50 °C, the oxygen permeability of poly(**1a**) increased to 37.8 mL·20 mm·m^{-2}·day^{-1}·atm^{-1}, probably because the process temperature was close to the glass transition temperature of the polymer (70 °C). The 10 % weight loss temperature in nitrogen of this polymer was 340 °C.

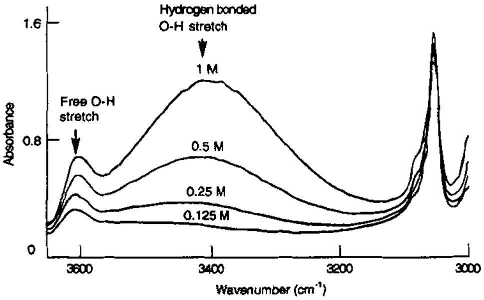


Figure 5. O-H stretch region IR data for various concentrations of **1a** in CH_2Cl_2 at 25 °C, after substraction of the spectrum of pure CH_2Cl_2 at the same temperature.

Table 4. Oxygen Permeability of Several Polymers

polymer	log P_{O2}[a]
Poly(ethylene)	3.477
Poly(ethylene terephthalate)	2.279
Nylon 6	2
Poly(ethylene naphthate)	1.699
Poly(**1a**)[b]	0.792
Poly(vinylidenechloride)	0.699
Poly(ethylene-*co*-vinylalcohol)	-0.824

a) P_{O2} = mL • 20 mm • m^{-2} • day^{-1} • atm^{-1}

b) No elongation.

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