Efficient Fixation of Carbon Dioxide into Poly(glycidyl methacrylate) Containing Pendant Crown Ether

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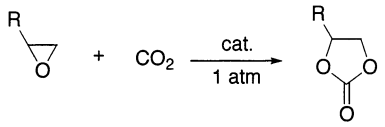
ABSTRACT: The copolymers (**CP1**−**CP4**) of glycidyl methacrylate (GMA) and methacrylate derivatives bearing 15-crown-5-ether (**1**−**4**) with M_n of 9100−12 300 were prepared under radical conditions, and they were employed for the fixation of CO_2 using NaI as a catalyst in nitromethane. The conversion of oxirane groups to carbonate by fixation of CO_2 increased remarkably compared to the homopolymer of GMA. In the case of **CP1**, the reaction proceeded readily even in a dilute reaction system. Poly-GMA could convert into the corresponding polymer containing a carbonate moiety by the introduction of crown ether into the polymer backbone.

Introduction

The fixation of carbon dioxide, which is a prominent greenhouse gas, into organic compounds is very interesting from an economical and an environmental point of view.[1] The use of CO_2 as a starting material for the preparation of chemicals is a practical strategy to solve the problems of CO_2. The reaction of oxirane with CO_2 has been investigated enthusiastically as a possible and effective method. In previous studies using oxiranes, carbonates were prepared effectively using amines, phosphines, quaternary ammonium salts, alkali metal salts, halostannanes, and transition-metal complexes as catalysts.[1,2] An advantage of these procedures is resulting carbonates can be utilized as precursors for further functionalization, including polymer synthesis.[3] However, in most of these reactions, high CO_2 pressure (>20 atm) is necessary to incorporate CO_2. We recently reported the reaction of CO_2 and oxirane in the presence of catalytic amounts of an alkali metal salt such as LiBr or NaI to afford a five-membered cyclic carbonate under an atmospheric pressure of CO_2 (Scheme 1).[4] Further, we have examined the fixation of CO_2 into poly(glycidyl methacrylate) (**PGMA**), which has the advantage of easy separation from the reaction mixture.[5]

Our successful fixation was generally conducted in a homogeneous reaction system. However, a limited amount of solvent such as DMF and *N*-methylpyrrolidone (NMP) was required because of the low solubility of the metal salts in organic solvents. Therefore, we believe that introduction of a crown ether into the polymer may enhance the fixation irrespective of solvents and concentration by self-assembly and neighboring group effects. In the previous report,[4] we described preliminary results on the influence of a crown ether additive on the reaction. This paper deals with several derivatives of poly(glycidyl metahcrylate) containing pendant crown ethers and examines their CO_2 fixation behavior.

Scheme 1



Experimental Section

Measurements. ^{1}H and ^{13}C NMR spectra were recorded on either a Bruker DMX-500 or a JEOL AL-300 spectrometer, using tetramethylsilane (TMS) as an internal standard in chloroform-*d* ($CDCl_3$) and dimethyl-d_6 sulfoxide. IR spectra were recorded on a Jasco FT/IR-230 spectrometer. Number-average molecular weights (M_n) and polydispersity ratios (M_w/M_n) of polymers were estimated by gel permeation chromatography (GPC) on a Shimadzu HPLC-LC6A system with refractive index detector and two consecutive polystyrene gel columns (shim-pack GPC-802 and GPC-804, whose limitations of size exclusion are 5.0×10^3 and 4.0×10^5, respectively), and tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 mL/min at 40 °C using a calibration curve of polystyrene standards.

Materials. Unless stated otherwise, all the chemicals and reagents were obtained commercially and used without further purification. Glycidyl methacrylate (Tokyo Kasei Kogyo Co., Inc.), acetonitrile (Kanto Chemical Co., Inc., >99.5%), dimethylformamide (DMF) (Kanto Chemical Co., Inc., >99.5%), and nitromethane (Kanto Chemical Co., Inc., >96%) were distilled over CaH_2. Toluene (Kanto Chemical Co., Inc., >99.5%) and diethyl ether (Kanto Chemical Co., Inc., >99.0%) were distilled from sodium benzophenone ketyl before use. 2-Hydroxymethyl-15-crown-5 (Tokyo Kasei Kogyo Co., Inc., Extra Pure), thallium ethoxide (Aldrich, 98%), methacryloyl chloride (Tokyo Kasei Kogyo Co., Inc., >80.0%), and 15-crown-5-ether (Tokyo Kasei Kogyo Co., Inc., >97%) were used as received. Methacryloyloxymethyl-15-crown-5 (**1**),[6] 2-(2-bromoethyloxy)tetrahydropyran (**5**),[7] 2-(6-bromohexyloxy)tetrahydropyran (**6**),[8] and 2-(12-bromododeceyloxy)tetrahydropyran (**7**)[9] were prepared according to reported procedures.

Preparation of 4-(Tetrahydropyran-2-yloxy)-2-oxabutyl-15-crown-5 (8). Dry toluene (12 mL) and 2-hydroxymethyl-15-crown-5 (1.00 g, 4.5 mmol) were added to a round-bottom flask equipped with argon gas inlet. To the mixture was added thallium ethoxide (1.10 g, 4.5 mmol) in one portion, and the solution was stirred for 10 min under argon at room temperature. The solvent was removed under reduced pressure, and then the residue was dissolved in 30 mL of dry acetonitrile. To this solution was added **5** (0.94 g, 4.5 mmol),

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and the solution was refluxed for 14 h. After filtration through a short column of alumina, the eluate was evaporated under reduced pressure and the residue was purified by chromatography on alumina (ethyl acetate eluent) to give 1.00 g (2.9 mmol) of **8** as a colorless oil; yield 63%. ^{1}H NMR ($CDCl_3$): δ 1.43−1.46 (m, 4 H, −CH_2−C), 1.51−1.69 (m, 1 H, −CH_2−C), 1.72−1.80 (m, 1 H, −CH_2−C), 3.43−3.78 (m, 27 H, −CH_2−O and C−CH−O), 4.57 ppm (t, 1 H, O−CH−O, J = 3.5 Hz). ^{13}C NMR ($CDCl_3$): δ 19.78, 25.81, 30.93 (−CH$_2$−C), 62.48, 66.95, 66.97, 70.65, 70.91, 70.93, 70.96, 71.10, 71.14, 71.29, 71.39, 71.91, 71.95 (−CH$_2$−O), 79.06 (C−CH−O), 99.22 ppm (O−CH−O). IR (neat): 2864 (−CH$_2$−), 1121 (O−C−O), 1079 cm^{-1} (C−O−C). Anal. Calcd for $C_{18}H_{34}O_8$: C, 57.12; H, 9.06. Found: C, 57.34; H, 8.90.

Preparation of 8-(Tetrahydropyran-2-yloxy)-2-oxaoctyl-15-crown-5 (9). **9** was prepared as described for **8** from 2-hydroxymethyl-15-crown-5 (1.58 g, 7.0 mmol) and **6** (1.86, 7.0 mmol) to give a colorless oil (2.00 g, 4.6 mmol); yield 66%. ^{1}H NMR ($CDCl_3$): δ 1.36−1.85 (m, 14 H, −CH_2−C), 3.34−3.86 (m, 27 H, −CH_2−O and C−CH−O), 4.57 ppm (s, 1 H, O−CH−O). ^{13}C NMR ($CDCl_3$): δ 19.71, 25.51, 25.97, 26.11, 29.59, 29.73, 30.79 (−CH$_2$−C), 62.35, 67.56, 70.27, 70.41, 70.62, 70.73, 70.80, 70.87, 70.98, 71.05, 71.61, 71.86 (−CH$_2$−O), 78.67, 78.74 (C−CH−O), 98.86 ppm (O−CH−O). IR (neat): 2864 (−CH$_2$−), 1121 (O−C−O), 1079 cm^{-1} (C−O−C). Anal. Calcd for $C_{22}H_{42}O_8$: C, 68.80; H, 9.74. Found: C, 68.54; H, 9.55.

Preparation of 14-(Tetrahydropyran-2-yloxy)-2-oxatetradeceyl-15-crown-5 (10). **10** was prepared as described for **8** from 2-hydroxymethyl-15-crown-5 (1.10 g, 5.0 mmol) and **7** (1.72 g, 5.2 mmol) to give a colorless oil (1.62 g, 3.1 mmol); yield 62%. ^{1}H NMR ($CDCl_3$): δ 1.09−1.18 (m, 16 H, −CH_2−C), 1.34−1.43 (m, 8 H, −CH_2−C), 1.51−1.59 (m, 1 H, −CH_2−C), 1.65−1.72 (m, 1 H, −CH_2−C), 3.18−3.71 (m, 27 H, −CH_2−O and C−CH−O), 4.54 ppm (s, 1 H, O−CH−O). ^{13}C NMR ($CDCl_3$): δ 20.96, 25.90, 26.14, 26.48, 26.63, 29.82, 29.87, 29.89, 29.96, 29.99, 30.02, 30.15, 31.18, 33.20 (−CH$_2$−C), 62.74, 63.43, 68.09, 70.64, 70.94, 70.98, 71.15, 71.32, 71.39, 71.41, 72.03, 72.06 (−CH$_2$−O), 79.11 (C−CH−O), 99.23 ppm (O−CH−O). IR (neat): 2858 (−CH$_2$−), 1125 (O−C−O), 1079 cm^{-1} (C−O−C). Anal. Calcd for $C_{28}H_{54}O_8$: C, 64.83; H, 10.49. Found: C, 64.49; H, 10.11.

Preparation of 4-Hydroxy-2-oxabutyl-15-crown-5 (11). To the solution of **8** (1.00 g, 2.9 mmol) in methanol (12 mL) was added 1 mol/L HCl(aq) (1.3 mL), and the mixture was stirred at room temperature for 15 h. After removal of solvents, **11** (0.67 g, 2.7 mmol) was obtained as a colorless oil. It was used without further purification; yield 88%. ^{1}H NMR ($CDCl_3$): δ 2.12 (br, 1 H, −OH), 3.53−3.88 ppm (m, 25 H, −CH_2−O). ^{13}C NMR ($CDCl_3$): δ 61.60 (−CH$_2$−OH), 69.95, 70.26, 70.40, 70.43, 70.65, 70.97, 71.14, 76.57 (−CH$_2$−O), 78.54 ppm (⟩CH−O). IR (neat): 3380 (−OH), 2863 (−CH$_2$−), 1110 cm^{-1} (C−O−C). Anal. Calcd for $C_{13}H_{26}O_7$: C, 53.05; H, 8.90. Found: C, 52.87; H, 9.12.

Preparation of 8-Hydroxy-2-oxaoctyl-15-crown-5 (12). **12** was prepared as described for **11** from **9** (2.00 g, 4.6 mmol) to give a colorless oil (1.58 g, 4.5 mmol); yield 98%. ^{1}H NMR ($CDCl_3$): δ 1.35−1.40 (m, 4 H, −CH_2−C), 1.55−1.59 (m, 4 H, −CH_2−C), 1.79 (br, 1 H, −OH), 3.41−3.85 ppm (m, 25 H, −CH_2−O). ^{13}C NMR ($CDCl_3$): δ 25.53, 25.89, 29.54, 32.70 (−CH$_2$−C), 62.87 (−CH$_2$−OH), 70.22, 70.41, 70.59, 70.73, 70.87, 70.92, 71.01, 71.47, 71.54, 71.59, 71.85 (−CH$_2$−O), 78.68 ppm (−CH−O). IR (neat): 3380 (−OH), 2863 (−CH$_2$−), 1099 cm^{-1} (C−O−C). Anal. Calcd for $C_{17}H_{34}O_7$: C, 58.26; H, 9.78. Found: C, 58.15; H, 9.53.

Preparation of 14-Hydroxy-2-oxatetradeceyl-15-crown-5 (13). **13** was prepared as described for **11** from **10** (1.55 g, 3.0 mmol) to give a colorless oil (1.35 g, 2.9 mmol); yield 97%. ^{1}H NMR ($CDCl_3$): δ 1.19−1.27 (m, 16 H, −CH_2−C), 1.45−1.52 (m, 4 H, −CH_2−C), 1.99 (s, 1 H, −OH), 3.36−3.40 (m, 4 H, −CH_2−O), 3.55−3.77 (m, 21 H, −CH_2−O) ppm. ^{13}C NMR ($CDCl_3$): δ 26.13, 26.45, 29.80, 29.93, 29.95, 29.99, 33.16 (−CH$_2$−C), 63.37 (−CH$_2$−OH), 70.61, 70.91, 70.95, 71.12, 71.29, 71.36, 71.38, 72.00, 72.05 (−CH$_2$−O), 79.10 ppm (⟩CH−O). IR (neat): 3395 (−OH), 2856 (−CH$_2$−), 1105 cm^{-1} (C−O−C). Anal. Calcd for $C_{23}H_{46}O_7$: C, 63.56; H, 10.67. Found: C, 63.32; H, 10.92.

Preparation of 4-Methacryloyloxy-2-oxabutyl-15-crown-5 (2). **11** (1.35 g, 4 mmol), triethylamine (0.5 g, 5 mmol), and dry diethyl ether (10 mL) were added to a round-bottom flask equipped with argon gas inlet and thermometer. To the solution was added dropwise methacryloyl chloride (0.41 g, 4 mmol) at 0 °C for 5 min, and the mixture was stirred at room temperature for 1 h. The reaction mixture was extracted with diluted HCl(aq), washed with water, and dried over $MgSO_4$. After filtration, ether layer was evaporated under reduced pressure. The residue was purified by chromatography on alumina (eluent ethyl acetate) to obtain 0.75 g (1.8 mmol) of **2** as a colorless oil; yield 45%. ^{1}H NMR ($CDCl_3$): δ 1.88 (s, 3 H, −CH_3), 3.48−3.77 (m, 23 H, −CH_2−O−C), 4.22 (t, 2 H, −C(=O)−O−CH_2^-, J = 4.8 Hz), 5.49 (s, 1 H, CH_2=), 6.03 ppm (s, 1 H, CH_2=). ^{13}C NMR ($CDCl_3$): δ 18.73 (−CH$_3$), 64.25, 69.69, 70.68, 70.91, 70.96, 70.98, 71.18, 71.28, 71.35, 71.46, 71.65, 72.00 (−CH$_2$−O), 79.07 (⟩CH−O), 126.12 (CH$_2$=), 136.58 (=C⟨), 167.76 ppm (⟩C=O). IR (neat): 2863 (−CH$_2$−, −CH$_3$), 1716 (−C(=O)−O−C), 1633 (⟩C=C⟨), 1120 cm^{-1} (C−O−C). Anal. Calcd for $C_{17}H_{30}O_8$: C, 56.34; H, 8.34. Found: C, 56.08; H, 8.25.

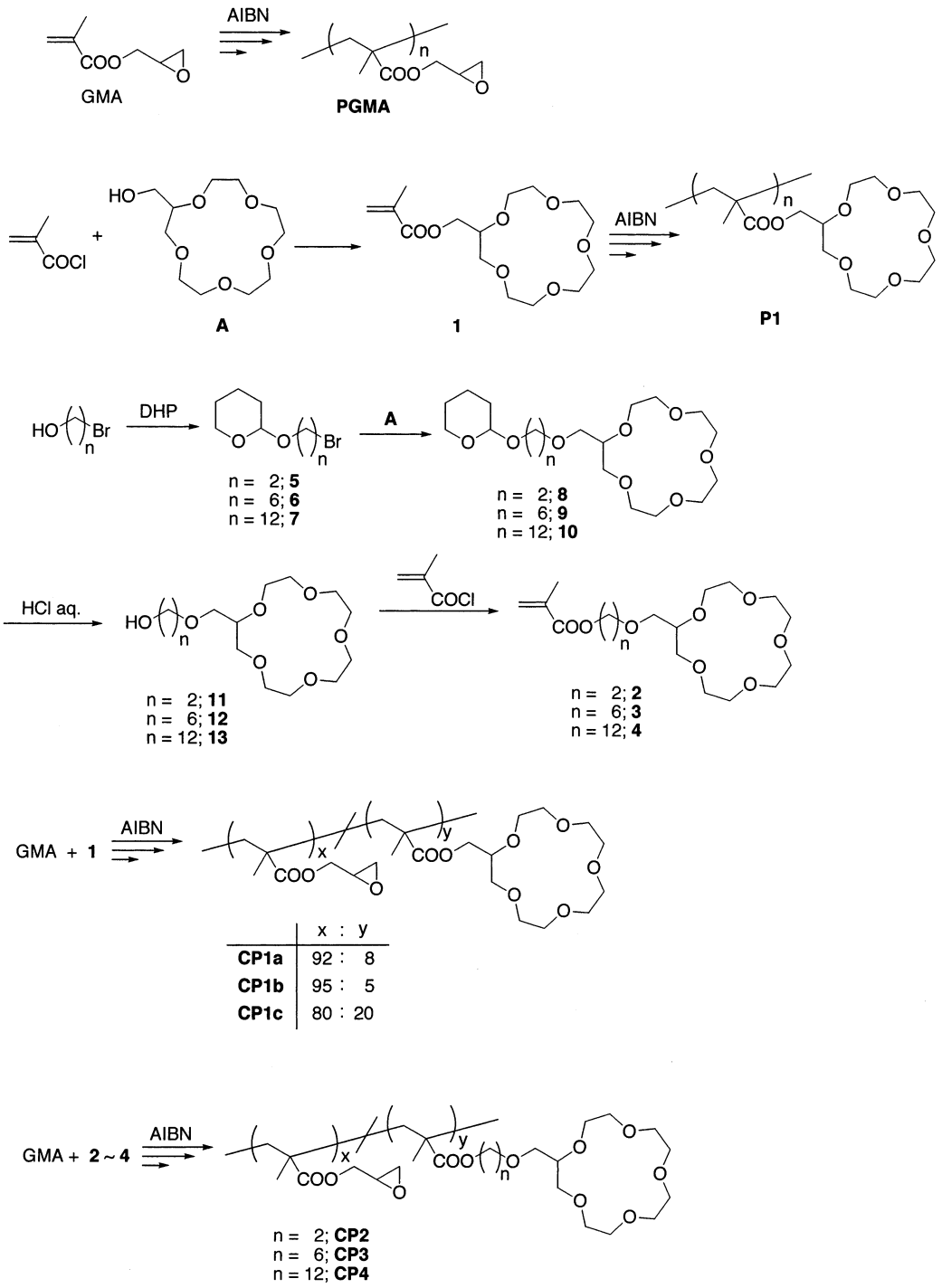
Preparation of 8-Methacryloyloxy-2-oxaoctyl-15-crown-5 (3). **3** was prepared as described for **2** from **12** (1.35 g, 4.0 mmol), triethylamine (0.50 g, 5.0 mmol), and methacryloyl chloride (0.41 g, 4 mmol) to give a colorless oil (0.75 g, 1.7 mmol); yield 45%. ^{1}H NMR ($CDCl_3$): δ 1.39 (t, 4 H, −CH_2−C, J = 3.6 Hz), 1.58 (t, 2 H, −CH_2−C, J = 6.7 Hz), 1.68 (t, 2 H, −CH_2−C, J = 6.9 Hz), 1.94 (s, 3 H, −CH_3), 3.42−3.76 (m, 23 H, −CH_2−O−C) 4.14 (t, 2 H, −C(=O)−O−CH_2−, J = 6.6 Hz), 5.55 (s, 1H, CH_2=), 6.09 ppm (s, 1H, CH_2=). ^{13}C NMR ($CDCl_3$): δ 18.29 (−CH$_3$), 25.79, 25.83, 28.59, 29.52 (−CH$_2$−C), 64.67, 70.27, 70.41, 70.61, 70.72, 70.79, 70.90, 70.99, 71.06, 71.48, 71.60, 71.83 (−CH_2−O), 78.67 (⟩CH−O), 125.17 (CH$_2$=), 136.52 (=C⟨), 167.48 ppm (⟩C=O). IR (neat): 2863 (−CH$_2$−, −CH$_3$), 1716 (−C(=O)−O−C), 1616 (⟩C=C⟨), 1120 cm^{-1} (C−O−C). Anal. Calcd for $C_{21}H_{38}O_8$: C, 60.27; H, 9.15. Found: C, 60.56; H, 9.21.

Preparation of 14-Methacryloyloxy-2-oxatetradeceyl-15-crown-5 (4). **4** was prepared as described for **2** from **13** (1.30 g, 2.8 mmol) and methyacryloyl chloride (0.31 g, 0.3 mmol) to give a colorless oil (0.87 g, 1.7 mmol); yield 64%. ^{1}H NMR ($CDCl_3$): δ 1.19−1.31 (m, 16 H, −CH_2−C), 1.45−1.50 (m, 2 H, −CH_2−C), 1.57−1.63 (m, 2 H, −CH_2−C), 1.87 (s, 3 H, −CH_3), 3.36 (t, 2 H, −CH_2−O−C, J = 6.7 Hz), 3.39−3.42 (m, 2 H, −CH_2−O−C), 3.51−3.79 (m, 19 H, −CH_2−O−C, ⟩CH−O) 4.07 (t, 2 H, −C(=O)−O−CH_2−, J = 6.7 Hz), 5.48 (s, 1 H, CH_2=), 6.17 ppm (s, 1 H, CH_2=). ^{13}C NMR ($CDCl_3$): δ 18.73 (−CH$_3$), 26.37, 26.48, 29.00, 29.65, 29.87, 29.90, 29.95, 29.97, 29.99, 30.03 (−CH$_2$−C), 65.23, 65.24, 70.64, 70.94, 70.98, 71.16, 71.32, 71.40, 71.42, 72.03, 72.06 (−CH$_2$−O), 79.12 (⟩CH−O), 125.53 (CH$_2$=), 136.95 (=C⟨), 167.96 ppm (⟩C=O). IR (neat): 2856 (−CH$_2$−, −CH$_3$), 1718 (−C(=O)−O−C), 1635 (⟩C=C⟨), 1128 cm^{-1} (C−O−C). Anal. Calcd for $C_{27}H_{50}O_8$: C, 64.51; H, 10.03. Found: C, 64.26; H, 9.91.

Polymerization. In a typical procedure, 4 mmol of total monomer, 0.02 g (0.12 mmol, 3 mol %) of AIBN, and DMF (2 mL) were fed into a glass tube. After three freeze−pump−thaw cycles, the glass tube was sealed under vacuum, and the reaction mixture was heated at 60 °C for 20 h. The reaction mixture was diluted with DMF and poured into diethyl ether (200 mL) to precipitate a resulting polymer. The polymer was collected by filtration and dried in vacuo. ^{1}H NMR (DMSO-d_6): δ 0.79−1.50 (m, −CH_3), 1.90−2.08 (m, −CH_2−C), 2.64 (s, −CH_2−O−C), 2.85 (s, −CH_2−O−C), 3.24 (s, ⟩CH−O), 3.56−3.95 (m, −CH_2−O−C), 4.48 ppm (s, −C(=O)−O−CH_2−). ^{13}C NMR (DMSO-d_6): δ 16.30, 18.20 (−CH$_3$), 43.80 (−CH$_2$−C), 44.17 (⟩C⟨), 44.51 (−CH$_2$−O), 48.51 (⟩CH−O), 52.88, 53.40, 64.92, 66.21, 69.72, 70.00 (−CH$_2$−O), 175.81, 176.60 ppm (⟩C=O). IR (KBr): 1731 (−C(=O)−O−C), 1149 (C−O−C), 906 cm^{-1} (oxirane).

Fixation of CO_2 into the Polymer. In a typical procedure, the polymer containing 1 mmol of oxirane groups, catalyst (NaI, NaBr, or NaCl, 1.5 or 5.0 mol %), and solvent (1−5 mL)

Scheme 2



were added into a glass tube. After degassing by a freeze−pump−thaw cycles, the glass tube was flowed CO_2 gas under atmospheric pressure and heated at 100 °C. The reaction mixture was dissolved in DMF and poured into diethyl ether (100 mL) to precipitate a polymer. The polymer was collected by filtration and dried in vacuo. Yield = 93−100%. ^{1}H NMR (DMSO-d_6): δ 0.81−0.99 (m, −CH_3), 1.82 (br, −CH_2−C), 3.50−3.83 (m, −CH_2−O−C), 4.20−4.45 (m, −C(=O)−O−CH_2−), 4.64 (s, −CH_2−O−C(=O)−O), 5.09 ppm (s, 〉CH−O−C(=O)−O). ^{13}C NMR ($CDCl_3$): δ 16.65, 18.23 (−CH$_3$), 44.09 (−CH$_2$−C), 44.47 (〉C〈), 53.12, 53.26, 65.71, 69.76, 69.96 (−CH$_2$−O), 73.89 (〉CH−O), 154.73 (−O−C(=O)−O−), 175.59, 176.25 ppm (C−C(=O)−O−). IR (KBr): 1797 (carbonate), 1733 (ester), 1169 cm^{-1} (C−O−C).

Results and Discussion

Copolymerization. A methacrylate derivative containing crown ether (CMA), **1**, was prepared according to a previous report.[6] Analogous compounds CMA (**2**−**4**) were prepared by the modified Parkers' procedure illustrated in Scheme 2.[8]

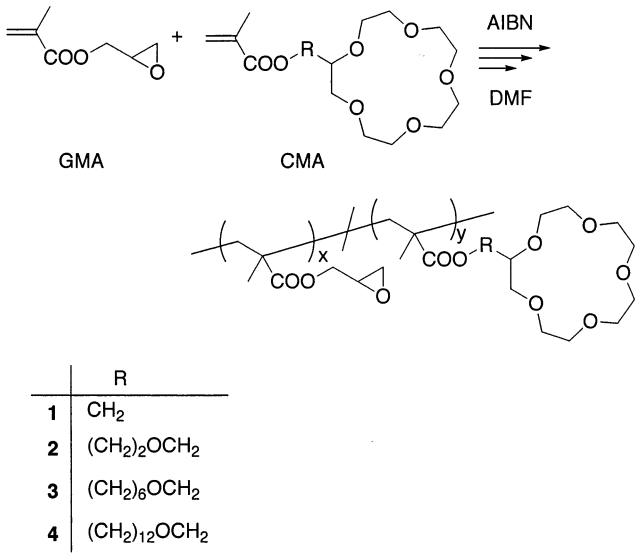
The radical copolymerization of GMA with **1**−**4** using AIBN as an initiator afforded the corresponding copolymers (**CP1**−**4**, M_n = 9100−12 300) in good yields. The homopolymerization of **1** under the same condition afforded the polymer **P1**. The M_n and M_w/M_n of the resulting polymers are summarized in Table 1 (Scheme 3). The ratio of crown ether unit in **CP**s was in accord

Table 1. Radical Copolymerization of GMA with CMA[a]

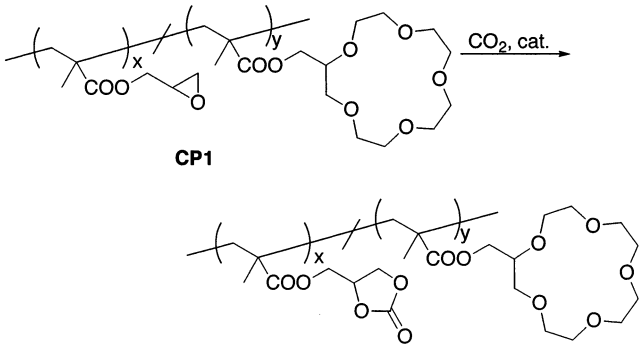
entry	feed composition (mol %) GMA	CMA [R]	yield (%)[b]	composition[c] *x*:*y*	M_n (M_w/M_n)[d]	polymer
1	100		92		11400 (2.38)	**PGMA**
2	90	**1** [CH_2] 10	90	92:8	10500 (2.46)	**CP1a**
3	95	**1** [CH_2] 5	90	95:5	12300 (3.16)	**CP1b**
4	80	**1** [CH_2]20	88	80:20	11100 (2.12)	**CP1c**
5[e]	0	**1** [CH_2] 100	85		1800 (1.10)	**P1**
6	90	**2** [$(CH_2)_2OCH_2$] 10	89	92:8	9200 (1.31)	**CP2**
7	90	**3** [$(CH_2)_6OCH_2$] 10	93	90:10	9100 (2.41)	**CP3**
8	90	**4** [$(CH_2)_{12}OCH_2$] 10	95	91:9	9800 (2.68)	**CP4**

[a] Conditions: total monomer 4 mmol, 3 mol % AIBN, DMF 2 mL, 60 °C for 20 h. [b] Ether-insoluble parts. [c] Estimated by comparing the integrated values of the ^{1}H NMR signal of the methine proton of oxirane unit (3.24 ppm) with methylene protons of crown ether unit (3.56−3.95 ppm). [d] Estimated by GPC (THF, polystyrene standards). [e] 5 mol % of AIBN.

Scheme 3



Scheme 4



with the feed composition. The **CP**s are soluble in common solvents such as chloroform, ethyl acetate, and THF.

Fixation of CO_2. Fixation of CO_2 into the **CP** was carried out in nitromethane solution (Scheme 4 and Table 2) because the obtained polymers are soluble in nitromethane, but NaI insoluble. Thus, it is suitable to clarify the intrinsic effect of crown ether unit upon the fixation. The yields of resulting polymer were quantitative, indicating the fixation proceeded without a side reaction such as the cleavage of backbone. In the fixation of CO_2 into **PGMA** using NaI as a catalyst, the conversion of oxirane into five-membered cyclic carbonate groups was about 13% (entry 1 in Table 2). On the other hand, when nonimmobilized 15-crown-5-ether was used as an additive, CO_2 could be fixed efficiently to give the copolymer bearing cyclic carbonate group (entry 2 in Table 2). Further, in the copolymer of GMA and **1** (**CP1a**), CO_2 could be incorporated smoothly similar to the above (entry 7 in Table 2). These results may indicate that 15-crown-5-ether increases the solubility of NaI into nitromethane and works effectively CO_2 fixation. The fixation of CO_2 was developed in the **CP1a**−**c**, in which the ratios of oxirane and crown ether units were varied from 100/2.5 to 80/20. With **PGMA** with 15-crown-5-ether, the fixation was decreased in proportion to the amount of crown ether (entries 5 and 6 in Table 2). With **CP1a**−**c**, however, no apparent difference of the conversions of oxirane into carbonate groups was observed (entries 9 and 10 in Table 2). It was assumed that the catalyst was mounted on the polymer by an appropriate amount of the crown ether moiety distributed along the polymer main chain by random copolymerization. The effects of sequences of the crown ether moieties of the polymer backbone on the reaction have not been clarified in this work. The information on the effects may be obtained by the use of the block copolymers prepared by the living radical technique.

Table 2. Fixation of CO_2 into the Polymers in CH_3NO_2 Solution Using NaI as Catalyst

entry	polymer crown ether unit (mol %)	15C5 (mol %)[b]	time (h)	fixation of CO_2[a] (%)
1	**PGMA** (−)		24	13
2	**PGMA** (−)	10	24	99
3	**PGMA** (−)	10	15	64
4	**PGMA** (−)	10	12	55
5	**PGMA** (−)	5	24	56
6	**PGMA** (−)	2.5	24	33
7	**CP1a** (10)		24	99
8	**CP1a** (10)		18	69
9	**CP1b** (5)		24	95
10	**CP1c** (20)		24	98

[a] Estimated by comparing the integrated values of the ^{1}H NMR signal of the methine proton of oxirane unit (3.24 ppm) with that of cyclic carbonate unit (5.09 ppm). [b] 15-Crown-5-ether.

The structure of the obtained polymer was confirmed by spectral data. In ^{1}H NMR analysis, as the fixation proceeded, while three signals assignable to methylene and methine protons at 2.6, 2.8, and 3.2 ppm based on oxirane group decreased, the new signals of methylene and methine protons due to the cyclic carbonate group appeared at 4.26, 4.64, and 5.09 ppm, respectively (Figure 1). These signals were utilized for the estimations of conversion of oxirane to carbonate groups. When the fixation proceeded quantitatively, the IR spectra of the obtained polymer showed no peak assignable to oxirane around 900 cm^{-1}, while the absorption of

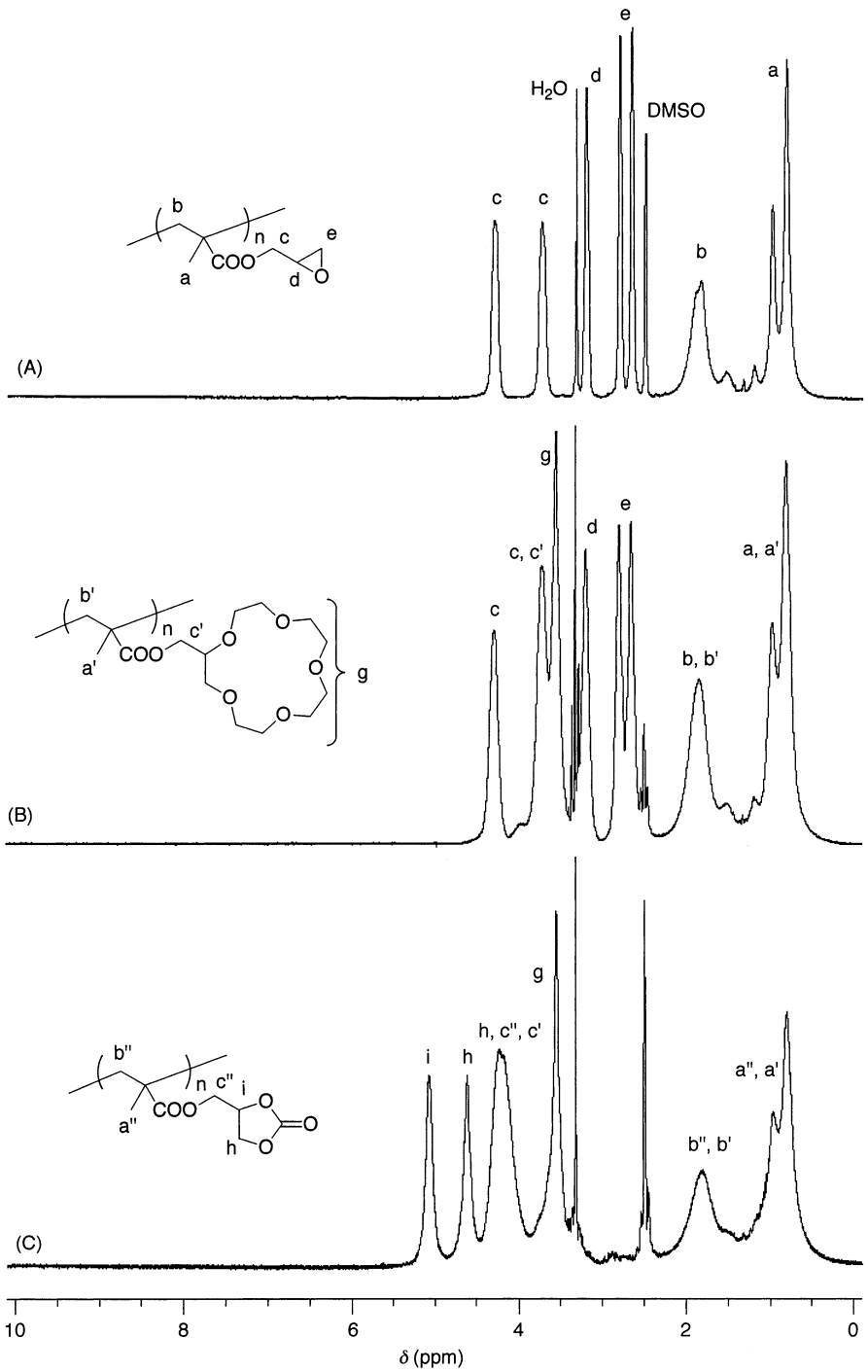


Figure 1. ^{1}H NMR spectra (a) **PGMA** (entry 1 in Table 1), (b) **CP1a** (entry 2 in Table 1), and (c) the polymer obtained by fixation into **CP1a** (entry 6 in Table 2).

carbonyl group due to cyclic carbonate was observed around 1800 cm^{-1}.

Next, we examined the effects of concentration on the fixation into **CP**s (Figure 2). In the case of PGMA with 15-crown-5-ether, the fixation ratio decreased as the amount of nitromethane increased (line b), while the conversion of **CP1a** was kept to 80% irrespective of the amount of the solvent (line a). These suggested that the catalyst, NaI, was supported on the polymer by the crown ether moiety and located in highly assembled oxirane moieties.[10] Thus, the polymer backbone, which can hold both the catalyst and the oxirane units with high local concentration, seems to provide an effective reaction environment to afford the polymer having cyclic carbonate moieties. In the case of **PGMA** with **P1**, the conversion decreased remarkably by dilution, and it was lower than that observed in the combination of **PGMA** and the nonimmobilized crown ether (line c). This is explained by steric hindrance of polymer structure bearing the catalyst, which should prevent an association with the substrate units, oxirane groups. Such results may support the speculation on the efficient incorporation of CO_2 into **CP1** mentioned above, in which both the catalyst and oxirane groups were mounted on the same polymer backbone.

The effects of length of side chain attached to crown ether group on the fixation were examined by changing the amounts of solvent. The results are illustrated in

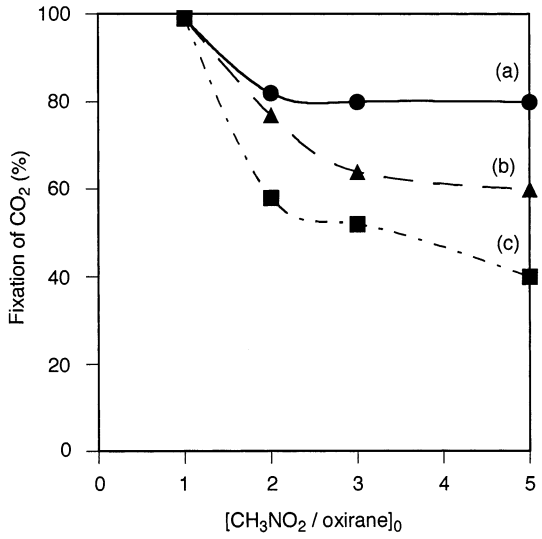


Figure 2. Effect of concentration of polymer structure on the fixation of CO_2 into (a) **CP1a**, (b) **PGMA** and 15-crown-5-ether (10 mol %), and (c) **PGMA** with **P1** (10 mol %). Conditions: oxirane unit 1 mmol, NaI 1.5 mol % in nitromethane at 100 °C for 24 h.

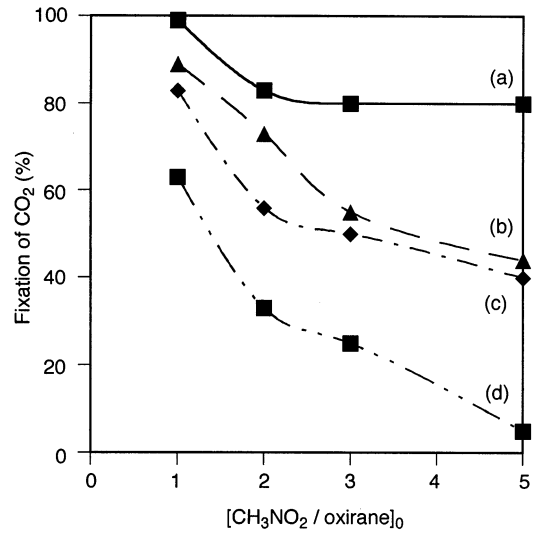
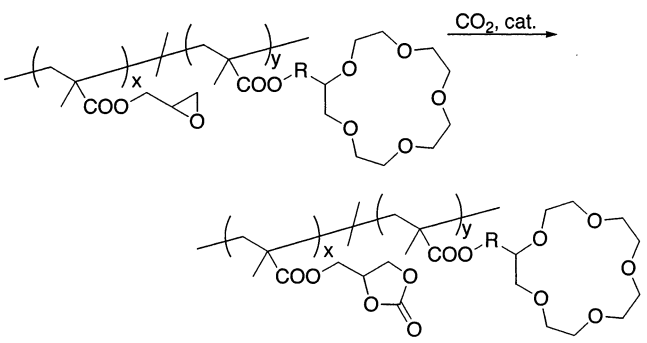


Figure 3. Effect of concentration of side chain length on the fixation of CO_2 into (a) **CP1a**, (b) **CP2**, (c) **CP3**, and (d) **CP4**. Conditions: oxirane unit 1 mmol, NaI 1.5 mol % in nitromethane at 100 °C for 24 h.

Figure 3 (Scheme 5). The effects of dilution were observed in the examples having a longer spacer such as **CP2**−**4**. In the case of **CP4** (n = 12), especially, the decrement was similar to the case using **P1** (line c in Figure 2). These results suggested that NaI was essentially complexed with crown ether moiety and participates to the reaction. In addition, when NaI was supported nearby main chain (a shorter spacer), the activation of neighboring oxirane group occurred readily to afford cyclic carbonate groups quantitatively irrespective of the concentration. When the polymer having a longer spacer, the crown ether groups were thought to move more freely like "crown ether monomer". Nishikubo et al. reported that the introduction of a long alkyl spacer between polymer main chain and catalyst reduced steric hindrance and increased catalytic activity in the reaction of low molecular weight of oxirane with CO_2.[11] In our study, oxirane groups were bonded to the same polymer backbone with the crown ether moieties.

Scheme 5



	R
CP2	$(CH_2)_2OCH_2$
CP3	$(CH_2)_6OCH_2$
CP4	$(CH_2)_{12}OCH_2$

Table 3. Fixation of CO_2 into the Polymer Using Various Sodium Salts Using 1.5 mol % Catalyst

entry	polymer	catalyst	fixation of CO_2[a] (%)
1	**PGMA**	NaCl	0
2	**PGMA**	NaBr	3
3	**PGMA**	NaI	13
4	**CP1a**	NaCl	10
5	**CP1a**	NaBr	71
6	**CP1a**	NaI	99

[a] Estimated by comparing the integrated values of the ^{1}H NMR signal of the methine proton of oxirane unit (3.24 ppm) with that of cyclic carbonate unit (5.09 ppm).

Consequently, the effect of local concentration seemed to appear more clearly rather than that of steric hindrance.

The catalytic activities of other sodium salts were examined to clarify the applicability of our reaction system (Table 3). Of the three sodium salts, NaI and NaBr showed good catalytic activities in the fixation. The order of the catalytic activity for the fixation in the both polymers with and without crown ether moiety was NaI > NaBr > NaCl. A salt that consists of a more nucleophilic anion and a Lewis acidic cation is generally more active to the oxirane.[12,13] However in our reaction system, NaCl was insoluble even in the presence of crown ether groups. This seemed to be the reason why NaCl did a less applicable catalyst but does not explain the intrinsic activity of the sodium salts shown in this work.

The solubility of catalyst is an important factor to proceed the fixation efficiently as mentioned above. Therefore, polymers **CP1**−**4** bearing crown ether moieties should to be usable in various solvents. Next, the efficiencies of the fixation on the polymer **CP**s in toluene and DMF were examined. These results are summarized in Table 4. In toluene, the enhancement of the fixation by the crown ether was appreciable (entries 1 and 2), but the conversion was 18% in the use of **CP1**. Furthermore, the obtained products included the insoluble parts in the solvents such as THF, DMF, and NMP. This may be caused by assembling the polymer after the fixation of CO_2, which results in the formation of cross-linking polymer. Consequently, the solubility of the resulting polymer having cyclic carbonate groups seems to be an important factor to proceed the fixation effectively. In DMF, the conversions of fixation were

Scheme 6

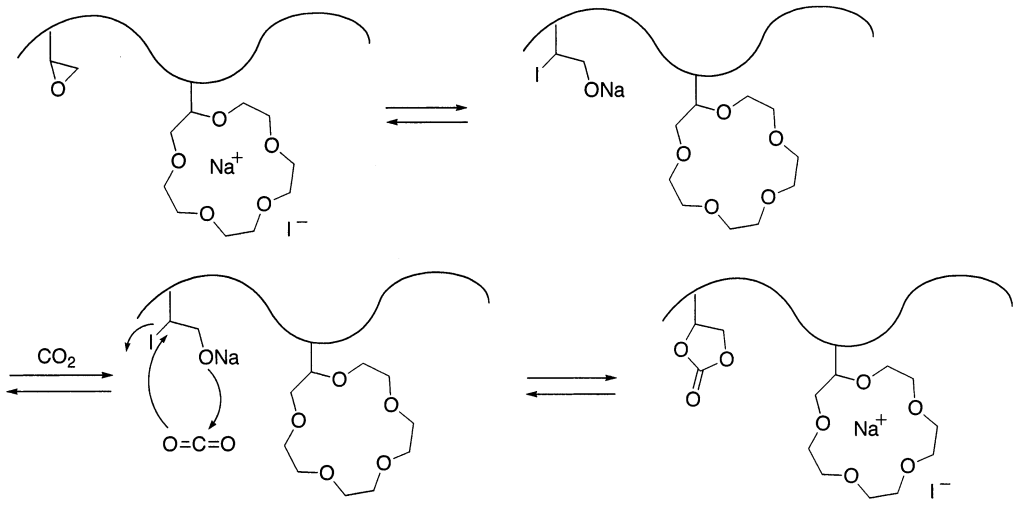


Table 4. Fixation of CO_2 into the Polymer in Toluene or DMF

entry	polymer	solvent	catalyst (mol %)	fixation ratio of CO_2[a] (%)
1	**PGMA**	toluene	NaI (5)	0 (61)[b]
2	**CP1a**	toluene	NaI (5)	18
3	**PGMA**	DMF	NaI (1.5)	95 (91)[b]
4	**CP1a**	DMF	NaI (1.5)	>99

[a] Estimated by comparing the integrated values of the ^{1}H NMR signal of the methine proton of oxirane unit (3.24 ppm) with that of cyclic carbonate unit (5.09 ppm). [b] Added 10 mol % 15-crown-5.

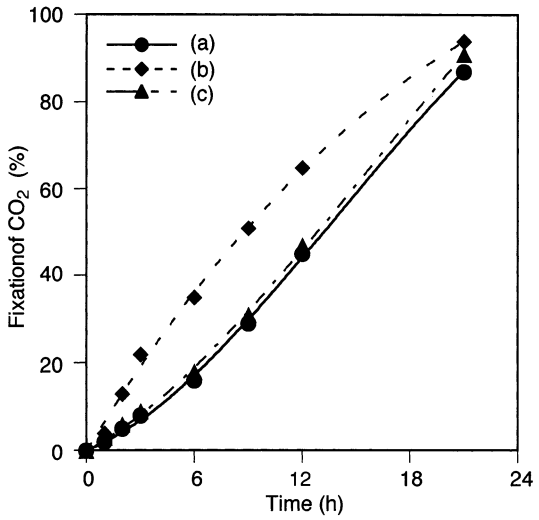


Figure 4. Relationship between the time and fixation of CO_2: (a) **PGMA** in DMF, (b) **CP1b** in DMF, and (c) **CP1b** in nitromethane. [Oxirane] = 1 M, NaI (1.5 mol %) at 100 °C.

quantitative regardless of the presence of crown ether (entries 3 and 4 in Table 4). Previously, we examined the reaction of oxiranes with CO_2 in the presence of crown ether. The report concludes that crown ether acted as a deactivator of the catalyst.[4] However, in this work, it behaved as an activator in toluene and nitromethane. To examine such differences of the results, the relationship between the time and fixation of CO_2 was investgated (Figure 4). The results demonstrate that the apparent effect, brought about by introducing the crown ether moiety into the polymer, on the rate of fixation could not be observed in DMF (lines a and b). We assumed that the binding ability of the crown ether for sodium cation was abated since DMF was a strongly competitive ligand for the Na^+ ion.[14,15] The kinetic study also showed that the use of nitromethane afforded the best result (line c). This seems to demonstrate that Na^+ ion is coordinated efficiently with the crown ether, and then, the Lewis acidity of sodium cation was increased in a solvent that shows moderate polarity. In the solvent like DMF, sodium cation may be stabilized much more compare to the case in nitromethane because of the electron-donating character of DMF.

Scheme 6 shows the plausible mechanism of the fixation. NaI was activated by complexing with crown ether moieties supported on polymer backbone. Immobilized catalyst assembles neighboring oxiranes to construct the effective reaction environment on the fixation of CO_2. In this environment, the activated catalyst coordinated with neighboring oxiranes, and then, the recycled catalyst was retracted to crown ether moieties after the fixation of CO_2 through the nucleophilic attack of the oxygen of oxirane to the center carbon of CO_2. In addition, it may be said that the reaction in the procedure is an equilibrium one because Sharpless and co-workers have reported the CO_2 elimination reaction from cyclic carbonate catalyzed by LiCl to give the corresponding oxirane compound.[16]

Summary

In this article, the fixation of carbon dioxide into the polymer containing oxirane and crown ether moieties was demonstrated to proceed effectively. The effects of crown ether on the fixation were shown clearly in comparison with the analogous polymer without crown ether moieties. From these experimental results, it was concluded that the crown ether moiety contributed to the solvation and activation of the alkali salt catalysts. In addition, the copolymer is thought to provide the effective reaction environment by introducing crown ether moieties to the polymer backbone. In other words, the catalytic site is located near oxirane groups. This seemed to enable the noticeable efficient fixation, which was not affected by concentration of the reaction system. Further research for optimization of the fixation system is in progress.

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