Polymer Reaction of Epoxide and Carbon Dioxide. Incorporation of Carbon Dioxide into Epoxide Polymers

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ABSTRACT: Polymeric epoxides can be converted to corresponding five-membered cyclic carbonates effectively by the reaction with carbon dioxide. For instance, poly(glycidyl methacrylate) (PGMA) was quantitatively converted to a polymethacrylate bearing a five-membered cyclic carbonate group (PDOMA) by the polymer reaction with carbon dioxide using alkali metal or quaternary ammonium halide salt as a catalyst. The salts having more Lewis acidic cation and more nucleophilic anion acted as more effective catalysts. Kinetic analyses of the polymer reaction show that the reaction rate can be expressed by the empirical equation: $-d[\text{epoxide}]/dt = k[\text{epoxide}][\text{catalyst}]^m$, where m depends on the Lewis acidity of the catalyst and molecular weight of the epoxide. The rate of the reaction is independent of the pressure of carbon dioxide. Further, various polymeric epoxides such as GMA copolymers, poly(glycidyl acrylate), and poly(vinylbenzyl glycidyl ether) could be converted to the corresponding polymers bearing five-membered cyclic carbonate moieties by the reaction with carbon dioxide, whereas the presence of an aromatic group in the structure of the polymer could retard the reaction with carbon dioxide.

Introduction

In the previous communication, we have reported that poly(glycidyl methacrylate) (PGMA) can be converted to a polymethacrylate bearing a five-membered cyclic carbonate group (PDOMA) by the quantitative polymer reaction with carbon dioxide using a conventional catalyst system.[1] The reaction of epoxide polymers with carbon dioxide is one of the most inexpensive methods to incorporate carbon dioxide into organic compounds because of easy separation of both original and produced polymers from the reaction system and successful solid-state reaction.[2] More recently, it has been reported that the reaction of epoxide with carbon dioxide quantitatively proceeds under an atmospheric pressure at rather low temperature (~100 °C) without side reaction.[3–5] Furthermore, we have reported that a polymer bearing a cyclic carbonate group reacted with amine easily and quantitatively to obtain the polymer carrying hydroxyurethane moieties,[6] and the versatility of polymers bearing cyclic carbonate groups as highly polar polymers has been pointed out by Katz[7] on the basis of the usefulness of cyclic carbonates as polar solvents.[8,9] However, a vinyl monomer bearing a cyclic carbonate group such as (2-oxo-1,3-dioxolan-4-yl)methyl methacrylate (DOMA) is extremely sensitive to the polymerization and difficult to handle.[6,9–14] Thus, the quantitative polymer reaction of epoxide polymers with carbon dioxide can be the most effective method of obtaining cyclic carbonate polymers (Scheme 1).

Recently, we have found that popular alkali metal halides can act as one of the most effective catalysts for the reaction of epoxides and carbon dioxide.[5] Their catalytic activity increases due to the more Lewis acidic cation part and the nucleophilic halide anion; *i.e.*, lithium chloride is basically the most active catalyst. We have observed that the rate of the reaction of epoxide and carbon dioxide is first order with respect to the concentration of epoxide and catalyst and is independent of the concentration (pressure) of carbon dioxide. These results prompted us to attempt the application of these structure–activity relationships of the catalysts and kinetic features to the polymer reaction to construct a more effective carbon dioxide fixation system. In this paper, we wish to report the details of the reaction of polymeric epoxide and carbon dioxide, *i.e.*, the structure–activity relationship of the catalyst on the polymer reaction, kinetic features of the polymer reaction of PGMA and carbon dioxide, and the reaction of various epoxide polymers with carbon dioxide.

Results and Discussion

Structure–Activity Relationship of the Catalyst on the Reaction of PGMA and Carbon Dioxide. The reaction of PGMA (M_n 29 000, M_w/M_n 2.23) with carbon dioxide was carried out at 100 °C for 2 h in NMP in the presence of 0.02 mol/L of a salt as a catalyst under atmospheric pressure. Conversions of epoxide to a five-membered cyclic carbonate group could be estimated by ^{1}H-NMR spectra and were confirmed by quantitative analysis of epoxide groups by titration using hydrochloride acid.[15,16] The results are summarized in Table 1. Typical ^{1}H-NMR spectra and GPC curves are shown in Figures 1 and 2, respectively. Since ^{1}H-NMR and IR spectra of resulting polymers exhibit features characteristic of PGMA and PDOMA and an increase of the polydispersity index of the polymer was not observed in every case, any side reaction can be neglected in this reaction. The spectra of the polymers obtained by using lithium chloride, lithium bromide, or benzyltrimethylammonium chloride as catalysts are identical with those of PDOMA. Thus, PDOMA can be synthesized easily by the polymer reaction of PGMA and carbon dioxide using these active catalysts. Since DOMA is an unstable monomer, the polymer reaction method is superior to the polymerization method to obtain PDOMA.[6]

Salts having a more Lewis acidic cation and more nucleophilic anion are found to be more effective catalysts, as observed in the reaction of monomeric epoxide and carbon dioxide. It should be noted that catalytic activities of benzyltrimethylammonium salts in the polymer reaction were higher than expected from the

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Scheme 1

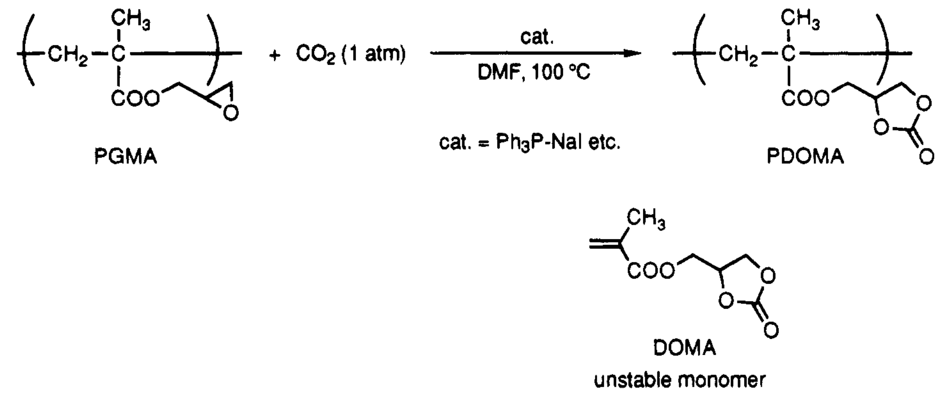


Table 1. Reaction of PGMA and Carbon Dioxide Catalyzed by Salt MS[a]

	incorporation ratio (%)[b]			
X	Li	Na	K	$PhCH_2NMe_3$
F	0[c]	0[c]	4	63
Cl	99	74[c]	47	100
Br	98	74	55	41
I	8	8	14	10

[a] In NMR (0.2 (mol unit)/L) under atmospheric pressure for 2 h catalyzed by 20 mmol/L of salt. [b] Estimated by ^{1}H−NMR spectra. [c] Heterogeneous system.

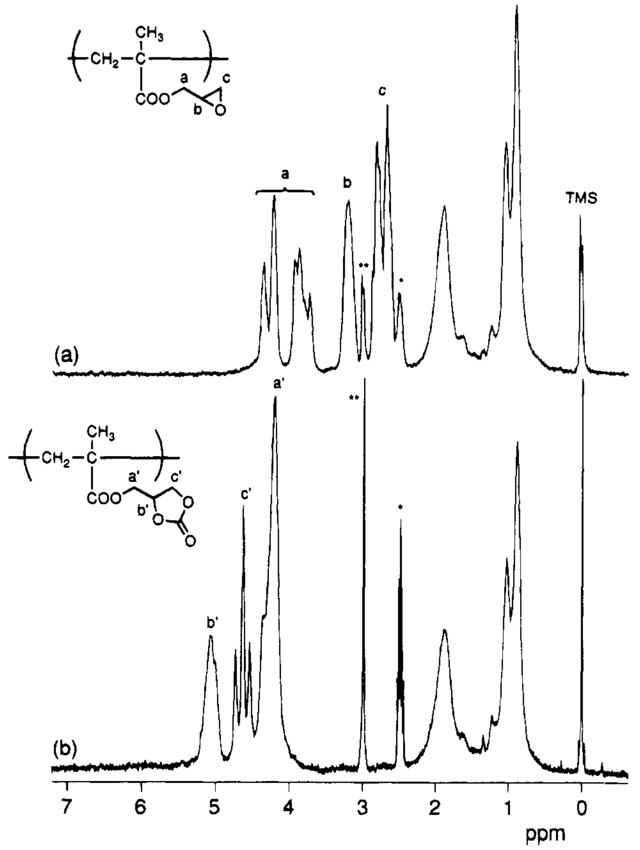


Figure 1. ^{1}H-NMR (90 MHz, 120 °C, DMSO-d_6) spectra of (a) PGMA and (b) PDOMA obtained by the reaction with carbon dioxide. * denotes solvent (DMSO-d_6) and ** denotes water.

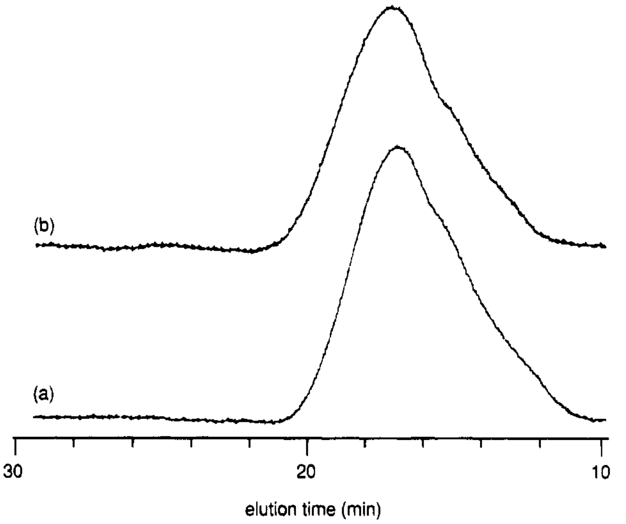


Figure 2. GPC profile of (a) PGMA and (b) PDOMA obtained by the reaction with carbon dioxide.

results of the reaction of monomeric epoxide with carbon dioxide. The hydrophobic character of the quaternary ammonium group seemed to enhance the local concentration of halide anion around the hydrophobic polymer chain. A similar effect has been reported in the quaternary ammonium salt catalyzed reaction of epoxide with acid chloride.[17,18] However, the full picture of these "hydrophobic effects" became clear through the kinetic investigation, as discussed below.

Kinetics of the Reaction of PGMA and Carbon Dioxide. As reported previously, the rate of the reaction of monomeric epoxide and carbon dioxide is first order with respect to the concentration of both catalyst and epoxide, respectively, and is independent of the concentration of carbon dioxide.[5] Thus, the kinetic analysis of the reaction of PGMA with carbon dioxide was carried out at 100 °C in NMP. The concentration of PGMA was set to 0.2 (mol unit)/L to maintain a lower viscosity in the reaction system. Series of bromide salts were used as the catalysts because of their higher solubility in NMP.

Figure 3 shows the first-order plot of the reaction of PGMA and carbon dioxide catalyzed by various bromide salts. A linear relationship was observed in every case, and therefore, the reaction of PGMA and carbon dioxide was confirmed to be first order with respect to the concentration of epoxide regardless of the catalyst. On the other hand, the carbon dioxide pressure showed no effect on the incorporation ratio of carbon dioxide into PGMA at all, as shown in Figure 4.

To evaluate the kinetic order with respect to the catalyst, the reaction was carried out at 100 °C in the presence of various concentrations of lithium bromide as shown in Figure 5. In these attempts, PGMA of M_n 21 800 (M_w/M_n 2.41) was used. The apparent rate constant, which is the function of the concentration of the catalyst, was evaluated from the slope of the first-order plots. A plot of the logarithm of the apparent rate constant *vs* the logarithm of concentration of the cata-

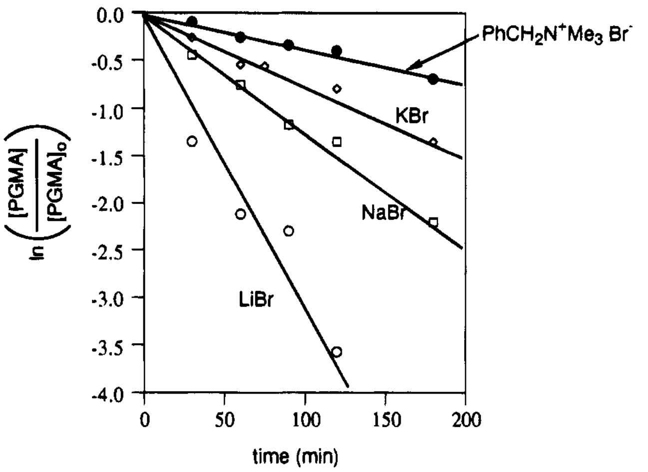


Figure 3. First-order plot of the reaction of PGMA and carbon dioxide in the presence of various bromide salts (19.5 mmol/L) in NMP at 100 °C.

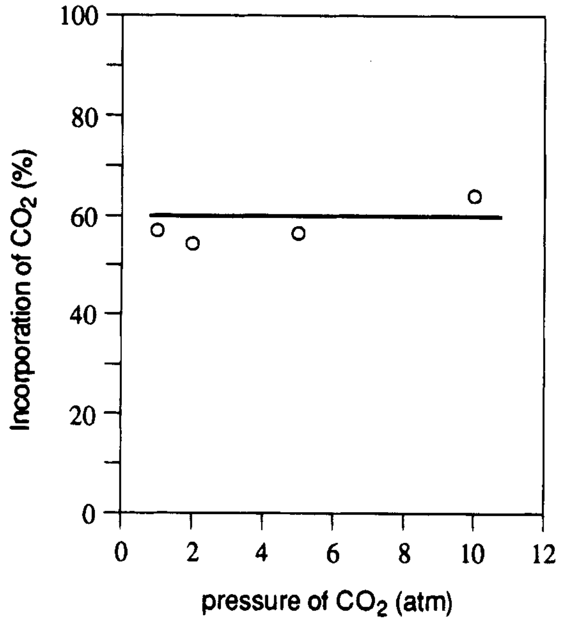


Figure 4. Incorporation of carbon dioxide into PGMA in the presence of lithium bromide (19.5 mmol/L) for 30 min in NMP at 100 °C.

lyst gives a straight line, as shown in Figure 6, and the slope of the line, which is thought to indicate the kinetic order with respect to the concentration of the catalyst, was 1.45. It was found that the reaction of epoxide and carbon dioxide was not generally first order with respect to the concentration of the catalyst in the case of the polymer system. When the rate of the reaction is expressed by the empirical equation (1)

$$-\mathrm{d}[\text{epoxide}]/\mathrm{d}t = k[\text{epoxide}][\text{catalyst}]^m \qquad (1)$$

$m = 1.45$ for lithium bromide and PGMA of M_n 21 800.

To confirm the "polymer effect" on the reaction of epoxide with carbon dioxide, the series of epoxides of different molecular weights were allowed to react with carbon dioxide using a series of bromide salts as catalysts. Glycidyl pivalate (GP) was used as the model monomeric epoxide. Low molecular weight PGMA was prepared by telomerization of GMA (Scheme 2). The kinetic orders with respect to the concentration of the catalysts was evaluated on the basis of the empirical equation (1). In every case, a simple linear relationship between log k' and log[catalyst] was observed. The results are summarized in Tables 2 and 3.

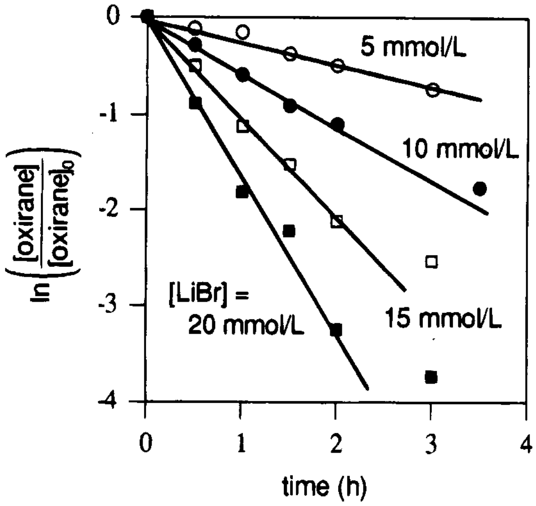


Figure 5. First-order plot of the reaction of PGMA and carbon dioxide in the presence of various concentrations of lithium bromide in NMP at 100 °C.

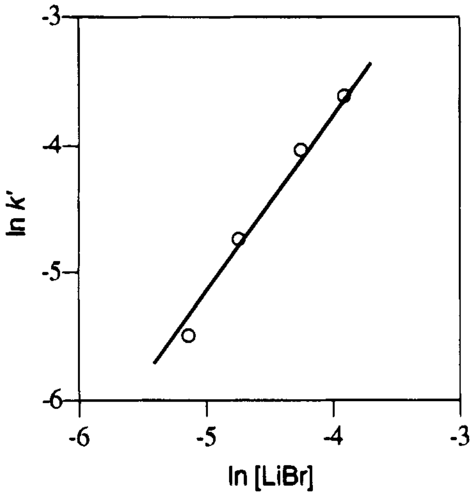
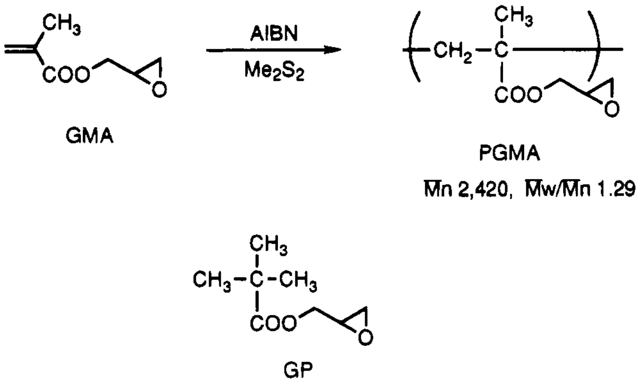


Figure 6. Relationship between [LiBr] and apparent rate constant at 100 °C in NMP for the reaction of PGMA and carbon dioxide.

Scheme 2



It is clear that the apparent kinetic order with respect to the concentration of the catalyst (m) depends on the Lewis acidity of the catalyst and molecular weight of the epoxide. In the case of monomeric epoxide GP, m is close to unity regardless of the catalyst. However, in the case of the larger molecular weight of the epoxide, m deviated from unity. The deviation depends on the Lewis acidity of the catalyst. Although the reason for the deviation is not clear at the present time, m increased in the case of a Lewis acidic catalyst such as a lithium salt and decreased in the case of a non-Lewis

Table 2. Effect of the Lewis Acidity of the Catalyst on the Kinetic Order with Respect to the Concentration of the Catalyst

	m^a	
catalyst	substrate PGMA[b]	GP
LiBr	1.45	1.02
NaBr	1.12	1.05
KBr	0.82	*c*
$PhCH_2N^+Me_3Br^-$	0.64	0.96

[a] Kinetic order with respect to the concentration of the catalyst. [b] M_n 21 800, M_w/M_n 2.41. [c] Not determined.

Table 3. Effect of the Molecular Weight of Epoxide on the Kinetic Order with Respect to the Concentration of the Catalyst[a]

epoxide	mol wt	M^b
GP	158.2	1.02
PGMA	2450	1.32
PGMA	21800	1.45

[a] Lithium bromide was used as a catalyst in NMP at 100 °C. [b] Kinetic order with respect to the concentration of lithium bromide.

Table 4. Rate Constant of the Reaction of Oxirane and Carbon Dioxide

oxirane	catalyst	k^a ($min^{-1} \cdot L^m \cdot mol^{-m}$)
PGMA (M_n 21 800)	LiBr	0.943
PGMA (M_n 21 800)	NaBr	0.583
PGMA (M_n 21 800)	KBr	0.391
PGMA (M_n 21 800)	$PhCH_2N^+Me_3Br^-$	0.122
PGMA (M_n 2450)	LiBr	1.33
GP	LiBr	1.88

[a] Rate constant. *m* is kinetic order with respect to the concentration of catalyst, see Tables 2 and 3.

acidic catalyst such as a quaternary ammonium salt. Although the change of kinetic order normally indicates the change of the reaction mechanism, a corresponding situation could not be supposed in this case.

Based on these kinetic orders, rate constants *k* as the function of the catalyst and epoxide are summarized in Table 4. Since the dimension of *k* depends on the catalyst and molecular weight of epoxide, *k*'s cannot be simply compared to each other. However, *k* can be an indicator of the reactivity of substrate and catalytic power. A more Lewis acidic salts showed more catalytic activity. Thus, the apparent high activity of quaternary ammonium salt (Table 1) came from its low kinetic order. Further, the higher molecular weight of epoxide showed a lower reactivity to carbon dioxide although the decrease of the reactivity is not so significant.

Reactions of Various Polymeric Epoxides with Carbon Dioxide. To reveal the effect of polymer structure on the reactivity of the polymer reaction, reactions of typical polymeric epoxides, *i.e.*, GMA copolymer, poly(glycidyl acrylate) (PGA),[19] and poly(vinylbenzyl glycidyl ether) (PVBGE),[20] with carbon dioxide were examined.

The copolymers of GMA with methyl methacrylate (MMA), acrylonitrite (AN), and styrene (St) were synthesized by radical copolymerization and were allowed to react with carbon dioxide at 100 °C in NMP for 30 min in the presence of 0.02 mol/L of lithium bromide. The initial concentration of the epoxide group was set to 0.2 mol/L in every case. The incorporation ratios were estimated by ^1H-NMR spectra, and the results are summarized in Table 5.

Table 5. Reaction of Copolymers of GMA with Carbon Dioxide[a]

	composition[b] (mol/mol)			incorporation of carbon
comonomer	GMA	comonomer	M_n (M_w/M_n)[c]	dioxide[b] (%)
MMA	26	74	50 600 (1.33)	75
	49	51	54 100 (1.42)	72
	74	26	62 800 (1.41)	75
AN	24	76	47 100 (1.56)	37
	45	55	64 300 (1.66)	74
	70	30	65 400 (1.91)	70
St	27	73	23 600 (1.33)	46
	50	50	36 200 (1.34)	54
	74	26	47 800 (1.46)	62

[a] In NMP (0.2 (mol epoxide unit)/L) at 100 °C for 30 min using LiBr (19.5 mmol/L) as the catalyst under atmospheric pressure. [b] Determined by ^1H-NMR. [c] Estimated by GPC.

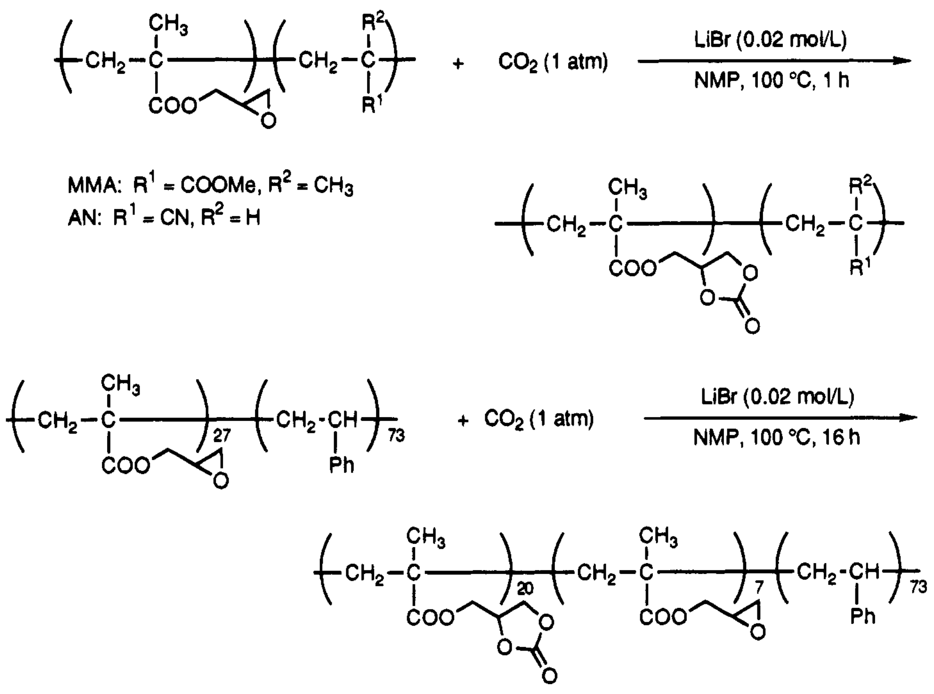
The incorporation of carbon dioxide into PGMA was 74% under these reaction conditions, and copolymers of GMA with MMA and AN were as reactive as PGMA. However, incorporation of carbon dioxide into the GMA−AN copolymer was inhibited when the composition of AN was raised to 76%, probably because of the presence of an acidic α-proton of the nitrile group. Quantitative incorporation of carbon dioxide into these copolymers could be achieved by the reaction for 1 h to obtain DOMA−MMA or DOMA−AN copolymers without any detectable side reaction (Scheme 3). Since DOMA is an unstable monomer, the polymer reaction method may be superior to the copolymerization method for obtaining PMMA or PAN modified by a five-membered cyclic carbonate group.

On the other hand, the reactivity of the GMA−St copolymer decreased as the composition of St increased. Actually, when a GMA−St copolymer (composition of St, 73 mol %) was allowed to react with carbon dioxide for 16 h, incorporation of carbon dioxide attained only 73% (Scheme 3). The aromatic ring neighboring the epoxide group may retard the reaction. It is speculated that the change of the higher order structure of the GMA−St copolymer, which can be induced by the interaction between the aromatic ring and five-membered cyclic carbonate group,[21] increases the steric hindrance around the remaining epoxide group to depress the reactivity. Another possibility is that the aromatic ring changes polarity around the epoxide group to decrease its reactivity. However, we have already reported that an aromatic solvent did not disturb the polymer reaction when the catalyst is homogeneously dispersed in the reaction system.[1] Thus, the effect of St composition on the reactivity cannot be explained by the change of the polarity of the polymer chain.

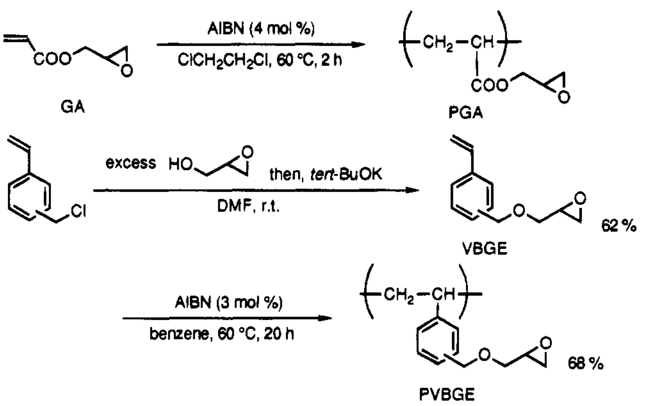
PGA and PVBGE were prepared by the radical polymerization of glycidyl acrylate (GA) and vinylbenzyl glycidyl ether (VBGE), respectively (Scheme 4). VBGE, which has been prepared[20] from (chloromethyl)styrene by acetoxylation and hydrolysis, followed by condensation with epichlorophydrin, was synthesized by simple condensation of (chloromethyl)styrene and glycidol using potassium *tert*-butoxide in 62% yield.

PGA (M_n 260 000, M_w/M_n 1.36) was allowed to react with carbon dioxide at 100 °C in NMP for 2 h under atmospheric pressure in the presence of 0.02 mol/L of lithium bromide to obtain the corresponding polyacrylate bearing a five-membered cyclic carbonate group (PDOA) without any side reaction (Scheme 5). Its structure was confirmed by ^1H-NMR and IR spectra. PDOA was soluble in NMP, DMF, and DMSO, but insoluble in methanol, chloroform, and THF. Since polymerization of the corresponding monomer, (2-oxo-1,3-dioxolan-4-yl)methyl acrylate (DOA), usually af-

Scheme 3



Scheme 4



forded a cross-linked gel,[10–14] this polymer reaction is a better method for obtaining soluble PDOA and its derivatives.

When PVBGE (M_n 5400, M_w/M_n 2.35) was allowed to react with carbon dioxide at 100 °C in NMP for 3 h under atmospheric pressure in the presence of 0.2 mol/L of lithium bromide, conversion of epoxide to a five-membered cyclic carbonate group attained 95%. Although PVBGE has a high reactivity to carbon dioxide, the reactivity of PVBGE is less than that of nonaromatic polymeric epoxides such as PGMA, as observed in the reaction of the Sr–GMA copolymer.

Experimental Section

General Information. ^{1}H-NMR spectra were recorded on a JEOL PMX-60 SI (60 MHz) or on a JEOL EX-90 (90 MHz), using a tetramethylsilane as an internal standard. IR spectra were recorded on a JEOL JIR-5300. Gel permeation chromatography (GPC) analyses were carried out to estimate molecular weights with a Tosoh Co. HLC-8020 equipped with TSK gel G5000HXL, TSK gel G4000HXL, and TSK gel G2500HXL, detected with a UV-8011 at 270 nm, eluted by DMF (containing 10 mmol/L of lithium bromide, 1 mL/min, 30 °C), and calibrated by polystyrene standards.

Materials. Glycidyl methacrylate, methyl methacrylate, acrylonitrile, styrene, (chloromethyl)styrene, and glycidol were commerically available and were used after distillation. Poly(glycidyl methacrylate) (PGMA) and its copolymers were prepared according to the literature.[16] Glycidyl acrylate and poly(glycidyl acrylate) (PGA) were prepared according to the literature.[19] *N*-Methyl-2-pyrrolidinone (NMP) was distilled on calcium hydride and stored over molecular sieves 4A. Organic and inorganic salts were commercially available and were used after drying overnight *in vacuo*. Other chemicals were reagent grade and used without further purification.

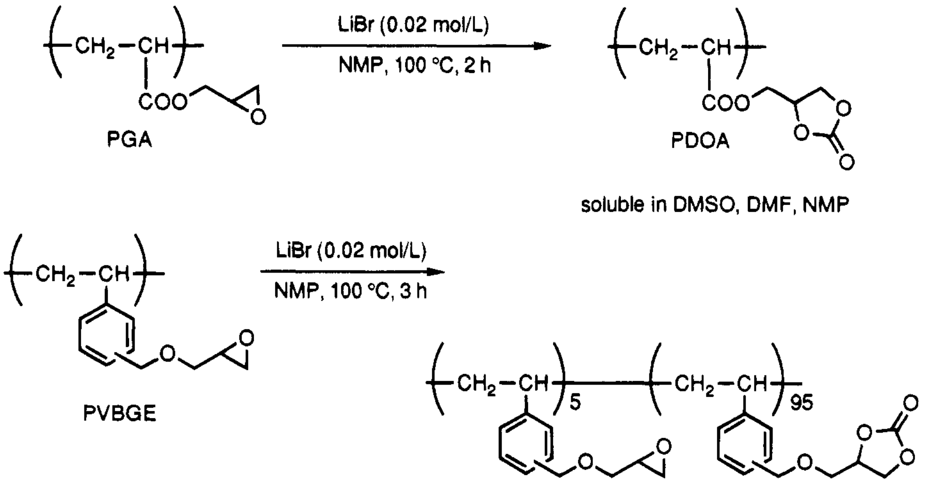
Reaction of Polymeric Epoxide with Carbon Dioxide: Typical Procedure. A mixture of 142 mg (1.00 mmol unit) of PGMA and 8.7 mg (0.10 mmol, 10 mol unit %) of lithium bromide was placed in a two-necked flask equipped with rubber septum and a balloon filled with carbon dioxide. After the atmosphere was replaced with carbon dioxide, 10.0 mL of NMP was introduced using a syringe though a rubber septum to dissolve the mixture. The solution was allowed to stand at 100 °C for 2 h with continuous stirring. After addition of 2.0 mL of DMF, the solution was poured into 100 mL of methanol with vigorous stirring. The white precipitate was separated by filtration, washed thoroughly with methanol, and dried over phosphorous pentoxide *in vacuo*.

Incorporation Ratio of Carbon Dioxide. The ^{1}H-NMR spectrum of the polymer was measured in DMSO-d_6 at 100 °C. The integration of 5.3–3.6 ppm corresponds to 5H of the PDOMA unit and 2H of the PGMA unit. The integration of 3.4–2.4 ppm corresponds to 3H of the PGMA unit. The incorporation ratio of carbon dioxide was estimated from the ratio of these integrations.

Reaction of PGMA with Carbon Dioxide under Higher Pressure. A solution of 142 mg (1.00 mmol unit) of PGMA and 8.7 mg (0.10 mmol, 10 mol unit %) of lithium bromide in 5.0 mL of NMP was placed in a stainless-steel autoclave. The atmosphere was replaced by carbon dioxide, and then carbon dioxide was introduced under the mentioned pressure. The autoclave was allowed to stand at 100 °C for 30 min. After addition of 2 mL of DMF, the solution was poured into 80 mL of methanol with vigorous stirring. The white precipitate was separated by filtration, washed thoroughly with methanol, and dried over phosphorus pentoxide *in vacuo*. The incorporation ratio of carbon dioxide was estimated by the ^{1}H-NMR spectrum in DMSO-d_6 at 100 °C.

Glycidyl Pivalate (GP). To a solution of 9.67 g (13.1 mmol) of glycidol, 614 mg (5.0 mmol) of 4-(dimethylamino)-pyridine, and 11.22 g (112 mmol) of triethylamine in 100 mL of dichloromethane was added dropwise 12.20 g (101 mmol) of pivaloyl chloride at 0 °C. The reaction mixture was allowed to stand for 6 h. After addition of 200 mL of water, the aqueous layer was extracted by ethyl acetate four times. The organic layer was combined, washed with 1.2 M aqueous

Scheme 5



hydrochloric acid followed by aqueous sodium hydrogen carbonate, dried over magnesium sulfate and evaporated *in vacuo*. The residue was chromatographed on silica gel [hexane:ethyl acetate (2/1 v/v)] and distilled *in vacuo* to afford 8.8 g (55%) of glycidyl pivalate (GP) as a colorless liquid. Bp: 61.0–62.0 °C/6 mmHg (lit.[22] 71 °C/15 mmHg). ^{1}H-NMR (90 MHz, $CDCl_3$): δ 4.41 (dd, $J = 3.1$ and 12.3 Hz, 1H), 3.92 (dd, $J = 5.7$ and 12.3 Hz, 1H), 3.30–3.08 (m, 1H), 2.83 (t, $J = 5.1$ Hz, 1H), 2.64 (dd, $J = 2.6$ and 5.1 Hz, 2H), 1.23 (s, 9H). IR (KBr): 1732, 1285, 1155, 912 cm^{-1}.

Reaction of GP with Carbon Dioxide. A mixture of 158 mg (2.00 mmol) of GP, the mentioned amount of catalyst, and 128 mg of naphthalene as an internal standard were placed in a two-necked flask equipped with rubber septum and a balloon filled with carbon dioxide. After the atmosphere was replaced with carbon dioxide, 10.0 mL of NMP was introduced using a syringe through the rubber septum to dissolve the mixture. The solution was allowed to stand at 100 °C with continuous stirring. Periodically, a small portion of the reaction mixture was removed through the rubber septum and diluted by deuterated chloroform. Conversion of GP to cyclic carbonate was estimated by the ^{1}H-NMR spectrum on the basis of the aromatic proton of naphthalene.

Telomerization of GMA. A solution of 1.42 g (10 mmol) of GMA and 330 mg (2 mmol, 20 mol) of AIBN in 20 mL of dimethyl disulfide was degassed and sealed *in vacuo*. The solution was allowed to stand at 60 °C for 24 h. The reaction mixture was poured into a large amount of ether. The white precipitate was filtered, washed thoroughly with ether, and dried *in vacuo*. The Telomer of GMA (824 mg, 58%) was obtained as a white powder: M_n 2420, M_w/M_n 1.29.

3,4-η-[[(2,3-Epoxypropyl)oxy]methyl]styrene (VBGE). To a solution of 45.8 g (300 mmol) of 3,4-η-(chloromethyl)-styrene and 11.4 g (150 mmol) of glycidol in 50 mL of DMF was added dropwise a solution of 13.5 g (120 mmol) of potassium *tert*-butoxide in 50 mL of DMF at room temperature under an argon atmosphere. The dark green reaction mixture was allowed to stand at room temperature for 7 h and poured into a large amount of water. The aqueous layer was extracted by ethyl acetate several times. The organic layer was combined and washed by water followed by brine. The organic layer was dried over magnesium sulfate and evaporated *in vacuo*. The residue was chromatographed on silica gel [hexane:ethyl acetate (9/1 v/v)] to afford 14.2 g (62%) of 3,4-η-[[(2,3-epoxypropyl)oxy]methyl]styrene (VBGE) as a colorless oil. VBGE was used for polymerization after distillation. R_f value: 0.15 [hexane:ethyl acetate (9/1 v/v)]. Bp: 114–117 °C/0.5 mmHg (lit.[20] 100–104 °C/0.15 mmHg). ^{1}H-NMR (90 MHz, DMSO-d_6): δ 7.55–7.13 (m, 4H), 6.76 (dd, $J = 11.0$, 17.8 Hz, 1H), 5.82 (dd, $J = 17.8$, 1.3 Hz, 1H), 5.26 (dd, $J = 11.0$, 1.3 Hz, 4.53 (s, 2H), 3.88–3.67 (m, 1H), 3.43–3.05 (m, 2H), 2.83–2.44 (m, 2H).

Poly[1-[3,4-η-[[(2,3-epoxypropyl)oxy]methyl]phenyl]-ethylene] (PVBGE). A solution of 1.91 g (10.0 mmol) of freshly distilled VBGE and 48 mg (0.29 mmol, 2.9 mol %) of AIBN in 10 mL of benzene was degassed and sealed *in vacuo*. The solution was allowed to stand at 60 °C for 24 h. The reaction mixture was poured into a large amount of methanol. The highly viscous precipitate was separated out by decantation, washed thoroughly by methanol, and dried *in vacuo* to obtain 1.30 g (68%) of poly[1-[3,4-η-[[(2,3-epoxypropyl)oxy]-methyl]phenyl]ethylene] (PVBGE) as a colorless gum. ^{1}H-NMR (90 MHz, DMSO-d_6): δ 7.25–6.05 (m, 4H), 4.55–4.00 (br, 2H), 3.80–2.55 (m, 5H), 2.20–0.80 (m, 3H).

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