Macromolecules **1994,** *27,* 6239–6244

Articles

Self-Catalyzed Carbon Dioxide Incorporation System. The Reaction of Copolymers Bearing an Epoxide and a Quaternary Ammonium Group with Carbon Dioxide

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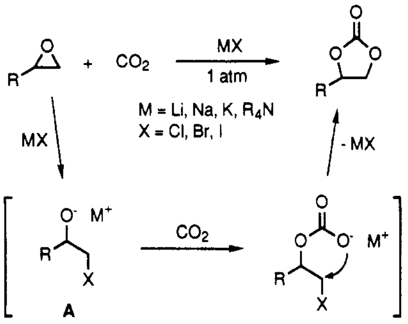
Received April 19, 1994; Revised Manuscript Received August 1, 1994[⊗]

ABSTRACT: Copolymers of glycidyl methacrylate (GMA) and *N*-benzyl-*N*-[2-(methacryloyloxy)ethyl]-*N*,*N*-dimethylammonium bromide (**1b**) were synthesized by radical copolymerization in acetonitrile using AIBN as an initiator to obtain copolymer-6 (GMA:**1b** = 94:6) and copolymer-10 (GMA:**1b** = 90:10), respectively. When copolymer-6 was reacted with carbon dioxide at 100 °C in NMP for 24 h, 86% of the epoxide group was converted to the five-membered cyclic carbonate moiety by self-catalyzation. When the powder of copolymer-6 was exposed to carbon dioxide under an atmospheric pressure at 140 °C for 500 min, incorporation of carbon dioxide into copolymer-6 was attained up to 76%. Similarly, incorporation of carbon dioxide into copolymer-10 at 130 °C for 500 min in the solid state was attained up to 75%. A cross-linked copolymer, copolymer-5C, was synthesized by radical copolymerization of GMA, **1b**, and divinylbenzene (93:5:2) and exposed to carbon dioxide to attain 61% of incorporation at 140 °C for 500 min.

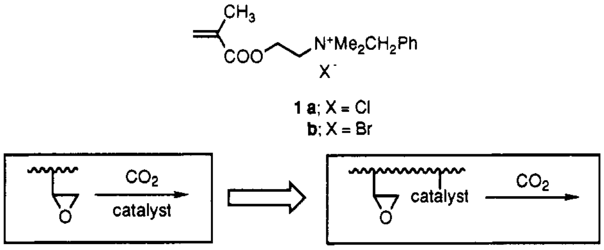
Introduction

Carbon dioxide reacts with various epoxides in the presence of alkali metal or quaternary ammonium halides as catalysts under atmospheric pressure to afford five-membered cyclic carbonates.[1-5] We have reported that the reaction proceeds *via* nucleophilic attack of the halide anion on the epoxide ring followed by cyclization after the facile incorporation of carbon dioxide (Scheme 1).[5] Since ring opening of the epoxide is the rate-determining step, more nucleophilic halide anion exhibits higher catalytic activity. This reaction is one of the most versatile methods of incorporating carbon dioxide into organic molecules because of its easy operation, quantitative yield, and versatility of five-membered cyclic carbonates.[6-14] Especially, incorporation of carbon dioxide into the epoxide polymer, such as poly(glycidyl methacrylate) (PGMA), by polymer reaction[15] is advantageous on the view point of easy separation of the polymer from the reaction mixture, successful solid-state reaction,[16] and production of reactive polymers.[17,18] Since a polymer system can be easily modified by copolymerization, copolymerization of the epoxide monomer with a catalytic functional group may enable a self-catalyzed carbon dioxide incorporation system. Although it has been reported that an epoxide having a quaternary ammonium group at the β-position reacts with carbon dioxide under very mild conditions by a self-catalyzation manner,[13] the mole ratio of the epoxide and ammonium group cannot be controlled in such a system. Since it can be easily controlled by the copolymerization system, a flexible self-catalyzed carbon dioxide incorporation system is expected to be constructed by the copolymerization of monomers containing epoxide and catalytic functional groups, respectively. In this paper, reactions of carbon dioxide with novel copolymers obtained from glycidyl methacrylate (GMA) as an epoxide monomer and *N*-benzyl-*N*-[2-(methacryloyloxy)ethyl]-*N*,*N*-dimethylammonium bromide (**1b**) as a comonomer having a catalytic functional group are described.

Scheme 1



Scheme 2



Experimental Section

General. ^{1}H-NMR spectra were recorded on a JEOL PMX-60 SI (60 MHz) or JEOL EX-90 (90 MHz) spectrometer, using tetramethylsilane as an internal standard. IR spectra were recorded on a JEOL JIR-5300 spectrometer. Gel permeation chromatography (GPC) analyses were carried out to estimate molecular weights with a Tosoh Co. HLC-8020 instrument

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[⊗] Abstract published in *Advance ACS Abstracts*, September 1, 1994.

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equipped with TSKgel G5000HXL, TSKgel G4000HXL, and TSKgel G2500HXL, detected with a UV-8011 instrument at 270 nm, eluted by a 10 mmol/L solution of lithium bromide in *N*,*N*-dimethylformamide (1 mL/min, 40 °C), and calibrated by polystyrene standards. Differential scanning calorimeter (DSC) analyses and thermogravimetric analyses (TGA) were carried out on a SEIKO SSC-5000 instrument equipped with an aluminum cell at a heating rate of 10 K/min. Dispersion of the grain size was evaluated on a Shimadzu SALD-2000 instrument dispersed in 2-propanol.

Materials. Glycidyl methacrylate and divinylbenzene were commercially available, and used after distillation. Poly(glycidyl methacrylate) was prepared according to the literature.[19] Reagent grade 2-(dimethylamino)ethyl methacrylate was commercially available and used without further purification. Acetonitrile, *N*,*N*-dimethylformamide (DMF), and *N*-methylpyrrolidin-2-one (NMP) were distilled on CaH$_2$ and stored over molecular sieves (4A). Other chemicals were reagents grade and used without further purification.

***N*-Benzyl-*N*-[2-(methacryloyloxy)ethyl]-*N*,*N*-dimethylammonium Bromide (1b).** To a solution of 2.11 g (13.4 mmol) of benzyl bromide in 10 mL of toluene was added 1.57 g (10.0 mmol) of 2-(dimethylamino)ethyl methacrylate dropwise at 0 °C. The white precipitate was separated and washed thoroughly with acetone. After drying under vacuum, 2.24 g (68%) of **1b** was obtained as white crystals. ^{1}H-NMR (60 MHz, CD$_3$OD): δ 7.56 (s, 5H, Ar), 6.24–6.10 (m, 1H, –CH=), 5.77–5.60 (m, 1H, –CH=), 4.85–4.51 (m, 2H, –COOCH$_2$–), 4.68 (s, 2H, PhCH$_2$–), 3.98–3.69 (m, 2H, –CH$_2$N$^+$≡), 3.17 (s, 6H, –CH$_3$), 2.07–1.93 (m, 3H, –CH$_3$). IR (KBr): 1721, 1295, 1172, 1154, 771, 722 cm^{-1}. Anal. Calcd for C$_{15}$H$_{22}$BrNO$_2$: C, 54.89; H, 6.76; N, 4.27. Found: C, 54.54; H, 6.76; N, 4.26.

Copolymer-6. A solution of 677.7 mg (4.77 mmol) of GMA, 83.0 mg (0.25 mmol, 5.3 mol %) of **1b**, and 22.2 mg (0.14 mmol) of AIBN in 5.0 mL of acetonitrile was heated at 60 °C in a sealed tube for 33 h. Insoluble material was filtered off, and the filtrate was poured into 100 mL of ether. The precipitate was separated out and washed thoroughly with ether followed by water. After drying under vacuum, 429.2 mg (56%) of copolymer-6 was obtained as a white powder.

Copolymer-10 was obtained using 645.9 mg (4.54 mmol) of GMA, 165.0 mg (0.50 mmol, 11 mol %) of **1b**, and 23.8 mg (0.14 mmol) of AIBN in a similar manner as described above.

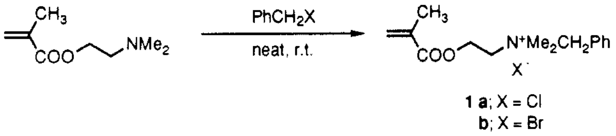
Poly-1b. A solution of 342.1 mg (1.0 mmol) of **1b** and 4.8 mg (0.03 mmol) of AIBN in 3.0 mL of methanol was heated at 70 °C in a sealed tube for 24 h. The clear reaction mixture was poured into 50 mL of acetone. The precipitate was separated out and washed thoroughly with acetone. After drying under vacuum, 279.7 mg (82%) of poly-**1b** was obtained as a white powder. ^{1}H-NMR (90 MHz, CD$_3$OD): δ 7.9–7.2 (m, 5H, Ar), 5.3–3.7 (m, 6H, –CH$_2$–), 3.7–2.8 (br, 6H, –CH$_3$), 2.7–0.7 (m, 5H, –CH$_2$– and –CH$_3$). IR (KBr): 1728, 1479, 1456, 1147, 768, 717 cm^{-1}. T_g was not observed below the decomposition temperature (120 °C).

Copolymer-5C. A solution of 705.1 mg (4.96 mmol) of GMA, 95.5 mg (0.29 mmol) of **1b**, 16.2 mg (0.12 mmol) of divinylbenzene, and 33.6 mg (0.20 mmol) of AIBN in 3.0 mL of acetonitrile was heated at 60 °C in a sealed tube for 24 h. The reaction mixture was washed thoroughly with Soxlet extractor with acetone followed by ether. After drying under vacuum, 567.6 mg (69%) of the cross-linked polymer was obtained as a white powder. IR (KBr): 1724, 1480, 1445, 1250, 1148 cm^{-1}.

Reaction of Copolymer-6 with Carbon Dioxide in NMP. A solution of 47.7 mg (0.29 mmol/epoxide) of copolymer-6 in 0.60 mL of NMP was stirred at 100 °C for 24 h under an atmospheric pressure of carbon dioxide. After addition of 1 mL of DMF, the white precipitate was filtered off and the filtrate was poured into 100 mL of ether. The precipitate was separated out and washed thoroughly with ether. After drying under vacuum, 41.1 mg (70%, as an 86% carbon dioxide-incorporated polymer estimated by ^{1}H-NMR) of polymer was obtained as a pale yellow powder.

Reaction of Copolymers with Carbon Dioxide in the Solid State. The copolymer (*ca.* 9 mg) was placed in a TGA sample cell without capping. The cell was set in a TGA instrument flowing with 400 mL/min carbon dioxide, and the weight of the polymer was measured precisely. The furnace was heated to the mentioned temperature, and the sample was annealed at the temperature for 500 min while monitoring the weight of the sample.

Scheme 3



1 a; X = Cl
b; X = Br

A Mixture of PGMA and Poly-1b. A solution of 84.4 mg (0.59 mmol/unit) of PGMA and 13.2 mg (0.040 mmol/unit, 6.8 mol % of the GMA units) of poly-**1b** in 1 mL of DMF was poured into 50 mL of ether. The precipitate was separated out and washed thoroughly with ether. After drying under vacuum, a mixture of PGMA and poly-**1b** was obtained as a white powder.

Results and Discussion

Self-Catalyzed Carbon Dioxide Incorporation System. GMA was used as an epoxide monomer. To disperse the catalytic functional group in the system homogeneously, methacrylic acid ester bearing a quaternary ammonium halide group, which is expected to copolymerize with GMA in a random manner, was selected. To be free from Hoffmann degradation, *N*-benzyl-*N*-[2-(methacryloyloxy)ethyl]-*N*,*N*-dimethylammonium halide **1** was designed as a comonomer. Although chloride is the most active catalyst,[5] noncrystalline **1a** could not be purified by recrystallization. Thus, **1b** was synthesized from 2-(dimethylamino)ethyl methacrylate and benzyl bromide in 68% yield and used as a comonomer.

Copolymers of GMA and **1b** were prepared by the radical copolymerization using AIBN as an initiator at 60 °C in acetonitrile. Since the resulting polymers were unimodal and their ^{1}H-NMR and IR spectra exhibited features characteristic of PGMA and poly-**1b**, desired random copolymerization was confirmed and a possible side reaction of the bromide anion and the epoxy group could be neglected.[5,20–22] The obtained polymers are denoted as copolymer-6 and copolymer-10 that correspond to the unit ratio of **1b** in the copolymers. A homopolymer of **1b** was also prepared by radical polymerization of **1b** in methanol. Further, the cross-linked copolymer copolymer-5C was prepared by the radical copolymerization of GMA, **1b**, and divinylbenzene (93:5:2) in acetonitrile.

Self-Catalyzed Carbon Dioxide Incorporation in the Solution State. Copolymer-6 was reacted with carbon dioxide at 100 °C in NMP for 24 h under atmospheric pressure. A small amount of the cross-linked polymer was precipitated during the reaction, and conversion of the epoxide group in copolymer-6 into the five-membered cyclic carbonate moiety by self-catalyzation was attained up to 86%, which was estimated by a ^{1}H-NMR spectrum of the soluble part of the resulting polymer. To estimate the catalytic activity of the ammonium group in copolymer-6, PGMA was reacted with carbon dioxide under a similar condition using benzyltrimethylammonium bromide as a catalyst. No cross-linked polymer was observed, and the incorporation ratio of carbon dioxide into PGMA was attained up to over 99%.[15] These results indicated that catalytic activity and selectivity of the copolymerized quaternary ammonium group on reaction of the epoxide moiety and carbon dioxide were less than those of the monomeric quaternary ammonium salt in the case of a solution-state reaction. Although the quaternary ammonium group was dispersed in these systems on the macroscopic scale, it might be localized around the neighboring epoxide group on the microscopic scale in the case of a copolymer system. Such a local heterodispersity

Scheme 4

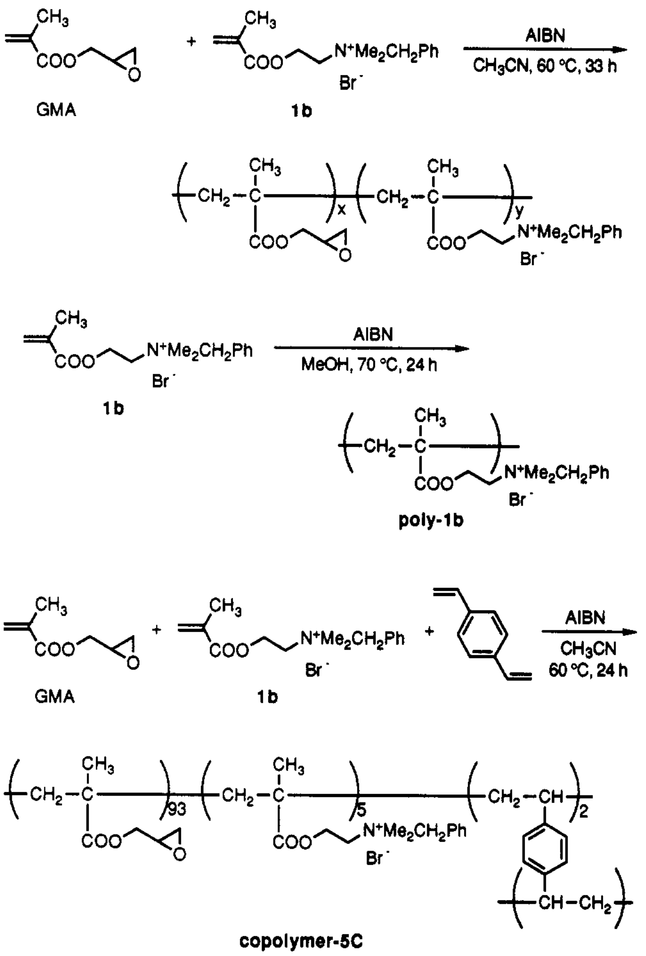


Table 1. Radical Copolymerization of GMA and 1b[a]

feed ratio (mol %)			composition[c]			
GMA	1b	yield[b] (%)	x	y	M_n (M_w/M_n)[d]	polymer
95	5	56	94	6	34 000 (2.00)	copolymer-6
90	10	81	90	10	20 000 (1.41)	copolymer-10

[a] Polymerizations were carried out using 3 mol % of AIBN as an initiator in acetonitrile ([methacrylate] = 1.0 mol/L) at 60 °C for 33 h. [b] Ether-insoluble part. [c] Estimated by ^{1}H-NMR spectra. [d] Estimated by GPC (eluted by DMF, 10 mM LiBr, based on PSt standards), detected by RI detector.

should be emphasized in a diluted solution system, decreasing the total catalytic activity. It should also decrease the selectivity of the reaction (see below).

Self-Catalyzed Carbon Dioxide Incorporation in the Solid State. Before the solid-state reactions of the copolymers with carbon dioxide, their thermal behaviors in nitrogen and carbon dioxide atmospheres were investigated using TGA (Figures 2 and 3). Thermal behavior of PGMA and poly-**1b** were independent of the atmosphere. Poly-**1b** began to decompose slowly at 120 °C, while PGMA was stable below 160 °C. On the other hand, copolymer-6 began to decompose at 100 °C in a nitrogen atmosphere and rapidly decomposed above 130 °C to afford the cross-linked gel. Since weight decrease of copolymer-6 was larger than those of PGMA and poly-**1b** and the decomposition temperature of copolymer-6 was lower than those of PGMA and poly-**1b**, bromide ion-catalyzed decomposition of the glycidyl ester group can be a main pathway of thermal decomposition of copolymer-6. Thus, copolymer-6 was heated at 100 °C in a nitrogen atmosphere, and the vaporized products were combined in a liquid nitrogen trap. Figure 4 shows the ^{1}H-NMR spectrum of the resulting mixture, and the signals due to benzyl bromide, benzyl ether, and the aldehyde group were observed. Although details of the decomposition reaction are not clear at this time, it is obvious that the bromide ion reacted with the epoxide and the ammonium group above 100 °C to give these products.[20-22] Therefore, it is nothing to be wondered that drastic weight increase of copolymer-6 was observed on heating in a carbon dioxide atmosphere above 100 °C, which clearly indicates the occurrence of a self-catalyzed solid-state reaction of copolymer-6 with carbon dioxide because the reaction of the epoxide and carbon dioxide is initiated by the

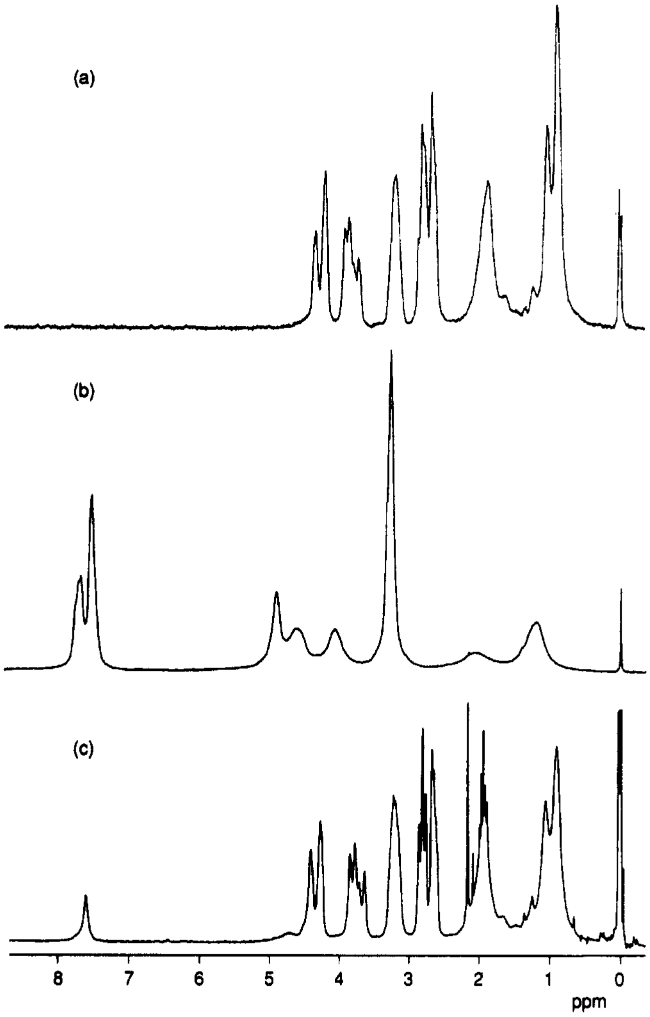


Figure 1. ^{1}H-NMR spectra of (a) PGMA (90 MHz, DMSO-d_6), (b) poly-**1b** (90 MHz, CD_3OD), and (c) copolymer-6 (90 MHz, DMSO-d_6).

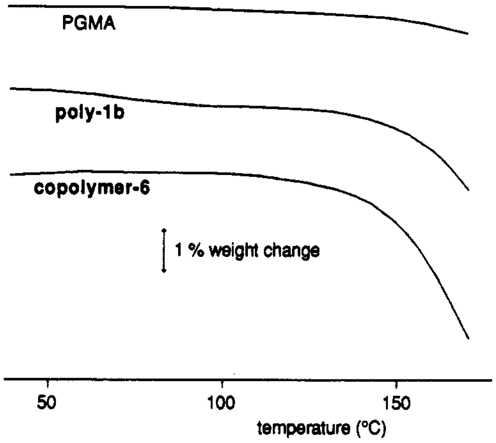


Figure 2. TGA profiles of PGMA, poly-**1b**, and copolymer-6 under a nitrogen atmosphere on heating at 10 K/min.

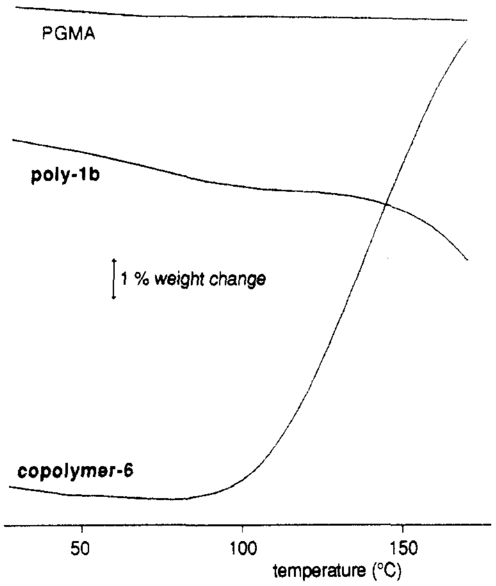
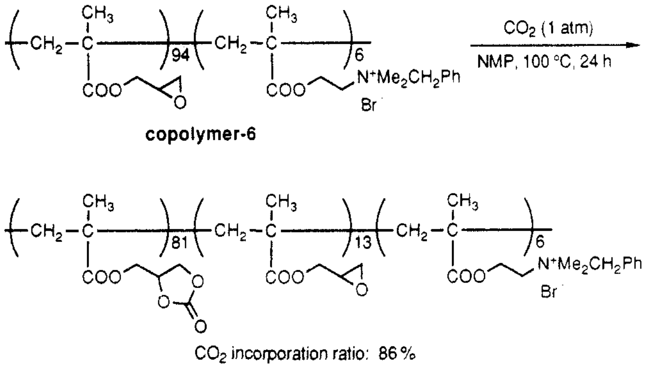


Figure 3. TGA profiles of PGMA, poly-**1b**, and copolymer-**6** under a carbon dioxide atmosphere on heating at 10 K/min.

Scheme 5



nucleophilic attack of the bromide anion on the epoxide group (Scheme 1).[5] The highly reactive alkoxy intermediate **A** can be considered as a common intermediate for the decomposition and incorporation. Since decomposition of the polymer to decrease its weight was superior to incorporation of carbon dioxide above 160 °C, further investigations of the solid-state reaction of copolymers with carbon dioxide were carried out at 100–160 °C.

Powders of copolymer-**6** and copolymer-**10** were exposed to carbon dioxide under atmospheric pressure at various temperatures. The incorporation ratios were estimated from the weight increase of the copolymers as shown in Figures 5 and 6, respectively. In every case, carbon dioxide was incorporated into the copolymer rapidly at the initial stage of the reaction, although the rate of the incorporation was depressed immediately and saturation of the incorporation appeared. The incorporation of carbon dioxide at the initial stage of the reaction was accelerated at higher temperature, although the saturation appeared earlier. When the reaction was carried out over 140 °C, the incorporation ratio decreased at the later stage of the reaction. Totally, the highest incorporation ratio was observed by the reaction at 130–140 °C, i.e., 76% for copolymer-**6** at 140 °C and 75% for copolymer-**10** at 130 °C. Although the incorporation of carbon dioxide into copolymer-**10** was faster than that of copolymer-**6**, saturation appeared earlier at lower temperature. Consequently, the maximum incorporation ratio was independent of the composition of the catalytic functional group in the copolymers. Contrary to the solution-state reaction, the reaction of copolymer-**6** with carbon dioxide was faster than that of PGMA catalyzed by 6 mol % of benzyltrimethylammonium bromide in the case of the solid-state reaction.[16] Since the solid state is a highly concentrated system, the higher local concentration of the catalytic functional group in a copolymer system might not be a disadvantageous point in the case of a solid-state reaction, and completely homogeneous dispersion of the catalytic functional group on the copolymer chain might result in the more effective incorporation reaction.[15]

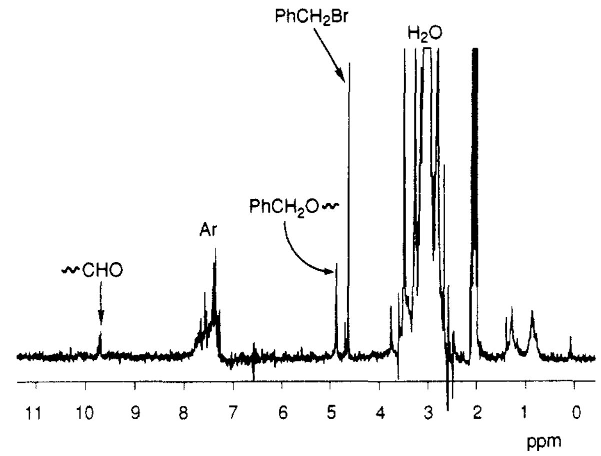


Figure 4. ^{1}H-NMR spectrum (90 MHz, acetone-d_6) of the volatile products obtained by the degradation of copolymer-**6** under a nitrogen atmosphere at 100 °C for 24 h.

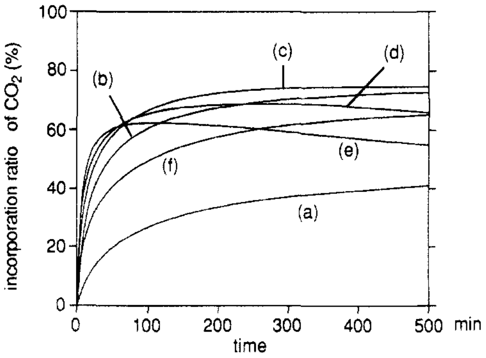


Figure 5. Incorporation of carbon dioxide into copolymer-**6** by the solid-state self-catalyzed polymer reaction under atmospheric pressure at (a) 100 °C, (b) 130 °C, (c) 140 °C, (d) 150 °C, and (e) 160 °C and (f) incorporation of carbon dioxide into PGMA catalyzed by 6 mol % of benzyltrimethylammonium bromide at 140 °C.

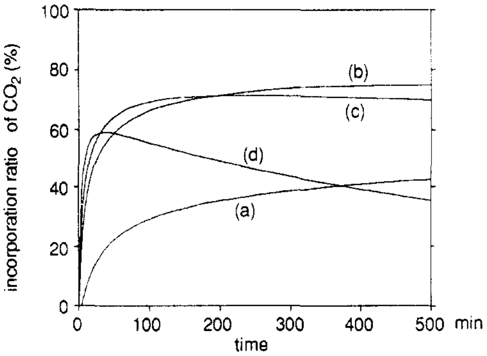


Figure 6. Incorporation of carbon dioxide into copolymer-**10** by the solid-state self-catalyzed polymer reaction under atmospheric pressure at (a) 100 °C, (b) 130 °C, (c) 140 °C, and (d) 160 °C.

The obtained polymers became insoluble in any solvent at the early stage of the reaction, even at 100 °C as observed in the solid-state reaction of PGMA and carbon dioxide.[16] Although the characteristic IR absorptions of both $\nu_{C=O}$ of the five-membered cyclic carbonate group at 1800 cm^{-1} and ν_{C-O-C} of the remaining epoxide group at 910 cm^{-1}

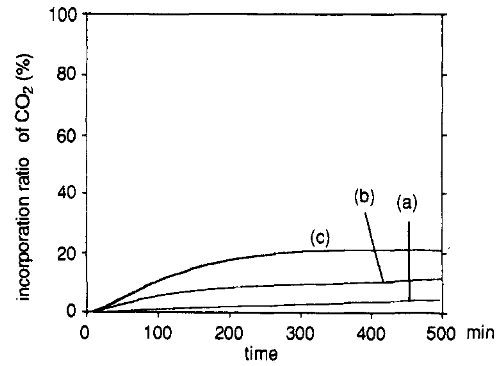


Figure 7. Incorporation of carbon dioxide into a mixture of PGMA and poly-**1b** by the solid-state polymer reaction under atmospheric pressure at (a) 100 °C, (b) 130 °C, and (c) 160 °C.

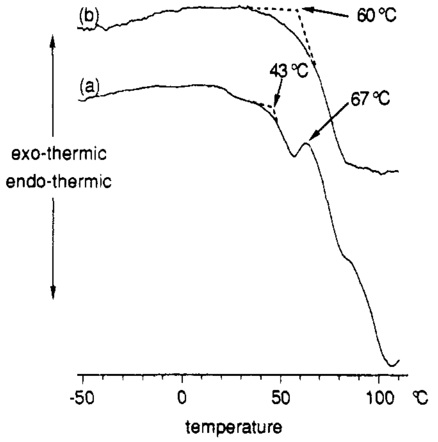


Figure 8. DSC profiles of the mixture of PGMA and poly-**1b** (6 mol %): (a) first scan and (b) second scan (after annealing at 110 °C).

were observed in the resulting polymer, the intensity of the absorption of the epoxide group was lower than that expected from the incorporation ratio and the relative ϵ value of these groups in each case.[23] Cross-linking by the simultaneous polymerization of the epoxide group initiated by the alkoxy intermediate **A** might occur. For example, after the reaction of copolymer-6 with carbon dioxide at 100 °C for 500 min, 41% of the incorporation ratio was estimated by weight increase of the polymer, while epoxide: carbonate = 46:54 as the unit ratio was estimated from its IR spectra. Assuming that the difference between these values came from the polymerization of the epoxide unit, it can be estimated that 24% of the epoxide group was converted to a poly(oxyethylene) unit in this case. Although such a side reaction was not observed in the reaction of PGMA and carbon dioxide in the solution state,[15] inter- and/or intramolecular reactions of **A** and the epoxide group can occur in a concentrated solid-state system.[16]

A mixture of PGMA and poly-**1b** (6 mol %) was exposed to carbon dioxide as shown in Figure 7 to examine the difference between copolymerization and a homopolymer mixture system. The incorporation ratio was lower than those of the copolymer system. To analyze the compatibility of PGMA (T_g = 43 °C)[19] and poly-**1b** (T_g > 120 °C), the thermal behavior of the mixture was analyzed by DSC, as shown in Figure 8. T_g of PGMA and exothermic transition at 67 °C were observed in the first scan, and only a single T_g at 60 °C was observed in the second scan. These results clearly showed that a homogeneous alloy of PGMA and poly-**1b** was formed by heating above 67 °C. Therefore, the low incorporation ratio of the homopolymer mixture system is not due to phase separation of the system but is due to the low local concentration of the catalytic functional group around the epoxide group because the quaternary ammonium group was strictly fixed in the polymer chain.

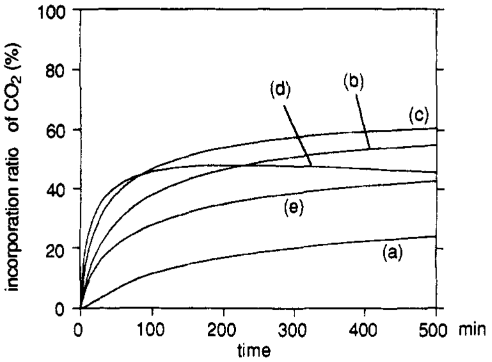


Figure 9. Incorporation of carbon dioxide into well-grained copolymer-5C by the solid-state self-catalyzed polymer reaction under atmospheric pressure at (a) 100 °C, (b) 130 °C, (c) 140 °C, and (d) 160 °C and (e) reaction of copolymer-5C without graining at 140 °C.

Since the incorporation of carbon dioxide into the copolymers occurred even after cross-linking, the reaction of the cross-linked polymer copolymer-5C with carbon dioxide was carried out. When well-grained copolymer-5C (average diameter was 150 μm) was exposed to carbon dioxide under atmospheric pressure, weight increase of copolymer-5C due to self-catalyzed incorporation of carbon dioxide was observed, as shown in Figure 9. The incorporation efficiency was, however, slightly lower than those of copolymer-6, i.e., the incorporation ratio at 140 °C for 500 min was 61%. Restricted mobility of the catalytic functional group in the cross-linked system might decrease the apparent catalytic activity. Surprisingly, when copolymer-5C was exposed to carbon dioxide without graining (diameter was about 1.5 mm), carbon dioxide was effectively incorporated into the bulk as well as the well-grained gel as shown in Figure 9(e), although the incorporation rate slightly decreased. It became clear that restricted mobility of the catalytic functional group in the system and the surface area are not essential for the incorporation of carbon dioxide in the solid-state system as the catalytic functional group was homogeneously dispersed in the system.

Conclusions

Effective self-catalyzed incorporation of carbon dioxide into linear or cross-linked copolymers having both epoxide and quaternary ammonium groups was demonstrated under atmospheric pressure. These polymers are expected to be applied as novel carbon dioxide incorporation materials. At this time, the complication of simultaneous polymerization of the epoxide group was unavoidable in the self-catalyzed carbon dioxide incorporation system. On the basis of the information that we have accumulated on the reaction of epoxide and carbon dioxide, the more effective and selective self-catalyzed carbon dioxide incorporation system will be constructed by the optimization of the epoxide and catalyst system.

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(23) The mole ratio of five-membered cyclic carbonate and epoxide can be calculated from their characteristic IR absorptions at 1800 (carbonate, $\nu_{\mathrm{C=C}}$) and 910 cm^{-1} (epoxide, $\nu_{\mathrm{C-O-C}}$), respectively, using the following equation:

$$\frac{[\mathrm{carbonate}]}{[\mathrm{carbonate}] + [\mathrm{epoxide}]} = \frac{A}{A + E}$$

where A denotes abs(1800 cm^{-1})/abs(910 cm^{-1}) and E denotes ϵ(1800 cm^{-1})/ϵ(910 cm^{-1}). The value of E calibrated by the corresponding homopolymers is 21.