Efficient Gas−Solid Phase Reaction of Atmospheric Carbon Dioxide into Copolymers with Pendent Oxirane Groups: Effect of Comonomer Component and Catalyst on Incorporation Behavior

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ABSTRACT: The appropriate choice of catalysts and comonomers improved the selectivity of the gas−solid-phase reaction of carbon dioxide into copolymers from glycidyl methacrylate (GMA), which transforms the pendent oxirane moieties to cyclic carbonate moieties. Benzyltributylammonium chloride ($BnBu_3NCl$) exhibited good and selective catalytic behavior owing to its appropriate mobility in the copolymer film and moderate catalytic activity. *n*-Butyl methacrylate proved to be an effective comonomer, resulting in higher incorporation efficiency and better selectivity by preventing the cross-linking reaction, allowing one to obtain soluble polymers bearing cyclic carbonate structure.

Introduction

Gas−solid phase reactions are one of the most environmentally benign chemical transformations, because they are free from volatile organic compounds.[1−8] However, the densely existing reactive groups and the heterogeneity often prevent the selective reactions that can be attained in the corresponding solution phase reactions. For example, we have developed the gas−solid-phase incorporation of carbon dioxide into oxirane containing polymers prepared from radical (co)polymerizations of glycidyl methacrylate (GMA).[5−8] This reaction can convert the polymers carrying oxirane groups into those carrying cyclic carbonate groups, potentially applicable as highly dielectric materials, polymer blends, and photopolymers.[9−17] However, this gas−solid-phase incorporation involves the concomitant cross-linking of oxirane that makes the resulting polymer insoluble, resulting in limiting the application of the products. Although the cross-linking reaction may be suppressed in the reaction using the copolymers of GMA and methyl methacrylate (MMA) with low oxirane contents at the temperatures below their glass transition temperatures (T_g), high carbon dioxide incorporation ratios could not be attained.[7] The low incorporation ratios may be ascribed to the higher T_gs of the copolymers with high MMA content arisen from the higher T_g of polyMMA (T_g = 122 °C) than polyGMA (T_g = 77 °C), i.e., the copolymers prepared from methacrylates with longer alkyl chain will be effective to attain the high incorporation ratios. It should be mentioned that the longer side chain in the copolymers is possible to suppress the nucleophilic addition of alkoxide to oxirane to improve the selectivity of the carbonate formation. Accordingly, we investigated the gas−solid-phase incorporation of carbon dioxide into the copolymers of GMA and various methacrylates (Scheme 1). Furthermore, various ammonium halides were examined as the catalyst to optimize the reaction conditions.

Experimental Section

Materials. Methyl methacrylate (MMA, Kanto Chemical), ethyl methacrylate (EMA, Tokyo Kasei Kogyo), *n*-butyl methacrylate (BMA, Tokyo Kasei Kogyo), *n*-hexyl methacrylate (HMA, Tokyo Kasei Kogyo), diethylene glycol methyl ether methacrylate (DGMMA, Tokyo Kasei Kogyo), and GMA (Kanto Chemical) were dried over CaH_2 and distilled under reduced pressure. Acetonitrile (ACN, Kanto Chemical) was dried over CaH_2 and distilled under nitrogen atmosphere. Benzyltrimethylammonium chloride ($BnMe_3NCl$, Kanto Chemical), benzyltriethylammonium chloride ($BnEt_3NCl$, Kanto Chemical), benzyltributylammonium chloride ($BnBu_3NCl$, Aldrich), tetramethylammonium chrolide (Me_4NCl, Wako Chemical), tetraethylammonium chloride (Et_4NCl, Wako Chemical), tetrabutylammonium chloride (Bu_4NCl, Kanto Chemical), tetrapentylammonium chloride ((n-$C_5H_{11})_4NCl$, Kanto Chemical), tetrahexylammonium chloride ((n-$C_6H_{13})_4NCl$, Aldrich), tetraheptylammonium chloride ((n-$C_7H_{15})_4NCl$, Kanto Chemical), tetrabutylammonium bromide (Bu_4NBr, Aldrich), and tetrabutylammonium iodide (Bu_4NI, Kanto Chemical) were used as received. Tetrabutylammonium fluoride (Bu_4NF) was used after extraction from silica gel supported Bu_4NF (Aldrich) with acetonitrile prior to use. The amounts of catalysts are indicated as molar percent toward oxirane groups in the copolymers. Radical copolymerization procedure was described in the previous reports. The copolymers and copolymer films were prepared as reported. Other materials were used as received unless otherwise noted.

Measurements. ^1H nuclear magnetic resonance (NMR) spectra were measured on a JEOL JNM-LA-270 instrument using tetramethylsilane as an internal standard (270 MHz). Fourier transform infrared (FT-IR) spectra were measured on a Horiba FT-210 instrument. Size exclusion chromatography (SEC) measurements were performed on a Tosoh HLC-8120 GPC equipped with Tosoh TSK-gel α-M, α-4000, α-3000, and α-2500 tandem columns using *N,N*-dimethylformamide (DMF) containing 50 mM lithium bromide and 50 mM phosphoric acid as an eluent at 40 °C. Polystyrene standards were used for calibration. Thermogravimetric analyses (TGA) were performed on a Seiko TG/DTA6000 (EXSTER6000). Differential scan calorimetry (DSC) measurements were performed on Seiko DSC-220 under nitrogen atmosphere (scan rate: 10 °C/min).

Gas—Solid Phase Reaction of Carbon Dioxide and Copolymer Film.[3] A typical procedure is shown as follows. Copolymer films were prepared from the acetonitrile or tetrahydrofuran solutions containing the catalysts. A TGA sample

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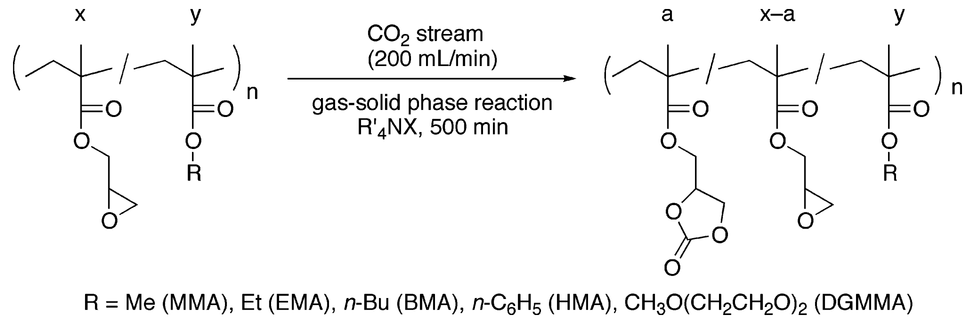
Scheme 1. Gas−Solid Phase Incorporation of Carbon Dioxide into Films of Copolymers Prepared from Radical Copolymerization GMA and Various Methacrylates[a]



[a] R = Me (MMA), Et (EMA), *n*-Bu (BMA), *n*-C_6H_5 (HMA), $CH_3O(CH_2CH_2O)_2$ (DGMMA).

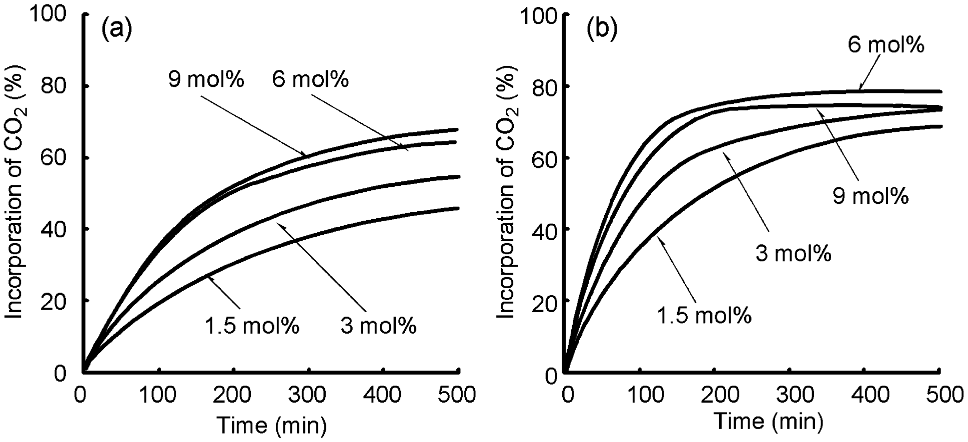


Figure 1. Gas-solid-phase incorporation of carbon dioxide into poly(GMA_{33}-MMA_{67}) using various amount of $BnMe_3NCl$ at 110 (a) and 120 °C (b).

pan containing copolymer film (5 mg) was placed in the TGA instrument under carbon dioxide atmosphere (gas flow rate: 200 mL/min). Temperature was raised to reaction temperature and the incorporation behavior was investigated with gravimetric changes monitored by TGA.

Results and Discussion

Effect of Catalyst on Gas—Solid-Phase Incorporation of Carbon Dioxide into Film of Poly(GMA_{33}-*co*-MMA_{67}). The effect of catalyst amount was examined in the carbon dioxide incorporation reaction into poly(GMA_{33}-*co*-MMA_{67}) at 110 and 120 °C using $BnMe_3NCl$ (Figure 1). All the resulting polymers were insoluble in any common organic solvents. In the reaction at 110 °C, the carbon dioxide incorporation rate increased as the increase of the catalyst amount. The incorporation rates in the reactions with 6 and 9 mol % of the catalysts were almost identical, probably because the excess amount of the catalyst resulted in considerable degree of the concomitant cross-linking that consumed the oxirane moiety. This presumption agrees with the result of the reaction at 120 °C, in which the carbon dioxide incorporation ratios decreased for the catalyst concentration as 6 mol % > 9 mol % > 3 mol % > 1.5 mol %. This result revealed that the appropriate amount of catalyst must be used to attain the selective reaction, and hence the following experiments were conducted using 6 mol % of catalysts.

Table 1. Gas−Solid Phase Incorporation of Carbon Dioxide into Film of Poly(GMA_{33}-*co*-MMA_{67}) Using Various Ammonium Chlorides[a]

run	catalyst[b]	temp (°C)	incorporation ratio (%)[c]
1	$BnMe_3NCl$	110	62
2	$BnMe_3NCl$	120	71
3	$BnEt_3NCl$	110	66
4	$BnEt_3NCl$	120	72
5	$BnBu_3NCl$	110	76
6	$BnBu_3NCl$	120	79
7	Et_4NCl	110	53
8	Et_4NCl	120	63
9	Bu_4NCl	110	77
10	Bu_4NCl	120	66
11	$(n\text{-}C_5H_{11})_4NCl$	110	73
12	$(n\text{-}C_5H_{11})_4NCl$	120	63
13	$(n\text{-}C_6H_{13})_4NCl$	110	78
14	$(n\text{-}C_6H_{13})_4NCl$	120	63
15	$(n\text{-}C_7H_{15})_4NCl$	110	80
16	$(n\text{-}C_7H_{15})_4NCl$	120	63

[a] Reaction conditions: CO_2 flow rate 200 mL/min, 500 min. [b] 6 mol % relative to GMA unit molar content. [c] Estimated by weight increase measured by TGA.

Various ammonium chlorides were examined to optimize the catalyst in the reactions at 110 and 120 °C (Table 1). When benzyltrialkylammonium chlorides were used, $BnBu_3NCl$ was the most effective catalyst. The better reactivity of $BnBu_3NCl$ is postulated to correlate with its compatibility and flexibility; i.e., the salt with longer alkyl chains will be more compatible with the copolymer than salts with less organic groups, and its flexibility will give sufficient mobility in the solid-state polymer. Accordingly, more flexible tetraalkylammonium chlorides were also examined. Although Me_4NCl is not compatible with the film, the salts having longer alkyl chains than ethyl group are compatible with the film. At 110 °C, the catalysts having alkyl groups longer than butyl group resulted in the good incorporations, whereas Et_4NCl incorporated carbon dioxide moderately. On the other hand, the incorporation ratios decreased at 120 °C (runs 10, 12, 14, and

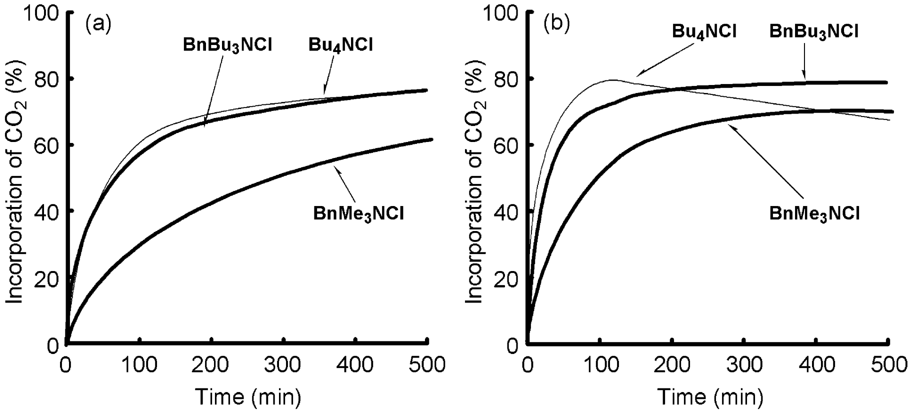


Figure 2. Time vs carbon dioxide incorporation ratio curves in the gas−solid-phase reaction of carbon dioxide and poly(GMA$_{33}$-*co*-MMA$_{67}$) using 6 mol % of BnMe$_3$NCl, BnBu$_4$NCl, and Bu$_4$NCl at 110 (a) and 120 (b) °C.

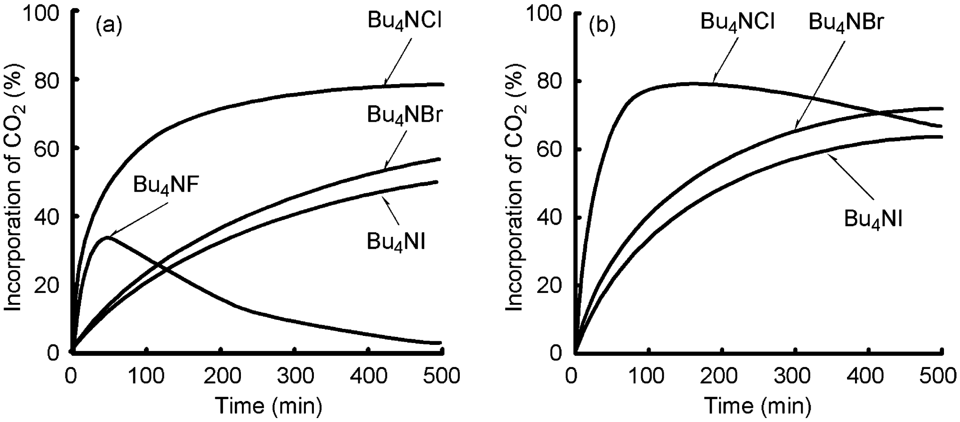


Figure 3. Time vs carbon dioxide incorporation ratio curves in the gas−solid-phase reaction of carbon dioxide and poly(GMA$_{33}$-*co*-MMA$_{67}$) using 6 mol % of tetrabutylammonium halides at 110 (a) and 120 (b) °C.

16). The incorporation ratios vs time for BnMe$_3$NCl, BnBu$_3$NCl, and Bu$_4$NCl are shown in Figure 2. The incorporation ratios increased with increasing the reaction time for benzyltrialkylammonium salts at both temperatures. The incorporation ratio using Bu$_4$NCl also increased as time proceeded at 110 °C (Figure 2a), while the decrease of the incorporation ratio was observed in the latter stage of the reaction at 120 °C (Figure 2b). Other tetraalkylammonium chlorides also showed the same tendency, indicating that these highly active salts may initiate the ring-opening polymerization of the resulting five-membered cyclic carbonate via elimination of carbon dioxide. That is, the appropriate reaction time must be set in the reactions employing the catalysts with high activities, while the reactions using the moderate catalysts are suitable to avoid the following undesired side reactions. Despite the improved incorporation ratio, all the resulting polymers were insoluble in any common organic solvents unfortunately.

The effect of halides in ammonium salt catalysts, which affect the catalytic efficiency in the reaction of oxiranes and carbon dioxide in the solution state,[18,19] was also examined (Figure 3). At 110 °C, the initial reaction rates using Bu$_4$NF and Bu$_4$Cl are significantly faster than those using Bu$_4$NBr and Bu$_4$NI. However, the incorporation ratio in the reaction using Bu$_4$NF decreased after 36 min, and the final incorporation ratio was only 1.5%. The high nucleophilicity of fluoride would have enhanced the ring-opening of oxirane to form the alkoxide in which the fluoride is not labile enough to produce five-membered cyclic carbonate. That is, the selectivity in the reaction using Bu$_4$NF prefers the anionic polymerization of oxiranes and, moreover, the resulting five-membered cyclic carbonate over the cyclic carbonate formation.

Effect of Comonomer Component on Gas—Solid-Phase Incorporation of Carbon Dioxide into Film of PGMA-Based Copolymers. To optimize the comonomer component, the gas−solid-phase incorporation of carbon dioxide was examined for various GMA-based copolymers, prepared from radical copolymerization of GMA and methacrylates, using 6 mol % of BnBu$_3$NCl as a catalyst (Table 2). The reactions were conducted at 100 and 110 °C in order to avoid the side reactions consuming the resulting cyclic carbonate. Although the carbon dioxide incorporation into poly(MMA$_{33}$-*co*-GMA$_{67}$) gave insoluble polymers (runs 1 and 2), the copolymers composed of the comonomers with longer alkyl chains gave soluble or swellable polymers (runs 3−8). The carbon dioxide incorporation ratios were higher in the reactions for poly(EMA$_{34}$-*co*-GMA$_{66}$) and poly(BMA$_{31}$-*co*-GMA$_{69}$). By contrast, the copolymer bearing ether chain gave the insoluble products with relatively lower carbon dioxide incorporation ratios (run 9). These results suggest that this gas−solid-phase carbon dioxide incorporation depends on the T_g and length of alkyl chain in the comonomer component. The lower T_g may provide high mobility to catalysts and high permeability of carbon dioxide into the film. A plausible reason for the unsuccessful result in the reaction of poly(DGMMA$_{35}$-*co*-GMA$_{65}$) is the increased polarity by the diethylene

Table 2. Gas−Solid Phase Incorporation of Carbon Dioxide into Films of Oxirane-Containing Copolymers Using $BnBu_3NCl^a$

run	copolymer^b (M_n, M_w/M_n)^c	T_g (°C)^d	temp (°C)	CO_2 incorporation ratio (%)^e	solubility^f (M_n, M_w/M_n)^c
1	poly(MMA_{33}-*co*-GMA_{67})	105	100	51	X
2	(20000, 1.73)		110	76	X
3	poly(EMA_{34}-*co*-GMA_{66})	74	100	71	○ (31200, 4.00)
4	(23000, 1.85)		110	73	△
5	poly(BMA_{31}-*co*-GMA_{69})	48	100	82	○ (24800, 2.40)
6	(21200, 2.15)		110	77	△
7	poly(HMA_{35}-*co*-GMA_{65})	25	100	54	○ (25900, 2.70)
8	(22900, 2.50)		110	50	○ (26500, 3.84)
9	poly($DGMMA_{35}$-*co*-GMA_{65}) (26400, 2.41)	−23	100	59	X

[a] Reaction conditions: CO_2 flow rate 200 mL/min, 500 min, catalyst amount = 6 mol %. [b] The copolymer compositions were determined by ^1H NMR spectroscopy. [c] Estimated by SEC (DMF, polystyrene standards). [d] Determined by DSC. [e] Estimated by weight increase measured by TGA. [f] Solubility in DMF. (○) soluble; (△) partially soluble or swell; (X) insoluble. BMA: *n*-butyl methacrylate. DGMMA: diethylene glycol methyl ether methacrylate. EMA: ethyl methacrylate. GMA: glycidyl methacrylate. HMA: *n*-hexyl methacrylate. MMA: methyl methacrylate.

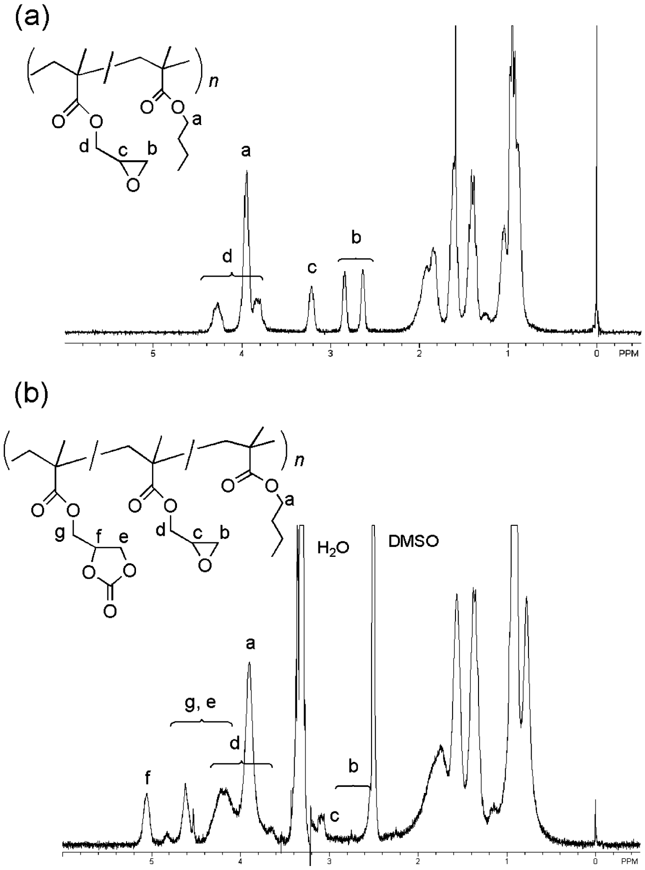


Figure 4. ^1H NMR spectra of poly(BMA_{31}-*co*-GMA_{39}) (a, 270 MHz, $CDCl_3$) and the polymer obtained by its gas−solid-phase reaction with carbon dioxide using $BnBu_3NCl$ at 100 °C (b, 270 MHz, d_6-DMSO).

glycol chain, which is supposed to be inappropriate for the permeation of less polar carbon dioxide.

The soluble polymers obtained by the reactions at 100 °C (Table 2, runs 3, 5, and 7) were characterized by ^1H NMR spectroscopy and SEC analysis. As an example, Figure 4 shows the ^1H NMR spectrum of poly(BMA_{31}-*co*-GMA_{39}) and the polymer obtained by its gas−solid-phase reaction with carbon dioxide at 100 °C. The ^1H NMR spectrum clearly shows the signals assignable to the cyclic carbonate at 4.2−5.2 ppm, whose integral ratio to those assignable to the oxirane allows us to calculate the carbon dioxide incorporation ratio as 91%. The incorporation ratio higher than that determined by

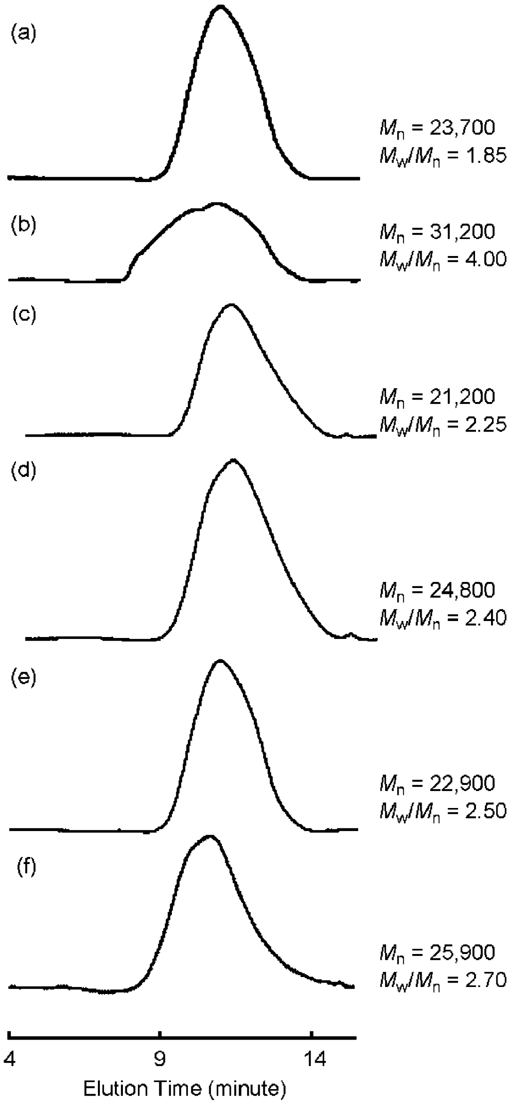


Figure 5. SEC profiles of poly(EMA_{34}-*co*-GMA_{66}) (a), poly(BMA_{31}-*co*-GMA_{39}) (c), poly(HMA_{35}-*co*-GMA_{65}) (e), and the polymers obtained by their gas−solid-phase reaction with carbon dioxide using $BnBu_3NCl$ at 100 °C (b, d, and f, respectively).

TGA (82%) is ascribable to the consumption of the oxirane groups by intra- or intermolecular polymerization, where the solubility of the resulting polymer suggests that the intramolecular polymerization is predominant. Figure 5 shows the SEC profiles of the original and the resulting polymers. Whereas the SEC profile of the polymer after the reaction of poly(EMA$_{34}$-*co*-GMA$_{66}$) at 100 °C shows an obvious shoulder at the high molecular weight region (Figure 5a,b), those of the copolymers containing the longer side chains exhibit negligible shoulders (Figure 5c−f). This result correlates well with the molecular weight distributions increased by the reactions; i.e., the reactions of the copolymers with longer alkyl side chain exhibit better selectivity in the incorporation of carbon dioxide to afford cyclic carbonate. Both the reactions of poly(HMA$_{35}$-*co*-GMA$_{65}$) at 100 and 110 °C gave the soluble polymers, while the reaction at 100 °C gave the polymer with the lower molecular weight distribution owing to the better selectivity.

Conclusions

This paper has described the effects of the comonomer component and catalyst on the gas−solid phase reaction of carbon dioxide into copolymers prepared from GMA and various methacrylates. For example, carbon dioxide is incorporated very selectively in the reaction with poly(BMA$_{31}$-*co*-GMA$_{69}$) film at 100 °C using $BnBu_3NCl$ to afford a soluble polymer carrying carbonate groups. This gas−solid-phase reaction depends on the T_g of the reactant polymer and the length of the side chain; i.e., lower T_g leads to acceleration of the incorporation of carbon dioxide and longer alkyl chain enhances the selectivity of the reaction but slows the carbon dioxide incorporation rate.

Because this gas−solid-phase reaction may convert various oxirane-carrying polymers into carbonate-carrying polymers, the potential application of this method includes the fabrication of ion-conducting materials based on the high affinity of carbonate groups to alkali metals via simple procedure.

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