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DIRECT INCORPORATION OF CARBON DIOXIDE INTO POLY(GLYCIDYL METHACRYLATE-CO-ACRYLONITRILE) USING QUATERNARY AMMONIUM SALT CATALYST AND ITS APPLICATION TO POLYMER BLENDS

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DIRECT INCORPORATION OF CARBON DIOXIDE INTO POLY(GLYCIDYL METHACRYLATE-CO-ACRYLONITRILE) USING QUATERNARY AMMONIUM SALT CATALYST AND ITS APPLICATION TO POLYMER BLENDS

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ABSTRACT

The study is related to an integrated process for the utilization of carbon dioxide to polymer blends via a copolymer bearing cyclic carbonate group. Poly(glycidyl methacrylate-co-acrylonitrile) [poly(PGMA-co-AN)] was converted to a poly[(2-oxo-1,3-dioxolane-4-yl) methyl methacrylate-co-acrylonitrile] [poly(DOMA-co-AN)] by the polymer reaction with carbon dioxide using quaternary ammonium salt as a catalyst. Among the quaternary salts tested, the one having a larger alkyl group and more nucleophilic counter anions, exhibited better catalytic activity in the addition of CO_2 to poly(GMA-co-AN). In a semibatch reaction system, pseudo first-order rate equation agreed with the experimental results. The miscibility of poly(DOMA-co-AN) with styrene/acrylonitrile (SAN, 25 wt% of AN) copolymer or methyl methacrylate/ethyl acrylate (MMA-EA, 7 wt% of EA) copolymer has been investigated both by differential scanning calorimetry (DSC) and visual inspection of the blends. Poly(DOMA-co-AN) formed clear films when blended with SAN or MMA-EA. DSC analysis also showed that poly(DOMA-co-AN)

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containing blends were miscible in the whole composition ranges. The glass transition temperatures (T_g) of the polymer blends closely matched the Fox equation.

Key Words: Carbon dioxide; Addition; Poly(glycidyl methacrylate-co-acrylonitrile); Quaternary ammonium salt; Blends

INTRODUCTION

Recently, the chemistry of carbon dioxide and the carbon dioxide fixation have received much attention both from an economical and environmental point of view: utilization of the least expensive carbon source and reduction of global warming gas. The reaction of carbon dioxide with oxiranes to produce cyclic carbonates has been of great interest as a useful method for its fixation by chemical processes.[1,2] Polymers bearing five-membered cyclic carbonate groups can be used as new polymeric materials for optical and electric devices.[3–5] They can also be applied as polymeric polar solvents for inorganic electrolytes and as hot dyes in nonlinear optical films.

The synthesis of cyclic carbonates from the reaction of carbon dioxide with oxiranes has been widely studied by using Lewis acids, transition-metal complexes, organometallic compounds, and alkali metal salts in the presence of crown ethers or quaternary ammonium salts under high pressure.[6–9] The reaction mechanism and catalytic effects for the synthesis of five-membered cyclic carbonates under atmospheric pressure using low molecular weight or polymer-supported quaternary onium salts were also reported.[10–12] It is known that a vinyl monomer bearing a cyclic carbonate group such as (2-oxo-1,3-dioxalane-4-yl) methyl methacrylate (DOMA) is extremely sensitive to the polymerization and difficult to handle.[13–15] Thus, the quantitative polymer reaction of epoxide polymers with carbon dioxide can be one of the most effective methods to obtain cyclic carbonate polymers. The reaction of poly(glycidyl methacrylate) (PGMA) with carbon dioxide to produce poly(-DOMA) was previously studied by several authors.[13,16,17] Blends of poly(-DOMA) bearing cyclic carbonate groups with some commercial polymers have also been reported for a more versatile application of the polymer.[18]

In this study, we propose an integrated process for the chemical fixation of carbon dioxide to polymer materials via cyclic carbonates as shown in Fig. 1. First, we synthesized poly(glycidyl methacrylate-co-acrylonitrile) [poly(PGMA-co-AN)] from glycidyl methacrylate (GMA) and acrylonitrile (AN). Then, CO_2 was incorporated into the copolymer to form poly[(2-oxo-1,3-dioxolane-4-yl) methyl methacrylate-co-acrylonitrile] [poly(DOMA-co-AN)]. Finally, blends of poly(DOMA-co-AN) with styrene/acrylonitrile (SAN, 25 wt% of AN) copolymer or methyl methacrylate/ethyl acrylate (MMA-EA, 7 wt% of EA) copolymer were prepared to test their miscibility.

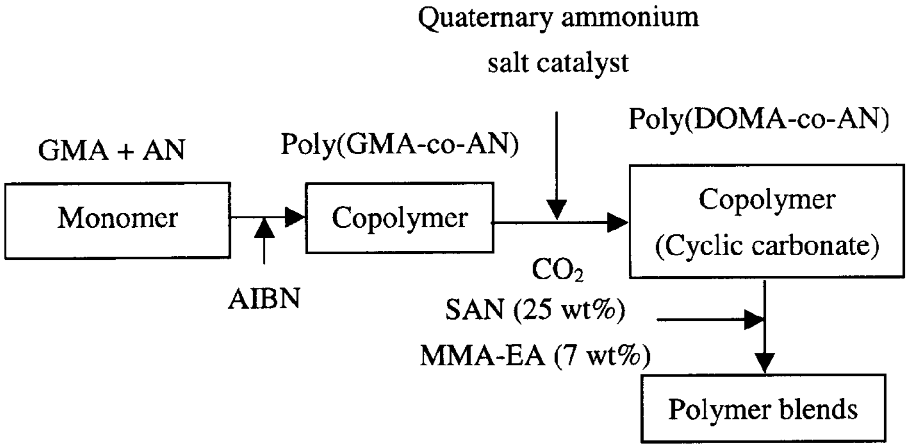


Figure 1. Integrated process for the catalytic fixation of carbon dioxide to polymer materials.

Miscibility of the blends was investigated by using differential scanning calorimetry (DSC) and optical clarity test.

EXPERIMENTAL

Materials

Glycidyl methacrylate (GMA, Junsei), acrylonitrile (AN, Junsei), methyl methacrylate (MMA, Junsei), and ethyl acrylate (EA, Junsei) monomers were washed with an aqueous sodium hydroxide solution, rinsed with distilled water, then dried over calcium chloride. Other reagents were reagent grades and used as received. Quaternary ammonium salts, such as tetrabutyl ammonium chloride (TBAC), tetrabutyl ammonium bromide (TBAB), tetrabutyl ammonium iodide (TBAI), tetraoctyl ammonium chloride (TOAC), and tetrahexyl ammonium chloride (THAC) were all reagent grades and were used as purchased without further purification. N-methyl-2-pyrrolidinone (NMP, Junsei), N,N′-dimethyl formamide (DMF, Junsei), dimethyl sulfoxide (DMSO, Junsei), and α,α'-azobisisobutyronitrile (AIBN, Junsei) were used as received. Styrene/acrylonitrile (SAN, Mw: 165,000; AN contents: 25 wt%) were purchased from Aldrich.

Polymer Synthesis

A radical copolymerization of GMA (12 g) with AN (4 g) [poly(GMA-co-AN)] was prepared in dimethyl sulfoxide (DMSO,260 mL) using α,α'-azobisisobutyronitrile (AIBN, 0.15 g) as an initiator at 7°C for 24 hours under nitrogen atmosphere, then the solution was poured into distilled water to give a precipitate. The copolymer was recovered using an excess of methanol and dried in vacuum at 30°C for 12 hours.

Copolymerization of MMA (4.7 g) and EA (0.4 g) was performed in acetonitrile (50 mL) using AIBN (0.1 g) at 70°C for 24 hours under nitrogen atmosphere. A copolymer with EA compositions (7 wt%) in feed was prepared. Hereafter, the copolymer will be designated as MMA-EA (7 wt%) for brevity. The copolymer was recovered using an excess of methanol and was purifed by chloroform/methanol reprecipitation.

Synthesis of Poly(DOMA-co-AN) by Direct Incorporation of Carbon Dioxide to Poly(GMA-co-AN)

The synthesis of a copolymer of DOMA and AN [poly(DOMA-co-AN)] from poly(GMA-co-AN) and CO_2 was carried out using quaternary ammonium salts as shown in Sch. 1. One-half mmol of catalyst was introduced to a 250 mL four-neck semibatch reactor containing a mixture of 4 g of poly(GMA-co-AN) and 120 mL of DMSO, and the solution was heated to a desired temperature (100°C). Reaction was started by stirring the solution under a slow stream of CO_2 (10 mL/min) and continued for 10 hours. The yield of CO_2 addition to the epoxide polymer was calculated using ^{1}H-NMR and gel permeation chromatography (GPC, Waters 244) in a similar way as reported by Sakai et al.[16] The copolymer composition of poly(GMA-co-AN) was first determined from the ratio of area in the copolymer using the ^{1}H-NMR spectrum. The ratio of area for the copolymer peak is 75.5:24.5 (GMA:AN). Then, the sample of reaction mixture was taken and analyzed to check the amount of CO_2 in poly(GMA-co-AN) using GPC. The yield of CO_2 addition is defined as follows:

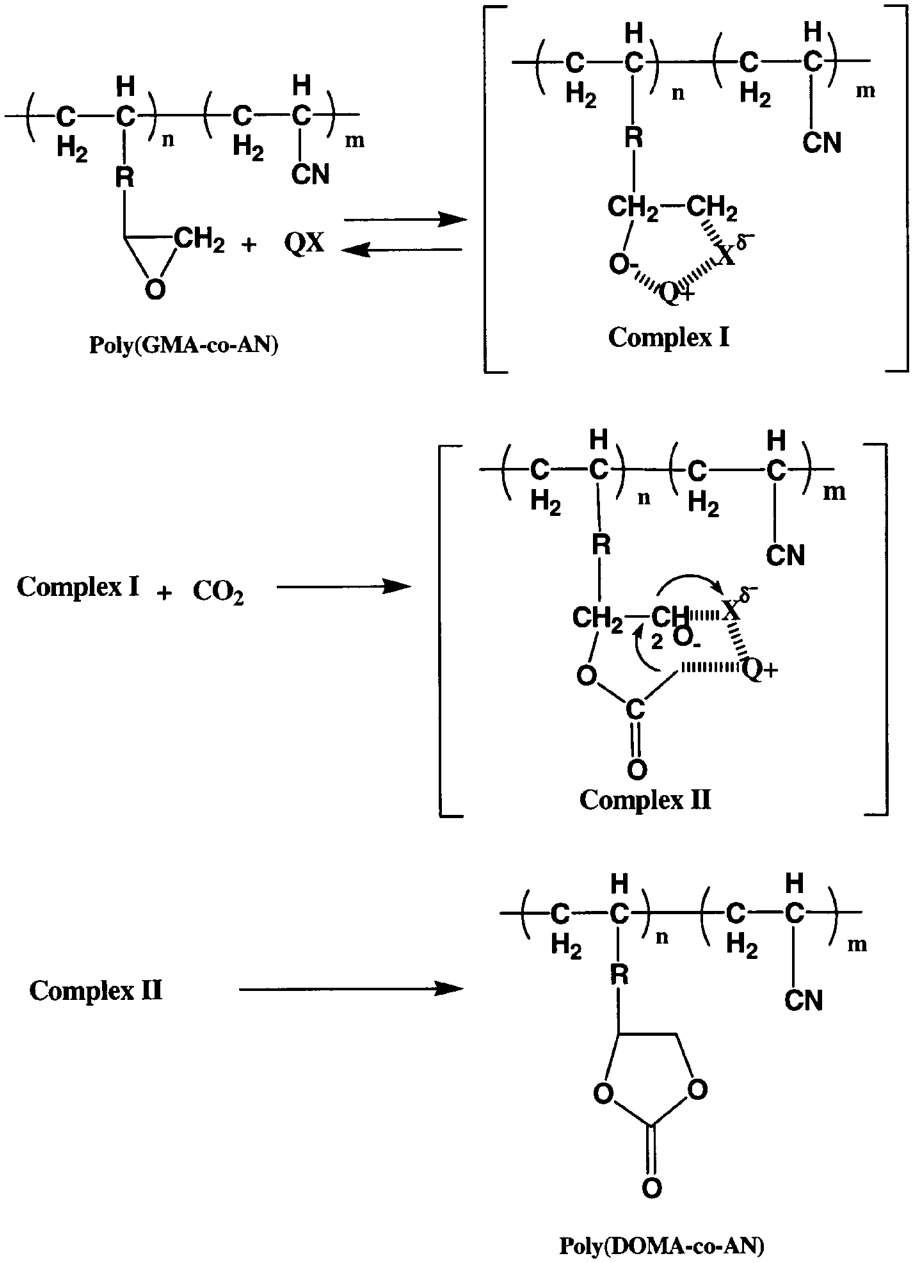
$$\text{Yield of } CO_2 \text{ addition } (\%)$$

$$= \frac{\text{Number of unit of cyclic carbonate group in poly(DOMA-co-AN)}}{\text{Number of unit of epoxide group in poly(GMA-co-AN)}} \times 100$$

The identification of poly(DOMA-co-AN) was performed by ^{1}H-NMR and FTIR spectroscopy.

Preparation of Blends

To prepare blend films, weighed amounts of poly(DOMA-co-AN) and SAN (25 wt%) or MMA-EA (7 wt%) with a given composition were cast from 10 wt% solution in DMF. The films were dried under vacuum for 3 days at room temperature.



Scheme 1. Reaction mechanism of the synthesis of poly(DOMA-co-AN) by the incorporation of carbon dioxide into poly(GMA-co-AN).

Measurements

^{1}H-NMR spectra were recorded with a Bruker 300 MHz NMR spectrophotometer. For the measurement, 1.5 mg of sample was dissolved in 0.5 mL of solvent(dimethyl-d_6-sulfoxide(DMSO-d_6)) in a 5 mL tube at 25°C. FTIR spectra were obtained by an Analect FX6160 FTIR spectrometer. Thin films of blends were prepared by direct casting on a glass. The solvent was removed by drying in a vacuum oven at room temperature for 2 weeks. The thickness of the films were in the range of 2–3 µm. Thirty-two scans at a resolution of 2 cm^{-1} were signal averaged. The molecular weight of polymers was determined from a GPC (Waters 244). The measurement was conducted using an RI detector, DMF as an eluent with a flow rate of 1.0 mL/min at 25°C. Polystyrene was used as a standard for calibration. Glass transition temperatures (T_g) were measured using a differential scanning calorimetry (DSC, Perkin Elmer) calibrated with pure indium as a standard. Experiments were carried out in a nitrogen atmosphere. In order to avoid the thermal history from the samples packed in the aluminum pan and to eliminate any small traces of solvent, samples were heated to 450 K at a heating rate of 10°C/min. All the glass transition temperatures were taken as the half-height point of the heat capacity jump in the second scan.

RESULTS AND DISCUSSION

Synthesis of Poly(DOMA-co-AN) from Poly(GMA-co-AN) with Carbon Dioxide

The conversion of the epoxide ring in poly(GMA-co-AN) to the five-membered cyclic carbonate group in poly(DOMA-co-AN) could be identified by ^{1}H-NMR and FTIR spectra. The characteristic peaks are as follows: $4.0 \sim 4.5$ (-O$\underline{H_2}$-, in side chain), $5.0 \sim 5.2$ (-$\underline{H}$CO-, in cyclic carbonate), $4.5 \sim 4.8$ ppm (-OC$\underline{H_2}$-, in cyclic carbonate). The IR-spectrum of the poly-(DOMA-co-AN) exhibited an absorption peak at 1800 cm^{-1} ($C=O$ of cyclic carbonate), whereas the peak was not observed on the IR spectrum for poly(GMA-co-AN). Table 1 also includes the molecular weights and glass transition temperatures of poly(GMA-co-AN) and poly(DOMA-co-AN), as well as SAN (25 wt%) and MMA-EA (7 wt%).

Kinetic Studies in a Semi-batch Reactor

For the addition reaction of CO_2 to poly(GMA-co-AN), the following elementary reaction steps can be proposed according to the mechanism shown in Sch. 1, where we set R = poly(GMA-co-AN), P = poly(DOMA-co-AN), and QX = quaternary ammonium salt catalyst:

Table 1. Molecular Weights and Glass Transition Temperatures of Polymers

Sample	M_W[a]	M_n[a]	M_w/M_n[a]	T_g (°C)[b]
Poly(GMA-co-AN)[c]	114,000	71,000	1.61	72
Poly(DOMA-co-AN)[d]	121,000	88,000	1.38	64
SAN (25 wt%)[e]	165,000	113,000	1.46	108
MMA-EA (7 wt%)[f]	124,000	108,000	1.15	120

[a] Weight average molecular weight measured by GPC.

[b] Number average molecular weight measured by DSC.

[c] Prepared with 12 g of GMA, 4 g of acrylonitrile, and 260 mL of DMSO at 70°C for 24 hours

[d] Prepared with 4 g of poly(GMA-co-AN), 120 mL of DMSO, and 0.5 mmol of TOAC at 100°C for 12 hours.

[e] Supplied by Aldrich Chemical Co., Inc.

[f] Prepared with 4.7 g of MMA, 0.4 g of EA, and 50 mL of acetonitrile at 70°C for 24 hours.

$$R + QX \underset{k_2}{\overset{k_1}{\rightleftarrows}} RQX^* \tag{1}$$

$$RQX^* + CO_2 \xrightarrow{k_3} P + QX \tag{2}$$

k_1, k_2, and k_3 are reaction rate constants.

The rate of formation of P can be written as:

$$dP/dt = k_3[CO_2][RQX^*] \tag{3}$$

Adopting a steady-state approximation method for the activated complex RQX*, the net rate of the RQX* formation can be written as Eq. (4):

$$d[RQX^*]/dt = k_1[R][QX] - k_2[RQX^*] - k_3[CO_2][RQX^*] = 0 \tag{4}$$

Rearranging this equation, one can obtain Eq. 5:

$$[RQX^*] = k_1[R][QX]/(k_2 + k_3[CO_2]) \tag{5}$$

Substituting Eqs. (3) to (5), the rate of formation of P can be written as:

$$dP/dt = k_1k_3[R][CO_2][QX]/(k_1 + k_3[CO_2]) \tag{6}$$

When the addition reaction of CO_2 to poly(GMA-co-AN) is carried out in a semi-batch reactor with a constant flow of CO_2, the absorption rate of CO_2 into the solvent can be assumed much faster than that of CO_2 addition reaction with poly(GMA-co-AN). Therefore, the concentration of dissolved CO_2 in a solvent can be assumed constant.

The rate of product formation is:

$$dP/dt = k'[R][QX] \tag{7}$$

where k' is $k_1k_3[CO_2]/(k_2 + k_3[CO_2])$.

Since the catalyst concentration does not change during the reaction, the pseudo first-order rate equation can be applied.

$$\mathrm{dP/dt = -dR/dt = k[R]} \tag{8}$$

Integration of Eq. (8) gives Eq. (9).

$$\mathrm{ln[poly(GMA\text{-}co\text{-}AN)]_0/[poly(GMA - co - AN)]) {=} kt} \tag{9}$$

From the slope of the linear plot between ln[poly(GMA-co-AN)]$_0$/[poly(GMA-co-AN)] vs. time, one can estimate the pseudo first-order rate constant k.

Structure-Activity Relationship of the Catalysts

The catalytic activity of a quarternary ammonium salt usually depends on the corresponding catalyst cation and counter anion.[19,20] In order to understand the effects of the cation structure in the reaction of poly(GMA-co-AN) and CO_2, quaternary ammonium chloride catalysts of different alkyl cations TOAC, THAC, and TBAC were used at 100°C. The yield of CO_2 addition with catalysts of different alkyl chain lengths are summarized in Table 2. The amount of CO_2 added to poly(GMA-co-AN) was calculated from the difference of molecular weight of poly(DOMA-co-AN) and poly-(GMA-co-AN). The yield of CO_2 addition increased in the order of TBAC < THAC < TOAC. The addition rate of CO_2 into poly(GMA-co-AN) increased with an alkyl chain length of the cation of quaternary am-

Table 2. Yield and Amount of CO_2 Addition to Poly(GMA-co-AN) for Different Cations or Anions of Quaternary Ammonium Salts

				Unit		
Material	Cat.	Mn[a]	Amount[b]	Epoxide	Cyclic Carbonate	Yield of CO_2 Addition (%)
Poly(GMA-co-AN)	–	71,000	–	374	–	–
Poly(DOMA-co-AN)	TOAC	84,000	13,100	77	297	79.7
	THAC	83,000	12,400	92	282	75.3
	TBAC	82,000	11,900	104	270	72.1
	TBAB	81,000	10,800	129	245	65.4
	TBAI	80,000	9,000	152	222	59.3

Reaction condition: 4.0 g of poly(GMA-co-AN), 0.5 mmol of catalysts, 120 mL of DMSO at 100°C for 10 hours.

[a] Number average molecule weight.

[b] The amount of CO_2 added to poly(GMA-co-AN).

monium salts. The catalyst cation having a large alkyl group is easily dispersed in organic solvent. Bulky quaternary salt, having longer distances between cation and anion, is generally known to exhibit higher activity in activating anions.[19] This explains why they are more effective in nucleophilic attack of the anion to the oxirane ring of poly(GMA-co-AN). Figure 2 shows the plots of ln($[C_{AO}]/[C_A]$) vs. time for the different cations of quaternary ammonium salts. Since good straight lines are obtained, the reaction can be considered as pseudo first-order with respect to [poly(GMA-co-AN)]. From the slope, the reaction rate constant was determined as 0.19 h^{-1} for TOAC, 0.17 h^{-1} for THAC, and 0.15 h^{-1} for TBAC, respectively.

In order to understand the effects of anions in the reaction of poly(GMA-co-AN) and CO_2, quaternary ammonium salt catalysts of different anion (Cl^-, Br^-, I^-) were used. Table 2 also shows that the addition rate of CO_2 increased in the order of $I^- < Br^- < Cl^-$. When the different halide ions are used for the quaternary ammonium salts in the reaction of poly(GMA-co-AN) and CO_2, the solvation of the anion is an important factor for the liquid phase reaction.[19] In an aprotic solvent, like DMSO, in the case of

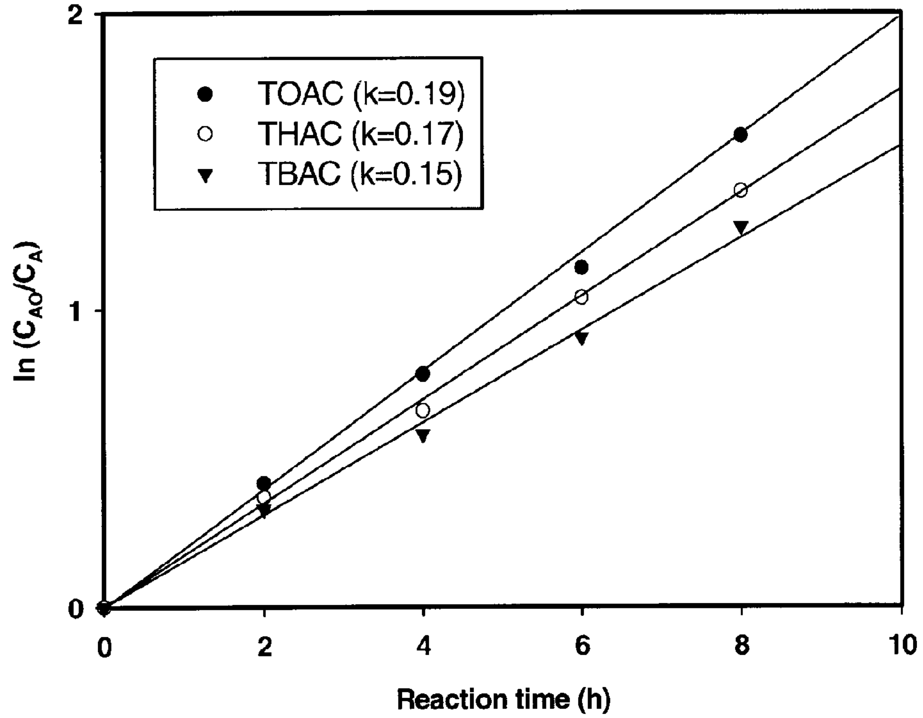


Figure 2. First-order plot of the CO_2 addition reaction to poly(GMA-co-AN) with different cations of quaternary ammonium salts at 10°C (k (h^{-1}) is rate constant; [C_A] denotes the concentration of poly(GMA-co-AN); solvent is DMSO.

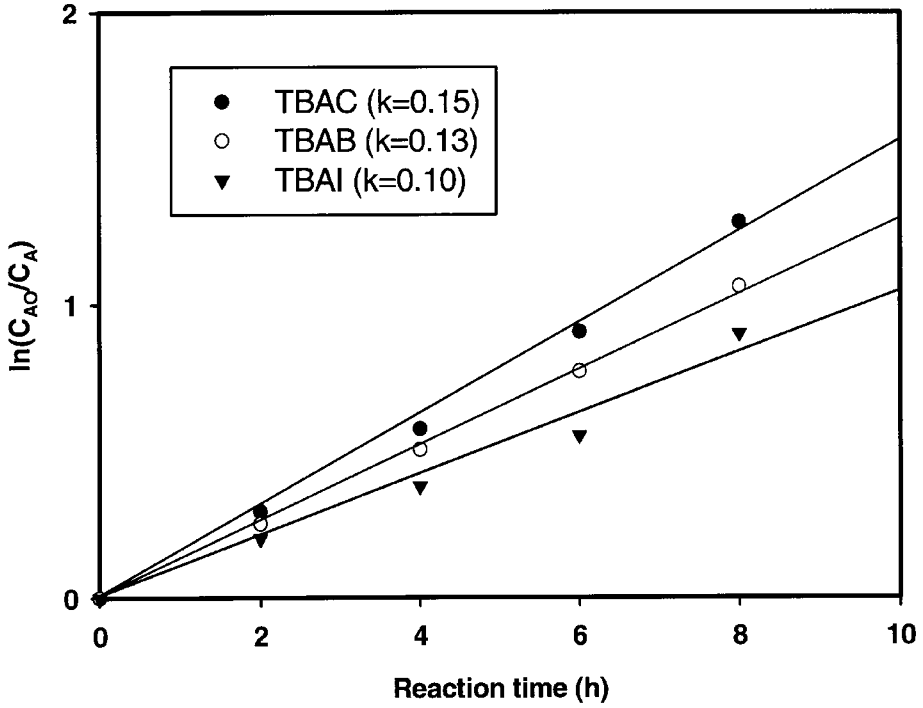


Figure 3. First-order plot of the CO_2 addition reaction with different anions of quaternary ammonium salts at 100°C (solvent is DMSO).

poly-(DOMA-co-AN) synthesis, stronger solvation may be expected for a soft anion like I^- than for a hard anion like Cl^-. Therefore, the order of nucleophilicity will increase in the order of $I^- < Br^- < Cl^-$, which agrees with the order of the reactivity of the quaternary ammonuim halides. It can be suggested that high nucleophilicity of Cl^- in an aprotic solvent enhances the attack of the anion to epoxide ring of poly(GMA-co-AN).[12] Figure 3 shows the linear plot of Eq. (9), and the pseudo first-order rate constant was obtained as 0.15 h^{-1} for TBAC, 0.13 h^{-1} for TBAB, and 0.10 h^{-1} for TBAI.

Effect of Solvents

The degree of association of the catalyst depends on the cation, anion, and solvent. The formation of ion pairs and their physical and chemical properties are strongly influenced by interaction with the solvent.[19] Table 3 shows the yield of CO_2 addition in the reaction of poly(GMA-co-AN) and CO_2 with various solvents. When we used aprotic solvents of low polarity, such as toluene and cyclohexane, we could not obtain poly(DOMA-co-AN) at all, because both the cation and anion of the ion pair were too poorly

Table 3. Yield and Amount of CO_2 Addition to Poly(GMA-co-AN) for Different Solvents

Material	Solvent	Mn[a]	Amount[b]	Unit Epoxide	Unit Cyclic Carbonate	Yield of CO_2 Addition (%)
Poly(GMA-co-AN)	–	71,000	–	1067	–	–
Poly(DOMA-co-AN)	NMP	85,000	13,000	66	303	82.2
	DMF	83,000	12,000	91	278	75.2
	DMSO	82,000	11,900	104	270	72.1

Reaction condition: 4.0 g of poly(GMA-co-AN), 120 mL of different solvents at 100°C for 10 hours using 0.5 mmol of TBAC catalyst.

[a] Number average molecule weight.

[b] The amount of CO_2 added to poly(GMA-co-AN).

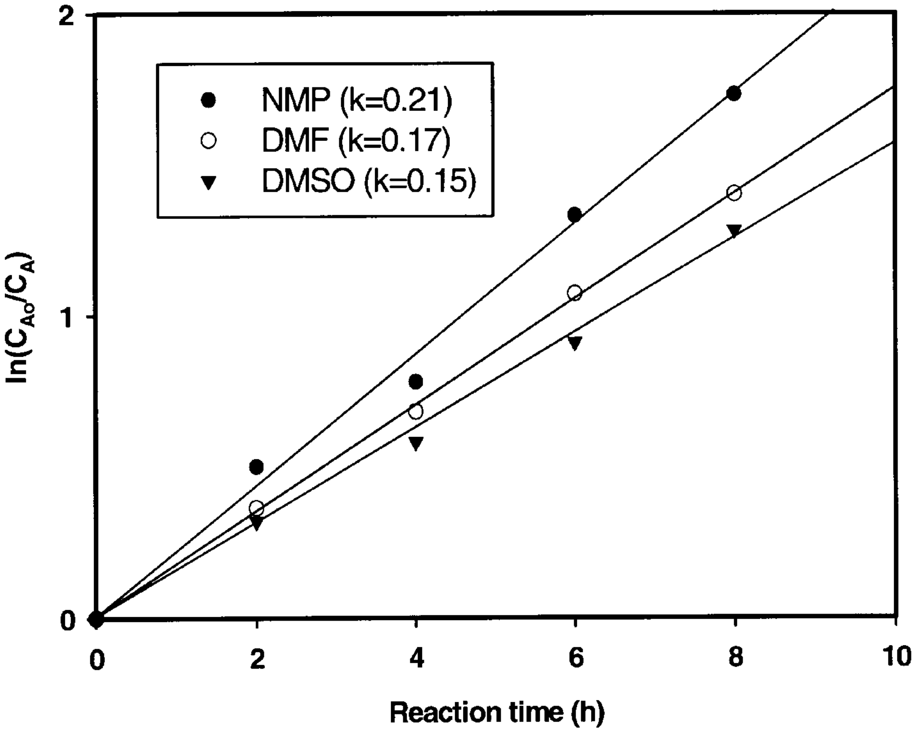


Figure 4. First-order plot of the CO_2 addition reaction to poly(GMA-co-AN) with different solvents at 100°C (catalyst is TBAC).

solvated. However, we could obtain a polymer in high polar aprotic solvent such as DMF and NMP. Figure 4 shows the plots of the ln($[C_{AO}]/[C_A]$) vs. time for the different solvents. From the slope the pseudo first-order rate constant was 0.21 h^{-1} for NMP, 0.17 h^{-1} for DMF, and 0.15 h^{-1} for DMSO in the presence of TBAC as a catalyst. In the preceding experiments on the effect of catalyst structure, however, we used DMSO for commercial purposes because of its lower price than DMF or NMP.

Blends of Poly(DOMA-co-AN) with SAN (25 wt%) or MMA-EA(7 wt%)

In order to develop an integrated process for the application of the cyclic carbonate group containing copolymers to polymer blends, the miscibility study of polymer blends with poly(DOMA-co-AN) and other conventional polymers are necessary. Therefore, we report the miscibility behavior of the blends containing either of the two copolymers, SAN and MMA-EA. In order to examine the degree of miscibility of the poly-(DOMA-co-AN)/SAN (25 wt%) and poly(DOMA-co-AN)/MMA-EA (7 wt%) blends, optical clarity was first investigated. Table 4 shows that all the poly(DOMA-co-AN) with SAN (25 wt%) or MMA-EA (7 wt%) blends form clear films, which implies that the blends are miscible over the whole concentration ranges. The optical appearance of blends often provides the first clue on miscibility. If the refractive indices of the two

Table 4. Optical Clarity and Glass Transition Temperatures of the Blends of Poly(DOMA-co-AN) with SAN (25 wt%) or MMA-EA (7 wt%)

Composition of Poly(DOMA-co-AN)	Optical Clarity	T_g (°C)
Poly(DOMA-co-AN)/SAN		
0.0	–	108
0.2	Clear	98
0.4	Clear	87
0.6	Clear	75
0.8	Clear	68
1.0	–	64
Poly(DOMA-co-AN)/MMA-EA		
0.0	–	120
0.2	Clear	102
0.4	Clear	89
0.6	Clear	79
0.8	Clear	70
1.0	–	64

polymers are not sufficiently different, however, a transparent blend sometimes indicates that the size of any heterogenity present is much smaller than the wavelength of visible light. Many works of calorimetric, spectroscopic, light or neutron scattering, and other experimental techniques, therefore, have been reported to determine the miscibility of polymer blends more accurately.[21,22]

For the detailed study of the miscibility of polymer blends, we measured the glass transition temperature of the blend component polymers. Each blend of different poly(DOMA-co-AN) compositions with SAN (25 wt%) or MMA-EA (7 wt%) exhibited a single glass transition temperature between the two T_gs of each polymer (Table 4). This result indicates that these blends are miscible over the entire composition ranges. Figures 5 and 6 show the T_g values of the blends with different poly(DOMA-co-AN) weight fractions. The dotted line represents the T_g of the blends estimated by the Fox equation,[23,24] where the enthalpy of mixing is neglected. W_A and W_B are the weight fractions of A and B components, respectively.

$$\frac{1}{T_g} = \frac{W_A}{T_{gA}} + \frac{W_B}{T_{gB}} \tag{10}$$

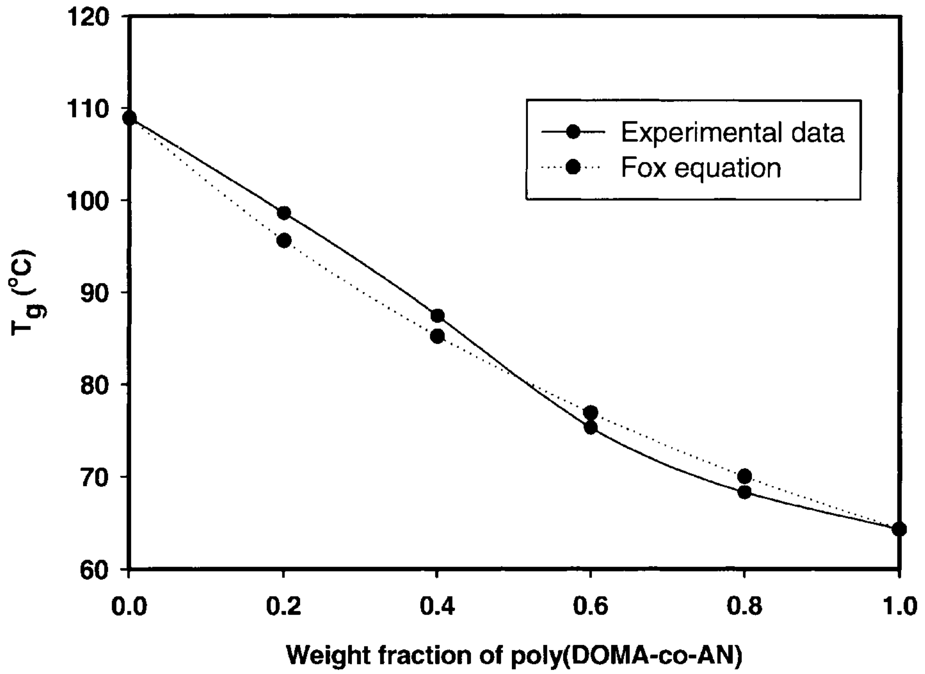


Figure 5. Glass transition temperatures of poly(DOMA-co-AN)/SAN (25 wt%) blends as a function of poly(DOMA-co-AN) weight fraction.

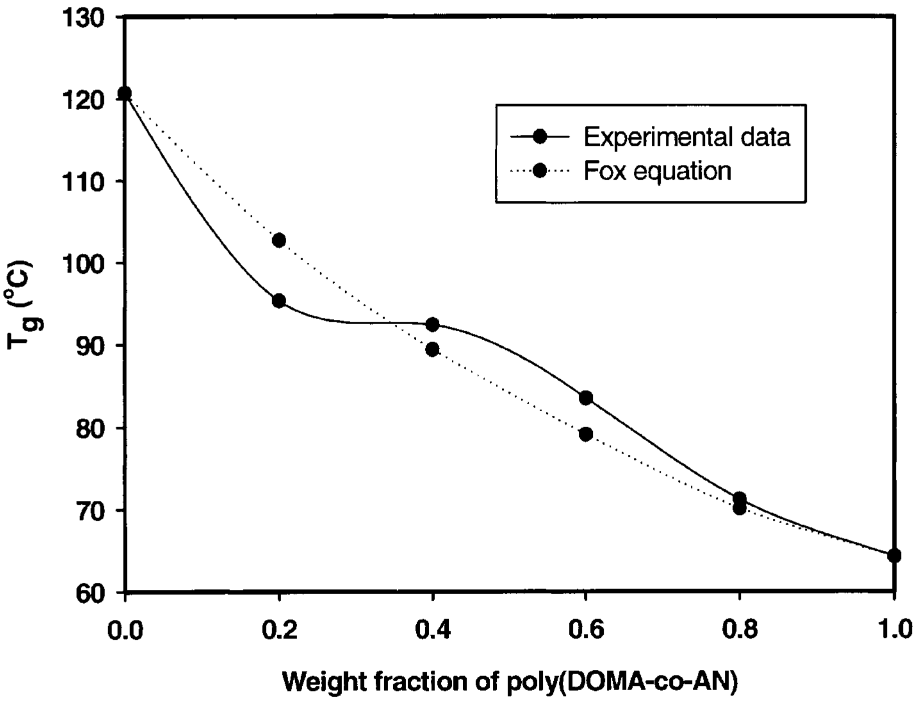


Figure 6. Glass transition temperatures of poly(DOMA-co-AN)/MMA-EA (7 wt%) blends as a function of poly(DOMA-co-AN) weight fraction.

This composition dependence of the experimental data gives "S-shaped" curves relative to the Fox equation for the blend. The result suggests that there is a strong specific interaction between poly(DOMA-co-AN) with SAN (25 wt%) or MMA-EA (7 wt%) blends.[25] This behavior may be ascribed to two factors as follows.[26] First, the existence of strong intermolecular interaction between the two different polymer chains in the blend, such as dipole-dipole interaction; and/or hydrogen bonding consequently, to increase the miscibility in the polymer blend. This would cause a positive deviation in the T_g composition curve. The second aspect is in connection with the destruction of self-association, which gives a positive contribution to free volume that should be taken into account. The intermolecular interaction may come from both carbonyl group and proton group, as well as the cyano group in the component polymers. Consequently, T_g behavior is the result of a balance between the two factors considered above, giving in these systems the Fox ideal behavior for the T_g-W dependence. More details on the intermolecular interaction in these blends will be reported elsewhere, along with their potential practical application.

CONCLUSION

In the synthesis of poly(DOMA-co-AN)] from poly(GMA-co-AN) and CO_2, quaternary ammonium salts showed good catalytic activity. Also, the quaternary ammonium salts of larger structure and more nucleophilic counter anion exhibited higher CO_2 addition to the epoxide groups of poly(GMA-co-AN). The addition of CO_2 into poly(GMA-co-AN) was effective when high dipolar aprotic solvent, such as DMSO, NMP, and DMF were used for the reaction. The synthesis of poly(DOMA-co-AN) from the reaction of poly(GMA-co-St) with CO_2 can be considered to be pseudo first order with the concentration of poly(GMA-co-St). An integrated process has been developed for the catalytic conversion of carbon dioxide to useful polymer materials by blending poly(DOMA-co-AN) with SAN or MMA-EA. It was found that the blends of the poly(DOMA-co-AN) with SAN (25 wt%) or MMA-EA (7 wt%) showed single T_gs over the entire blend compositions with "S-shaped" T_g-composition dependence.

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