

Synthesis of Poly(2-oxo-1,3-dioxolane-4-yl) Methyl Methacrylate by Polymer Reaction of Carbon Dioxide and Miscibility of Its Blends with Copolymers of Methyl Methacrylate and Ethyl Acrylate

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ABSTRACT: Polymeric epoxides were converted to corresponding five-membered cyclic carbonates in an effective manner. Poly(glycidyl methacrylate) (PGMA) was converted to a poly(2-oxo-1,3-dioxolane-4-yl) methyl methacrylate (PDOMMA) by the polymer reaction with carbon dioxide using tetraoctylammonium chloride (TOAC) as a catalyst. The miscibility of blends of PGMA or PDOMMA with copolymers of MMA and ethyl acrylate (MMA-EA) of two different EA compositions (2 and 5 wt %) was investigated by differential scanning calorimetry (DSC). The films of PGMA or PDOMMA and MMA-EA (2 and 5 wt %) blends were cast from *N,N*-dimethylformamide solution. An optical clarity test and DSC analysis showed that PDOMMA blends were miscible over the entire composition range, but PGMA was immiscible with the MMA-EA copolymers. It was also found that the miscibility of PDOMMA with 2 wt % MMA-EA copolymer was better than that of DOMMA with 5 wt % MMA-EA copolymer. The different miscibility behaviors were investigated in terms of Fourier transform IR spectra and interaction parameters based on the binary interaction model. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2161–2169, 2001

Key words: blends; polymer reaction; carbon dioxide; poly(glycidyl methacrylate); poly(2-oxo-1,3-dioxolane-4-yl) methyl methacrylate; miscibility; Fox equation

INTRODUCTION

Carbon dioxide is a major issue because it is considered to be responsible for the greenhouse effect. An attractive strategy to deal with this situation is to convert CO₂ into valuable substances. Consequently, new technologies are being inves-

tigated to convert CO₂.^{1,2} One approach may be the application of CO₂ as a monomer for the synthesis of a polymer material. Polymers bearing five-membered cyclic carbonate groups have been of interest as new polymeric materials for optical and electrical applications, and these polymers have some other possible uses such as polymeric polar solvents for inorganic electrolytics and hot dyes in nonlinear optical films.^{1,2}

The synthesis of cyclic carbonates from the reaction of CO₂ with oxirane was performed using Lewis acids, transition-metal complexes, and organometallic compounds as catalysts under high

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pressure.³ The synthesis of five-membered cyclic carbonates under mild conditions in the presence of metal halides or a phase transfer catalyst was also reported.³

In this work poly(glycidyl methacrylate) (PGMA) was converted to a polymethacrylate bearing a five-membered cyclic carbonate group by a polymer reaction with carbon dioxide and a catalyst. In general, a vinyl monomer bearing a cyclic carbonate group such as (2-oxo-1,3-dioxolane-4-yl) methyl methacrylate (DOMMA) is extremely sensitive to polymerization and difficult to handle. Thus, the quantitative polymer reaction of epoxide polymers with carbon dioxide can be the most effective method of obtaining cyclic carbonate polymers.⁴ The polymers containing pendant five-membered cyclic carbonate groups can also be considered as starting materials for the synthesis of functional polymers. Blends of polymers bearing a cyclic carbonate group with some commercial polymers were developed in this laboratory for more versatile applications of the polymers.^{1,5}

Therefore, blends of PGMA or poly(2-oxo-1,3-dioxolane-4-yl) methyl methacrylate (PDOMMA) with a copolymer of MMA and ethyl acrylate (MMA-EA) were also prepared. The miscibility of the blends was investigated by using differential scanning calorimetry (DSC) and the binary interaction model, as well as an optical clarity test.

EXPERIMENTAL

Materials

The GMA, MMA, and EA monomers were washed with an aqueous sodium hydroxide solution, rinsed with distilled water, and then dried over calcium chloride. Other reagents such as tetraoctylammonium chloride (TOAC), dimethyl sulfoxide (DMSO), acetonitrile, azobisisobutyronitrile (AIBN), and *N,N*-dimethylformamide (DMF) were reagent grade and were used as purchased without further purification.

Polymer Synthesis

Radical polymerization of GMA (40 mmol) in DMSO (30 mL) was performed using AIBN (5 mg) as an initiator at 70°C for 10 h under a nitrogen atmosphere. Then the solution was poured into distilled water to attain a precipitate.

The obtained polymer was reprecipitated twice and dried in a vacuum at 30°C for 12 h. Copoly-

merization of MMA and EA in acetonitrile was performed by a method similar to the polymerization of GMA. Two copolymers were prepared with different EA compositions (2 and 5 wt %) in the feed. The polymers were recovered using an excess of methanol and were purified by chloroform/methanol reprecipitation.

Synthesis of PDOMMA by Direct Incorporation of Carbon Dioxide to PGMA

PDOMMA was synthesized from PGMA and CO₂ using the TOAC catalyst as shown in Scheme 1. The catalyst (5 mmol) was introduced to a 250-mL three-necked pyrex reactor containing a mixture of 0.6 g of PGMA and 30 mL of DMSO, and the solution was heated to 100°C. The reaction was started by stirring the mixture under a stream of CO₂ (10 mL/min) and was continued for 24 h.

Preparation of Blends

Films of PGMA or PDOMMA and 2 and 5 wt % MMA-EA blends with various concentrations were prepared by casting 3 wt % of the blend solution in DMF on glass plates. The films were dried under a vacuum for 3 days at room temperature.

Measurements

Structure Identification

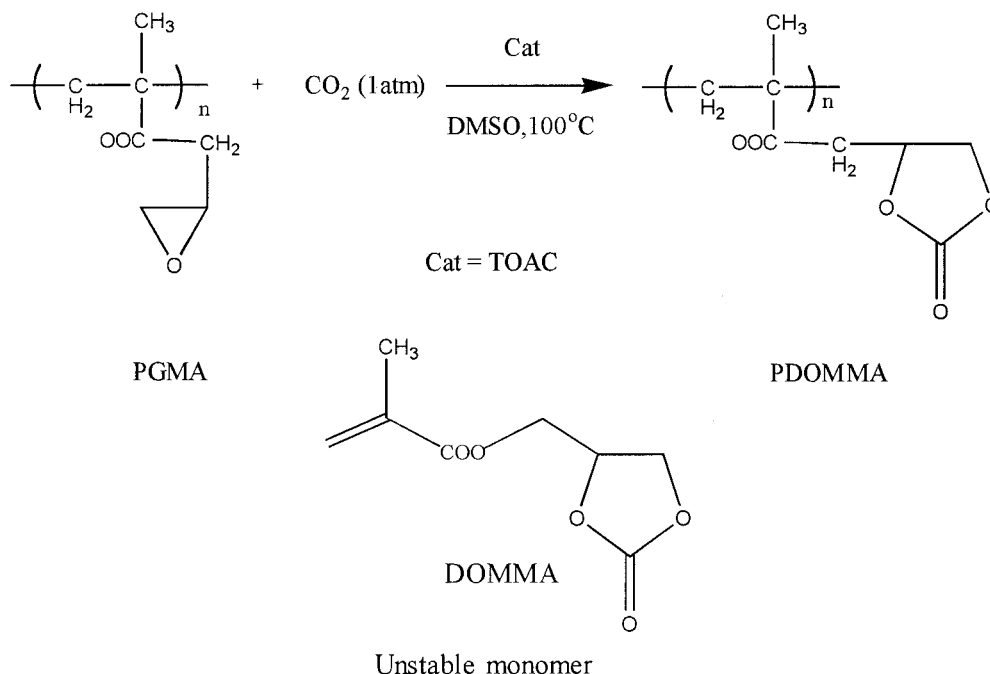
Fourier transform IR (FTIR) spectra were obtained by an Analect FX6160 FTIR spectrometer. Thin films of the blends were prepared by direct casting on glass. The solvent was removed by drying in a vacuum oven at room temperature for 2 weeks. The thickness of the films was 2–3 μm. Thirty-two scans at a resolution of 2 cm⁻¹ were signal averaged. The ¹H-NMR spectra were recorded with a Bruker 300-MHz NMR spectrophotometer. The measurements were made by dissolving 1.5 mg of sample in 0.5 mL of DMSO-*d*₆ solvent in a 5-mL tube at 25°C.

Molecular Weight

The molecular weights of the polymers were determined with a gel permeation chromatograph (Waters 244). The measurements were conducted using an RI detector and DMF as an eluent with a flow rate of 1.0 mL/min at 25°C. Polystyrene was used as the standard for calibration.

Thermal Analysis

The glass-transition temperatures were measured using a differential scanning calorimeter



Scheme 1 PDOMMA synthesis via incorporation of carbon dioxide into PGMA.

calibrated with pure indium as a standard. Experiments were carried out in a nitrogen atmosphere. The samples were heated to 450 K at a heating rate of 10°C/min to avoid the thermal history from the samples packed in the aluminum pan and to eliminate any small traces of solvent. All the glass-transition temperatures were taken as the half-height point of the heat capacity jump in the second scan.

prior to the polymerization of DOMMA to obtain PDOMMA.

The conversion of the epoxide ring (in PGMA) to the five-membered cyclic carbonate group (in PDOMMA) could be identified by ¹H-NMR, and their IR spectra are shown in Figures 1 and 2, respectively.

The IR spectrum of the PDOMMA exhibited an absorption peak at 1800 cm⁻¹ (C=O of cyclic car-

RESULTS AND DISCUSSION

Structure Identification of PDOMMA from Reaction of PGMA and Carbon Dioxide

The reaction of PGMA with carbon dioxide was carried at 100°C for 24 h in DMSO using 0.05 mmol of TOAC as a catalyst under atmospheric pressure. It is known that the rate-determining step of the epoxide-CO₂ reaction involves the nucleophilic attack of an anion to the oxirane ring.^{6,7} The highly nucleophilic Cl⁻ anion in an aprotic solvent is also known to enhance the attack of the anion on the epoxide ring of PGMA.⁸ Thus, PDOMMA can be easily synthesized by the polymer reaction of PGMA and carbon dioxide using active catalysts. Because DOMMA is an unstable monomer, the polymer reaction method is supe-

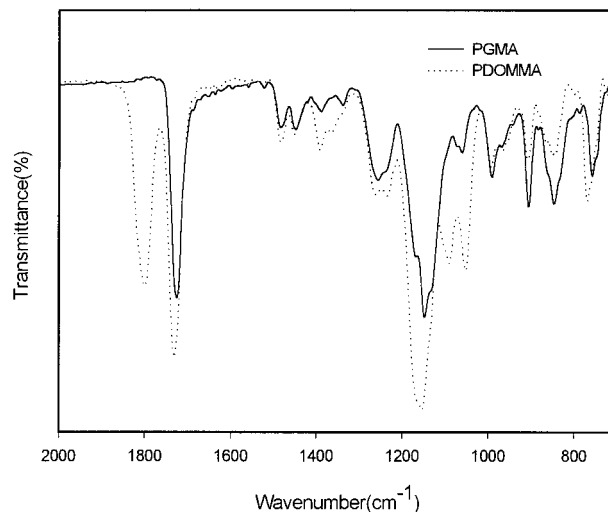


Figure 1 FTIR spectra of PGMA and PDOMMA.

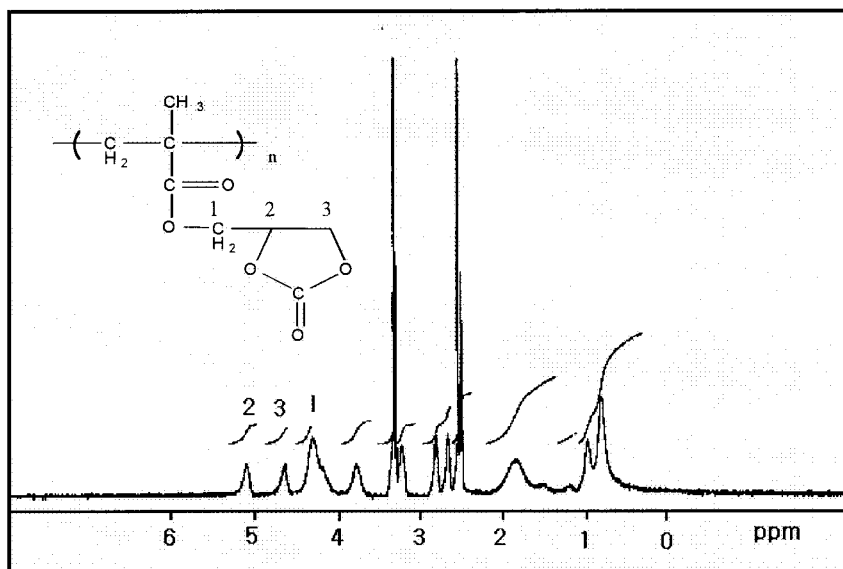


Figure 2 The $^1\text{H-NMR}$ spectrum of PDOMMA.

bonate). $^1\text{H-NMR}$ analysis also confirmed the formation of PDOMMA. The characteristic peaks were as follows: 4.0–4.5 ppm ($-\text{OCH}_2-$, in side chain), 5.0–5.3 ($-\text{HCO}-$, in cyclic carbonate), 4.5–4.8 ($-\text{OCH}_2-$, in cyclic carbonate). Table I lists the molecular weights and glass-transition temperatures (T_g) of PGMA and PDOMMA.

Synthesis of MMA-EA Copolymers

Radical copolymerizations of MMA with EA of two different EA comonomer compositions (2 and 5 wt % in the feed) were carried out in acetonitrile at 60°C for 30 h using AIBN as an initiator. The comonomer contents of the synthesized polymers were identified by $^1\text{H-NMR}$ and the comonomer compositions for the produced copolymers were 1.9 and 4.9 wt %, respectively. Therefore, these were almost identical to the compositions in the

feed. These copolymers were blended with PGMA or PDOMMA. The molecular weights and glass-transition temperatures of these copolymers are summarized in Table I.

Blends of PGMA or PDOMMA with 2 and 5 wt % MMA-EA

The optical appearance of blends often provides the first clue on their miscibility. All the blend films investigated in this study were transparent. It seemed that all the blends were miscible. If the sample was transparent to visible light, then light was not being substantially scattered; thus, we could conclude that no domain larger than about 4000 \AA was in the blend sample. Because visible light spans the $4000\text{--}7000 \text{ \AA}$ region, the phase that can be detected through scattering visible light is 4000 \AA in diameter or larger. Hence, the

Table I Characteristics of Polymer Samples

Sample	M_w^a	M_n^a	M_w/M_n	T_g ($^\circ\text{C}$)	Refractive Index ^b
PGMA	75,000	58,000	1.28	60.8	1.420
PDOMMA	126,000	76,000	1.65	49.2	1.417
MMA-EA					
2 wt %	217,000	165,000	1.31	125.5	1.489
5 wt %	132,000	121,000	1.09	122.4	1.490

^a The molecular weights are in polystyrene equivalents.

^b The refractive indices were estimated by the group contribution method according to Van Krevelen.¹¹

Table II Glass-Transition Temperatures of PGMA or PDOMMA with 2 and 5 wt % MMA-EA Blends

	Composition of		T_g (°C)	
	Copolymer	PGMA	PGMA	MMA-EA
PGMA/MMA-EA	2 wt % EA	0.0	—	125.5
		0.2	61.3	68.3
		0.4	61.9	71.8
		0.6	63.0	79.4
		0.8	63.7	85.5
		1.0	60.7	—
	5 wt % EA	0	—	122.4
		0.2	63.2	83.4
		0.4	65.9	83.9
		0.6	66.9	85.1
		0.8	67.0	86.0
		1.0	60.7	—
			PDOMMA	Blends
	PDOMMA/MMA-EA	2 wt % EA	0.0	0.0
0.2			0.2	87.0
0.4			0.4	72.4
0.6			0.6	60.2
0.8			0.8	66.4
1.0			1.0	49.2
5 wt % EA		0.0	0.0	122.4
		0.2	0.2	85.0
		0.4	0.4	73.1
		0.6	0.6	55.0
		0.8	0.8	53.2
		1.0	1.0	49.2

refractive indices of the components must differ to contrast the separated phases. Actually, the critical domain size for transparency was reported to be approximately 1000 Å.^{9,10} Many studies on calorimetric, spectroscopic, light or neutron scattering, and other experimental techniques were conducted to more accurately determine the miscibility of polymer blends.⁵ In fact, the differences in the refractive index of the polymers investigated in this study were not large, as shown in Table I. Therefore, the optical clarity results may provide inaccurate conclusions on the miscibility. Thus, the glass-transition temperature behavior of the blends was further considered using DSC.¹¹

Glass-Transition Temperatures of Blends

Table II shows the T_g of the blends as a function of the blend composition for the blends of PGMA and MMA-EA copolymers of two different co-

monomer compositions. For all the PGMA/MMA-EA blends, there were two T_g values observed for the blends of various compositions. Careful inspection of Table II indicates that there was no significant change in the T_g of PGMA. However, Figure 3 shows that the T_g of the copolymer (2 wt % MMA-EA) was remarkably decreased when a small amount of PGMA (0.2 wt %) was added; then it was slightly increased with the increase of the PGMA weight fraction above 0.2. For the PGMA/MMA-EA (5 wt %) blend, the T_g of MMA-EA had similar behavior to that observed for the blend of PGMA/MMA-EA (2 wt %). As for the limited miscibility, there were two separated T_g values between the two T_g values of each component. In a highly phase separated polymer blend system, the T_g values of the individual components remain unchanged. The initial rapid decrease in T_g may therefore be related to the partial miscibility of PGMA with the copolymers, giv-

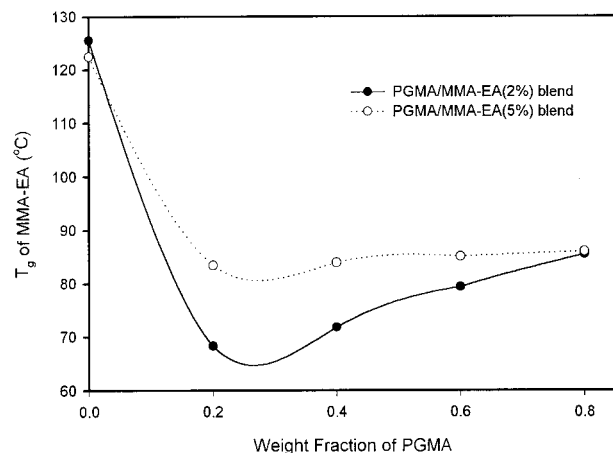


Figure 3 The glass-transition temperatures of MMA-EA for PGMA/MMA-EA (2 and 5 wt %) blends as a function of the PGMA weight fraction.

ing rise to a significant plasticization effect by PGMA on the copolymers. The trend is more significant when the EA content in the copolymer is lower. The plasticization effect seemed to not take place however when more PGMA was added to the copolymers, perhaps because of the lack of miscibility between the two components.

On the other hand, each blend of different PDOMMA compositions with 2 and 5 wt % MMA-EA exhibited a single T_g between the two T_g val-

ues of the each polymer. This result indicated that these blends were miscible over the entire composition range. Figures 4 and 5 show the T_g values of PDOMMA/MMA-EA blends as a function of the PDOMMA weight fraction. The solid lines in these figures represent the T_g of blends estimated by the Fox equation,⁷ where the enthalpy of mixing is neglected:

$$\frac{1}{T_g} = \frac{W_A}{T_{gA}} + \frac{W_B}{T_{gB}} \quad (1)$$

W_A and W_B are the weight fractions of the A and B components, respectively. The Fox equation fit well to the experimental data within experimental errors. Of more interest was the S-shaped T_g versus the PDOMMA composition curve for the PDOMMA/MMA-EA (2 wt %) blends as shown in Figure 4. This result suggested that there was a specific interaction between PDOMMA and the copolymer containing 2 wt % EA composition.¹² However, this was not observed in Figure 5 for the PDOMMA/MMA-EA (5 wt %) blends. Figure 6 shows the FTIR spectra of the carbonyl vibration for the PDOMMA/MMA-EA (2 wt %) copolymer blends.

The peaks around 1650 and 1680 cm^{-1} represent C=O in the ester group of the EA. The peak

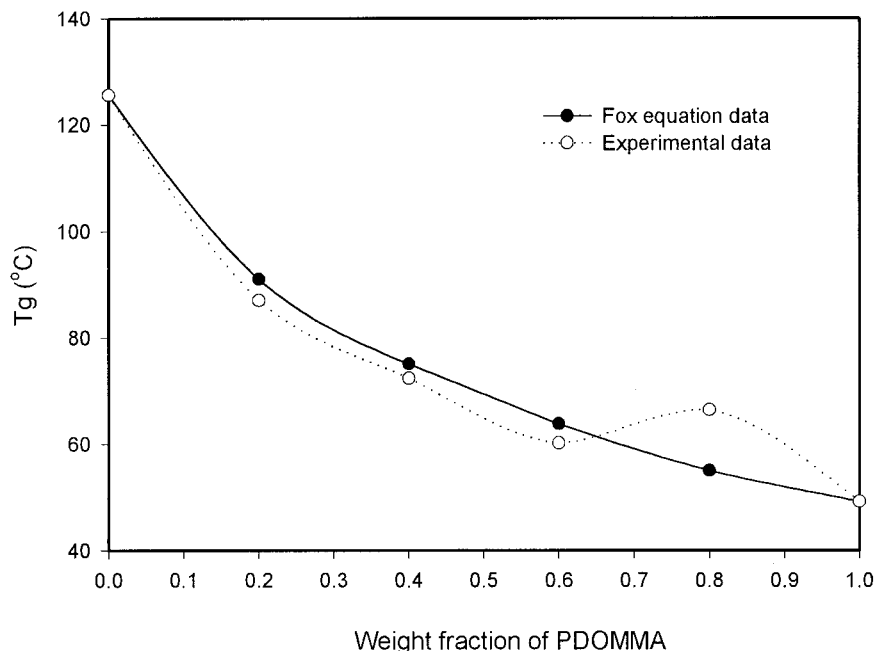


Figure 4 The glass-transition temperatures of PDOMMA/MMA-EA (2 wt %) blends as a function of the PDOMMA weight fraction.

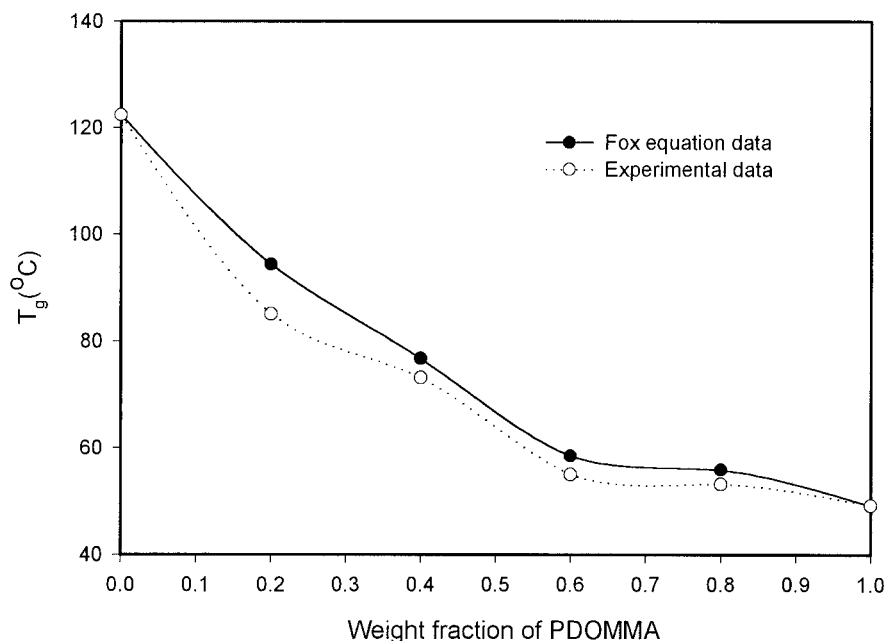


Figure 5 The glass-transition temperatures of PDOMMA/MMA-EA (5 wt %) blends as a function of the PDOMMA weight fraction.

due to C=O in the ester group of the MMA-EA copolymer shifted toward a lower wave number when the PDOMMA composition was higher than 60%. This peak was further shifted toward a lower wave number as the PDOMMA contents increased. For example, the peak was observed at 1680 cm^{-1} for the 20/80 composition, whereas it was observed at 1650 cm^{-1} for the 80/20 compo-

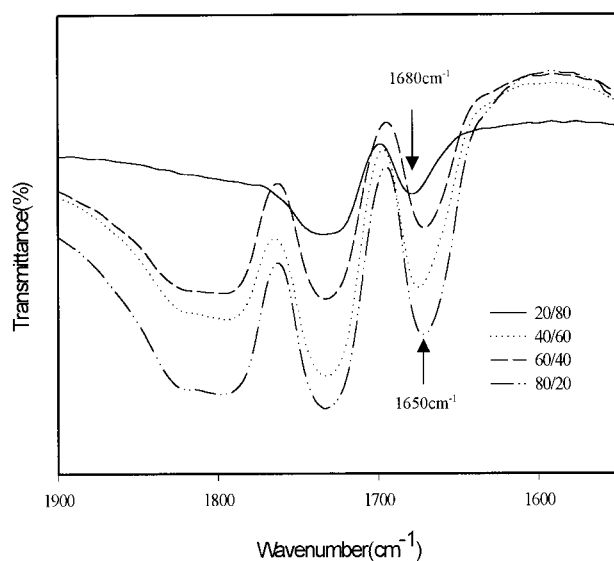


Figure 6 FTIR spectra of the carboxyl vibration region for PDOMMA/MMA-EA (2 wt %) blends.

sition. This peak shift due to C=O in the ester group of the MMA-EA copolymer at around 1650 cm^{-1} may indicate a specific interaction. The better miscibility of PDOMMA bearing a cyclic carbonate than PGMA with the MMA-EA copolymer may be due to the interaction between the ester group in the MMA-EA copolymer and the cyclic carbonate group in PDOMMA.¹³⁻¹⁵ Similar FTIR spectral results were observed for PDOMMA/MMA-EA (5 wt %) blends but the peak shifts were not large in comparison to that of PDOMMA/MMA-EA (2 wt %) blends. This difference may be related to the non-S-shaped T_g versus the PDOMMA composition curve in Figure 5. A comparison of Figures 4 and 5 thus indicates that the interaction between component polymers was larger in the PDOMMA/MMA-EA (2 wt %) blends than for PDOMMA/MMA-EA (5 wt %) blends, although both of the two blend systems were miscible over the entire composition range.

Polymer-Polymer Interaction Parameter

The basic approximation embodied in the Flory-Huggins treatment¹⁶ is of the mean-field nature, ignoring the local concentration fluctuations around individual segments. The mean-field approximation is fairly satisfactory when the mixture consists of all long chain molecules. In such mixtures

Table III Segmental Interaction Parameters for Blends of PGMA or PDOMMA with 0.4 Weight Fraction of 2 and 5 wt % MMA-EA

Blend System	2 wt % MMA-EA	5 wt % MMA-EA
PGMA	$\chi_{\text{PGMA/MMA}} = 0.0051$	$\chi_{\text{PGMA/MMA}} = 0.0063$
	$\chi_{\text{PGMA/EA}} = 0.0470$	$\chi_{\text{PGMA/EA}} = 0.0501$
	$\chi_{\text{MMA/EA}} = 0.1090$	$\chi_{\text{MMA/EA}} = 0.0950$
PDOMMA	$\chi_{\text{PDOMMA/MMA}} = 0.0035$	$\chi_{\text{PDOMMA/MMA}} = 0.0054$
	$\chi_{\text{PDOMMA/EA}} = 0.0281$	$\chi_{\text{PDOMMA/EA}} = 0.0387$
	$\chi_{\text{MMA/EA}} = 0.1090$	$\chi_{\text{MMA/EA}} = 0.0950$

the chains assume ideal Gaussian conformation unperturbed by the excluded volume effect.

Assuming that the above equilibrium condition is in the blend systems, Kim and Burn¹⁵ derived an expression to determine the Flory–Huggins polymer–polymer interaction parameter (χ_{12}) of the partially miscible mixture without a solvent. Taking a mixture of two polymers in the absence of solvent into consideration and assuming that equilibrium is reached, the Flory–Huggins free energy of mixing (ΔG_m) for the systems consisting of two polymers can be written as follows¹⁷:

$$\frac{\Delta G_m}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi_{12} \phi_1 \phi_2 (m_1 n_1 + m_2 n_2) \quad (2)$$

where n_i is the number of moles of the i th component in the mixture; $\phi_i = (m_i n_i)/(m_i n_i + n_j m_j)$ is the volume fraction of the i th component ($i, j = 1, 2$ and $i \neq j$); χ_{12} is the Flory–Huggins interaction parameter; the subscripts 1 and 2 denote polymers 1 and 2, respectively; and m_i is essentially the degree of polymerization, relating the molar volumes V_1 and V_2 of the polymers to a fictitious molar volume V_o of one submolecule of polymer.

The chemical potential of the mixing of component i is obtained as the partial derivative of eq. (1) with respect to n_i :

$$\frac{\Delta \mu_1}{RT} = \ln \phi_1 + \left(1 - \frac{m_1}{m_2}\right) \phi_2 + m_1 \chi_{12} \phi_2^2 \quad (3)$$

$$\frac{\Delta \mu_2}{RT} = \ln \phi_2 + \left(1 - \frac{m_2}{m_1}\right) \phi_1 + m_2 \chi_{12} \phi_1^2 \quad (4)$$

At equilibrium the chemical potential of each component must be the same in both phases.

For a blend of a homopolymer (A) and a copolymer (B), where A consists of segments of type 1

and B of segments of types 2 and 3, the binary interaction model gives the effective interaction parameter X_{AB} in terms of the interaction between the constituents¹⁸ as

$$X_{AB} = \beta \chi_{12} + (1 - \beta) \chi_{13} - \beta(1 - \beta) \chi_{23} \quad (5)$$

where β represents the mole fraction of component 2 in the copolymer.

The miscibility should only be expected if X_{AB} is negative; if it is positive, its magnitude is as small as possible. When $0 < \chi_{12} \leq \chi_{13} < \chi_{23}$, the repulsion between the different segments comprising the copolymer is stronger than the repulsion between the homopolymer and copolymer segments.

Using eqs. (2) and (3) we can derive χ_{12} . The various segmental interaction parameters thus obtained are summarized in Table III. These values were small and positive, indicating that the interactions were weakly repulsive. Table III shows the typical values for the blend of 40% MMA-EA (2.5 wt %) compositions. Tables IV and V show that the values of X_{AB} were higher in the PGMA/MMA-EA (2.5 wt %) blends than in the

Table IV Interaction Parameters (X_{AB}) for PGMA and 2 and 5 wt % MMA-EA Blends

Blends	Composition		
	EA	PGMA	X_{AB}
PGMA/MMA-EA	2 wt %	0.2	0.0043
		0.4	0.0032
		0.6	0.0038
		0.8	0.0041
	5 wt %	0.2	0.0044
		0.4	0.0037
		0.6	0.0040
		0.8	0.0041

Table V Interaction Parameters (X_{AB}) for PDOMMA and 2 and 5 wt % MMA-EA Blends

Blends	Composition		X_{AB}
	EA	PDOMMA	
PDOMMA/MMA-EA	2 wt %	0.2	0.0028
		0.4	0.0010
		0.6	0.0019
		0.8	0.0030
	5 wt %	0.2	0.0040
		0.4	0.0005
		0.6	0.0025
		0.8	0.0033

PDOMMA/MMA-EA (2.5 wt %) blends. These results suggested that the miscibility of PDOMMA/MMA-EA blends was better than that of PGMA/MMA-EA blends, which was in agreement with the T_g behavior of the blends as discussed previously. The X_{AB} values of PDOMMA/MMA-EA (2 wt %) were also found to be generally lower than those of the PDOMMA/MMA-EA (5 wt %), meaning that the interaction between components was larger in the former blends than in the latter.

CONCLUSION

Carbon dioxide was effectively added to the epoxide ring of PGMA to produce the corresponding cyclic carbonate, PDOMMA. The TOAC catalyst showed good catalytic activity, even at the atmospheric pressure of carbon dioxide. An integrated process was developed for the catalytic conversion of carbon dioxide to useful polymer materials by blending PDOMMA with the copolymer of MMA and EA. It was found that the blends of the CO_2 containing PDOMMA/MMA-EA copolymer showed a single T_g over the entire blend composition range, but PGMA/MMA-EA blends exhibited two T_g values. The better miscibility of PDOMMA containing blends was explained in terms of a specific interaction between the ester group of the MMA-EA copolymer and the cyclic carbonate group in PDOMMA, which was determined from the FTIR spectra. Based on the bi-

nary interaction model, the values of X_{AB} were much lower for the PDOMMA/MMA-EA (2 wt %) than the PGMA/MMA-EA (2 wt %) blends, suggesting that the interaction between components was larger in the former than in the latter blends. It was also found from the DSC results and X_{AB} values that the miscibility of PDOMMA/MMA-EA (2 wt %) blends was better than that of PDOMMA/MMA-EA (5 wt %) blends.

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