Synthesis of Poly[(2-oxo-1,3-dioxolan-4-yl)methyl vinyl ether-*co-N*-phenylmaleimide] and Its Miscibility in Blends with Styrene-Acrylonitrile or Poly(vinyl chloride)

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ABSTRACT: The aim of the study was to investigate the synthesis of a copolymer bearing cyclic carbonate and its miscibility with styrene/acrylonitrile copolymer (SAN) or poly(vinyl chloride) (PVC). (2-Oxo-1,3-dioxolan-4-yl)methyl vinyl ether (OVE) as a monomer was synthesized from glycidyl vinyl ether and CO_2 using quaternary ammonium chloride salts as catalysts. The highest reaction rate was observed when tetraoctylammonium chloride (TOAC) was used as a catalyst. Even at the atmospheric pressure of CO_2, the yield of OVE using TOAC was above 80% after 6 h of reaction at 80°C. The copolymer of OVE and *N*-phenylmaleimide (NPM) was prepared by radical copolymerization and was characterized by FTIR and ^{1}H-NMR spectroscopies and differential scanning calorimetry (DSC). The monomer reactivity ratios were given as r_1 (OVE) = 0.53–0.57 and r_2 (NPM) = 2.23–2.24 in the copolymerization of OVE and NPM. The films of poly(OVE-*co*-NPM)/SAN and poly(OVE-*co*-NPM)/PVC blends were cast from *N*-dimethylformamide. An optical clarity test and DSC analysis showed that poly(OVE-*co*-NPM)/SAN and poly(OVE-*co*-NPM)/PVC blends were both miscible over the whole composition range. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1809–1815, 2000

Key words: carbon dioxide; glycidyl vinyl ether; cyclic carbonate; poly[OVE-*co*-NPM]; miscibility; polymer blends

INTRODUCTION

Carbon dioxide plays an important role in global warming. An attractive strategy to deal with this situation is to convert CO_2 into a valuable substance. Consequently, new technologies are being investigated to catalytically convert CO_2. One approach may be the application of CO_2 as a monomer for the synthesis of polymer materials. Of special interest are the reactions of CO_2 with oxiranes or some polymers containing pendant epoxide groups, because they lead to the production of cyclic carbonates.[1] These cyclic carbonates can be used as aprotic polar solvents, electrolytes for batteries, and sources for reactive polymer synthesis.[2] The polar polymers are of interest for optical, magnetic, and electronic applications.

The synthesis of cyclic carbonates from the reaction of CO_2 with oxirane was performed using Lewis acids, transition-metal complexes, and organometallic compounds as catalysts under high pressure. But some authors reported the synthe-

sis of five-membered cyclic carbonates under mild conditions in the presence of metal halides or phase transfer catalysts.[3–6] One example is the synthesis of the functional monomer (2-oxo-1,3-dioxolan-4-yl)methyl vinyl ether (OVE), which contains both reactive vinyl ether and cyclic carbonate groups, from the reaction of glycidyl VE (GVE) with carbon dioxide.[7] In our previous article[8] kinetic studies on the synthesis of OVE were carried out using quaternary salts as catalysts. In a semibatch reactor, in which a slow stream of CO_2 was continuously passed, a pseudo-first-order rate equation fit the experimental results well. However, in a batch autoclave reactor with high CO_2 pressure, the reaction was proportional to both the concentration of GVE and CO_2, showing second-order kinetics.

In the present study we propose an integrated process for the conversion of CO_2 to functional polymers. First we synthesized OVE from CO_2 and GVE using quaternary ammonium chlorides as catalysts. Then the copolymerization of OVE with *N*-phenylmaleimide (NPM) was carried out. We investigated the monomer reactivity ratios and thermal stability of the copolymer. The blends of poly(OVE-*co*-NPM) and styrene/acrylonitrile (SAN) or poly(vinylchloride) (PVC) were also prepared, and the miscibility of the blends was examined by optical clarity and differential scanning calorimetry (DSC) analysis.

EXPERIMENTAL

Materials

The GVE (Seimi Chemical Co., Ltd.) and solvents were used after distillation on CaH_2. Quaternary ammonium salts, such as tricaprylylmethylammonium chloride (Aliquat 336), tetrabutylammonium chloride (TBAC), tetraoctylammonium chloride (TOAC), and tetrapropylammonium chloride (TPAC), were all reagent grade and used without further purification. The SAN (AN content = 40 wt %, M_w = 160,000) and PVC (M_w = 165,000) were supplied by LG Chem. Co. Ltd., Korea.

Synthesis of OVE from GVE and Carbon Dioxide

The synthesis of OVE from GVE and CO_2 was carried out using a quaternary ammonium salt catalyst as shown in Scheme 1. The catalyst (1 mmol) was introduced into a 150-mL, three-necked Pyrex reactor containing the mixture of 10
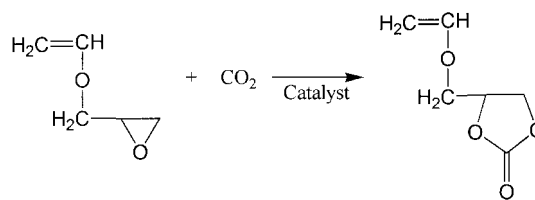
Scheme 1   The synthesis of OVE from GVE and CO_2.

mmol of GVE and 50 mL of NMP, and the solution was heated to a desired temperature (60–100°C). The reaction was started by stirring the solution under a slow stream of CO_2 (10 mL/min) and continued for 6–24 h. Periodically, a small portion of the reaction mixture was taken and analyzed by a gas chromatograph (HP5890A) equipped with a 10 wt % OV-101/chromosorb W column to check the degree of reaction.

Copolymer Synthesis

Radical copolymerization of OVE (5 mmol) with NPM (5 mmol) was performed using azobisisobutyronitrile (AIBN, 5 mg) as an initiator at 60°C for 10 h under a nitrogen atmosphere, and then the solution was poured into diethyl ether to yield a precipitate. The obtained polymer was reprecipitated twice and dried *in vacuo* at 60°C for 12 h. The molecular weight of the copolymer was measured using polystyrene as the standard with gel permeation chromatography (Waters 244). Dimethylformamide (DMF) was used as an effluent.

Preparation of Blends

To prepare blend films, weighed amounts of poly(OVE-*co*-NPM) (67.7 wt % NPM) and SAN (40 wt % AN) or PVC with a given composition were cast from a 10 wt % solution in DMF. The films were slowly dried in a petri dish at room temperature and then kept under a vacuum to constant weight.

Measurements

Structure Identification

The chemical structure of OVE and the polymer was identified by FTIR (Mattson Polaris) and ^{1}H-NMR spectroscopy (Teol PMX-60SI).

Molecular Weight

The molecular weight of polymers was determined by gel permeation chromatography (Wa-
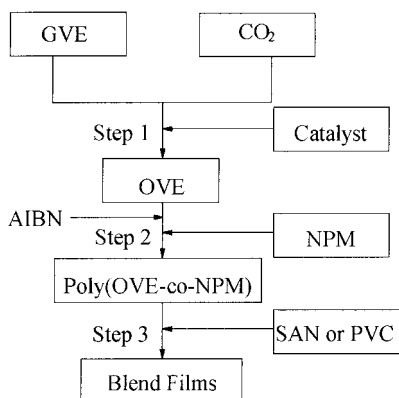
Figure 1   An integrated process for the catalytic conversion of CO_2 to polymer materials.

Figure 2   First-order plots of $\ln([GVE]_0/[GVE])$ vs. time for various quaternary ammonium chloride catalysts at 80°C.

ters 244). The measurement was conducted using a relative intensity detector in DMF at a flow rate of 1.0 mL/min at 25°C. Polystyrene was used as the standard for calibration.

Thermal Analysis

The glass-transition temperature (T_g) was measured using DSC (Perkin–Elmer DSC-7500). Thermograms of the blends were obtained at a heating rate of 10°C/min. All the glass-transition temperatures were recorded at the half-height of the heat capacity jump. The thermal stability was examined with a TGA instrument (Shimadzu DT30A) at a scanning rate of 10°C/min in nitrogen.

constant. If the rate constant is k', the disappearance rate of GVE is expressed as

$$-r_{GVE} = -d[GVE]/dt = k'[GVE] \tag{1}$$

Integration of eq. (1) gives eq. (2):

$$\ln([GVE]_0/[GVE]) = k't \tag{2}$$

where $[GVE]_0$ is the initial concentration of GVE.

RESULTS AND DISCUSSION

Figure 1 shows the overall procedure for chemical fixation of CO_2 with GVE to polymers via cyclic carbonate (OVE). Step 1 involves the synthesis of OVE from GVE and CO_2 with quaternary ammonium salts as catalysts. Step 2 concerns radical copolymerization of OVE with NPM. Step 3 includes the preparation of blends of poly(OVE-*co*-NPM) with another commercial resin like SAN or PVC.

Synthesis of OVE

When the reaction is carried out in a semibatch reactor with a constant flow of CO_2, only the concentration of GVE varies because the concentration of dissolved CO_2 in NMP can be assumed
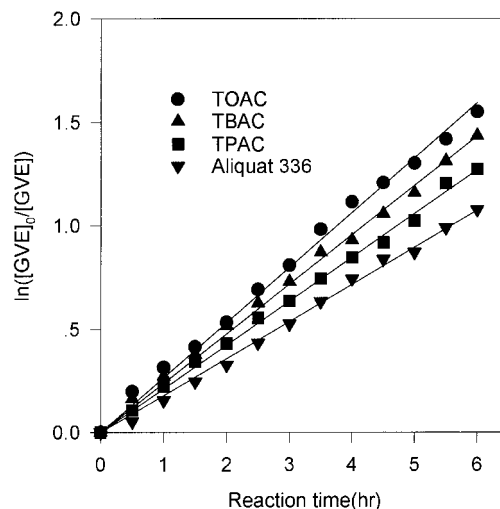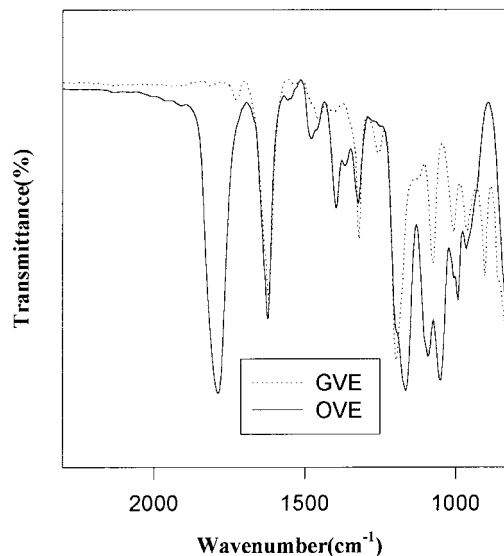

Figure 3   FTIR spectra of GVE and OVE.

Figure 4 A ^{1}H-NMR spectrum of OVE.
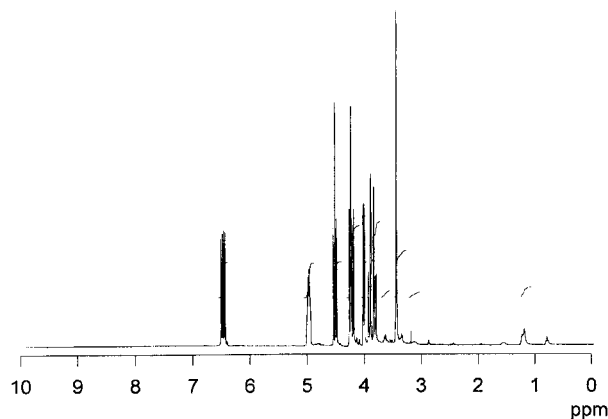

Figure 6 A ^{1}H-NMR spectrum of poly(OVE-*co*-NPM).

The synthesis of OVE was carried out with various quaternary ammonium salt catalysts and the first-order plots are shown in Figure 2. Because the plots of ln([GVE]$_0$/[GVE]) versus time give good straight lines, the reaction can be considered as first order with respect to [GVE]. The reaction rate constant can be estimated from the slope. The highest rate constant was observed when TOAC was used as a catalyst, which was probably due to its high alkyl chain length and the high nucleophilicity of the chloride anion. It is known that the rate-determining step of the epoxide–CO$_2$ reaction involves nucleophilic attack of an anion to the oxirane ring. According to the mechanism proposed by Kihara et al.,[1] bulky quatern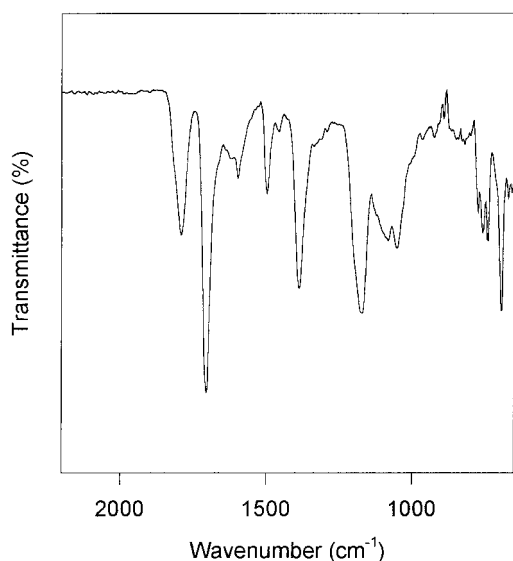ary salts, which have longer distances between cations and anions, are generally known to exhibit higher activity in activating anions. The high nucleophilicity of the Cl$^-$ anion in an aprotic solvent is also known to enhance the attack of the anion to the epoxide ring of GVE.[9] The yield of OVE with TOAC at 80°C for 6 h was 80%.

The order of the catalytic activity in Figure 2 can also be explained by the concept of accessibility. The accessibility of the cation may be defined as a factor of the attraction between the cation and anion. A qualitative parameter for characterizing accessibility was suggested based on the strong dependence of the electrostatic interaction on the distance of the closest approach between the cation and anion (which is determined by the steric factor). This parameter, termed q, is simply the sum of the reciprocals of the carbon number of linear alkyl chains attached to a central nitrogen atom of the quaternary ammonium cation.[10] The

Figure 5 An FTIR spectrum of poly(OVE-*co*-NPM).

Table I   Mole Fraction of OVE and Parameters for Finneman–Ross Method in Copolymerization of OVE and NPM

M_1[a]	m_1[b]	F[c]	f[d]	f/F^2	$(f - 1)/F$
10	5.2	0.11	0.05	4.13	−8.64
30	16.1	0.43	0.19	1.03	−1.88
50	33.3	1.00	0.50	0.5	−0.50
70	62.5	2.33	1.67	0.31	0.29
90	73.2	9.00	2.73	0.03	0.19

[a] Moles of OVE in the feed.
[b] Moles of OVE in the copolymer measured by ^{1}H-NMR spectra.
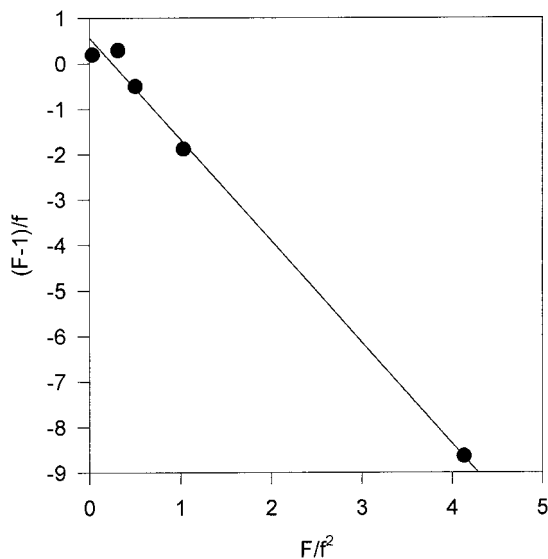[c] $F = M_1/M_2$.
[d] $f = m_1/m_2$.

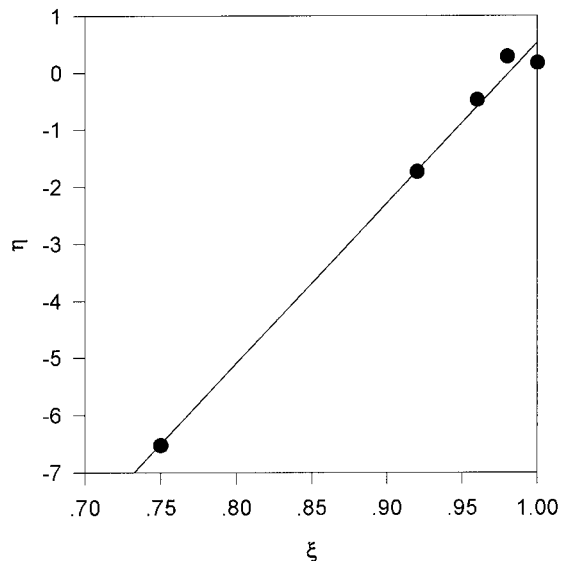**Figure 7**   Fineman–Ross plot for poly(OVE-*co*-NPM).

Figure 8   Kelen–Tudos plot for poly(OVE-*co*-NPM).

quaternary ammonium cation with a q value of greater than 1 is considered accessible. The q value of TOAC is $\frac{1}{2}$ ($=\frac{1}{8}+\frac{1}{8}+\frac{1}{8}+\frac{1}{8}$); that of TBAC, TPAC, and Aliquat 336 is $\frac{1}{1}$ ($=\frac{1}{4}+\frac{1}{4}+\frac{1}{4}+\frac{1}{4}$), $\frac{4}{3}$ ($=\frac{1}{3}+\frac{1}{3}+\frac{1}{3}+\frac{1}{3}$), and $\frac{11}{8}$ ($=\frac{1}{8}+\frac{1}{8}+\frac{1}{8}+\frac{1}{1}$), respectively. Therefore, Aliquat 336 is the most accessible and shows the lowest catalytic activity because of its high interaction between nitrogen and the anion, which inhibits the attack of the chloride anion to the epoxide ring.

Figure 3 shows the IR spectrum of OVE prepared from the addition reaction of GVE and CO_2 at 80°C for 24 h. The IR spectra of OVE and GVE show that an absorption peak at 910 cm^{-1} (C—O—C of oxirane) decreased whereas an absorption peak at 1790 cm^{-1} (C=O of cyclic carbonate) appeared in OVE. ^{1}H-NMR (Fig. 4) analysis also confirmed the formation of OVE. The characteristic peaks (ppm) are as follows: 4.97

(1H, in the cyclic carbonate ring), 4.6 (2H, in the cyclic carbonate ring), and 4.2 (2H, in the side chain CH_2).

Synthesis of OVE-*co*-NPM Copolymer

Radical copolymerization of OVE with NPM was carried out using AIBN in acetonitrile at 60°C for 10 h. The poly(OVE-*co*-NPM) was identified by FTIR and ^{1}H-NMR spectra. The FTIR spectrum of poly(OVE-*co*-NPM) in Figure 5 exhibited characteristic peaks of a cyclic carbonate C=O band at 1790 cm^{-1}, an ether C—O band at 1720 cm^{-1}, and an NPM C=O band at 1700 cm^{-1}. The ^{1}H-NMR analysis shown in Figure 6 confirms the formation of poly(OVE-*co*-NPM). The characteristic peaks (ppm) are identified as follows: 4.8–5.0 (1H, OCH$_2$C$\underline{H}$CH$_2$), 4.56 (2H, OC$\underline{H}_2$CHCH$_2$), and 6.8–7.2 (5H, aromatic).

In order to estimate the monomer reactivity ratios for the copolymer, the copolymer composition was calculated by high resolution ^{1}H-NMR spectroscopy. The monomer conversion was adjusted to be less than 10% and the monomer concentration ratio ([OVE]/[NPM]) in the feed was varied from 0.11 to 9.0. From the integrated areas at the resonance peaks, which are due to the —CH proton for OVE (4.8–5.0 ppm) and the —CH in the aromatic ring for NPM (6.8–7.2 ppm), the composition of OVE and NPM in the copolymer can be determined. The mole fractions of OVE and NPM in the feed and copolymer are shown in Table I. The Finneman–Ross plot of the copoly-

Table II   Parameters for Kelen–Tudos Method in Copolymerization of OVE and NPM

F	f	C	D	ξ	η
0.05	4.13	0.24	−2.09	0.75	−6.53
0.19	1.03	0.97	−1.83	0.92	−1.74
0.50	0.5	2.00	−1.00	0.96	−0.48
1.67	0.31	3.23	0.93	0.98	0.28
2.73	0.03	33.33	5.70	1.00	0.17

$C = F^2/f$, $D = F(f-1)f$, $\alpha = (C_{min}/C_{max})^{1/2}$, $\xi = C/(\alpha + D)$, $\eta = D/(\alpha + C)$.
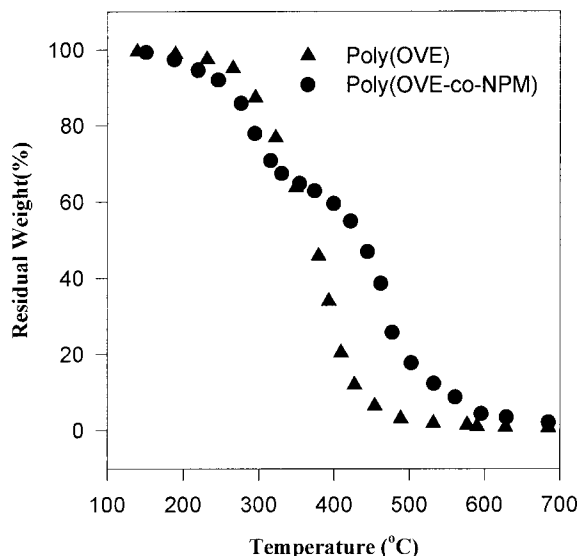
Figure 9 TGA thermograms of poly(OVE) and poly(OVE-co-NPM).

mer of OVE (M_1) and NPM (M_2) is shown in Figure 7. The monomer reactivity ratios can be estimated from the slope and intercept as r_1 = 0.57 and r_2 = 2.23. The monomer reactivity ratios can also be evaluated by the Kelen–Tudos method as shown in Table II and Figure 8. The monomer reactivity ratios can be estimated from the slope and intercept as r_1 = 0.53 and r_2 = 2.24. Because poly(OVE-co-NPM) shows r_1 < 1, r_2 > $1/r_1$, and $r_1 r_2$ > 1, this copolymer has a tendency to form a block copolymer.[11]

Figure 9 shows the TGA curves of poly(OVE) and poly(OVE-co-NPM). It should be noted that the copolymer shows higher thermal stability than poly(OVE) because of the presence of a bulky NPM group. Many N-substituted maleimides are used as comonomers for the maleimide copolymers with a vinyl comonomer by radical copolymerization. The maleimide copolymers are characterized by a high glass-transition temperature and they are thermostable at high temperatures.[12] The molecular weights of the copolymer

were determined as M_w = 112,000 and M_n = 53,000.

Miscibility of Poly(OVE-co-NPM)/SAN and Poly(OVE-co-NPM)/PVC Blends

Polymer miscibility has been the subject of considerable investigation from theoretical and practical standpoints. Many works of calorimetric, spectroscopic, light or neutron scattering, and other experimental techniques have reportedly investigated the miscibility of polymer blends. In this work DSC was used to study the miscibility of polymer blends.

Poly(OVE-co-NPM)/SAN and poly(OVE-co-NPM)/PVC blends were prepared by the solution casting method. In order to examine the degree of miscibility of the poly(OVE-co-NPM)/SAN blends, optical clarity was first investigated (Table III). All the poly(OVE-co-NPM) blends formed clear films when blended with SAN, which seems to mean that the blends are miscible over the whole concentration range. Table IV shows the optical clarity of poly(OVE-co-NPM)/PVC. As for the results for poly(OVE-co-NPM)/SAN blends, the films were clear over the whole concentration range.

The T_g of the polymer blends was measured using DSC for the detailed study of polymer miscibility. The T_g on the DSC thermograms was determined using the midpoint method. Figure 10 shows a typical DSC thermogram of poly(OVE-co-NPM)/PVC blends. The DSC thermogram exhibits the glass-transition temperature shift from the lowest T_g, which corresponds to that of the poly(OVE-co-NPM), to the highest T_g of PVC. One T_g value of the blends confirmed the miscibility of the poly(OVE-co-NPM)/PVC blends. A similar result was obtained for poly-(OVE-co-NPM)/SAN blends. The T_g data taken from the DSC thermograms are summarized in Tables III and IV.

Table III   Optical Clarity and Glass-Transition Temperature (T_g) of Poly(OVE-co-NPM)/SAN Blends

	Poly(OVE-co-NPM)	Poly(OVE-co-NPM)/SAN					SAN
		80/20	60/40	50/50	40/60	20/80	
Optical clarity	—	Clear	Clear	Clear	Clear	Clear	—
T_g (°C)	32.2	54.2	54.3	66.5	66.7	76.6	105

Table IV   Optical Clarity and Glass-Transition Temperature (T_g) of Poly(OVE-*co*-NPM)/PVC Blends

| | Poly(OVE-*co*-NPM) | Poly(OVE-*co*-NPM)/PVC | | | | | PVC |
		85/15	65/35	50/50	35/65	15/85	
Optical clarity	—	Clear	Clear	Clear	Clear	Clear	—
T_g (°C)	32.2	60.1	60.2	61.5	63.5	66.2	88.3

CONCLUSION

An integrated process was developed for the catalytic conversion of carbon dioxide with GVE to useful polymer materials via a cyclic carbonate, OVE. This integrated process could be one choice for the reduction and utilization of greenhouse gas. Poly(OVE-*co*-NPM) copolymers were prepared by radical copolymerization of OVE and NPM. It showed higher thermal stability than poly(OVE). The monomer reactivity ratios were estimated as r_1 (OVE) = 0.53–0.57 and r_2 (NPM) = 2.23–2.24. The blends of the CO_2 containing copolymer with SAN or PVC showed miscibility over the whole concentration range examined, which was based on DSC analyses and optical clarity.

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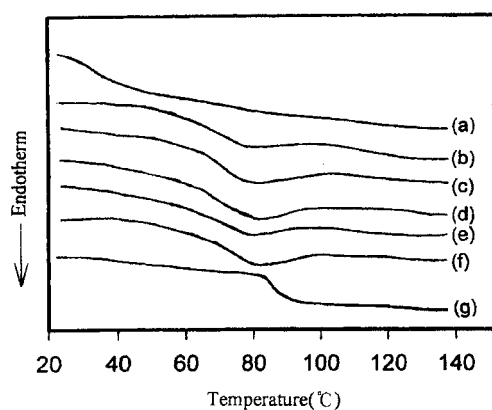
Figure 10   DSC thermograms of poly(OVE-*co*-NPM)/PVC blends and the percentage concentration of poly(OVE-*co*-NPM)/PVC: (a) 100/0, (b) 85/15, (c) 65/35, (d) 50/50, (e) 35/65, (f) 15/85, and (g) 0/100).