Chemical Fixation of Carbon Dioxide to Copolymers Bearing Cyclic Carbonate Group

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Abstract–This study is related to the investigation of the chemical fixation of carbon dioxide to copolymers bearing a cyclic carbonate group and their application to polymer blends. In the synthesis of (2-oxo-1,3-dioxolan-4-yl)methyl vinyl ether (OVE) from glycidyl vinyl ether (GVE) and CO_2, quaternary ammonium salt catalysts showed good yield of OVE. The results with long alkyl chain and with lower accessibility showed a higher catalytic activity. Mixed catalyst of PEG-4000 and NaI showed higher catalytic activity than NaI alone. The copolymer of OVE and acrylonitrile (AN) was prepared by radical copolymerization in acetonitrile at 60 °C. The monomer reactivity ratios were given as r_1(OVE)=0.36 and r_2(AN)=1.21 in the copolymerization of OVE and AN. The films of poly(OVE-co-AN)/PVC blends were cast from DMF. The poly(OVE-co-AN)/PVC blends showed good miscibility over whole composition ranges.

Key words: Chemical Fixation, Carbon Dioxide, Glycidyl Vinyl Ether, Cyclic Carbonate, Copolymer, Polymer Blends

INTRODUCTION

CO_2, CFC, NO_x and hydrocarbons are the main sources of the green house effect. Among these gases, CO_2 plays an important role in global warming. Therefore, the reduction of CO_2 is urgent. Some progress has been made by using various chemical and biological methods to fix and utilize CO_2. A useful method may be the application of CO_2 as a monomer for the synthesis of polymer materials. This method could use CO_2 as a useful polymer. Of special interest are the reactions of CO_2 with oxiranes or some polymers containing pendant groups, since they lead to the production of cyclic carbonates [Rokicki et al., 1984]. These cyclic carbonates can be used as sources for reactive polymer synthesis [Inoue et al., 1982]. The polar polymers are of interest for optical, magnetical and electronic applications.

The synthesis of cyclic carbonates from the reaction of CO_2 with oxirane has been performed using Lewis acids, transition-metal complexes, and organometallic compounds as catalysts under high pressure. But some authors reported the synthesis of 5-membered cyclic carbonates under mild conditions in the presence of metal halides or phase transfer catalysts [Nomura et al., 1980]. Recently, the successful synthesis of a new functional monomer (2-oxo-1,3-dioxolan-4-yl)methyl vinyl ether (OVE), containing both reactive vinyl ether and cyclic carbonate groups, has been described by the reaction of glycidyl vinyl ether (GVE) with carbon dioxide [Moon et al., 1997; Nishikubo et al., 1994]. However, detailed kinetic studies on the synthesis of OVE and its application to polymer blends have not been undertaken.

In the present study, the synthesis of OVE from CO_2 and

GVE was performed in view of the characteristics of quaternary ammonium salts as catalysts. We have also studied monomer reactivity ratio and thermal properties of the copolymer prepared from the OVE and acrylonitrile (AN). In addition, the blends of poly(OVE-co-AN) and PVC were prepared, and the miscibility of the polymer blends was examined by optical clarity and DSC.

EXPERIMENTAL

1. Materials

Glycidyl vinyl ether (GVE) (provided by Seimi Chemical Co. Ltd.), and N-methyl pyrollidinone (NMP) were used after distillation on CaH_2. Quaternary ammonium salts, such as tricaprylylmethylammonium chloride (Aliquat 336), tetrabutyl-ammonium chloride (TBAC), tetraoctyl ammonium chloride (TOAC) and tetrapropylammonium chloride (TPAC) were all in reagent grade and used as purchased without purification.

2. Synthesis of OVE from GVE and Carbon Dioxide

The OVE was synthesized in a semi-batch reactor under atmospheric pressure of CO_2. 1 mmol of catalyst was introduced to a 150 mL three-neck pyrex reactor containing the mixture of 10 mmol of GVE and 50 mL of NMP as solvent, and then the solution was heated to the 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 hours. Periodically, a small portion of the reaction mixture was taken and analyzed by gas chromatograph (HP5890A) equipped with FID using a 10 wt% OV-101/chromosorb W column. The identification of OVE was performed by FT-IR (Mattson Polaris), ^{1}H-NMR and ^{13}C-NMR (Jeol PMX-60 SI, TMS as an internal standard).

3. Synthesis of Poly(OVE-co-AN) and Preparation of Polymer Blends

Radical copolymerization of OVE (5 mmol) with acryloni-

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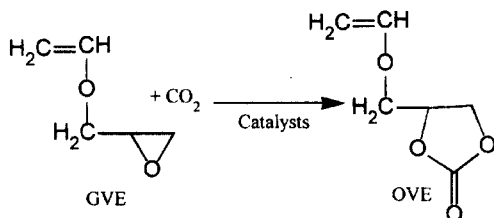E-mail: dwpark2@hyowon.cc.pusan.ac.kr

trile (AN, 5 mmol) was performed using AIBN (5 mg) as an initiator at 60 °C for 10 hr under N_2 atmosphere, and then the solution was poured into diethyl ether to give a precipitate. The obtained polymer was reprecipitated twice, and dried in vacuo at 60 °C for 12 hr. Polymer blends were prepared by solution casting method. A total of 0.4 g of poly(OVE-co-AN) (27 wt% AN) and PVC in weight fraction of poly(OVE-co-AN) of 0, 20, 40, 60, 80 and 100 was dissolved in 4 g of DMF at room temperature for at least 1 day. The films were dried slowly in a Petri dish at room temperature and then kept under vacuum to constant weight.

RESULTS AND DISCUSSIONS

1. Synthesis of OVE from GVE and CO_2

The synthesis of OVE was carried out by the reaction of GVE with carbon dioxide in the presence of various quarternary ammonium salt catalysts as shown in Scheme 1. The structure of OVE was confirmed and exhibited by FT-IR, ^{1}H-NMR and ^{13}C-NMR.

Fig. 1 shows the time variant concentration of GVE with different catalysts at 80 °C. The catalysts used were TOAC, TBAC, TPAC, Aliquat 336 and NaI. Since the plots of ln ([GVE]o/ [GVE]) vs. time give good straight lines, the reaction can be considered as pseudo first-order with respect to [GVE]. From the slope, the order of the rate constant was determined as TOAC>TBAC>TPAC>Aliquat 336>NaI.
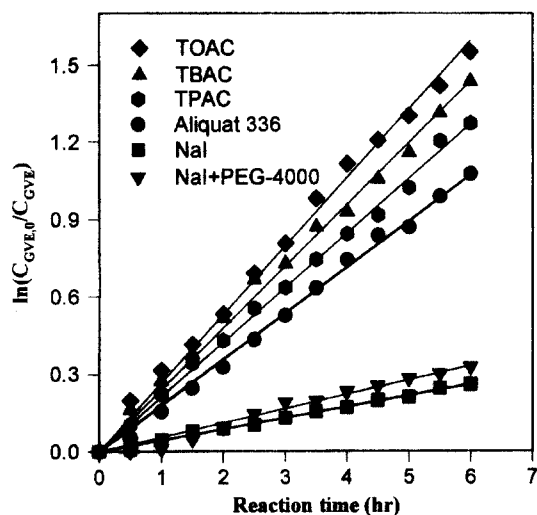

Scheme 1

Fig. 1. Linear plots of ln($C_{GVE,0}$/C_{GVE}) vs. reaction time for different catalysts.

The catalytic activity of quarternary ammonium salt usually depends on the corresponding catalyst cation and counter anion [Starks et al., 1994]. According to the mechanism proposed by Kihara et al. [1993], the rate determining step of the epoxide-CO_2 reaction was known to involve nucleophilic attack of an anion to oxirane ring. In addition, bulky quaternary salts, having longer distances between cations and anions, are generally known to exhibit higher activity in activating anions [Starks et al., 1994]. This explains why quaternary ammonium salt catalysts have higher catalytic activity than NaI and, especially, TO-AC is the most effective in nucleophilic attack of the anion to the oxirane ring of GVE.

The order of the catalytic activity in Fig. 1 can also be explained by the concept of accessibility. The accessibility of cations may be defined as a factor of the attraction between cations and anions. A qualitative parameter for characterizing accessibility was suggested based on the strong dependence of electrostatic interaction on the distance of the closest approach between cations and anions (which is determined by steric factor). This parameter, termed q, is simply the sum of the reciprocals of the carbon number of linear alkyl chains attached to central nitrogen atom of the quaternary ammonium cation [Starks et al., 1994]. The quaternary ammonium cation with a q value of greater than 1 is considered accessible. The q value of TOAC is 1/2(=1/8+1/8+1/8+1/8), that of TBAC, TPAC and Aliquat 336 is 1/1(=1/4+1/4+1/4+1/4), 4/3(=1/3+1/3+1/3+1/3) and 11/8(=1/8+1/8+1/8+1/1), respectively. Therefore, Aliquat 336 is the most accessible and shows the lowest catalytic activity due to its high interaction between nitrogen and anions, which inhibits the attack of chloride anions to the epoxide ring. In the case of catalyst anions, we reported that the rate constant with different halide anions of the quaternary ammonium salts decreases in the order of $Cl^->Br^->I^-$ [Park et al., 1998]. This is consistent with the nucleophilicity of the halide anions.

It is well known that cation-exchangeable phase transfer catalysts, such as crown ethers and polyethylene glycol (PEG), can form a complex with cations and increase higher catalytic activity than metal halide alone. The mixed catalyst of NaI and PEG-4000 showed higher rate constant (k'=7.5×10^{-2} hr^{-1}) than NaI alone (k'=4.3×10^{-2} hr^{-1}), because PEG-4000 forms complex metal cations and activates the halide anions to attack the epoxide ring of GVE. However, a mixed catalyst of KI and 18-crown-6 showed lower catalytic activity (k'=1.7×10^{-2} hr^{-1}) than KI alone (k'=3.8×10^{-2} hr^{-1}). Kihara et al. [1993] reported the effect of crown ether in the reaction of phenyl glycidyl ether and carbon dioxide. They suggested that the catalytic activity decreased due to the decrease of Lewis acidity of cations in the presence of a strong ligand such as crown ether for mixed catalyst.

2. Synthesis and Thermal Properties of Poly(OVE-co-AN)

Radical copolymerization of OVE with AN was carried out using AIBN as initiator in acetonitrile at 60 °C for 10 h. Poly(OVE-co-AN) was identified by an FT-IR spectrometer. The FT-IR spectrum of poly(OVE-co-AN) exhibited characteristic peaks of cyclic carbonate C=O band at 1,790 cm^{-1}, vinyl ether C-O band at 1,154 cm^{-1} and CN band at 2,250 cm^{-1}. In order to estimate the monomer reactivity ratio for the copolymer, the co-
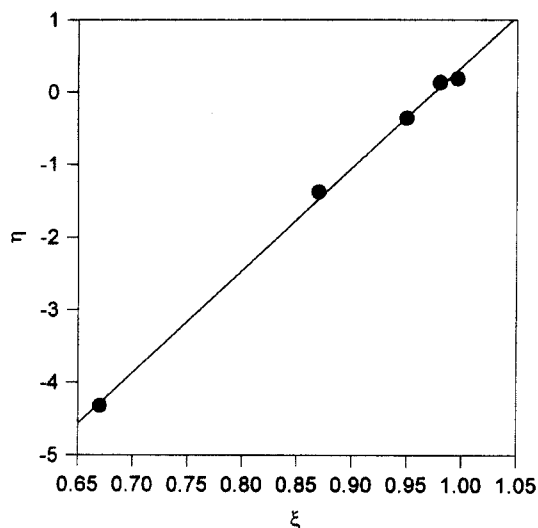
Fig. 2. Kelen-Todus plot of poly(OVE-co-AN).

Table 1. Mole fraction of OVE and parameter for Kelen-Tudos method in copolymerization of OVE and AN

$M_1^{(a)}$	$m_1^{(b)}$	F	f	C	D	ξ	η
12.2	9.5	0.14	0.11	0.18	−1.15	−4.32	0.67
30.0	24.2	0.43	0.32	0.58	−0.91	−1.38	0.87
50.0	38.3	1.00	0.62	1.61	−0.61	−0.36	0.95
71.6	57.3	2.52	1.34	4.74	0.64	0.13	0.98
88.0	67.7	7.33	2.38	22.73	4.25	0.19	1.00

$^{(a)}$Mole fraction of OVE in feed.
$^{(b)}$Mole fraction of OVE in copolymer measured by ^{13}C-NMR.
$F=M_1/M_2$, $f=m_1/m_2$, $C=F^2/f$, $D=F(f-1)/f$, $\alpha=(C_{min}/C_{max})^{1/2}$, $\xi=D/(\alpha+C)$, $\eta=C/(\alpha+C)$.

polymer composition was calculated by high resolution nuclear magnetic resonance spectroscopy [Randall, 1977]. The monomer conversion was adjusted to be less than 10% and the monomer ratio ([OVE]/[AN]) in the feed was varied from 0.14 to 7.33. By measuring areas of C=O peak (OVE) in 165 ppm and CN peak (AN) in 120 ppm, one can determine the mole fraction of OVE and AN in the copolymer. The mole fractions of OVE and AN both in the feed and copolymer are shown in Table 1. The monomer reactivity ratio was evaluated from a Kelen-Tudos plot (Fig. 2) and Table 1. From the slope and intercept, the monomer reactivity ratio could be estimated as $r_1=0.36$ and $r_2=1.21$.

The Q-e scheme of copolymerization is best considered an empirical approach to placing monomer reactivity on a quantitative basis. The values of Q and e are estimated as the reactivity of monomers in the copolymerization. Monomer reactivity is separated into Q, which is the resonance factor (steric factor) in the monomer, and the e, which describes the polar factor [Odian, 1991]. Q-e scheme can be used to give a general idea of the behavior to be expected from a comonomer pair that has not been studied. Copolymerization is more suitable between monomers of similar Q values and different e values.

The Q-e values of OVE for the copolymerization of OVE and AN were calculated based on the Q-e scheme of the copo-

Table 2. Parameters in copolymerization of OVE and AN

M_1	M_2	r_1	r_2	$r_1 \times r_2$	Q_1	e_1
AN	ST			0.01	0.48	1.23
OVE	AN	0.36	1.21	0.44	0.13	0.31

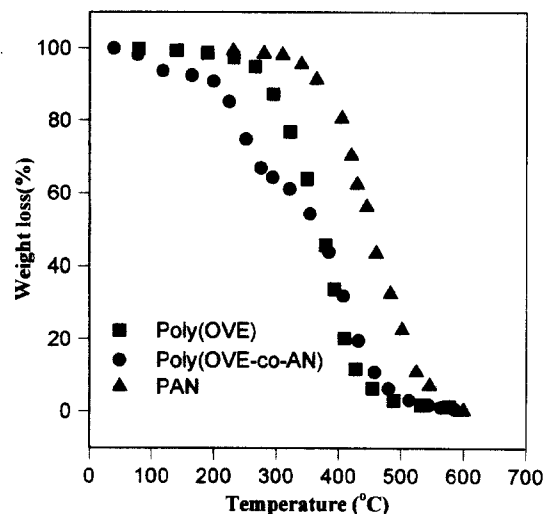ST : Styrene, Q=1, e=−0.8
AN : Acrylonitrile, Q=0.48, e=1.23

Fig. 3. TGA diagram of poly(OVE), poly(OVE-co-AN) and PAN.

lymerization of styrene (Q=1, e=−0.8) with acrylonitrile (Q= 0.48, e=1.23) [Brandrup, 1989] and listed in Table 2. Since Q values of OVE and AN are not so difficult, in the sense of a Q-e scheme in copolymerization one can confirm that it can be easily copolymerized. The Q value of OVE can further be saved to test the possibility of its copolymerization with other commercial polymers. Fig. 3 shows TGA curves of poly(OVE), poly(OVE-co-AN) and polyacrylonitirle (PAN). It was observed that the thermal stability of the polymer increased in the order PAN>poly(OVE-co-AN)>poly(OVE). Therefore, it could be noted that the copolymer showed better thermal stability than the homopolymer of OVE.

3. The Miscibility of Poly(OVE-co-AN)/PVC

Polymer miscibility has been the subject of considerable investigation from both theoretical and practical standpoints. A number of works of calorimetric, spectroscopic, light or neutron scattering, and other experimental techniques have been reported to investigate the miscibility of polymer blends. Of particular interest in the area of polymer blends is the application of DSC to study the miscibility on the molecular level.

In order to examine the degree of miscibility of the poly (OVE-co-AN)/PVC blends, optical clarity was first investigated (Table 3). All the poly(OVE-co-AN) formed clear films when blended with PVC. This means that the blends are miscible

Table 3. Optical clarity of poly(OVE-co-AN)/PVC blends

Poly(OVE-co-AN)/PVC composition	20/80	40/60	60/40	80/20
Optical clarity	Clear	Clear	Clear	Clear

Fig. 4. DSC thermodiagram of poly(OVE-co-AN)/PVC.

OVE   : (2-Oxo-1,3-dioxolan-4-yl)methyl vinyl ether
PAN   : polyacrylonitrile
PEG   : polyethylene glycol
Poly(OVE-co-AN) : copolymer of OVE with AN
PVC   : poly(vinyl chloride)
r_1(OVE) : monomer reactivity ratio of OVE
r_2(AN) : monomer reactivity ratio of AN
TBAC   : tetrabutylammonium chloride
Tg   : glass transition temperature
TOAC   : tetraoctylammonium chloride
TPAC   : tetrapropylammonium chloride

over the whole concentration ranges. For a detailed study of polymer miscibility, the Tg behavior of the polymer blends was tested by differential scanning calorimetry (DSC). DSC measurements of poly (OVE-co-AN)/PVC blends shown in Fig. 4 reveal the shift of glass transition temperature from the lowest Tg, which corresponds to the poly(OVE-co-AN) to the highest Tg of PVC. One Tg value of the blend confirmed the miscibility of the poly(OVE-co-AN)/PVC blends.

CONCLUSION

Carbon dioxide can be effectively added to the epoxide ring of GVE to produce the corresponding cyclic carbonate, OVE. Quaternary ammonium salt catalyst, together with the mixed catalyst of NaI and PEG-4000, showed good catalytic activity even at atmospheric pressure of carbon dioxide. The copolymer of the OVE and AN showed good thermal stability, and the monomer reactivity ratio of OVE(r_1) and AN(r_2) was 0.36 and 1.21, respectively. Since the blends of poly(OVE-co-AN) and PVC were miscible over the entire concentration ranges, catalytic fixation of carbon dioxide to polymers bearing cyclic carbonate as pendant group could be one of choices for the reduction and utilization of greenhouse gas.

ACKNOWLEDGEMENT

NOMENCLATURE

AN   : acrylonitrile
GVE   : glycidyl vinyl ether

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