

Synthesis of Phenoxymethyl Ethylene Carbonate Using Quaternary Ammonium Salt Catalysts Grafted onto Styrene-Vinylbenzylchloride-Montmorillonite Support

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Abstract—The synthesis of phenoxymethyl ethylene carbonate (PMEC) from carbon dioxide and phenyl glycidyl ether (PGE) was investigated using styrene-vinylbenzylchloride-montmorillonite supported quaternary ammonium salt catalysts. The catalysts were prepared by grafting the copolymer of styrene (ST) and vinylbenzyl chloride (VBC) onto montmorillonite (MMT) interlayers, followed by the quaternization using trialkylamines. The influence of VBC concentration, the structure of trialkylamine, and the type of support on the catalytic activity was discussed. Quaternary ammonium salt grafted onto organophilic ST-VBC-MMT intercalates showed higher conversion of PGE than that grafted onto montmorillonite interlayers since the former exhibits greater affinity for organic solvents than the latter does.

Key words: Phenylglycidyl Ether, Carbon Dioxide, Montmorillonite, Polystyrene, Supported Catalyst

INTRODUCTION

Quaternary onium salts are widely used as phase transfer catalysts in the field of organic synthesis [Starks et al., 1994; Sasson et al., 1997]. The quaternary onium salts bounded to polymer resins have been reported by several authors [Akelah et al., 1990; Nishikubo et al., 1990; Tomoi et al., 1986; Tundo et al., 1979; Wang et al., 1994]. Most published works on resin-bound quaternary onium salts use styrene-divinylbenzene related resins because large amount of technology is available on these resins due to their use as ion-exchange resin support [Starks et al., 1994]. The polymer-supported catalysts can be easily separated from reaction mixtures and can be reused, or they can be used in flow systems such as fixed-bed and fluidized-bed reactors.

However, the polymer-supported catalysts have yet some drawbacks such as diffusion limitations, high cost, tendency to swell, mechanical and thermal instability. Several inorganic supports, involving metal oxides [Venturello et al., 1982; Clark et al., 1995], zeolites [Tundo et al., 1985] and clays [Monsef-Mirzai et al., 1981; Ford, 1984] have been substituted for polymers. Clay material has high physical strength and chemical resistance towards acid and alkali treatment [Akelah et al., 1994; Awate et al., 2001; Kim et al., 2001]. Montmorillonite is one of the most widely used support for immobilized and anchored catalysts [Pinnavaia, 1983; Moronta et al., 2002]. It is naturally abundant material and available as inexpensive material.

The chemical fixation of carbon dioxide has received much attention from the view of an environmental problem. An attractive strategy to deal with this situation is converting CO₂ into valuable substances. The reaction of carbon dioxide with oxiranes leading

to 5-membered cyclic carbonates is well known among many examples [Kihara et al., 1993]. The synthesis of cyclic carbonates has been performed using Lewis acids, transition-metal complexes, and organometallic compounds as catalysts under high pressure [Kuran et al., 1984]. Some articles reported the synthesis of 5-membered cyclic carbonates under mild conditions in the presence of metal halides or quaternary ammonium salts [Nomura et al., 1980; Nishikubo et al., 1993; Moon et al., 1997, 1999].

In our previous work [Park et al., 1998], we reported the synthesis of 4-(phenoxymethyl)-1,3-dioxane-2-one (PMEC) from CO₂ and phenyl glycidyl ether (PGE) using monomeric quaternary salt catalysts. PMEC is a good example of cyclic carbonates having high polarity and high reactivity for introduction of functional groups. In the present study, the same reaction was performed using ST-VBC-MMT supported quaternary ammonium salt catalysts to facilitate their separation after reaction. Copolymers of styrene (ST) and vinylbenzylchloride (VBC) containing ammonium salt groups have been grafted onto montmorillonite interlayers by cation exchange process. VBC is often used for polystyrene supported catalysts to attach trialkylamine to the chlorine position [Nishikubo et al., 1993]. The remaining chloromethyl groups were modified to produce ammonium salt containing supported catalysts. Our research has focused on the effects of the amount of VBC, the structure of quaternary ammonium salts and the types of supports on the conversion of PGE in the synthesis of PMEC. A kinetic study on the reaction with the polymer-supported catalyst was also carried out in a semi-batch reactor with a continuous supply of carbon dioxide into the reactor.

EXPERIMENTALS

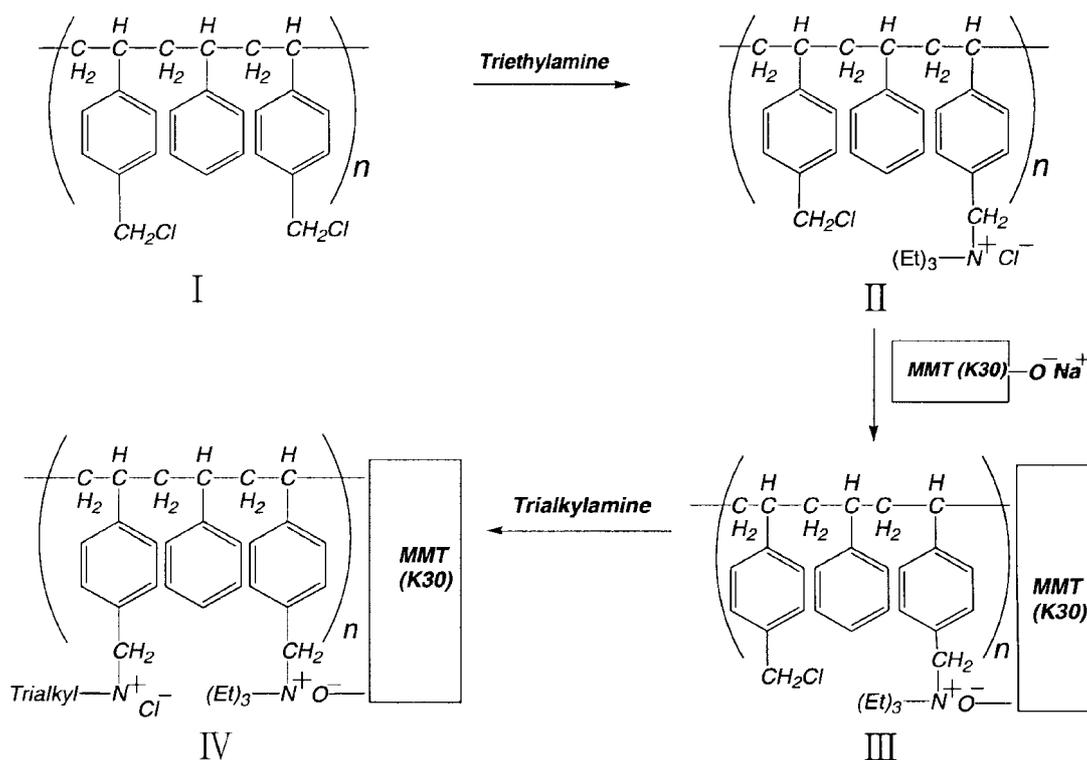
1. Materials

Phenyl glycidyl ether (PGE) and reaction solvents were used after distillation on CaH₂. Styrene and VBC were supplied from Aldrich and used after the removal of inhibitor. Trialkylamines, azobisisobu-

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[‡]This paper is dedicated to Professor Baik-Hyon Ha on the occasion of his retirement from Hanyang University.



Scheme 1.

tyronitrile (AIBN), methylene blue were used without further purification. Montmorillonite (MMT, K30) minerals were supplied by Fluka.

2. Preparation of ST-VBC-MMT Supported Ammonium Salt Catalysts

The grafting of copolymer ST and VBC containing ammonium groups onto montmorillonite interlayers was performed by the method reported previously [Akelah et al., 1994], as shown in Scheme 1. Copolymer (I) was prepared by the bulk polymerization of mixture of ST and VBC using AIBN as free radical initiator. The resulting copolymer was dissolved in acetone and treated with 2% triethylamine by stirring overnight at room temperature. The polymeric ammonium salt (II) was purified by reprecipitation in ethanol and dried under vacuum.

A suspension of 5 g of MMT in 150 mL water was stirred overnight and then 200 mL dioxane were added. To the stirred suspension, a solution of 7.5 g of the polymeric ammonium salt (II) in 50 mL acetone was added dropwise and stirring was continued for 24 h at room temperature. After filtration, the product was suspended in 100 mL DMF and allowed to stand overnight. To the stirred suspension, a solution of another 5 g of II in 50 mL acetone was added. After stirring for 24 h at room temperature, the white precipitate product was filtered, washed with acetone several times and dried at 100 °C under vacuum to give 13 g of the ST-VBC-MMT intercalate (III). To the suspension of 8 g of III, in 20 mL DMF, a solution of 6.5 g tributylamine dissolved in 20 mL benzene was added under stirring. After stirring overnight, ether was added and the product was filtered, washed with ether, and dried in vacuum to yield 10 g of IV. The amount of quaternary ammonium salt bound to polymer support was analyzed by an elemental analyzer (Vario EL). The mor-

phology of the polymer catalyst was analyzed by scanning electron micrograph (SEM, Hitachi S-4200).

The surfactant pillared clay was also prepared by stirring the sodium-exchanged MMT 5 g in 0.2 molar solution of the tetraalkylammonium chloride for 100 h at 60–70 °C [Varma et al., 1998]. The solution was filtered, washed repeatedly with distilled water and dried overnight in an oven (100–110 °C).

3. Addition Reaction of Phenylglycidyl Ether with Carbon Dioxide

The syntheses of PMEC from PGE and CO_2 using ST-VBC-MMT supported catalysts were carried out under atmospheric pressure of CO_2 . The catalyst was introduced to a 150 mL four-neck pyrex reactor containing the mixture of PGE (30 mmol) and solvent (50 mL), and the solution was heated up to 90 °C. Reaction was started by stirring the solution under a slow stream of CO_2 (10 mL/min). At a chosen interval, a small portion of reaction mixture was taken and analyzed by a gas chromatograph (HP6890A) equipped with HP-1 capillary column. The identification of 5-membered cyclic carbonates was performed by FT-IR (Mattson Polaris), $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ (Jeol PMX-60 SI, TMS as an internal standard).

RESULTS AND DISCUSSIONS

1. Preparation and Characterization of ST-VBC-MMT Supported Catalysts

The copolymers of ST and VBC in different ratios (30, 50, 70 mol% ST) were prepared by the bulk radical copolymerization. The inserting of ammonium moieties into chloromethyl groups requiring for the attachment into MMT interlayers was proceeded by the reaction with triethylamine. Fig. 1 shows the decrease of the absorp-

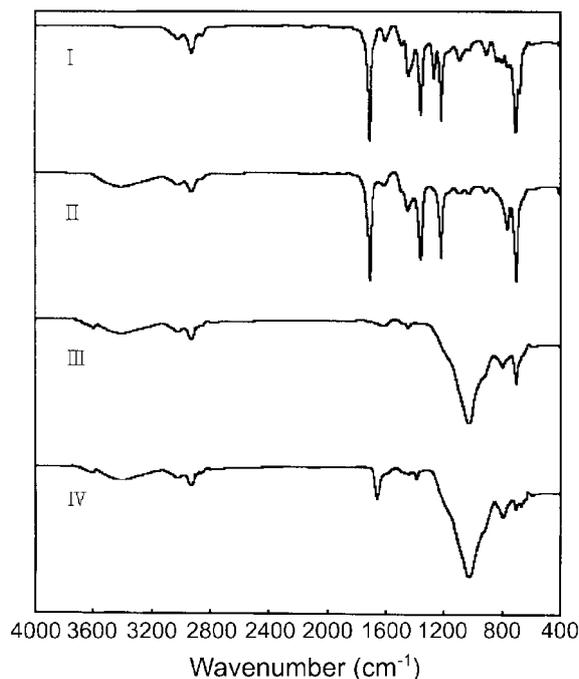


Fig. 1. Infrared spectra of support and catalyst shown in Scheme 1.

Table 1. The composition of ST-VBC-MMT support and the amount of attached nitrogen atom

Support no.	ST (mol%)	VBC (mol%)	Element content (%)			N (mmol/g)
			C	H	N	
III-a	70	30	32.2	4.65	0.33	0.24
III-b	50	50	22.9	3.42	0.35	0.25
III-c	30	70	25.7	3.79	0.31	0.22

tion band of chloromethyl group (710 cm^{-1}) from II to IV. The IR spectrum also shows an absorption band of $-\text{N}^+$ at $3,500\text{ cm}^{-1}$. Table 1 lists the composition and the amount of triethylammonium chloride group for different ST-VBC copolymers. The amount of ammonium salt increased with the increase of VBC from 30 to 70 mol%. Treatment of the polymeric ammonium salt (II) with MMT produced an ionic bond between them through the exchange of the inorganic cations of MMT interlayers with the positively charged

ammonium groups of the polymer. Akelah et al. [1994] reported that the solvation of the ST-VBC-MMT intercalate with DMF, which led to better grafted products, was attributed to the aprotic nature of the DMF and ST-VBC-MMT intercalate. The hydrophilic surfaces of MMT have changed to an organophilic nature by its treatment with polystyrene. The quaternization of the remaining chloromethyl groups of ST-VBC-MMT intercalate (III) was carried out by treatment with different trialkylamines. Table 2 shows the composition and the amount of the quaternized amine group for the ST-VBC-MMT supported catalysts. When tetrabutylamine was used, the attached amount of the pendant ammonium salt groups increased with the increase of VBC. However, this trend was not observed for the other trialkylamines because of their large molecular size.

2. Activity Test of ST-VBC-MMT Supported Catalysts

In order to study the effects of these parameters on the catalytic activity, the addition reaction of PGE and CO_2 at 90°C was performed with the catalysts of equal amount of attached quaternary ammonium salts. Therefore, 0.3 mmol of pendant benzyltributylammonium bromide residues was used with 30 mmol of PGE. Fig. 2 shows time variant conversion of PGE with different types of catalysts. Tetrabutylammonium chloride salt attached to MMT showed lower PGE conversion than that supported onto ST-VBC-MMT. The increase in the organophilic nature of the ST-VBC-MMT supported catalyst resulted in the increase of attraction of organophilic reagent PGE. The soluble polymer supported catalyst ST-VBC, prepared by the method reported previously [Kim et al., 2002], showed the highest conversion of PGE. However, this catalyst has a drawback of separation after reaction, since it needs another precipitation step for the reuse of the catalyst.

The effects of the chemical composition and polarity of polymer backbone are studied using C-1, C-4, and C-7. Fig. 3 shows the conversion of PGE with these catalysts in different solvents; toluene, DMF and DMAc. The catalyst containing 70% VBC segments (C-7) showed higher PGE conversion in all the three solvents than the catalyst C-1 that has 30% VBC units. This meant that the reaction carried out in the presence of more hydrophilic catalyst was more effective than that with less hydrophilic one. Thus reaction rate increased with decreasing the degree of hydrophobic styrene segments in the ST-VBC-MMT supported catalyst.

Even though the active sites are bound to polymer supports, solvent can also influence the reactivity of the catalyst [Sasson et al., 1997]. Fig. 3 shows that the conversion of PGE with toluene is higher

Table 2. The composition of supports and the attached amount of benzyltrialkyl ammonium chloride

Catalyst no.	ST (mol%)	VBC (mol%)	Amine	Element content (%)			Attached ammonium salt (mmol/g)	Polymer/g-cat (g)
				C	H	N		
C-1	70	30	TBA	32.0	4.82	3.09	1.41	0.40
C-2	70	30	THA	38.3	6.11	2.18	1.76	0.46
C-3	70	30	TOA	46.7	7.71	2.00	1.42	0.56
C-4	50	50	TBA	25.7	5.22	2.27	1.62	0.37
C-5	50	50	THA	23.0	4.14	1.88	1.34	0.29
C-6	50	50	TOA	26.8	4.74	2.02	1.45	0.34
C-7	30	70	TBA	25.6	3.90	1.97	2.20	0.32
C-8	30	70	THA	42.4	6.97	2.47	1.56	0.52
C-9	30	70	TOA	40.5	6.54	1.99	1.43	0.49

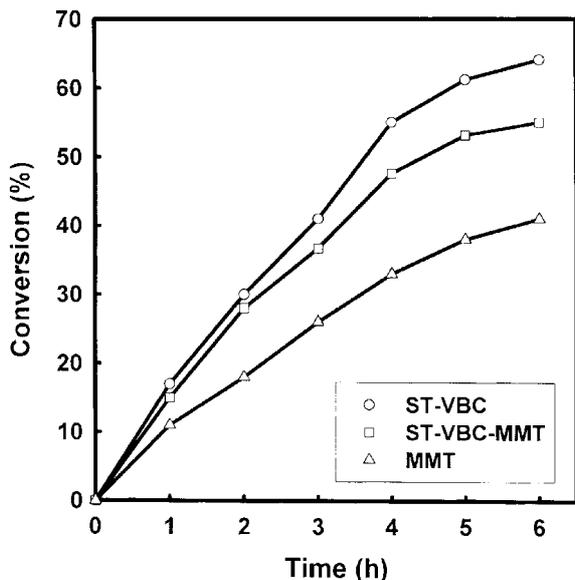


Fig. 2. Time variant conversion of PGE for different supported quaternary salt catalysts.

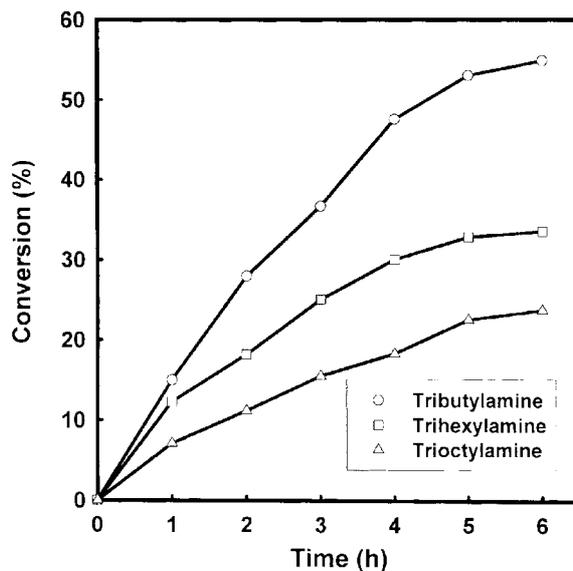


Fig. 4. Effect of the trialkylamine structure on the conversion of PGE.

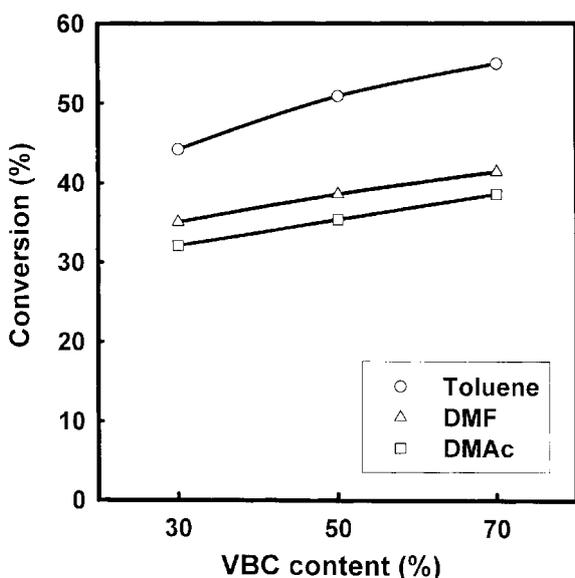


Fig. 3. Variation of PGE conversion with the content of vinylbenzylchloride in different solvents.

than that in DMF and DMAc. The solvent can affect nucleophilic attack of quaternary salt to the epoxide ring of PGE. Swelling is primarily due to the solvation of the interlayer ammonium cations and the interlayer distance can be increased remarkably in solvents, which have strong attractive forces to the intercalated active site and epoxide ring [Akelah et al., 1994]. The role of ST-VBC-MMT intercalate is to stimulate the contact between the catalyst and the epoxide ring and hence to improve the conversion of PGE.

Fig. 4 shows the effect of cation structure of the quaternary salt on the conversion of PGE. The catalyst prepared with tributylamine showed the highest conversion of PGE. In our previous work [Park et al., 1998] on the same reaction with unsupported liquid quaternary ammonium salts catalysts, the order of catalytic activity for

the salt was tetraoctyl->tetrahexyl->tetrabutyl->tetraethyl-ammonium salt. Bulky quaternary salts, having longer distances between cations and anions, are generally known to exhibit higher activity in activating anions. However, the immobilized catalyst from trihexyl or trioctyl amines show lower catalytic activity than that of tributylamine. The result indicates that the steric hindrance of bulky alkyl structure in the ST-VBC-MMT intercalate inhibits the approach of PGE to the supported active sites.

To test the stability of the polymer-immobilized catalyst, 4 successive experimental runs are carried out with the C-2 catalyst for the reaction of PGE and CO₂ in DMF at 90 °C. Each experimental run continued 6 h and then the used catalyst was separated and washed for the next run. Fig. 5 shows that the polymer-immobilized quaternary ammonium salt catalyst can be reused for at least

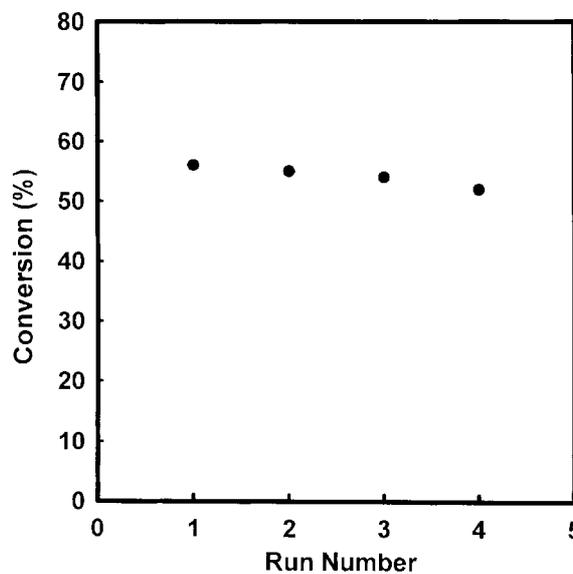


Fig. 5. Stability test of C-7 catalyst.

4 successive runs with a decrease of its initial activity of less than 10%. Surface analysis of the used catalysts by energy dispersive spectroscopy (EDS, Jeol JXA-8600) confirmed the maintenance of chloride group bound to the polymer support after 4th run.

3. Kinetic Studies in a Semi-Batch Reactor

For the addition reaction of CO₂ with PGE using polymer-supported catalysts, the following elementary reaction steps can be proposed, where we set R=PGE, P=PMEC, and QX=supported quaternary ammonium salt catalyst.



k_1 , k_2 and k_3 are reaction rate constants.

The rate of formation of P can be written as

$$dP/dt = k_3[CO_2][RQX^*] \quad (3)$$

The active intermediate RQX* has a very short lifetime because of its high reactivity, and it is present only in low concentrations. Therefore, pseudo-steady-state approximation, in which the net rate of formation RQX* equals to its rate of disappearance, can be applied. Since the addition reaction of CO₂ with PGE is carried out in a semi-batch reactor with a constant flow of CO₂, the concentration of PGE varies only because the concentration of dissolved CO₂ in solvent can be assumed constant.

$$dP/dt = k'[R][QX] \quad (4)$$

where k' is $k_3 k_1 [CO_2] / (k_2 + k_3 [CO_2])$.

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

$$\ln([PGE]_0/[PGE]) = kt \quad (5)$$

From the slope of the linear plot between $\ln([PGE]_0/[PGE])$ vs. time, one can estimate the pseudo first-order rate constant k . The addition of CO₂ with PGE was carried out using 1 mol% of C-7

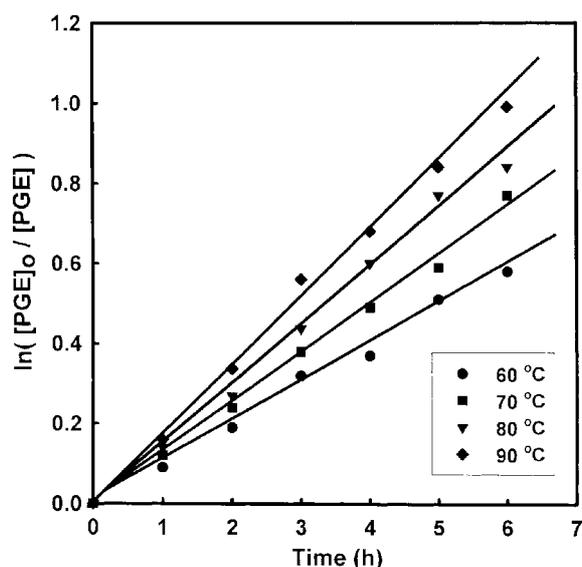


Fig. 6. First order plots of carbon dioxide addition with PGE for C-7 catalyst at different reaction temperatures.

catalyst in DMF at 60, 70, 80 and 90 °C. As shown in Fig. 6, the experimental data fit well to the pseudo first-order kinetics. The linear dependence of the pseudo first-order rate constants with the amount of catalyst was previously reported by Nishikubo et al. [1993]. This result indicates that the assumed reaction steps [Eqs. (1) and (2)] are reasonable for the reaction mechanism. The pseudo first-order rate constant k for 60, 70, 80 and 90 °C was 0.087, 0.098, 0.107 and 0.119 h⁻¹, respectively. From the Arrhenius plot, the apparent activation energy for the CO₂ addition reaction was estimated as 10.5 kJ/mol. The rate constants for the same reaction with the soluble ST-VBC supported benzyltributylammonium salt catalyst were 0.114, 0.180, 0.197 and 0.202 for 60, 70, 80 and 90 °C, respectively. The activation energy was 18.2 kJ/mol. From these results, one can see that the ST-VBC-MMT supported catalysts showed smaller reaction rate constants than the ST-VBC supported ones at the expense of the increased separation facility.

CONCLUSIONS

Carbon dioxide can be effectively added to the epoxide ring of phenyl glycidyl ether (PGE) to produce the corresponding 5-membered cyclic carbonate. The ST-VBC-MMT supported quaternary ammonium salts showed good catalytic activity even at the atmospheric pressure of carbon dioxide. The catalytic activity highly depends on the composition of VBC and the structure of trialkylamine, and the type of support. The catalyst can be reused for several times and considered to have high possibility of easy recovery. The addition reaction of CO₂ to PGE can be considered as pseudo-first order with the concentration of PGE, and the apparent activation energy was estimated as 10.5 kJ/mol.

ACKNOWLEDGEMENT

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NOMENCLATURE

AIBN : azobisisobutyronitrile
 DMAc : *N,N*-dimethyl acetamide
 DMF : dimethyl formamide
 MMT : montmorillonite
 PGE : phenyl glycidyl ether
 PMEC : phenoxyethyl ethylene carbonate
 QX : supported quaternary ammonium salt
 ST : styrene
 VBC : vinylbenzylchloride
 k : rate constant [h⁻¹]

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