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APPLICATION OF QUATERNARY AMMONIUM SALT AS CATALYST IN THE REACTION OF GLYCIDYL METHACRYLATE WITH CO_2

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Abstract – This study is related to the investigation of the characteristics of quaternary ammonium salt catalyst on the addition reaction of carbon dioxide and glycidyl methacrylate (GMA) to form (2-oxo-1,3-dioxolan-4-yl) methyl methacrylate (DOMA). Among the salts tested, the ones with higher alkyl chain length and with more nucleophilic counter anion showed a higher catalytic activity. The DOMA monomer was obtained in non polar solvent like toluene and cyclohexane, while poly (DOMA) could be directly obtained in aprotic dipolar solvent such as DMF. In order to facilitate recovery of catalyst, polymer-immobilized quaternary ammonium salt was prepared by copolymerization of styrene (ST), divinylbenzene (DVB) and vinyl benzene chloride (VBC). The catalyst with 2 wt% of DVB, 25 wt% of VBC and quaternized tributyl amine showed the highest catalytic activity, and its activity was maintained even up to 10 successive experimental runs.

Key words: Glycidyl Methacrylate, Carbon Dioxide Addition, Quaternary Ammonium Salts

INTRODUCTION

Chemical fixation of carbon dioxide is a very attractive subject in view of resource utilization and environmental problems. Various chemical and biological methods to fix and utilize CO_2 are under study. Among them, the application of carbon dioxide as a monomer for the synthesis of various polymers has received much attention in recent years. The reactions of carbon dioxide with oxiranes leading to 5-membered cyclic carbonates are well-known among many examples. These cyclic carbonates can be used as aprotic polar solvents, electrolytes for batteries and sources for reactive polymer synthesis [Inoue et al., 1982]. The polar polymers obtained from the cyclic carbonate and diamine 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, organometallic compounds as catalysts under high pressure [Nomura et al., 1980]. But some authors reported the synthesis of 5-membered cyclic carbonates under mild conditions in the presence of metal halides or phase transfer catalyst [Rokicki et al., 1984; Kihara et al., 1992; Nishikubo et al., 1994]. Especially, the successful synthesis of a new functional monomer (2-oxo-1,3-dioxolan-4-yl)methyl methacrylate (DOMA), containing both reactive methacrylate and cyclic carbonate groups, have been described by the reaction of glycidyl methacrlyate (GMA) with carbon dioxide in recent year [Kihara and Endo, 1992]. However, detailed kinetic studies have not been undertaken.

In the present study, synthesis of DOMA from the reaction of GMA and carbon dioxide was investigated using quaternary ammonium halides as catalyst. Kinetic studies are carried out in a high pressure batch reactor. The effects of quaternary cation, counter anion and solvent on the conversion of GMA are discussed to understand the reaction mechanism. In order to facilitate the recovery of catalyst, polymer-supported quaternary ammonium salt catalysts are also studied in this work.

EXPERIMENTAL

1. Materials

Glycidyl methacrylate (GMA) and reaction solvents were used after distillation on CaH_2. Quaternary ammonium salts, such as tricaprylylmethyl ammonium chloride (Aliquat 336), tetrabutylammonium chloride (TBAC), tetrabutylammonium bromide (TBAB), tetrabutylammonium iodide (TBAI), and tetraoctylammonium chloride (TOAC) were all reagent grade and used as purchased without purification.

2. Experimental

The syntheses of DOMA from GMA and CO_2 were carried out under both atmospheric and high pressure of CO_2. For the former case, the catalyst was introduced to a 150 mL three-neck pyrex reactor containing the mixture of GMA and solvent, and the solution was heated up to a desired temperature. 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 reaction mixture was taken and analyzed by gas chromatograph (HP5890A) equipped with a 10 wt% OV-101/chromosorb W column or 10 wt% SE-30/chromosorb W column and FID. The identification of 5-membered cyclic carbonates was performed by FT-IR (Mattson Polaris), ^{1}H-NMR and ^{13}C-NMR (Jeol PMX-60 SI, TMS as an internal standard).

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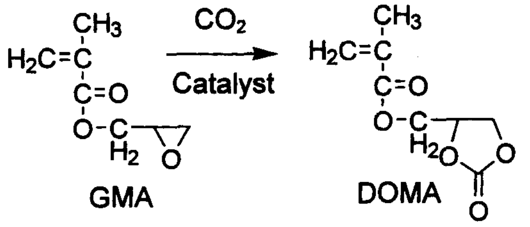
For the experiments with high CO_2 pressure, 100 mL of solvent containing both epoxide and catalyst was introduced to an autoclave (Parr 4841), and the reactor was pressurized to a desired level by a CO_2 cylinder. The variation of reactor pressure during the experiment was followed by a pressure transducer. The final reaction mixture was analyzed by the same method as described above.

Polymer-immobilized quaternary ammonium salt catalysts were prepared by copolymerization of styrene (ST), divinylbenzene (DVB), vinyl benzene chloride (VBC) according to the method of Tomoi and Ford [1981]. The amount of quaternary ammonium salt immobilized on polymer support was calculated by Volhard method [Tomoi and Ford, 1981]. The synthesis of DOMA from GMA and CO_2 using polymer-immobilized quaternary ammonium salts was carried out at atmospheric pressure of CO_2.

RESULTS AND DISCUSSIONS

The synthesis of DOMA was carried out by the reaction of GMA with carbon dioxide in the presence of various quarternary ammonium salt catalysts as shown in Scheme 1. The formation of 5-membered cyclic carbonates was characterized by an IR spectroscopy and absorption peak of C=O in the cyclic ring was identified at 1,790 cm^{-1} (Fig. 1). The ^{13}C-NMR and ^{1}H-NMR analysis also confirmed the synthesis of cyclic carbonates.



Scheme 1.

1. Effects of Catalyst Structure

The catalytic activity of quarternary ammonium salt usually depends on the corresponding catalyst cation and counter anion [Starks et al., 1994]. In order to understand the effects of cation structure on the conversion of GMA, quaternary ammonium chloride catalysts of different alkyl cation (tetrabutyl, tetrahexyl, and tetraoctyl) were used at 80 °C. The time variant conversions of GMA are shown in Fig. 2. The order of catalytic activity is determined as TOAC > THAC > TBAC in the reaction of GMA and CO_2. The rate determining step of the epoxide-CO_2 reaction involves nucleophilic attack of an anion to oxirane. According to the mechanism proposed by Kihara et al. [1993], 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 they are more effective in nucleophilic attack of the anion to the oxirane ring of GMA.

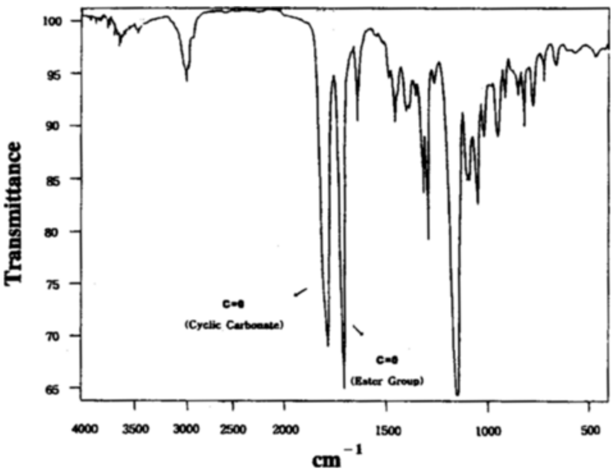


Fig. 1. FT-IR spectrum of DOMA.

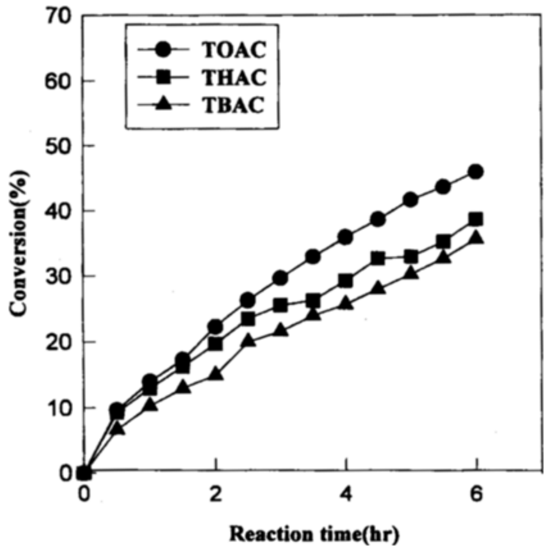


Fig. 2. Effects of quaternary ammonium cation on the conversion of GMA.

(Reaction condition: 30 mmol of GMA, 3 mmol of catalyst, 50 mL of toluene, T=80 °C)

Quaternary ammonium salts with different halide anion (chloride, bromide and iodie) were used to study the effect of counter anion on the conversion of GMA. The experimental results using toluene as solvent are as shown in Fig. 3. For the reaction of GMA and CO_2 in toluene, the conversion of GMA increased in the order of $Cl^- < Br^- < I^-$. This is contrary to other results on the synthesis of (2-oxo-1,3-dioxolan-4-yl)methyl vinyl ether (OVE) [Moon et al., 1997] and 4-phenylmethyl-1,3-dioxolane-2-one (PMO) [Park et al., 1997] using N-methyl pyrollidinone (NMP) as solvent. The solvation of anion is an important factor for the liquid phase reaction. In a protic solvent like toluene, in the case of DOMA synthesis, stronger solvation may be expected with a hard anion like Cl^- than with a soft anion like I^-. Therefore, the order of nucleophilicity will decrease in the order of $I^- > Br^- > Cl^-$, which accords with the order of the reactivity of quaternary ammonium halides. But, in the case of NMP, the order of nucleophilicity increases as $I^- < Br^- < Cl^-$, which was the order of catalytic activity in the synthesis of OVE and PMO. In both cases, the order of activity of halide anions is in accord with the order of nucleophilicity.

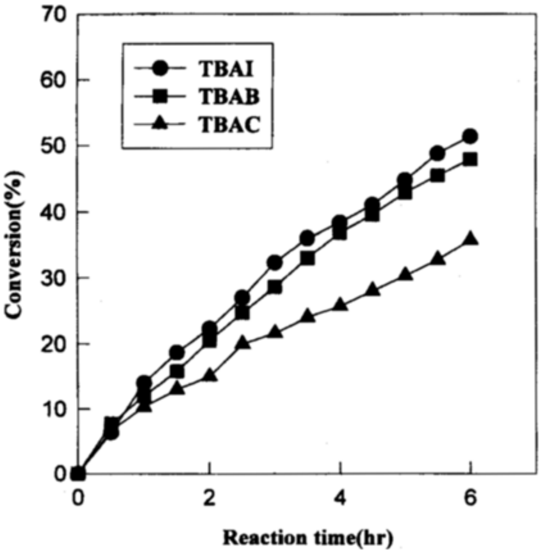


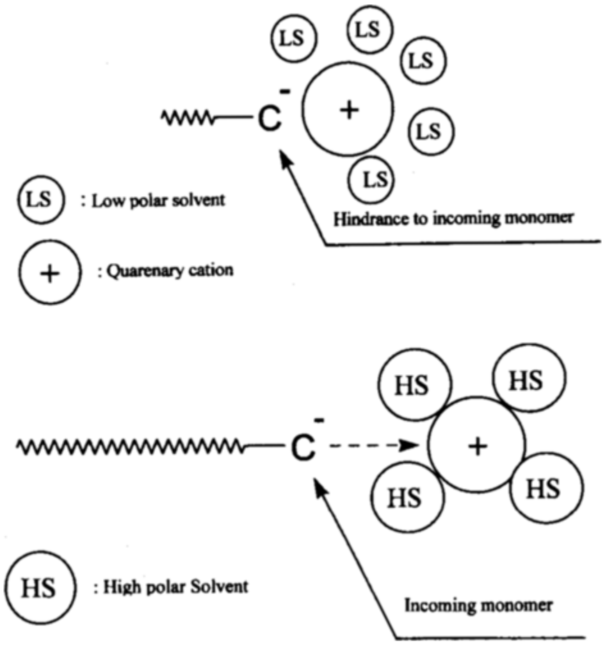
Fig. 3. Effects of counter anion on the conversion of GMA. (Reaction condition: 30 mmol of GMA, 3 mmol of catalyst 50 mL of toluene, T=80 °C)

Table 1. Effect of solvent on the product type

Solvent	Conversion (%)	Product
Toluene	44	M
Diglyme	35.7	M
DMF	96	P
THF	23.3	M
Cyclohexane	21.6	M

M=Monomer, P=Polymer, 30 mmol of GMA, 3 mmol of TBAC, 50 mmol of solvent, T=80 °C

Solvent can also give an important influence on the reaction path in polymerization. Table 1 shows types of product in the reaction of GMA and CO_2 with various solvents. Monomer type DOMA was obtained in non polar solvent like toluene and cyclohexane, and in aprotic solvent of low polarity like diglyme and THF. However, we can directly obtain the polymer of DOMA in high polar aprotic solvent such as DMF. The pendant cyclic carbonate of the polymer was identified by FT-IR spectrum. Therefore, it can be assumed that anionic polymerization as well as the addition reaction of GMA and CO_2 take place simultaneously in DMF. In the case of anionic polymerization as shown in Scheme 2, catalyst anion activates the vinyl group of GMA and the activated anionic site forms near to the vinyl group. Generally counter cation exists as free ion or ionic pair near anionic site. Therefore, polymerization rate depends on the polarity of solvent. Since bulky quaternary ammonium cation inhibits incoming monomer, polymerization has not taken place in low polar solvents. But in the case of high polar solvent like DMF, quaternary ammonium cation is away from the anionic site because of strong solvation. It enables the access of incoming monomer to the activated anion site.



Scheme 2. Effect of solvent polarity in the anionic polymerization.

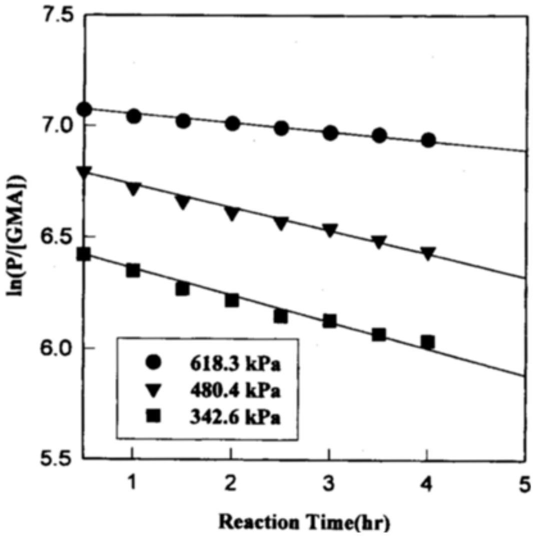


Fig. 4. Linear plot of ln(P/[GMA]) vs. time.

2. Kinetic Study in High Pressure Reactor

When the addition reaction between GMA and CO_2 is carried out in a batch reactor, both [GMA] and $[CO_2]$ vary with time. If we assume that the reaction rate is dependent on both reactants and follows second-order kinetics, the reaction rate of GMA can be expressed as Eq. (1) [Moon et al., 1997].

$$\ln\{P/[GMA]\} = k\{[CO_2]_0 - [GMA]_0\}t + \ln\{P_0/[GMA]_0\} \quad (1)$$

If CO_2 is the only component in the gaseous phase, we can easily estimate the extent of reaction by measuring P with time. Fig. 4 shows the plots of ln{P/[GMA]} vs. time at different P_0 of 342.6, 480.4 and 618.3 kPa at 80 °C with Aliquat 336 catalyst. Since each plot shows a good linear relationship, we can get $k\{[CO_2]_0 - [GMA]_0\}$ and $\ln\{P_0/[GMA]_0\}$ from the slope and intercept respectively. Replacing the initial concentration of dissolved carbon dioxides $[CO_2]_0$ in the slope by $H'P_0$, Eq. (2) and (3) can be obtained:

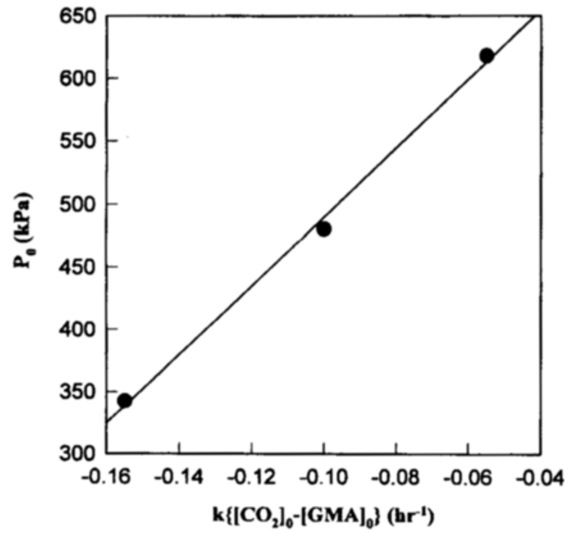


Fig. 5. Linear plot of P_0 vs. k $\{[CO_2]_0 - [GMA]_0\}$.

$$k\{[CO_2]_0 - [GMA]_0\} = k\{H'P_0 - [GMA]_0\} \qquad (2)$$

$$P_0 = \frac{k\{[CO_2]_0 - [GMA]_0\}}{kH'} + \frac{[GMA]_0}{H'} \qquad (3)$$

Here, P_0 is initial pressure of CO_2 and H' is the Henry's constant. Since the plot of P_0 vs. $k\{[CO_2]_0 - [GMA]_0\}$ in Fig. 5 gives another linear relationship, the reaction rate could be considered as second order. This is consistent to the mechanism of some other cyclic carbonate syntheses proposed in earlier reports [Moon et al., 1997; Park et al., 1997]. From the slope and intercept corresponding to 1/(kH') and 1/H', the second-order rate constant k and Henry's constant H' at 80 °C are estimated to be 0.56 L/mol·hr and 6.5×10^{-4} mol/L·kPa, respectively. This method is specially advantageous considering that sampling from a pressurized reactor and subsequent analysis of the reaction mixture are very difficult. The H' value of CO_2 in NMP is not known in the literature, but that of CO_2 in water at 80 °C is 1.3×10^{-4} mol/L·kPa [Perry, 1984].

3. Polymer-immobilized Catalyst

Polymer support was prepared by copolymerization of ST, VBC and DVB. Quaternary ammonium salt bounded on polymer support was obtained by the quaternization of tertiary amine to polymer support at room temperature, and the amount of quaternary ammonium salt formed on the polymer support was calculated by Volhard method. The composition of polymer support and the amount of attached quaternary salt are listed in Table 2.

Table 2. The composition of polymer support and the amount of immobilized quaternary salt

Catalyst	ST (wt%)	VBC (wt%)	DVB (wt%)	Attached amount/ g-support (mmol/g)
PIC-1	73	25	2	1.95
PIC-2	88	10	2	2.86
PIC-3	65	25	6	1.67
PIC-4	71	25	4	2.10
PIC-5	63	35	2	3.06
PIC-6	74	25	1	2.23

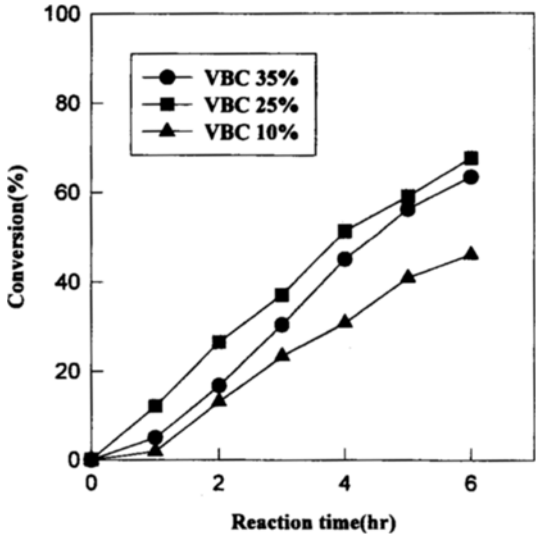


Fig. 6. Effect of amount of vinyl benzene chloride (VBC) on the conversion of GMA.

(Reaction condition: 30 mmol of GMA, 2 mmolar equv. catalyst, 50 mL of DMF, T=100 °C)

Correlation between catalytic activity and VBC amount in polymer support was investigated using the polymer-supported benzyltributylammonium chloride catalysts of 2 wt% DVB. The time variant conversions of GMA at different VBC amount are shown in Fig. 6. The catalytic activity increased gradually with the increase of VBC amount. When VBC amount is large the resulting catalyst may tend to be too high hydrophilic around the active site for some kind of reaction in that it inhibits diffusional approach of hydrophobic reagent into the catalyst zone. The hydrophilic-organophilic balance is a very important factor in the reaction using polymer-immobilized catalyst [Starks et al., 1994]. Therefore, it is nec-

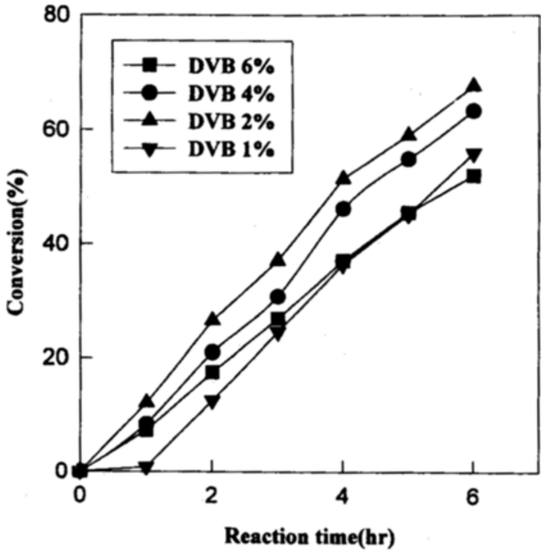


Fig. 7. Effect of amount of divinylbenzene (DVB) on the conversion of GMA.

(Reaction condition: 30 mmol of GMA, 2 mmolar equv. catalyst, 50 mL of DMF, T=100 °C)

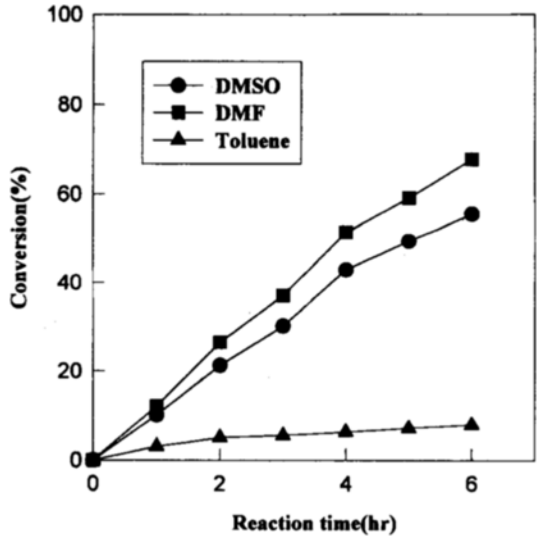


Fig. 8. Effect of solvent on the conversion of GMA.
(Reaction condition: 30 mmol of GMA, 2 mmolar equv. PIC-1 catalyst, 50 mL of DMF, T=100 °C)

essary for the polymer support to have this balance which enables easy diffusion of reagent to the catalytic site.

The amount of DVB as crosslinking agent also affect the conversion of GMA. The effect of crosslinking agent on the conversion was shown in Fig. 7. The catalytic activity showed a maximum at DVB amount of 2 wt%. When more amount of DVB was used, catalytic activity decreased with the increase of DVB amount. It may probably be due to the reduction of diffusion rate by low swelling ability of support. However, when too little was used (1 wt% of DVB), polymer support was very soft and flexible, and it would crumble, lose its shape, and mechanically deteriorate.

The effect of solvent in the reaction of GMA and CO_2 was also studied with polymer supported catalyst PIC-1. Fig. 8 shows the effect of solvent on the conversion of GMA. It was found that the polar solvents like DMSO and DMF showed higher conversion of GMA than toluene. It is generally known that the catalytic activity usually increases with increasing swelling power of solvent and that toluene shows slightly higher swelling ability than polar solvents [Nishikubo et al., 1993]. Although polystyrene bead might have high degree of swelling in toluene, the conversion was very low because of low nucleophilicity of chloride anion in toluene as described in non-supported catalyst experiments.

To test the stability of the immobilized catalyst, 13 successive experimental runs are carried out with the PIC-1 catalyst for the reaction of GMA and CO_2 in DMF at 100 °C. Each experimental run durated for 6 hours. Fig. 9 shows that the polymer-immobilized quaternary ammonium salt can be reused for at least 10 runs. After that time, the catalytic activity gradually decreased and it showed no catalytic activity at 13th run probably due to the mechanical deterioration of the catalyst.

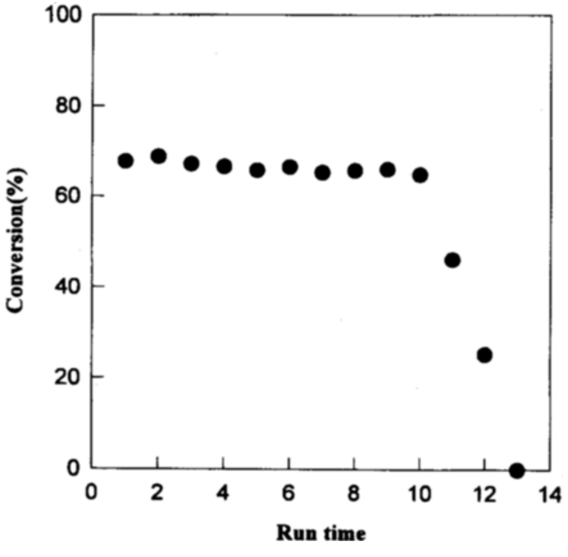


Fig. 9. Effect of catalyst recovery (DVB 2 %, VBC 25 %), tributyl amine quaternalized catalyst).

CONCLUSION

1. Quaternary ammonium salts showed a good catalytic activity in addition reaction of GMA and CO_2.

2. Among the salts tested, the ones with higher alkyl chain length and more nucleophilic counter anion showed higher conversion of GMA.

3. Polymer-immobilized quaternary salt catalyst showed good conversion of GMA and it had higher than 67 % of conversion even after 10 successive experimental runs. The amount of VBC and DVB was an important factor to determine the performance of the catalyst.

ACKNOWLEDGEMENT

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NOMENCLATURE

DMF	: N,N-dimethylformamide
DMSO	: dimethyl sulfoxide
DOMA	: (2-oxo-1,3-dioxolan-4-yl)methyl methacrylate
DVB	: divinylbenzene
GMA	: glycidyl methacrylate
HS	: high polar solvent
LS	: low polar solvent
NMP	: N-methyl pyrollidinone
P	: pressure of carbon dioxide
PIC	: polymer immobilized catalyst
ST	: styrene
TBAB	: tetrabutylammonium bromide
TBAC	: tetrabutylammonium chloride
TBAI	: tetrabutylammonium iodide
THAC	: tetrahexylammonium chloride
THF	: tetrahydrofuran
TOAC	: tetraoctylammonium chloride
VBC	: vinyl benzene chloride

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