

《Original》

## The Reaction of 4,4'-Dihydroxydiphenyl Methane with Glycidyl Methacrylate

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(Received May 31, 1979)

### Abstract

The reaction of 4,4'-dihydroxydiphenyl methane (4,4'-DPM) with glycidyl methacrylate (GMA) catalyzed by triethylbenzyl ammonium chloride (TEBAC) has been studied for the purpose of synthesis of electron beam curable prepolymer. The reaction was in good agreement with third-order kinetics, according to

$$-d[GMA]/dt = k[TEBAC][DPM][GMA]$$

and the apparent activation energy was about 33.4kcal/mole. However, the reaction rates were increased if the reaction proceeded after the mixtures exposed to air for 24 hrs at room temperature.

The effects of the catalyst and the difference in the reactivity between 2,2'-DPM to GMA were discussed. The plausible reaction mechanism was proposed on basis of experimental data obtained.

### 요 약

전자선경화성 prepolymer 를 합성하기 위해서 4,4'-Dihydroxydiphenyl methane (4,4'-DPM) 과 메타크릴산 글리시딜 (GMA)과의 반응을 열화벤질 트리에틸 암모늄 (TEBAC)을 촉매로 하여 진행시키고 그 반응 메커니즘을 고찰하였다. 반응은 3차 속도식

$$-\frac{d[GMA]}{dt} = k[TEBAC][DPM][GMA]$$

에 해당하였고 활성화 에너지는 33.4kcal/mole 이었다. 그러나 혼합물을 상온에서 24시간 방치한 후의 반응은 빠른 속도로 진행되었다. 촉매효과 및 2,2'-DPM 과 4,4'-DPM 의 GMA 에 대한 반응성을 비교 검토하였다. 얻어진 데이터를 기초로 하여 가능한 반응기구를 제시하였다.

### Introduction

The reactions of epoxides with compounds containing active hydrogen such as alcohols, carboxylic acids and amines have been studied

by many researchers from different points of view. However, relatively few reviews have been reported on the reaction of epoxides with phenols.

The reactions between epoxides and phenols were briefly reported by L. Shechter et al.<sup>1)</sup>

D.R. Boyd et al.<sup>2)</sup> K. Uno et al.<sup>3)</sup> M. Yoshino et al.<sup>4)</sup> E. Masuhara et al.<sup>5)</sup> and for chemical kinetics and reaction mechanism, the detailed researches were reported by T. Setsuda et al.<sup>6)~7)</sup> Y. Ishii et al.<sup>8)~9)</sup> S. Sakai et al.<sup>10)~12)</sup> However, they proposed different mechanisms according to the reaction conditions and the kind of reactants.

In this paper, for the purpose of synthesis of electron beam curable prepolymers, kinetics study on the reaction of 4,4'-dihydroxydiphenyl methane with glycidyl methacrylate in the presence of triethylbenzyl ammonium chloride catalyst in DMF solution was undertaken and the reaction mechanism was proposed.

### Experimental

**Phenol and formaldehyde (36% w/w)** were of reagent grade and used without further purification.

**Glycidyl methacrylate (GMA)** and **N,N-dimethyl formamide (DMF)** were of reagent grade and redistilled prior to use.

**Triethylbenzyl ammonium chloride (TEBAC)**. Benzyl chloride 3.27g, triethyl amine 3.43g, ethyl acetate 1.14g, N,N-dimethyl formamide (DMF) 2.8g were placed in three-necked flask equipped with a reflux condenser, and the reaction mixtures were refluxed for 1 hr, the precipitated white crystal was separated by filtration, washed with benzene, and unreacted reactant was removed by vacuum distillation<sup>13)</sup>

**4,4'-Dihydroxydiphenyl methane (4,4'-DPM)**. Phenol (94g) was condensed with formaldehyde (80g of 36% w/w) using p-toluene sulfonic acid as a catalyst for 9 hrs at 30°C, and 4,4'-DPM formed was separated and purified by recrystallization from large excess of water<sup>14)</sup>.

**2,2'-Dihydroxydiphenyl methane (2,2'-**

**DPM)**. Prepared by the condensation of phenol and formaldehyde for 30-120 min until about 70-95% of the formaldehyde had reacted in the presence of zinc acetate catalyst (1% to phenol). After removal of volatile matter by distillation, the product was separated by fractional distillation (160°C/1mm. Hg), and purified by recrystallization from water<sup>15)</sup>.

**The reaction of DPMs with GMA.** A quantity of DPMs dissolved in DMF was placed to 250ml flask equipped with a reflux condenser, and the mixtures were regulated at a constant temperature. After 30 minutes GMA and TEBAC were then added to the mixtures, and this time was considered as the reaction starting point.

The unreacted epoxy groups were determined according to pyridinium chloride in pyridine method<sup>17)</sup> withdrawing the samples from the reaction mixture during the course of the reaction.

### Results

Fig. 1 shows the NMR spectra of these dimers.

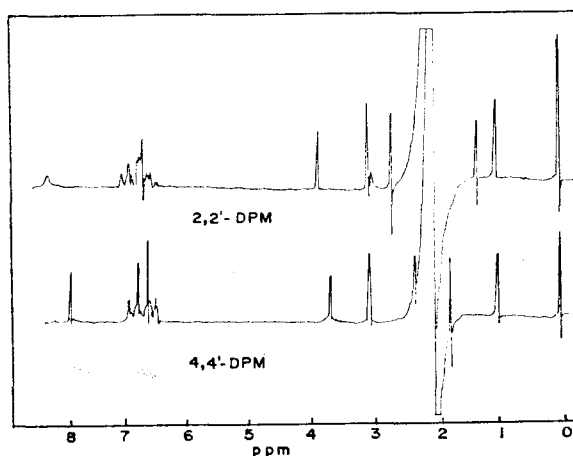


Fig. 1. NMR spectrum of 4,4'-DPM and 2,2'-DPM.

Methylene peaks were observed for the 2,2'-DPM at 3.94 ppm and 3.75 ppm corresponding to 4,4'-DPM, respectively. These

results were in good agreement with those described by Hirst et al.,<sup>16)</sup> 2,2'-DPM and 4,4'-DPM prepared by above methods had a melting point of 118°C and 159°C, respectively.

Fig. 2 is shown the result of the reaction of 1 mole of 4,4'-DPM (0.352mole/l) with 2 moles of GMA (0.704mole/l) in the presence of 2wt. % of TEBAC catalyst to the sample in DMF solution at 130°C.

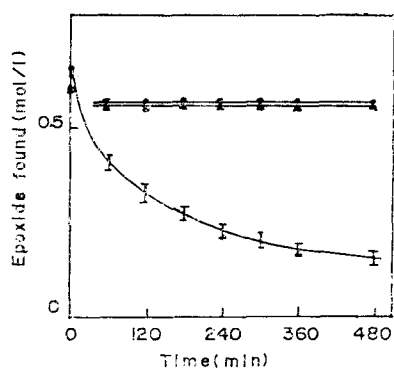


Fig. 2. Reaction of 4,4'-DPM with GMA at 130°C. 4,4'-DPM: 0.352mol/l, GMA: 0.704 mol/l. TEBAC:  $7.49 \times 10^{-3}$  mol/l. (●): GMA only, (▲): GMA+TEBAC, Solvent:DMF.

From the results shown in Fig. 2, it was found that epoxides disappeared rapidly at the initial stage and reached 78% conversion after 8 hrs had passed. The same reactions were repeated several times, and represented the range of error in Fig. 2 also. However, epoxide remained unchanged in the absence of 4,4'-DPM at the same conditions described above. From the results it was found that epoxy group was very stable in these conditions.

If we assume this reaction proceed obeying second-order rate law, the reaction rate can be represented as follows.

$$-\frac{dx}{dt} = k(a-x)(b-\frac{x}{2}) \quad \text{i)}$$

where,  $a$  and  $b$  are the initial concentrations of GMA and 4,4'-DPM, respectively, and  $x$

is the concentration decrease at time  $t$ . Since  $a=2b$

$$-\frac{dx}{dt} = \frac{1}{2}k(a-x)^2 \quad \text{ii)}$$

The integration yields,

$$\frac{1}{a-x} = \frac{1}{2}kt + \text{constant} \quad \text{iii)}$$

when  $t=0$ ,  $x=0$  and  $\text{constant} = \frac{1}{a}$ , Therefore

$$t = \frac{2}{k} \left( \frac{1}{a-x} - \frac{1}{a} \right) \quad \text{iv)}$$

Fig. 3 is shown a plot of the right side of this equation against time at various temperatures.

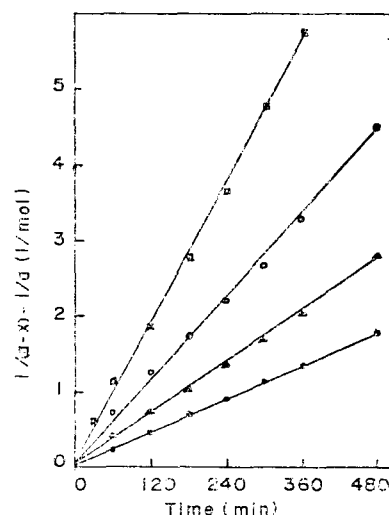


Fig. 3. Second-order plots for the reaction of 4,4'-DPM and GMA at various temperatures. (□): 140°C, (○): 130°C, (▲): 120°C, (●): 110°C) 4,4'-DPM : 0.352 mol/l, GMA:0.074 mol/l, TEBAC :  $7.49 \times 10^{-3}$  mol/l. Solvent : DMF.

Straight lines were obtained, and rate constants were  $1.82 \times 10^{-3}$  1/mole·min (110°C),  $2.86 \times 10^{-3}$  1/mole·min (120°C),  $4.68 \times 10^{-3}$  1/mole/min (130°C) and  $7.98 \times 10^{-3}$  1/mole·min (140°C), respectively. The apparent activation energy calculated from Arrhenius equation was 33.4 kcal./mole.

However, at the same conditions described above, if the mixtures were exposed to air for 24 hrs at room temperature, the reaction

were proceeded more rapidly, and obeyed nearly first-order rate law (Fig. 4).

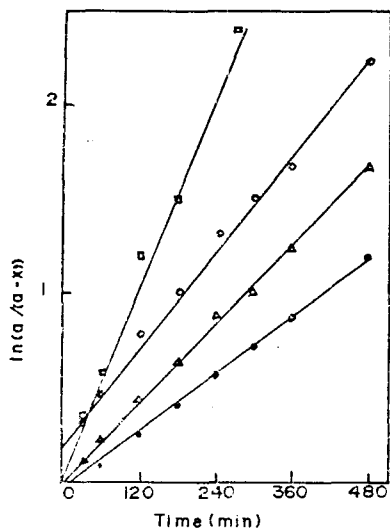


Fig. 4. First-order plots for the reaction of 4,4'-DPM and GMA at various temperatures after the mixtures exposed to air for 24hrs at room temperature. (□: 140°C, ○: 130°C, △: 120°C, ●: 100°C) 4,4'-DPM: 0.352 mol/l, GMA: 0.704 mol/l, TEBAC:  $7.49 \times 10^{-3}$  mol/l. Solvent: DMF.

To clarify this phenomena, the effect of water content was examined. Fig. 5, 6, 7 are shown NMR spectra of 4,4'-DPM, GMA and TEBAC mixtures in DMF solution (Fig. 5), those of mixtures after exposed to air for 3, 6 and 24 hrs (Fig. 6), those of mixtures and water (Fig. 7).

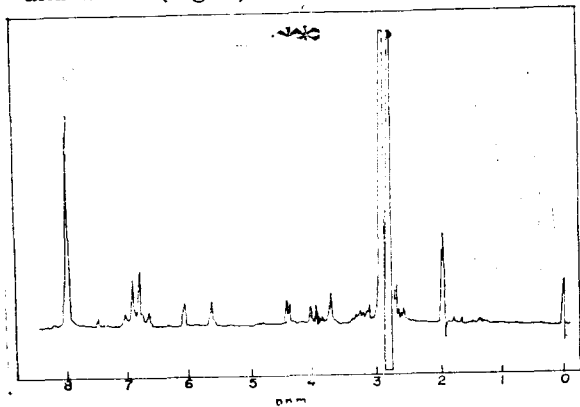


Fig. 5. NMR spectrum of 4,4'-DPM, GMA, DMF and TEBAC mixture.

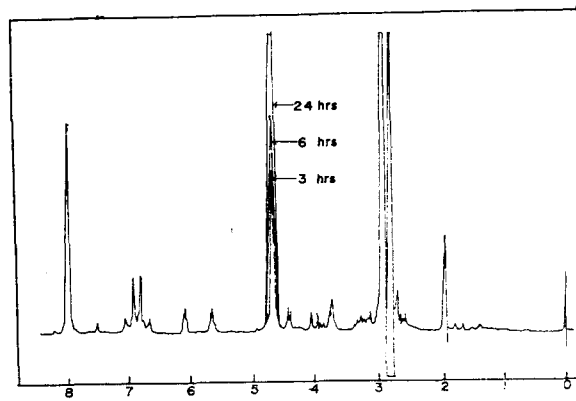


Fig. 6. NMR spectrum of 4,4'-DPM, GMA, DMF and TEBAC mixture exposed to air for 3, 6 and 24hrs at room temperature.

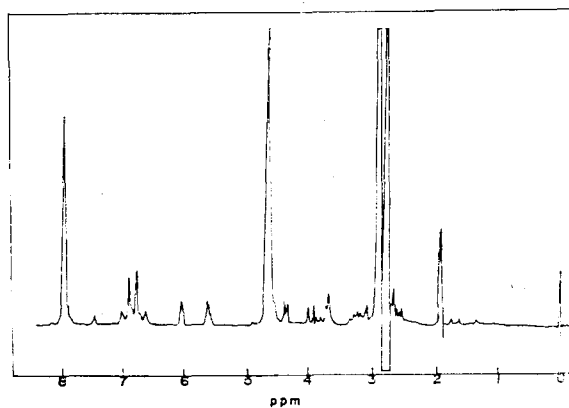


Fig. 7. NMR spectrum of 4,4'-DPM, GMA, DMF, TEBAC, and water mixture.

It was observed that intensity in the region of 4.7 ppm increased with increasing the times of exposing to air. Hence, it was concluded that the mixtures absorbed the water when they were exposed to air.

Fig. 8 shows the relationship between the  $1/(a-x) - 1/a$  and time when the reactions proceeded varying catalyst concentrations, and initial concentrations of 4,4'-DPM (0.352 mole/l) and GMA (0.704 mole/l) were kept constant.

Straight lines were obtained and the reaction rate constant was increased with increasing the concentration of the catalyst. The

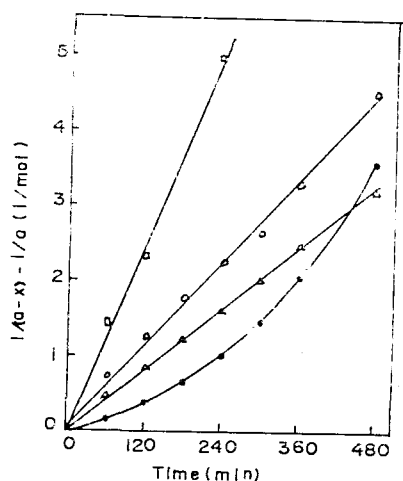


Fig. 8. Second-order plots for the reaction of 4,4'-DPM and GMA at various catalyst concentrations at 130°C. ( $\Delta$ :  $3.74 \times 10^{-3}$  mol/l,  $\circ$ :  $7.49 \times 10^{-3}$  mol/l,  $\square$ :  $14.98 \times 10^{-3}$  mol/l,  $\bullet$ : none) 4,4'-DPM: 0.352 mol/l, GMA: 0.704 mol/l. Solvent: DMF.

reaction rate constants were  $3.38 \times 10^{-3}$  l/mole·min ( $3.74 \times 10^{-3}$  mole/l),  $4.68 \times 10^{-3}$  l/mole·min ( $7.49 \times 10^{-3}$  mole/l),  $1.14 \times 10^{-2}$  l/mole·min ( $14.98 \times 10^{-3}$  mole/l), respectively. However, it was found that the reaction obeyed zero-order rate when the reaction was carried out without catalyst.

The initial rate constants were plotted

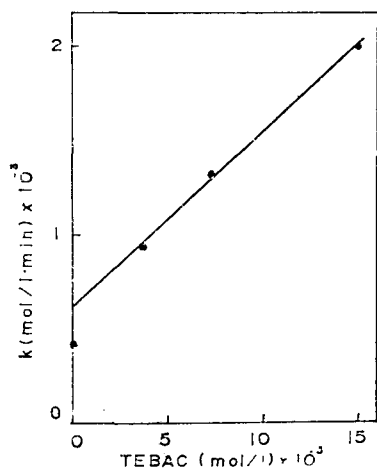


Fig. 9. The rate constant of the reaction as a function of catalyst concentrations at 130°C. 4,4'-DPM: 0.352 mol/l, GMA: 0.704 mol/l. Solvent: DMF.

against the catalyst concentrations in Fig. 9. From the slopes of the straight line, the order of the catalyst was estimated to be about one.

To determine the reaction order of 4,4'-DPM, the reaction proceeded varying the concentrations of 4,4'-DPM, and initial concentrations of GMA (0.704 mole/l) and catalyst ( $7.49 \times 10^{-3}$  mole/l) were kept constant.

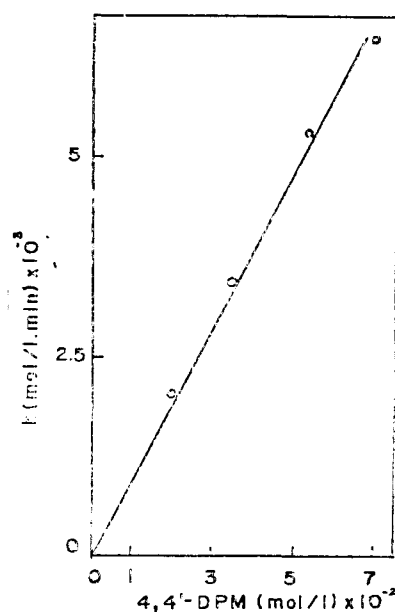


Fig. 10. Determination of the order of the reaction with respect to 4,4'-DPM. GMA: 0.704 mol/l, TEBAC:  $7.49 \times 10^{-3}$  mol/l. Solvent: DMF. Temp.: 130°C.

From the slopes of the straight line passing through the origin (Fig. 10), the reaction order of the 4,4'-DPM was estimated to be about one. On the basis of these results, the experimental kinetic equation was

$$-\frac{d[\text{GMA}]}{dt} = k[\text{TEBAC}][\text{DPM}][\text{GMA}]$$

Fig. 11 is shown the result of the reaction of 4,4'-DPM (0.352 mole/l) with GMA (0.704 mole/l) in the presence of KOH, TEBAC, diethanol amine (DEA), triethanol amine (TEA) catalysts, respectively.

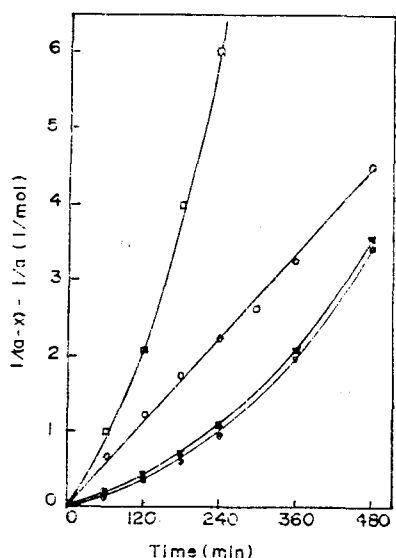


Fig. 11. Catalytic effect on the reaction of 4,4'-DPM with GMA at 130°C. (□: KOH ○:TEBAC, ■:DEA, ●:TEA) 4,4'-DPM: 0.352 mol/l, GMA: 0.704mol/l, catalyst concentration:7.49  $\times 10^{-3}$ mol/l. Solvent:DMF.

Here, each catalyst concentration was kept constant ( $7.49 \times 10^{-3}$  mole/l).

KOH was found to be effective catalyst for these reactions and the reaction was obeyed nearly first-order rather than second-order, whereas DEA and TEA were ineffe-

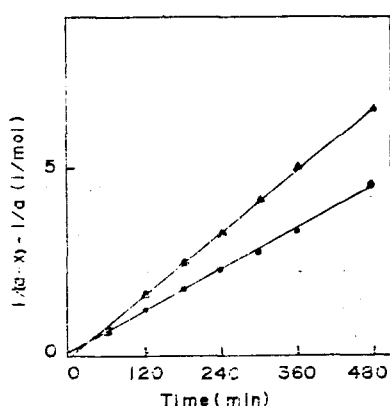


Fig. 12. Second-order plots for the reaction of 4,4'-DPM and 2,2'-DPM with GMA at 130°C. 4,4'-DPM (●) = 2,2'-DPM (▲):0.352mol/l, GMA:0.704 mol/l, TEBAC:  $7.49 \times 10^{-3}$ mol/l, Solvent : DMF.

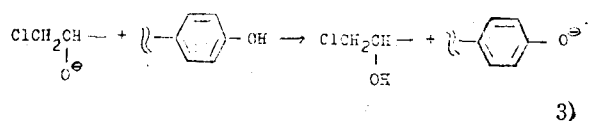
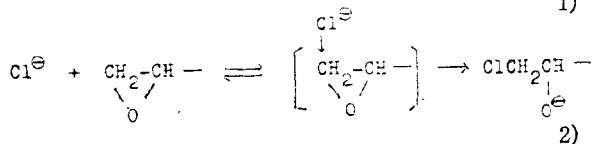
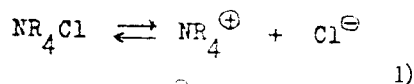
ctive just same as the reaction carried out without catalyst.

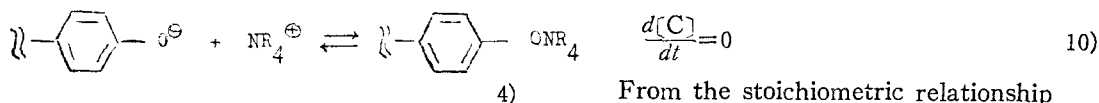
To compare the reactivity of 4,4'-DPM with 2,2'-DPM for GMA, the 4,4'-DPM (each 0.352 mole/l) was reacted with GMA (0.704 mole/l) in the presence of TEBAC ( $7.49 \times 10^{-3}$  mole/l) at 130°C, and it was found that the rate constants were  $6.77 \times 10^{-3}$  1/mole·min for 2,2'-DPM and  $4.68 \times 10^{-3}$  1/mole·min for 4,4'-DPM, respectively.

### Discussion

In the base-catalyzed reaction, three cases were reported, depending on the ionic tendency of the catalysts, on the ionizing power of the solvent, and acidity or basicity difference due to the substituent on the phenol or epoxide. For these reasons, they were divided into free ion mechanism, complex mechanism, or the intermediate of the two cases<sup>18)</sup>.

In the study on the reaction of benzoic acid with phenyl glycidyl ether, Uejima et al.<sup>19)</sup> suggested in the catalytic action of quaternary ammonium salt that anion adds to epoxide to form the strong base alcoholate anion and suggested that actual catalyst species of the reaction is  $\text{COONR}_4$ . Hence, it is anticipated that the catalytic action of TEBAC in the reaction of 4,4'-DPM with GMA is analogous to that mentioned above, that is;



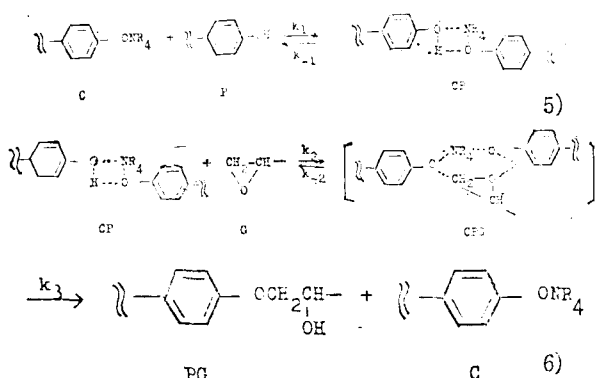


From the stoichiometric relationship

$$-\frac{d[\text{P}]}{dt} = -\frac{d[\text{G}]}{dt} \quad (11)$$

The overall reaction is considered to proceed as follows. The hydrogen bond, at first, is formed between 4,4'-DPM and quaternary ammonium salt of 4,4'-DPM, followed by termolecular reaction mechanism just as proposed by Uejima et al.

Taking into consideration the fact that the 4,4'-DPM has two phenolic hydroxyl groups isolated by methylene group at para position, the reactions can be considered to take place at each end of 4,4'-DPM competically. Therefore, when 1/2 mole of 4,4'-DPM reacts with 1 mole of GMA, the reaction mechanism is considered as follows;



Replacing CP and CPG obtained from eq. 10 and 11 into eq. 8, then overall rate equation is obtained as follows.

$$\begin{aligned} -\frac{d[\text{G}]}{dt} &= k_2[\text{CP}][\text{G}] - k_{-2}[\text{CPG}] \\ &= \frac{k_1 k_2 k_{-2} [\text{C}][\text{P}][\text{G}] + k_1 k_2 k_3 [\text{C}][\text{P}][\text{G}]}{k_{-1} k_{-2} + k_2 k_3 [\text{G}] + k_{-1} k_3} \\ &\quad - \frac{k_1 k_{-2}}{k_3} [\text{C}][\text{P}] + \frac{k_{-1} k_{-2}}{k_3} \\ &\quad \frac{k_1 k_{-2} [\text{C}][\text{P}] + k_1 k_3 [\text{C}][\text{P}]}{k_{-1} k_{-2} + k_2 k_3 [\text{G}] + k_{-1} k_3} \quad (12) \end{aligned}$$

If  $k_3$ , the rate of decomposition of CPG, is very large, this expression reduces to

$$-\frac{d[\text{G}]}{dt} = \frac{k_2 k_3 [\text{C}][\text{P}][\text{G}]}{k_2 [\text{G}] + k_{-1}} \quad (13)$$

The reaction velocity is the rate at which CP reacts with G, that is, in the case of  $k_2 [G] \ll k_{-1}$ , eq. 13 reduces to

$$-\frac{d[\text{G}]}{dt} = \frac{k_1 k_2}{k_{-1}} [\text{C}][\text{P}][\text{G}] = K[\text{C}][\text{P}][\text{G}] \quad (14)$$

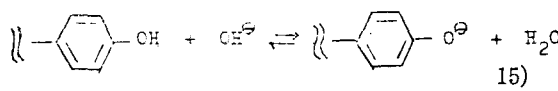
Eq. 14 is in good agreement with the equation obtained from experimental data.

where, C is the quaternary ammonium salt of 1/2 mole of 4,4'-DPM, P is 1/2 mole of 4,4'-DPM, G is the GMA, CP is the C and P complex formed by hydrogen bonding, CPG is the C, P and G termolecular complex, and  $k_1, k_{-1}, k_2, k_{-2}$  and  $k_3$  are the rate constants of the each reaction.

$$\begin{aligned} -\frac{d[\text{P}]}{dt} &= k_1[\text{C}][\text{P}] - k_{-1}[\text{CP}] \quad (7) \\ -\frac{d[\text{G}]}{dt} &= k_2[\text{CP}][\text{G}] - k_{-2}[\text{CPG}] \quad (8) \\ -\frac{d[\text{C}]}{dt} &= k_1[\text{C}][\text{P}] - k_{-1}[\text{CP}] - k_3[\text{CPG}] \quad (9) \end{aligned}$$

For the concentration of catalyst remained unchanged in overall reaction

The reason why the reaction rate was increased, when the reaction was proceeded after the mixture was exposed to air at room temperature, is considered as follows. Beside the reaction mentioned before, TEAC catalyst absorbs water to form quaternary ammonium hydroxide which had a strong ionizing power in DMF solution. These hydroxyl ions formed are then believed to produce phenoxide anions.

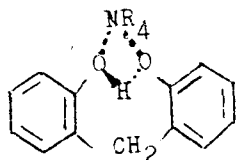


Considering from the fact that the mixtures were deeply colored in reddish brown as increasing the exposing time, the mixtures

were believed to be formed a complex in eq. 5. As a result, the overall reaction rate seems to be increased.

When KOH was used as a catalyst, from the fact that the reaction rate obeyed nearly first-order, this reaction is believed to proceed by ionic mechanism just as proposed by D. R. Boyd,<sup>2)</sup> and seems to accompany complex side reactions judging from the result that the excellent straight line did not obtained.

The greater reactivity of 2, 2'-DPM for the GMA compared to the 4, 4'-DPM may be ascribed to two factors. First, its easiness to form the acid-base complex in eq. 5 as follows



Second factor is considered the close proximity of ring hydroxyl group to each other provides an opportunity for hydrogen bonding to form phenoxide anions<sup>20)</sup>.

#### Acknowledgement

The authors wish to thank professor Myun Sup Kim of the Department of Chemical Engineering of Han Yang University for helpful advice during the course of this work.

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