

# A Novel Reaction of Epoxy Resins with Polyfunctional Active Esters

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## Synopsis

Addition reactions of commercial epoxy resins such as bisphenol-A diglycidylether (BADGE), ethylene glycol diglycidylether (EGGE), and *N,N*-diglycidylaniline (GAN) with various active esters such as di[S-(benzothizolyl)] thioadipate (BTAD), di(4-nitrophenyl) adipate (NPAD), di(S-phenyl) thioadipate (PTAD), and 4-nitrobenzoyl esters of polyfunctional phenols were carried out in neat using quaternary salts or crown ether-salts complexes as a catalyst at 50–130°C. The rate of addition reaction of BTAD was faster than that with other esters under the same reaction conditions. Furthermore, it was found that the rate of addition reaction of the epoxy resins with some active esters was strongly affected by the kind of epoxy resin, the structural formula of carboxylic acid, and the kind of catalyst. The reaction of epoxy resins with polyfunctional active esters proceeded quantitatively at the elevated temperatures. However, some of the mixtures of epoxy resin, polyfunctional active ester and the catalyst showed excellent storage stability at 30°C.

## INTRODUCTION

Epoxy resins have been widely used<sup>1-4</sup> industrially with suitable curing reagents as coatings, adhesives, prepregs, paints, composites, and others. It is also well known that the epoxy resins were modified with a large number of curing reagents such as polyfunctional amines, alcohols, phenols, carboxylic acids, carboxylic anhydrides, Lewis acids, and their complexes. However, the cured epoxy resins by the *prim*- or *sec*-amines, alcohols, phenols and carboxylic acids produced pendant hydroxyl groups in the skeleton. This is undesirable from the viewpoint of lipophilic property and electric property on the cured polymer in industrial applications.

Recently, Funahashi<sup>5,6</sup> reported addition reaction of arylcarboxylates with oxiranes catalyzed by *tert*-amines or potassium *tert*-butoxide at 140–200°C. Renner et al.<sup>7</sup> reported curing of epoxy resin to form a spirodilactone ring by polyfunctional esters of cyanoacetic acid. We have also reported syntheses of self-sensitized photosensitive polymers<sup>8</sup> by addition reaction of poly(glycidyl methacrylate) (PGMA) with nitroaryl cinnamates, insertion reaction<sup>9</sup> of epoxy compounds into aryl ester linkage in the polymer, and new synthesis of cyclic carbonates<sup>10</sup> by the reaction of epoxy compounds with  $\beta$ -butyrolactone using quaternary salts or crown ether-KBr complex as a catalyst under relatively mild reaction conditions. In a previous paper, we studied<sup>11</sup> the rate of addition

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reactions of pendant epoxide groups in PGMA with various active esters, the catalytic effect of reaction and the reaction mechanism in detail.

This article reports on novel curing of epoxy resins by some polyfunctional active esters using the quaternary salts or crown ether-potassium salts system as a catalyst, and storage stability of the mixtures.

## EXPERIMENTAL

### Materials

Commercial epoxy resins such as bisphenol-A diglycidylether (BADGE) (Yuka-Shell Epoxy Co. Ltd., Epicoat-828) ethylene glycol diglycidylether (EGGE) (Kyoeisha Yushi Co. Ltd., Epolight-40E) and *N,N*-diglycidylaniline (GAN) (Nippon Kayaku Co. Ltd., GAN), and reagent-grade catalysts such as tetramethylammonium bromide (TMAB), tetraethylammonium bromide (TEAB), tetrapropylammonium bromide (TPAB), tetrabutylammonium bromide (TBAB), tetrapentylammonium bromide (TPEAB), tetrahexylammonium bromide (THAB), tetraoctylammonium bromide (TOAB), tetrabutylammonium chloride (TBAC), tetrabutylammonium iodide (TBAI), tetrabutylammonium hydrogensulfate (TBAH), tetrabutylammonium perchlorate (TBAP), tetrabutylphosphonium bromide (TBPB), tetramethylammonium chloride (TMAC), tetraethylammonium chloride (TEAC), tetrapropylammonium chloride (TPAC), tetrapentylammonium chloride (TPEAC), benzyltriethylammonium bromide (BTEAB), benzyltriethylammonium chloride (BTEAC), dicyclohexyl-18-crown-6 (DCHC), potassium phenoxide (KOPh), potassium acetate (KOAc), potassium benzoate (KOBz), potassium thiocyanate (KSCN), potassium bromide (KBr), potassium iodide (KI), and tributylamine (TBA) were used without further purification. Di[S-(2-benzothiazolyl)] thioadipate (BTAD) (m.p. 131–132°C), di[S-(2-benzothiazolyl)] thiosebacate (BTSB) (mp. 122–123°C), and di[S-(2-benzothiazolyl)] thioisophthalate (BTIP) (m.p. 117–118°C) were synthesized by the reactions of 2-mercapto-benzothiazole with the respective acids chloride and then recrystallized twice from suitable solvents as reported previously.<sup>12</sup> Di(4-nitrophenyl)adipate (NPAD) (m.p. 123–124°C)<sup>13</sup> and di(S-phenyl) thioadipate (PTAD) (m.p. 79–81°C)<sup>13</sup> were prepared by the reaction of adipoyl chloride with 4-nitrophenol or thiophenol and then recrystallized twice from ethanol or hexane, respectively. 4-Nitrobenzoyl ester of poly(vinyl phenol) (VPNB) and 4-nitrobenzoyl ester of *p*-cresol-formaldehyde prepolymer (CNNB) were synthesized from the reaction of commercial poly(vinyl phenol) (Maruzen Oil Co. Ltd., Resin-M;  $M_w = 5500$ ) and the prepared *p*-cresol novolac ( $\bar{M}_w = 6$ ) with 4-nitrobenzoyl chloride in THF, precipitated into water, reprecipitated twice from THF into methanol, and dried at 50°C *in vacuo* in the manner reported<sup>9</sup> previously.

### Apparatus

The Infrared (IR) spectra were recorded on the JASCO model A-202 spectrophotometer.

### Measurement of Rate of Addition Reaction of Epoxide Groups with Ester Moieties

The mixture of epoxy resin (0.5 mmol), polyfunctional ester (0.5 mmol) and 1–7 mol% of the catalyst was prepared without solvent or in small amounts of THF. The mixture was coated on KBr or KRS (Composition:  $\text{TlCl} + \text{TlBr}$ ) plate, and then dried when the THF was used. The mixture on KBr or KRS plate was heated in the test chamber at suitable temperature. The rate of decrease of characteristic absorption at  $910\text{ cm}^{-1}$  due to oxirane ring was measured<sup>14</sup> by IR spectrophotometry.

### Measurement of Storage Stability of the Mixture of Epoxy Resin, Polyfunctional Active Ester and Catalyst

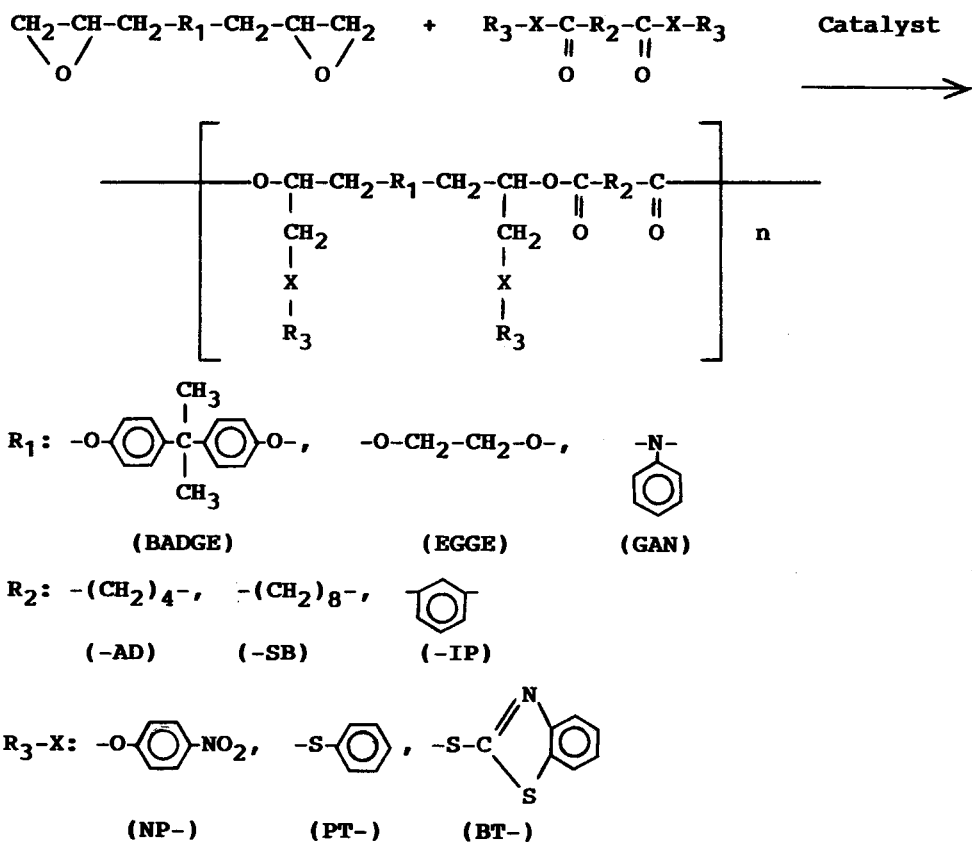
The mixture of epoxy resin (5 mmol), polyfunctional ester (5 mmol), and catalyst (0.25 mmol) was prepared in glass tubes and stored at  $30^\circ\text{C}$ . Curing of the mixture was confirmed by eye measurement and by disappearance of the absorption of  $910\text{ cm}^{-1}$  due to epoxide groups, using IR spectrophotometry.

## RESULTS AND DISCUSSION

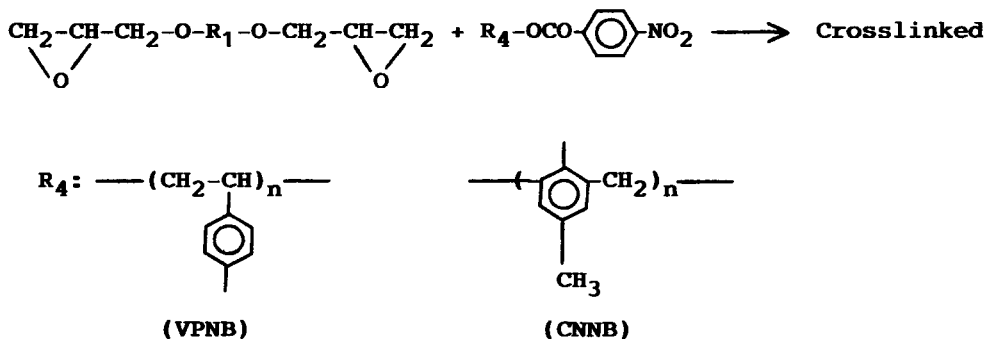
IR spectrum of the mixture prepared from epoxy resin BADGE, active ester TBIP and the catalyst TBAB showed characteristic absorptions at 1660 and  $910\text{ cm}^{-1}$  due to  $\text{C}=\text{O}$  of thioester and oxirane, respectively. However, the IR spectrum dramatically changed and showed disappearing absorptions at 1660 and  $910\text{ cm}^{-1}$  due to  $\text{C}=\text{O}$  of thioester and oxirane, an apparent strong absorption at  $1720\text{ cm}^{-1}$  due to  $\text{C}=\text{O}$  of ester group, and no absorption near  $3400\text{ cm}^{-1}$  due to  $-\text{OH}$  group, when the mixture was heated at  $120^\circ\text{C}$  for 2 h. This is evidence that addition reaction of the epoxy resin and the active ester catalyzed by TBAB proceeded selectively<sup>11</sup> without side reactions such as hydrolysis of epoxide groups or addition reaction of the epoxide with the hydroxyl groups.

The addition reactions of BADGE with BTAD, PTAD, and NPAD were carried out at  $110^\circ\text{C}$  using 5 mol% of TBAB as a catalyst (Fig. 1). The rate of reaction of BADGE with BTAD was much faster than those of BADGE with TPAD and NPAD, and the reaction of BADGE with BTAD proceeded quantitatively for 45 min. Also the reactivity of PTAD was located between those of BTAD and NPAD. This suggested that benzothiazolthioesters, phenylthioesters and phenyl esters of carboxylic acids might become new useful functional groups for the crosslinking reaction of epoxy resin.

As shown in Figure 2, the rates of BADGE with BTAD and BTSB which have flexible alkyl chains, were faster than that with BTIP, which is composed of a rigid benzene ring, when the reaction was carried out at  $70^\circ\text{C}$  using 5 mol% of TBAB. Also the reactivity of BTAD was higher than that of BTSB under the same conditions because of higher acidity of the former compound. It suggested that the reactivity of active ester to epoxy resin was also affected by the kind of carboxylic acid.



The rate of addition reaction of BADGE with BTIP was compared with those of EGGE and GAN at 70°C using TBAB as a catalyst (Fig. 3). Although the initial rate of BADGE was slightly faster than those of EGGE and GAN, the reactions of EGGE and GAN proceeded quantitatively for 40 min. However, the degree of conversion of BADGE was about 80% for 60 min. It seems that flexible ethylene glycol unit affords higher reactivity to EGGE at 70°C. Furthermore, the higher reactivity of GAN might be attributed to the self-catalyzing effect of the *tert*-amino group in GAN.



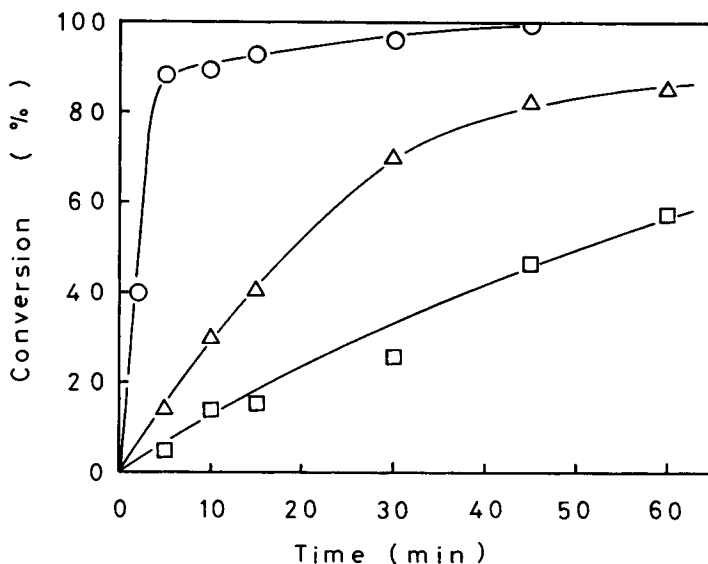


Fig. 1. The rate of addition reaction of BADGE with various esters of adipic acid using 5 mol% of TBAB at 110°C: (○) BTAD, (Δ) PTAD, (□) NPAD.

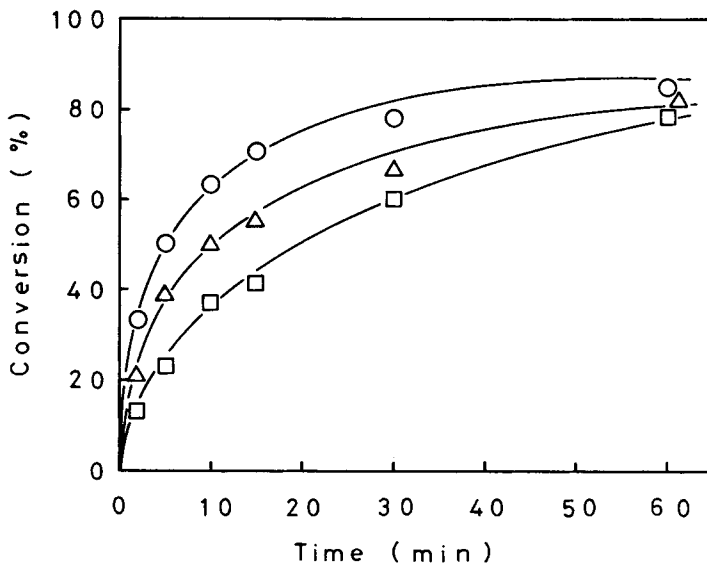


Fig. 2. The rate of addition reaction of BADGE with various esters of 2-mercaptobenzothiazole using 5 mol% of TBAB at 70°C: (○) BTAD, (Δ) BTSB, (□) BTIP.

The reactions of BADGE with polyfunctional active esters such as VPNB and CNNB, which have 4-nitrobenzoyl esters of phenols, were carried out using 5 mol% of TBAB as a catalyst at 100°C and 130°C, respectively (Fig. 4). Although the initial rates of the reaction with CNNB were faster than those with VPNB, the extent of conversion with VPNB was higher than those with CNNB for 60 min at both 100°C and 130°C, respectively. Furthermore, the cured resins of BADGE with VPNB and CNNB were insoluble in any solvents.

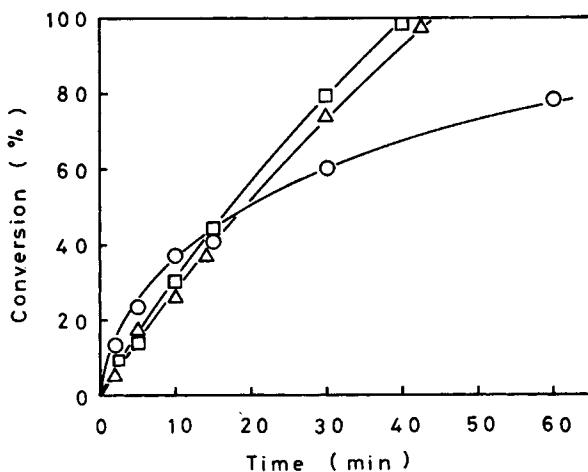


Fig. 3. The rate of addition reaction of BADGE, EGGE, and GAN with BTIP using 5 mol% of TBAB at 70°C: (○) BADGE, (□) EGGE, (Δ) GAN.

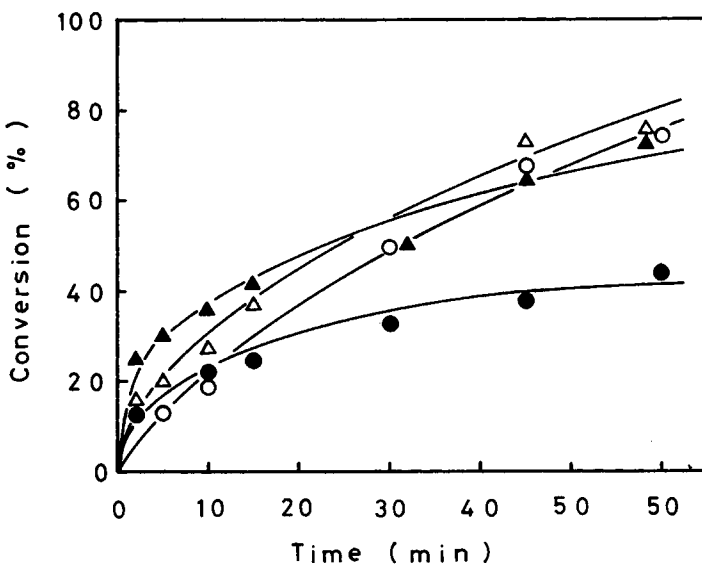


Fig. 4. The rate of addition reaction of BADGE with various esters of polyfunctional phenols using TBAB: (○) VPNB at 100°C, (Δ) VPNB at 130°C, (●) CNNB at 100°C, (▲) CNNB at 130°C.

The effect of alkyl chain in the catalyst was investigated in the reaction of BADGE with BTIP using symmetric quaternary ammonium salts at 70°C for 60 min (Fig 5). TMAC did not show catalytic activity. Although the activity of TPAC was higher than that of TEAC, the activities of TPAC and TPEAC were almost the same as the activity of TBAC under the same conditions when the catalysts have  $\text{Cl}^-$  as a counter ion. On the other hand, when the catalysts having  $\text{Br}^-$  as a counter ion were used, TBAB showed the highest activity, and also the activity of quaternary ammonium salts such as TEAB,

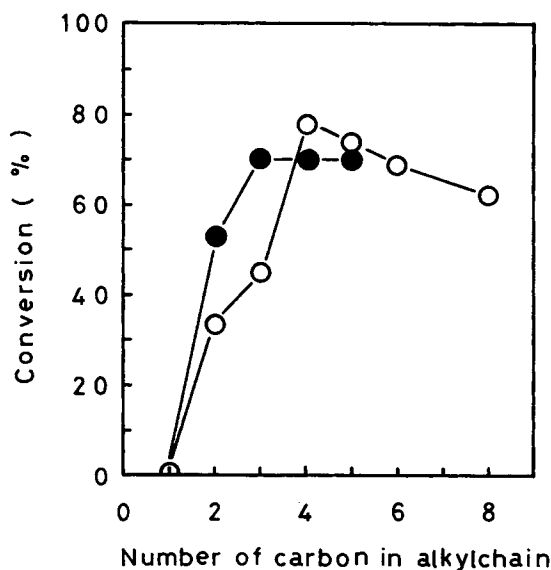


Fig. 5. Relation between the degree of conversion in reaction of BADGE with BTIP at 70°C for 60 min and the chain length in symmetric tetraalkylammonium salts: (●) ammonium salts having Cl<sup>-</sup>, (○) ammonium salts having Br<sup>-</sup>.

TPAB, TPEAB, THAB, and TOAB was depressed with ether increasing or decreasing of the carbon number of alkyl chain of the catalyst. In addition, TMAB did not show any activity for the reaction of BADGE with BTIP at 70°C for 60 min.

As shown in Figure 6, when symmetric tetrabutylammonium salts were used as a catalyst, TBAC and TBAB showed higher catalytic activity than

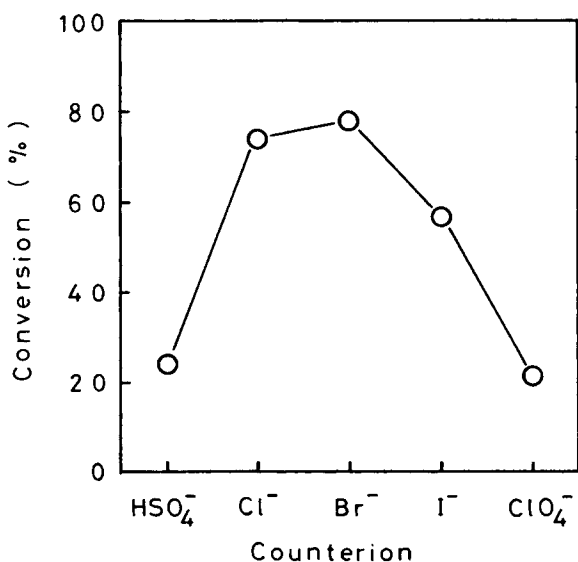


Fig. 6. Relation between the degree of conversion in reaction of BADGE with BTIP at 70°C for 60 min and the paired ion of tetrabutylammonium.

those of TBAI, TBAH, and TBAP in the reaction of BADGE with BTIP at 70°C for 60 min. Furthermore, TBPB, which is a quaternary phosphonium salt, showed the same activity with TBAC; and BTEAC and BTEAB, which are asymmetric quaternary ammonium salts, showed relatively high catalytic activity under the same conditions (Table I). However, the catalytic activity of *tert*-amine TBA was lower than that of TBAB or TBAC.

This means that the reaction of epoxy resin with active ester was strongly affected by the length of alkyl chain in the catalyst and kind of counter ion of the catalyst when quaternary salt was used as a catalyst, and the rate of reaction of epoxy resin with active ester might be adjusted by selecting the catalyst. In addition, it was found that the catalytic activity of quaternary salt in a addition reaction of the epoxide group<sup>11</sup> with the active ester was very similar to that of the quaternary salt as phase transfer catalyst<sup>15</sup> in a substitution reaction of the chloromethyl group with nucleophilic reagent.

Interestingly enough crown ether DCHC-potassium salts system also showed similar catalytic activity. As shown in Figure 7, the activity of DCHC/KOPh was higher than those of DCHC/KOAc and DCHC/KOBz, and the activity of DCHC/KOAc was located between DCHC/KOPh and DCHC/KOBz. This order in relationship of catalytic activity of DCHC complex was essentially the same as the order of alkalinities of the potassium salts.<sup>16</sup> In addition, as summarized in Table I, DCHC complexes with KBr, KI, or KSCN also showed the same high catalytic activity as quaternary ammonium salts. It suggested that crown ether-organic salts or inorganic salts systems might also be used as a useful catalyst for the reaction of epoxy resin with active ester.

The reaction of BADGE with active ester such as BTIP was also strongly affected by the amounts of the catalyst, finding that the rate of reaction increased with increasing the TBAB concentration (Fig. 8).

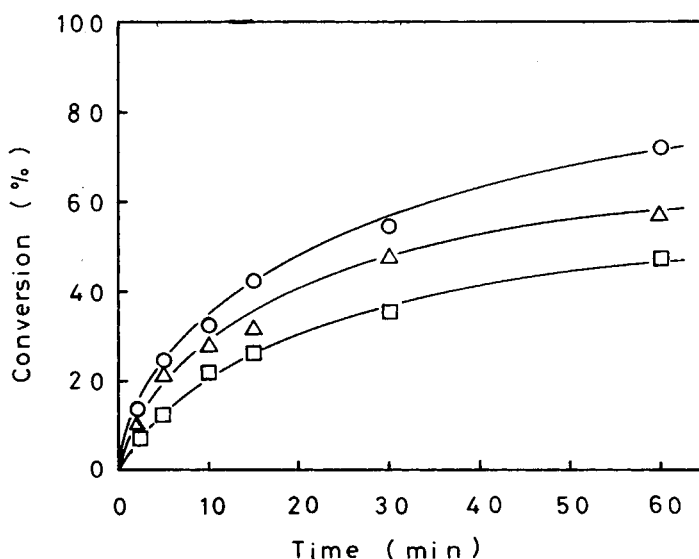


Fig. 7. The rate of addition reaction of BADGE with BTIP using crown ether-various salts system as a catalyst at 70°C: (○) DCHC-KOPh, (Δ) DCHC-KOAc, (□) DCHC-KOBz.



TABLE I  
Effect of Catalyst on Addition Reaction of BADGE with BTIP<sup>a</sup>

Run no.	Catalyst	Degree of reaction (mol%)
1	TBPB	69.5
2	BTEAC	54.9
3	BTEAB	64.6
4	DCHC/KSCN	68.5
5	DCHC/KBr	43.6
6	DCHC/KI	62.7
7	TBA	7.9

<sup>a</sup>The reaction of BADGE with BTIP was carried out using 5 mol% of the catalyst at 70°C for 60 min.

As shown in Figure 9, the reaction of BADGE with BTIP was extremely accelerated by heating and the highest degree of conversion was reached with 98% at 110°C for 60 min. The observed rates of the reaction in neat obey second order kinetics as do the reaction in solution,<sup>11</sup> and the rate constants at 50°C, 60°C, 70°C, and 90°C were  $2.74 \times 10^{-5}$ /mol min,  $2.26 \times 10^{-4}$ /mol min,  $5.35 \times 10^{-4}$ /mol min, and  $9.93 \times 10^{-4}$ /mol min, respectively.

Storage stability data of the mixtures of epoxy resins, esters and catalysts is summarized in Table II. The mixtures of BADGE, EGGE, and GAN with BTAD (which has high reactivity to epoxide) containing TBAB as a catalyst cured within 5–9 days. The mixtures of BADGE, EGGE and GAN with PTAD containing TBAB cured within 14–30 days. On the other hand, the mixtures of BADGE, EGGE, and GAN with NPAD containing TBAB cured

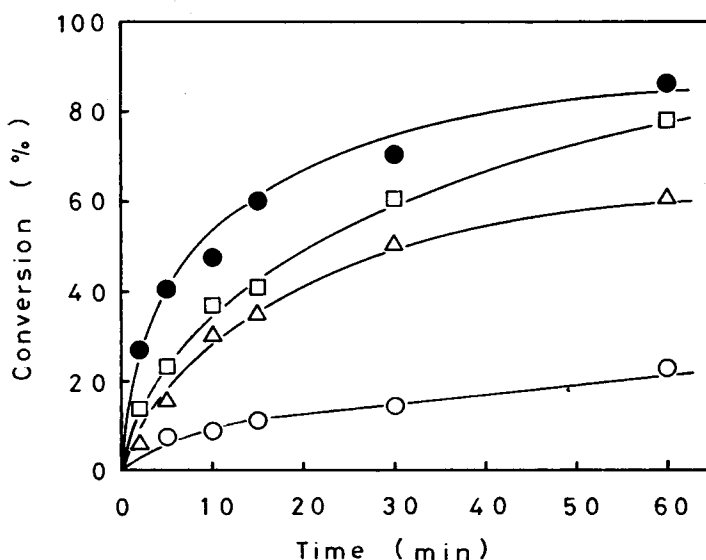


Fig. 8. The rate of addition reaction of BADGE with BTIP under various TBAB concentrations at 70°C: (○) 1 mol%, (△) 3 mol%, (□) 5 mol%, (●) 7 mol%.

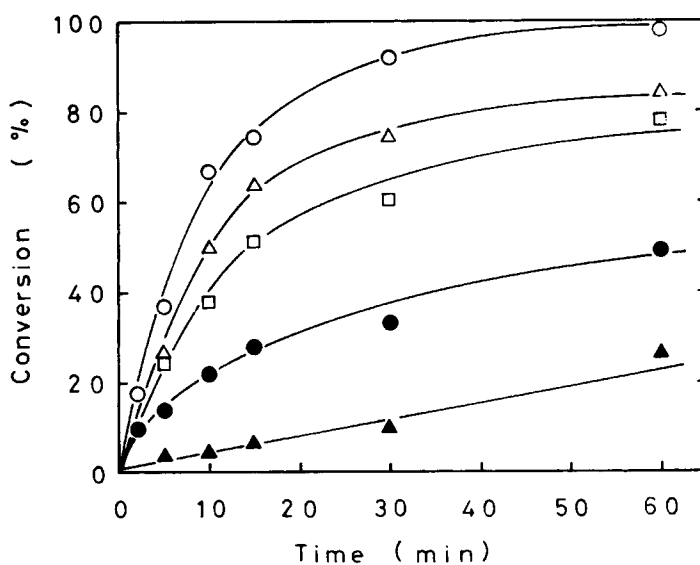


Fig. 9. The rate of addition reaction of BADGE with BTIP using 5 mol% of TBAB at various temperatures: (▲) 50°C, (●) 60°C, (□) 70°C, (Δ) 90°C, (○) 110°C.

TABLE II  
Storage Stability of Epoxy Resin with Polyfunctional Active Ester at 30°C<sup>a</sup>

Epoxy resin	Ester compound	Catalyst	Cured time (days)
BADGE	BTAD	TBAB	9
BADGE	PTAD	TBAB	16
BADGE	NPAD	TBAB	114
EGGE	BTAD	TBAB	8 <sup>b</sup>
EGGE	PTAD	TBAB	30 <sup>b</sup>
EGGE	NPAD	TBAB	140 <sup>b</sup>
GAN	BTAD	TBAB	5
GAN	PTAD	TBAB	19
GAN	NPAD	TBAB	60

<sup>a</sup>The reaction was carried out with 5 mmol of epoxy resin, 5 mmol of ester compound and 0.25 mmol of the catalyst.

<sup>b</sup>Confirmed by IR spectrometry.

in 114, 140, and 60 days under the same conditions, respectively. This suggested that the mixture of epoxy resins with NPAD containing TBAB as a catalyst have very excellent storage stability.

## CONCLUSIONS

From all these results, the following conclusions can be drawn:

1. Addition reaction of epoxy resins with active esters such as 2-mercapto-benzothiazole, thiophenol, and 4-nitrophenol of polyfunctional carboxylic

- acids or 4-nitrobenzoic acid of polyfunctional phenols catalyzed by quaternary salts or crown ether-inorganic or organic salts system were readily carried out.
2. Polyfunctional active esters might be used as new curing reagents for epoxy resins.
  3. Certain superior quaternary salts or the mixture of crown ether with organic and inorganic salts might be used as catalyst for new curing system of epoxy resins with polyfunctional active esters.
  4. Interestingly enough, the catalytic activity of the quaternary salts in addition reaction of the epoxide group with active esters was very similar to the activity of phase transfer catalyst in substitution reaction of the chloromethyl group with nucleophilic reagents.
  5. The rate of reaction and the storage stability of epoxy resin with the active ester might be adjusted by selecting the kind of ester and catalyst.

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Received May 28, 1986

Accepted September 12, 1986