Polymer Journal, Vol. 39, No. 8, pp. 845–852 (2007)


# Curing Behavior of Epoxy Resin Initiated by Amine-Containing Inclusion Complexes

Natsuki AMANOKURA,[1,2] Masami KANEKO,[2] Tetsuya SAHARA,[2] and Ryu SATO[1,†]

[1]*Department of Applied Chemistry, Faculty of Engineering, Iwate University, 4-3-5 Ueda, Morioka 020-8551, Japan*
[2]*R & D Laboratory for High-Performance materials, Nippon Soda Co., Ltd., 12-54 Goi-Minamikaigan, Ichihara 290-0045, Japan*

(Received January 31, 2007; Accepted May 17, 2007; Published July 3, 2007)

ABSTRACT: Imidazole derivatives and alkylamines are very useful as hardeners of epoxy resins. These amine compounds form inclusion complexes with 1,1,2,2-tetrakis(4-hydroxyphenyl) ethane (**TEP**). When these amine-containing inclusion complexes are reacted with epoxy resins, curing acceleration, pot life extension, and higher curing temperatures are observed.

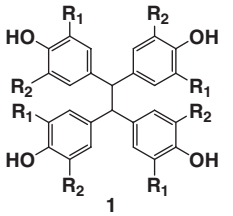
An explanation for this curing behavior is that guest molecule "amine compounds" are trapped in inclusion complex crystals. X-Ray crystal structure data shows the existence of O-H–N hydrogen bonding between host and guest molecules. With the imidazole molecule in the inclusion complex, hydrogen bonding prevents easy attack of the epoxy ring. Amine-**TEP** inclusion complexes show these enhanced curing behaviors when reacted with epoxy resins.
[doi:10.1295/polymj.PJ2006224]

KEY WORDS Amine-Containing Inclusion Complex / 1,1,2,2-Tetrakis(4-hydroxyphenyl) ethane / Epoxy Resin / Hydrogen Bond / Hardener / Curing Acceleration / Pot Life /

Epoxy resins have important roles in adhesives, sealants, coatings, etc.,[1] and their importance will only increase in the future. The properties of epoxy resins depend on both the structures of the epoxy monomers as well as those of hardeners. Imidazole derivatives and alkyl diamines are representative epoxy resin hardeners.[1] There are various methods of altering the reactivity of the hardener: one is design of molecular structure, and another is the formation of the complexes with acidic compounds. Therefore, many imidazole and alkyl diamine-acidic compound complexes have been proposed. For example, a phenol-1,8-diazabicyclo[5,5,0]undec-7-ene complex and its imidazole–carboxylic acid derivative have been reported.[1]

Our recent efforts have revolved around a study of inclusion complexes as stabilized guest molecules.[2,3] The formation of inclusion complexes enables an alternation of the properties of the trapped guest molecules within the inclusion complexes.[4,5]

We have reported that 1,1,2,2-tetrakis(4-hydroxyphenyl) ethane (**1a**) forms inclusion complexes with many organic solvents.[2] Furthermore, these inclusion complexes make it possible to stabilize unstable molecules, or to control the very strong activity of the guest. For instance, the stimulating property of 5-chlroro-2-methyl-4-isothiazoline-3-one (**CMI**) used as a bactericide, is weakened by forming an inclusion complex with **1a**.[3] Consequently, these phenol-type inclusion complexes are proposed as one approach to stabilize the epoxy resin hardener. This report describes the use of 1,1,2,2-tetrakis(4-hydroxyphenyl) ethane (**1a**), 1,1,2,2-tetrakis(3-methyl-4-hydroxyphenyl) ethane (**1b**), and 1,1,2,2-tetrakis(3,5-dimethyl-4-hydroxyphenyl) ethane (**1c**) as host molecules (Figure 1), forming inclusion complexes with various amine molecules. The reactivities of these amines are lowered by the protective effect of hydrogen bonding between the host molecule and the nitrogen atom of the guest molecule confined in the crystal lattice constructed by the hydrogen bonding between hosts. When these **1a** amine-containing inclusion complexes are used as epoxy hardeners, the starting points of the curing temperatures are shifted higher, and curing acceleration based on hydrogen bonding is observed.




1

$R_1$ = H, $R_2$ = H; **1a**
$R_1$ = $CH_3$, $R_2$ = H; **1b**
$R_1$ = $CH_3$, $R_2$ = $CH_3$; **1c**

**Figure 1.** The host compounds.

†To whom correspondence should be addressed (E-mail: n.amanokura@nippon-soda.co.jp).

## EXPERIMENTAL

*General*

$^1$H NMR measurements were performed using JEOL JNM ECP 500, JEOL EX 270, and Bruker AMX-400 instruments. X-Ray diffraction (XRD) was measured using a JEOL JDX-8020. Thermogravimetric-differential thermal analysis (TG-DTA) was performed using a RIGAKU Thermo plus TG-8120, and the differential scanning calorimetry (DSC) was measured with a RIGAKU Thermo plus TG-8230. The epoxy monomer (**4**) was purchased from TOHO KASEI Co., Ltd. The imidazoles and alkyldiamines were purchased from Tokyo Chemical Industry Co., Ltd., and Wako Pure Chemicals Industries Ltd. The solvents were used without further purification.

*Preparation of **1a** (1,1,2,2-tetrakis(p-hydroxyphenyl) ethane)*

A 40% glyoxal aqueous solution (29.0 g, 200 mmol), phenol (94.1 g, 1000 mmol), and glacial acetic acid (120.0 g, 2000 mmol) were mixed at −10 °C. To the resulting solution, sulfuric acid (78.5 g, 800 mmol) and phosphoric acid (19.6 g, 200 mmol) were added dropwise at −10 °C. After addition of the two acids, the solution was stirred at 0 °C for 4 h. The solution was added slowly to water and crushed ice (600 mL), and the resulting solution was stirred at 70 °C for 1 h. The precipitated solid was filtered, and the solid was recrystallized using 1,4-dioxane. **1a** was obtained by drying under vacuum at 110 °C for 2 h. (White powder, yield: 47 g, 57%), mp. 315–317 °C, $^1$H NMR (400 MHz, $CD_3OD$) $\delta$ 6.981 (d $J = 8.6$ Hz, 8H, Ar-H), 6.509 (d, $J = 8.6$ Hz, 8H, Ar-H), 4.529 (s, 2H, CH); $^{13}$C NMR (101 MHz, $CD_3OD$) $\delta$ 155.8, 137.3, 130.6, 115.7, 56.4.

*Preparation of **1b** (1,1,2,2-tetrakis(3-methyl-4-hydroxyphenyl) ethane)*

A 40% glyoxal aqueous solution (14.5 g, 100 mmol), 2-methyl-phenol (51.8 g, 480 mmol), and glacial acetic acid (60.0 g, 1000 mmol) were mixed at −10 °C. To the resulting solution, sulfuric acid (39.3 g, 400 mmol) and phosphoric acid (9.8 g, 100 mmol) were added dropwise at −10 °C. After addition of the two acids, the solution was stirred at 0 °C for 4 h. The solution was added slowly to water and crushed ice (600 mL), and then the resulting solution was stirred at 70 °C for 1 h. The precipitated solid was filtered, and the solid was recrystallized using 1,4-dioxane. **1b** was obtained by drying under vacuum at 110 °C for 2 h. (Reddish powder, yield: 17 g, 37%), mp. 290 °C; $^1$H NMR (400 MHz, $CD_3OD$) $\delta$ 6.843 (d $J = 2.1$ Hz, 4H, Ar-H), 6.822 (dd, $J_1 = 8.2$ Hz, $J_2 = 2.1$, 4H, Ar-H), 6.455 (d, $J = 8.2$ Hz, 4H, Ar-H), 4.426 (s, 2H, CH), 2.029 (s, 12H, $CH_3$); $^{13}$C NMR (101 MHz, $CD_3OD$) $\delta$ 153.8, 137.5, 132.2, 127.7, 124.7, 115.1, 56.3, 16.3.

*Preparation of **1c** (1,1,2,2, tetrakis(3,5-dimethyl-4-hydroxyphenyl) ethane)*

2,6-Dimethyl-phenol (122.0 g, 1000 mmol), methyl isobutyl ketone (14.0 g, 140 mmol) and *p*-toluene sulfuric acid (1.5 g, 8.7 mmol) were mixed at 50 °C. To the mixture solution, 40% glyoxal aqueous solution (35.4 g, 240 mmol) were added at 50 °C. After the addition of the 40% glyoxal aqueous solution, the solution was stirred at 60 °C for 2 h, at 100 °C for 4 h and at 150 °C for 2 h to remove the water and methyl isobutyl ketone. After the water and methyl isobutyl ketone were removed, the methyl isobutyl ketone (140 mL) was added again and the solution was stirred at room temperature for 1 h. A precipitated yellowish crystal was filtered. The obtained crystal was washed with methyl isobutyl ketone and methanol, and **1c** was obtained by drying under vacuum for 2 h at 100 °C. (Yellowish powder, yield: 39 g, 32%), mp. 310–312 °C; $^1$H NMR (400 MHz, $CD_3OD$) $\delta$ 6.929 (s, 8H, Ar-H), 4.613 (s, 2H, CH), 2.069 (s, 24H, $CH_3$); $^{13}$C NMR (101 MHz, $CD_3OD$) $\delta$ 151.4, 137.5, 129.3, 123.8, 55.1, 16.7.

## PREPARATIONS OF INCLUSION COMPLEXES CONTAINING IMIDAZOLES

*Method A*

*Preparation of **1a·2a** (imidazole) inclusion complex.* To a heterogeneous solution of ethyl acetate (150 mL) of **1a** (7.96 g, 20 mmol), imidazole (2.99 g, 44 mmol) was added under reflux and the heterogeneous solution was stirred for 3 h. After 3 h, the heterogeneous solution was left overnight at room temperature, and the white powder obtained was filtrated and dried under vacuum for 4 h at 80 °C. The **1a·2a** inclusion complex obtained was identified by $^1$H NMR, TG-DTA, and XRD. The inclusion ratio of the **1a·2a** inclusion complex was determined to be 1:2 from the $^1$H NMR spectrum. The XRD peak pattern of **1a·2a** was apparently different from those of **1a** and **2a**. (Yellowish crystal, yield: 92%. The release temperature of the guest was 177 °C based on results of the measurement of TG-DTA.

*Preparation of **1a·2b** (1-methylimidazole) inclusion complex.* **1a·2b** was prepared according to a procedure similar to that mentioned for **1a·2a**. The inclusion ratio of the **1a·2b** inclusion complex was determined to be 1:2 from the $^1$H NMR spectrum. The XRD peak pattern of **1a·2b** was apparently different from those of **1** and **2b**. (White powder, yield: 93%)

The release temperature of guest was 174 °C based on the result of the TG-DTA measurement.

*Preparation of **1a·2c** (2-methylimidazole) inclusion complex.* **1a·2c** was prepared according to a procedure similar to that mentioned for **1a·2a**. The inclusion ratio of the **1a·2c** inclusion complex was determined to be 1:2 from the $^1$H NMR spectrum. The XRD peak pattern of **1a·2c** was apparently different from those of **1a** and **2c**. (White powder, yield: 94%) The release temperature of the guest was 176 °C based on the result of the TG-DTA measurement.

*Preparation of **1a·2d** (4-methylimidazole) inclusion complex.* **1a·2d** was prepared according to a procedure similar to that mentioned for **1a·2a**. The inclusion ratio of the **1a·2d** inclusion complex was determined to be 1:2 from the $^1$H NMR spectrum. The XRD peak pattern of **1a·2d** was apparently different from those of **1a** and **2d**. (White powder, yield: 94%) The release temperature of the guest was 187 °C based on the result of the TG-DTA measurement.

*Preparation of **1a·2e** (2-n-propylimidazole) inclusion complex.* **1a·2e** was prepared according to a procedure similar to that mentioned for **1a·2a**. The inclusion ratio of the **1a·2e** inclusion complex was determined to be 1:2 from the $^1$H NMR spectrum. The XRD peak pattern of **1a·2e** was apparently different from those of **1** and **2e**. (White powder, yield: 95%) The release temperature of the guest was 188 °C based on the result of the TG-DTA measurement.

*Preparation of **1a·2f** (2-i-propylimidazole) inclusion complex.* **1a·2f** was prepared according to a procedure similar to that mentioned for **1a·2a**. The inclusion ratio of the **1a·2f** inclusion complex was determined to be 1:2 from the $^1$H NMR spectrum. The XRD peak pattern of **1a·2f** was apparently different from those of **1a** and **2f**. (White powder, yield: 93%) The release temperature of the guest was 180 °C based on the result of the TG-DTA measurement.

*Preparation of **1a·2g** (2-methyl-4-methylimidazole) inclusion complex.* **1a·2g** was prepared according to a procedure similar to that mentioned for **1a·2a**. The inclusion ratio of the **1a·2g** inclusion complex was determined to be 1:2 from the $^1$H NMR spectrum. The XRD peak pattern of **1a·2g** was apparently different from those of **1a** and **2g**. (White powder, yield: 91%) The release temperature of guest was 205 °C based on the result of the TG-DTA measurement.

*Preparation of **1a·2h** (2-Phenylimidazole) inclusion complex.* **1a·2h** was prepared according to a procedure similar to that mentioned for **1a·2a**. The inclusion ratio of the **1a·2h** inclusion complex was determined to be 1:2 from the $^1$H NMR spectrum. The XRD peak pattern of **1a·2h** was apparently different from those of **1a** and **2h**. (White powder, yield: 92%) The release temperature of the guest was 225 °C based on the result of the TG-DTA measurement.

*Preparation of **1a·2i** (1-n-Butylimidazole) inclusion complex.* **1a·2i** was prepared according to a procedure similar to that mentioned for **1a·2a**. The inclusion ratio of the **1a·2i** inclusion complex was determined to be 1:2 from the $^1$H NMR spectrum. The XRD peak pattern of **1a·2i** was apparently different from those of **1a** and **2i**. (White powder, yield: 95%) The release temperature of the guest was 180 °C based on the result of the TG-DTA measurement.

*Preparation of **1a·2j** (1-i-Butyl-2-methylimidazole) inclusion complex.* **1a·2j** was prepared according to a procedure similar to that mentioned for **1a·2a**. The inclusion ratio of the **1a·2j** inclusion complex was determined to be 1:2 from the $^1$H NMR spectrum. The XRD peak pattern of **1a·2j** was apparently different from those of **1a** and **2j**. (White powder, yield: 92%) The release temperature of the guest was 183 °C based on the result of the TG-DTA measurement.

*Method B*

*Preparation of **1a·2k** (2-ethyl-4-methylimidazole) inclusion complex.* **1a** (7.96 g, 20 mmol) was dissolved in methanol (200 mL) under reflux. To the methanol solution of **1a**, a methanol solution (50 mL) of the 2-ethyl-4-methylimidazole (**2k**) (4.85 g, 44 mmol) was added dropwise. After adding of the solution of **2k** was completed, the solution was stirred for 1 h and then was left overnight at room temperature. The precipitated yellowish crystal was filtrated and dried under vacuum for 4 h at room temperature. The obtained **1a·2k** inclusion complex was identified by $^1$H NMR, TG-DTA, and XRD. The inclusion ratio of the **1a·2k** inclusion complex was determined to be 1:2 from $^1$H NMR spectrum. The XRD peak pattern of **1a·2k** was apparently different from that of **1a**. Yield: 72%. The release temperature of the guest was 191 °C based on the result of the TG-DTA measurement.

*Preparation of **1a·2l** (1-benzyl-2-methylimidazole) inclusion complex.* **1a·2l** was prepared according to a procedure similar to that mentioned for **1a·2k**. The inclusion ratio of the **1a·2l** inclusion complex was determined to be 1:2 from the $^1$H NMR spectrum. The XRD peak pattern of **1a·2l** was apparently different from that of **1a**. (Yellowish crystal, yield: 72%) The release temperature of guest was 211 °C based on the result of the TG-DTA measurement.

*Preparation of **1b·2l** (1-benzyl-2-methylimidazole) inclusion complex.* **1b·2l** was prepared according to a procedure similar to that mentioned for **1a·2k** (**1b** (20 mmol, 10.00 g, **2l** (60 mmol, 10.17 g)). The inclusion ratio of the **1b·2l** inclusion complex was determined to be 1:4 from the $^1$H NMR spectrum. The XRD peak pattern of **1b·2l** was apparently different

from that of **1b**. (Yellowish crystal, yield: 21%). The release temperature of the guest was 168 °C from the result of the TG-DTA measurement.

## PREPARATIONS OF INCLUSION COMPLEXES CONTAINING ALKYLDIAMINES

*Method A*

*Preparation of **1a·3b** (1,3-diaminopropane) inclusion complex.* To a heterogeneous solution of ethyl acetate (150 mL) and **1a** (7.96 g, 20 mmol), 1,3-diaminopropane (3.26 g, 44 mmol) was added under reflux, and the heterogeneous solution was stirred for 3 h. After 3 h, the heterogeneous solution was left overnight at room temperature and the obtained yellowish powder was filtered and dried under vacuum for 4 h at 80 °C. The obtained **1a·3b** inclusion complex was identified by $^1$H NMR, TG-DTA, and XRD. The inclusion ratio of the **1a·3b** inclusion complex was determined to be 1:1 from the $^1$H NMR spectrum. The XRD peak pattern of **1a·3b** was apparently different from that of **1a**. (White powder, yield: 99%) The release temperature of the guest was 164 °C from the result of the TG-DTA measurement.

*Preparation of **1a·3c** (1,4-diaminobutane) inclusion complex.* **1a·3c** was prepared according to a procedure similar to that mentioned for **1a·3b**. The inclusion ratio of the **1a·3c** inclusion complex was determined to be 1:1 from the $^1$H NMR spectrum. The XRD peak pattern of **1a·3c** was apparently different from that of **1a**. (Yellowish powder, yield: 96%) The release temperature of the guest was 176 °C based on the result of the TG-DTA measurement.

*Preparation of **1a·3d** (1,6-hyxyldiamine) inclusion complex.* **1a·3d** was prepared according to a procedure similar to that mentioned for **1a·3b**. The inclusion ratio of the **1a·3d** inclusion complex was determined to be 1:1 from the $^1$H NMR spectrum. The XRD peak pattern of **1a·3d** was apparently different from that of **1a**. (Yellowish powder, yield: 99%) The release temperature of the guest was 176 °C based on the result of the TG-DTA measurement.

*Preparation of **1b·3a** inclusion complex.* **1b·3a** was prepared according to a procedure similar to that mentioned for **1a·3b**. The inclusion ratio of the **1b·3a** inclusion complex was determined to be 1:1 from the $^1$H NMR spectrum. The XRD peak pattern of **1b·3a** was apparently different from that of **1b**. (Yellowish powder, yield: 95%) The release temperature of the guest was 182 °C based on the result of the TG-DTA measurement.

*Preparation of **1c·3a** inclusion complex.* **1c·3a** was prepared according to a procedure similar to that mentioned for **1a·3b**. The inclusion ratio of the **1c·3a** inclusion complex was determined to be 1:1 from the $^1$H NMR spectrum. The XRD peak pattern of **1c·3a** was apparently different from that of **1c**. (Yellowish powder, yield: 99%) The release temperature of the guest was 167 °C based on the result of the TG-DTA measurement.

*Method B*

*Preparation of **1a·3a** (ethylenediamine) inclusion complex.* **1a** (7.96 g, 20 mmol) was dissolved in methanol (400 mL) under reflux. Ethylenediamine (2.40 g, 40 mmol) dissolved (**1a**) in methanol (50 mL) was added dropwise very slowly to the methanol solution of **1a** under reflux. While **3a** was being added, the precipitation of a yellowish powder began. The heterogeneous solution containing crystals was stirred for 3 h and then left overnight at room temperature. The obtained yellowish powder (**1a·3a**) was filtered and dried under vacuum for 4 h at room temperature. **1a·3a** was confirmed by $^1$H NMR, XRD and TG-DTA. The inclusion ratio of the **1a·3a** inclusion complex was determined to be 1:1 from the $^1$H NMR spectrum. The XRD peak pattern of **1a·3a** was apparently different from that of **1a** (Yield: 87%). The release temperature of the guest was 203 °C based on the result of the TG-DTA measurement.

*Crystallographic data.* Crystallographic data for inclusion complex **1a·2k** has been deposited with The Cambridge Crystallographic Data Centre: Deposition number CCDC-629549.[6]

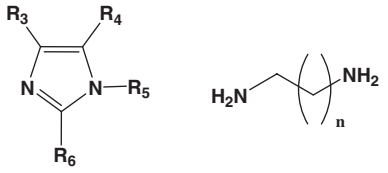
*DSC measurement of the epoxy monomer (**4**) with an inclusion complex.* To the epoxy monomer (**4**) (10.0 g) was added an inclusion complex (0.4 g as amine or imidazole component). This epoxy monomer (**4**) was mixed with the inclusion complex, and the mixture (about 4 mg) was measured by DSC.

*Measurements of glass transition points of epoxy resin (**4**) cured with **2k** and **1a·2k** inclusion complexes.* To the epoxy monomer (**4**) 10.0 g was added either **2k** (0.40 g) or an inclusion complex (1.25 g). This epoxy monomer (**4**) with hardener was mixed, and the mixture was heated and cured at 140 °C for 2 h in an incubator. The cured epoxy resins were measured using a TA Instruments Q100 DSC (conditions: −50 °C → 200 °C → −50 °C → 200 °C heat, cool, reheat cycle at 20 °C/min under a nitrogen atmosphere (50 mL/min) in an Al pan).

## RESULT AND DISCUSSION

*Formation of inclusion complexes containing amines*

Hosts **1a**, **1b**, and **1c** (Figure 1) easily formed inclusion complexes with various amines (Figure 2) by recrystallization from a solution of an amine in methanol or a slurry solution of ethyl acetate, as shown in Table I. These inclusion complexes were confirmed




2 3

**2a: $R_3$=H, $R_4$=H, $R_5$=H, $R_6$=H**

**2b: $R_3$=H, $R_4$=H, $R_5$=$CH_3$, $R_6$=H**

**2c: $R_3$=H, $R_4$=H, $R_5$=H, $R_6$= $CH_3$**

**2d: $R_3$= $CH_3$, $R_4$=H, $R_5$=H, $R_6$= H**

**2e: $R_3$= H, $R_4$=H, $R_5$=H, $R_6$= *n*-$C_3H_7$**

**2f: $R_3$= H, $R_4$=H, $R_5$=H, $R_6$= *i*-$C_3H_7$**

**2g: $R_3$= $CH_3$, $R_4$=H, $R_5$=H, $R_6$= $CH_3$**

**2h: $R_3$= H, $R_4$=H, $R_5$=H, $R_6$= Ph**

**2i: $R_3$= H, $R_4$=H, $R_5$= *n*-$C_4H_9$, $R_6$= H**

**2j: $R_3$= H, $R_4$=H, $R_5$= *i*-$C_4H_9$, $R_6$= $CH_3$**

**2k: $R_3$= $CH_3$, $R_4$=H, $R_5$= H, $R_6$= $C_2H_5$**

**2l: $R_3$= H, $R_4$=H, $R_5$= $CH_2Ph$, $R_6$= $CH_3$**

**3a: n= 1**

**3b: n=2**

**3c: n=3**

**3d: n=5**

**Figure 2.** The guest compounds.

by XRD and TG-DTA, and the host-guest ratios of the inclusions were determined by their $^1$H NMR spectra. The results show that all of the imidazoles tested formed inclusion complexes with **1a**, and the inclusion ratios are 1:2 (host:guest). Surprisingly, in the case of **1a** with **2l**, the ratio of inclusion is 1:2; however, in the case of **1b**, having a methyl group at the *o*-position with **2l**, the ratio of inclusion is 1:4. The higher ratio of inclusion means that more guest molecules are included by fewer host molecules. This fact is chemically important. It was thought that the higher ratio of **1b·2l**[7] arose from the more expansive space in the crystal lattice constructed by **1b** due to the steric hindrance of the methyl group of **1b** compared to **1a·2l**. On the other hand, alkyl diamines, such as ethylenediaimine, diethylenediamine, triethylenediamine, and tetraethylenediamine, form inclusion complexes with an inclusion ratio of 1:1 (Table I). The melting point of **2k** is 47–54 °C. On the other hand, the temperature of the guest-release of **1a·2k** is 184 °C. The **2k** molecule vaporized at a vapor pressure less than the boiling point. When **2k** (10 g) was put in a drying oven at 70 °C, **2k** disappeared within 1 day, but in the case of the inclusion complex **1a·2k**, no change in the structure and the weight at 70 °C was observed after one month. The fact that these inclusion complexes had no vapor pressure at 70 °C means that the guest molecule was highly stabilized within the inclusion complex.

### *Crystal structure of the **1a·2k** inclusion complex*

Preparation of a single-crystal of **1a·2k** (2-ethyl-4-methylimidazole) was successful[8] and a **1a·2k** crystal structure has been reported.[6] The result of a single-

**Table I.** Formation of inclusion complexes and inclusion ratio of host to guest

| Entry | | Guest | | Method | Host | H:G |
|---|---|---|---|---|---|---|
| 1 | | $R_3$=H, $R_4$=H, $R_5$=H, $R_6$=H | **2a** | A | **1a** | 1:2 |
| 2 | | $R_3$=H, $R_4$=H, $R_5$=$CH_3$, $R_6$=H | **2b** | A | **1a** | 1:2 |
| 3 | | $R_3$=H, $R_4$=H, $R_5$=H, $R_6$=$CH_3$ | **2c** | A | **1a** | 1:2 |
| 4 | | $R_3$=$CH_3$, $R_4$=H, $R_5$=H, $R_6$=H | **2d** | A | **1a** | 1:2 |
| 5 | | $R_3$=H, $R_4$=H, $R_5$=H, $R_6$=*n*-$C_3H_7$ | **2e** | A | **1a** | 1:2 |
| 6 | **2** | $R_3$=H, $R_4$=H, $R_5$=H, $R_6$=*i*-$C_3H_7$ | **2f** | A | **1a** | 1:2 |
| 7 | | $R_3$=$CH_3$, $R_4$=H, $R_5$=H, $R_6$=$CH_3$ | **2g** | A | **1a** | 1:2 |
| 8 | | $R_3$=H, $R_4$=H, $R_5$=H, $R_6$=Ph | **2h** | A | **1a** | 1:2 |
| 9 | | $R_3$=H, $R_4$=H, $R_5$=*n*-$C_4H_9$, $R_6$=H | **2i** | A | **1a** | 1:2 |
| 10 | | $R_3$=H, $R_4$=H, $R_5$=*i*-$C_4H_9$, $R_6$=$CH_3$ | **2j** | A | **1a** | 1:2 |
| 11 | | $R_3$=$CH_3$, $R_4$=H, $R_5$=H, $R_6$=$C_2H_5$ | **2k** | B | **1a** | 1:2 |
| 12 | | $R_3$=H, $R_4$=H, $R_5$=$CH_2Ph$, $R_6$=$CH_3$ | **2l** | B | **1a** | 1:2 |
| 13 | | $R_3$=H, $R_4$=H, $R_5$=$CH_2Ph$, $R_6$=$CH_3$ | **2l** | B | **1b** | 1:4 |
| 14 | | n = 1 | **3a** | B | **1a** | 1:1 |
| 15 | | n = 2 | **3b** | A | **1a** | 1:1 |
| 16 | **3** | n = 3 | **3c** | A | **1a** | 1:2 |
| 17 | | n = 5 | **3d** | A | **1a** | 1:1 |
| 18 | | n = 1 | **3a** | A | **1b** | 1:1 |
| 19 | | n = 1 | **3a** | A | **1c** | 1:1 |

Method A: heterogeneous system (solvent AcOEt) imidazoles tested were dissolved in ethyl acetate. Method B: homogeneous system-recrystallization from a solution of methanol.

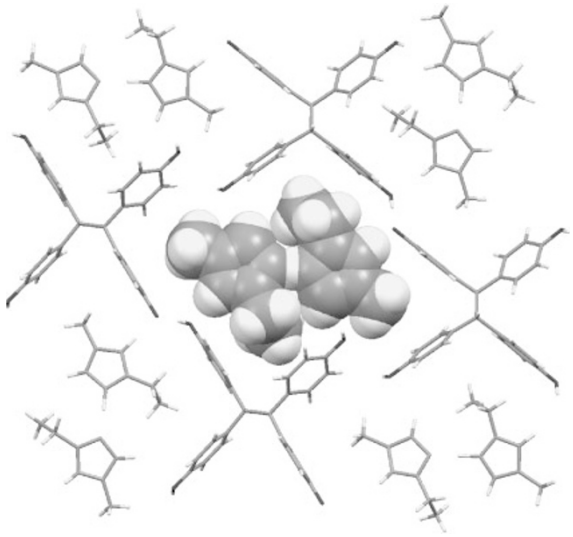


**Figure 3.** Crystal structure of **1a·2k**.

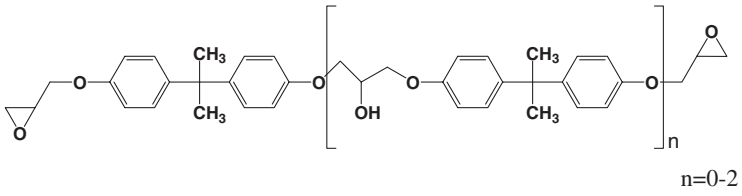
| | |
|---|---|
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| $a$ | 17.3516(10) Å |
| $b$ | 13.4628(13) Å |
| $c$ | 19.0518(11) Å |
| $\beta$ | 133.064(3)° |
| $R$ | 0.042 |

crystal X-ray structural analysis is shown in Figure 3. In the case of **1a·2k**, some hydrogen bonding is noticed as a characteristic feature of the crystal structure. Especially, of note is the hydrogen bonding between **1a** and **2k** (O(21)···N(72) 2.708 Å). The molecules (**1a**) confine **2k** in the **1a·2k** inclusion complex *via* this hydrogen bonding.

*Reaction of epoxy monomer with inclusion Catalysts*

The **1a·2k** and **1a·2l** inclusion complexes were reacted as hardeners with a representative epoxy monomer (**4**) (Figure 4).[9,10] The DSC results of the epoxy curing reactions (ramp room temp → 200 °C, or held at 80 °C) are shown in Figures 5 and 6, respectively. As shown in Figure 5a and b, the curing reactions of upon increasing the temperature showed very different curing behavior for the reaction of only **2l** with (**4**) and that of **1a·2l** with (**4**).

In the case of the reaction with only **2l**, the beginning of the curing reaction started at 106 °C, and the range from the starting temperature to termination was wide (Figure 5a), while in the case of the reaction with an inclusion complex, the beginning of the curing reaction was at 120 °C, and the range of the curing reaction was narrower (Figure 5b). These results indicate that the epoxy curing starting temperature with the inclusion complexes (**1a·2l**) was higher than that with only **2l**, and the catalytic activity of **2l** was weakened because **2l** was confined in the space constructed by **1a**. Furthermore, the **2l**'s nitrogen atom was bonded by hydrogen bonding between **1a** and **2l** until the collapse temperatures of the inclusion complex. However, upon reaching the collapse temperature of the




**4**

**Figure 4.** Epoxy monomer.

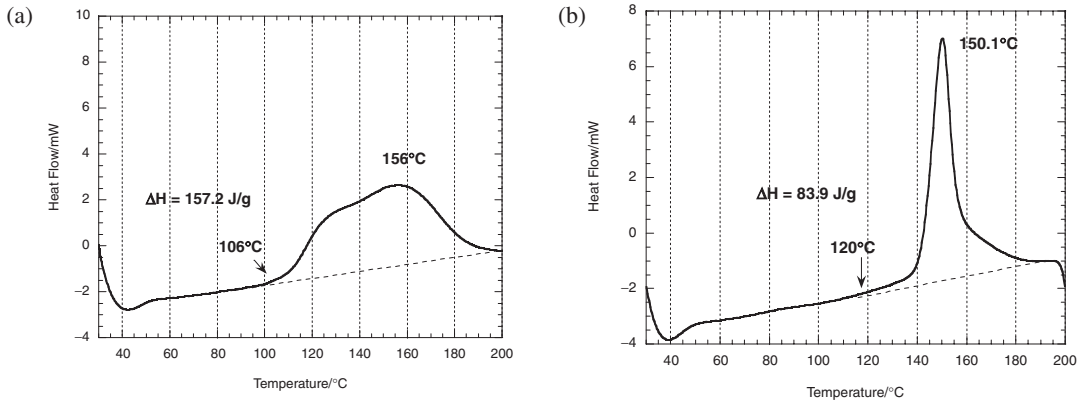



**Figure 5.** (a) DSC of **2l** with (**4**) (**2l**:**4** = 4:100). (b) DSC of **1a·2l** with (**4**) (**1a·2l**:**4** = 12.5:100).

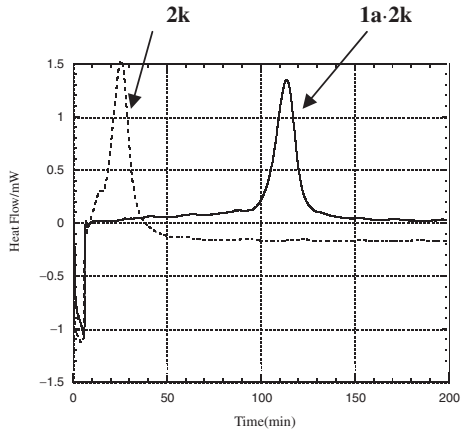



**Figure 6.** DSCs of **1a·2k** and **2k** with (**4**) at 80 °C.

inclusion complexes, **2l** was released all at once to the epoxy, and the curing reaction occurred rapidly. The curing reaction of **4** with the **1a·2k** inclusion complex also had unusual features when held at 80 °C. As shown in Figure 6, in the case of only **2k**, the epoxy curing reaction began within 30 minutes at 80 °C, while in the case of **1a·2k**, the curing reaction did not occur at 80 °C for more than 100 min. This feature can be explained in a similar manner as for the rising temperature reaction. That is, **2k** was not released from **1a·2k** until the collapse of the inclusion complex. It is known that the curing reaction of an epoxy resin is accelerated by adding a hydroxyl group. A hydroxyl group forms hydrogen bonds with the glycidyl ether of the epoxy, and the hydrogen bonding gives lower electron density on the neighboring carbon due to electron withdrawing.[11] The DSC results showed that solid-state **1a** in **1a·2k** also accelerated the reaction because the glycidyl ether was activated by the hydroxyl group of **1a**. When **1a** and **2k** were added separately to an epoxy monomer (**4**), the starting temperature was lower than that of the inclusion complex, but the accelerated curing reaction could not be confirmed. Namely, **1a** was stabilized by hydrogen bonding between **1a** and **2k** in **1a·2k** at low temperature, and therefore **2k** could not react with **4**. However, when the reaction was heated and the guest release point temperature was achieved, the collapsed **1a** formed hydrogen bonds with the glycidyl group, and the reactivity of **4** was activated. As a result, **2k** easily attacked the epoxy group, and the reaction occurred rapidly. (Figure 7)

In the case of measurements of gelation time by adding some compounds to epoxy resin at 130 °C (**1a·2k** inclusion complex collapse at over 120 °C in epoxy resin.), the gelation time of only **2k** was 4 min 11 sec, the one of the mixture (**1a** + **2k**) of **1a** with **2k** was 1 min 32 sec. Moreover, the gelation time of **1a·2k** inclusion complex was 2 min 13 sec, this gelation time was shorter compared with the case of only **2k** (the that of **1a·2k** longer was because of inclusion complex compared with **1a** + **2k**), As shown in Table II, by adding compounds (methanol, 1,4-butanediol, hydroquinone) that could not from inclusion complex with **2k**, however, having hydroxyl group in epoxy resin, their gelation times are 1 min 50 sec, 1 min 24 sec, and 1 min 27 sec, respectively. Their gelation times are more rapid compared with only **2k**. These results are analogized **1a** formed the hydrogen bond with glycidyl ether by the collapse of **1a·2k** and polymerization reaction of the epoxy is accelerated.

To offer proof that host (**1a**) does not react with **4**, the glass transition points of epoxy resin cured by

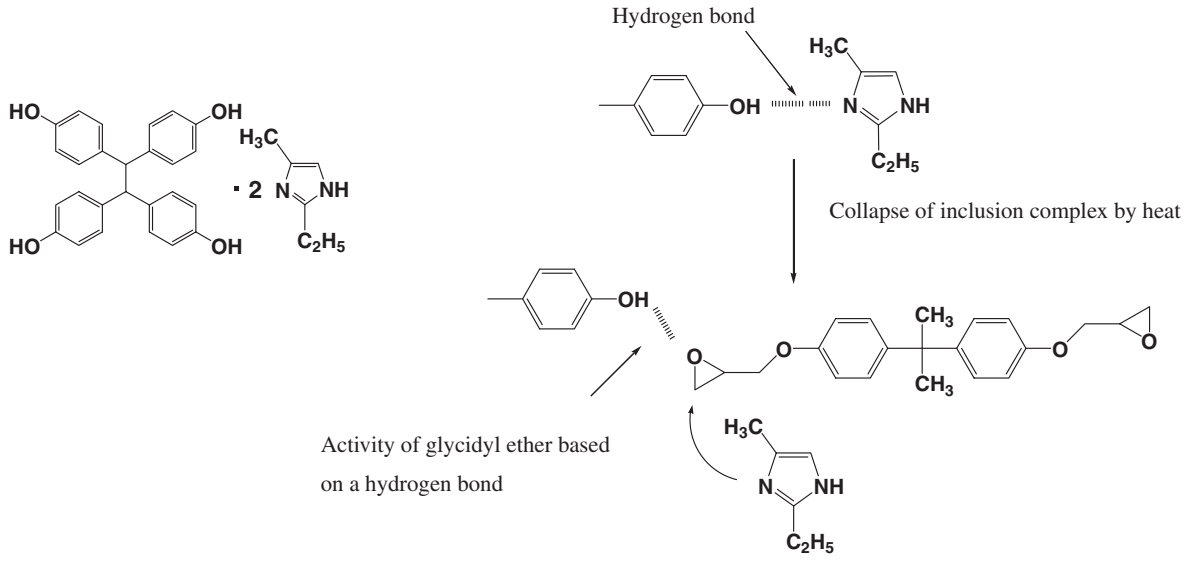



**Figure 7.** Activity of glycidyl ether based on **1a·2k** inclusion complex.

**Table II.** Gelation time of epoxy resin of hardener at 130 °C

| | Hardener + compound having O-H group | Gelation time |
|---|---|---|
| 1 | **1a** | 4 min 11 sec |
| 2 | **1a·2k** | 2 min 13 sec |
| 3 | **1a** + **2k** | 1 min 32 sec |
| 4 | **1a** + methanol + **2k** | 1 min 50 sec |
| 5 | Hydroquinone + **2k** | 1 min 24 sec |
| 6 | 1,4-butanediol + **2k** | 1 min 27 sec |

·: inclusion complex, +: mixture

Epoxy resin (**4**): 100, **1a**: 8.5, **2k**: 4, Methanol, hydroquinone, and 1,4-butanediol were added equal total of O-H based on O-H of **1a** to epoxy resin.

**1a·2k** inclusion complexes were measured. The glass transition points cured by **2k** alone were 55.2/141.9 °C (1st heating) and 136.4 °C (2nd heating), respectively.[12] Those cured by **1a·2k** inclusion complexes were 58.0/138.4 °C (1st heating) and 133 °C (2nd heating), respectively.[12] The glass transition points of epoxy cured by only **2k** are similar to those of **1a·2k** inclusion complexes. This fact shows that **1a** is only responsible for an acceleration effect and is uninvolved in the curing reaction.

## CONCLUSION

When amine-containing inclusion complexes were used as hardeners, the curing reactions had a unique feature-the reactivities of the inclusion complexes as hardener were weakened due to hydrogen bonding between host and guest in the inclusion complex. Furthermore, curing accelerations occurred due to the hydroxyl groups of the host. These inclusion complexes have the possibility to act as new functional hardeners of epoxy resins.

## REFERENCES AND NOTES


1. http://www.sumibe.co.jp/st-tec/report/report10epokisi.htm
2. a) H. Suzuki, *Tetrahedron Lett.*, **35**, 5015 (1994).
   b) H. Suzuki and H. Takagi, *Tetrahedron Lett.*, **34**, 4805 (1993).
3. H. Suzuki, H. Takagi, and R. Sato, *Tetrahedron Lett.* **38**, 4563 (1997).
4. a) K. Tanaka and F. Toda, *Chem. Rev.*, **100**, 1025 (2000).
   b) J. L. Atwood, J. E. D. Davies, F. Vogtle, J.-M. Lean, D. D. Macnicol, F. Toda, and R. Bishop, "Comprehensive Supramolecular Chemistry", Volume 6, PERGAMON, 1996.
   c) M. Yagi, S. Hirano, S. Toyota, F. Toda, P. Giastas, and I. M. Marvidis, *Heterocycles*, **59**, 735 (2003).
   d) S. Nagahama, K. Inoue, K. Sada, M. Mikiya, and A. Matsumoto, *Cryst. Growth Des.*, **3**, 247 (2003).
   e) H. Kaku, S. Tanaka, and T. Tsunoda, *Tetrahedron*, **58**, 3401 (2002).
   f) K. Kato, M. Sugahara, N. Tohnai, K. Sada, and M. Mikiya, *Eur. J. Org. Chem.*, 981 (2004).
   g) Y. Takai, T. Nakaoki, T. Takaeda, and M. Sawada, *Tetrahedron*, **58**, 4319 (2002).
   h) M. Farina, G. Allegra, and G. Natta, *J. Am. Chem. Soc.*, **86**, 516 (1964).
   i) K. Kishikawa, S. Tsubokura, S. Kohmoto, and M. Yamamoto, *J. Org. Chem.*, **64**, 7568 (1999).
   j) T. Hens, Q. Li, and T. C. W. Mak, *Eur. J. Org. Chem.*, 1115 (1999).
   k) M. R. Caira, A. Jacobs, L. R. Nassimbeni, and F. Toda, *Cryst. Eng. Comm.*, 150 (2003).
   l) F. Guo, W. S. Guo, and F. Toda, *Cryst. Eng. Comm.*, **5**, 45 (2003).
   m) S. Hirano, K. Yoshizawa, S. Toyota, F. Toda, and Z. Urabancyk-Lipkowska, *Mendeleev Commun.*, 141 (2003).
   n) K. Tanaka, M. Asami, and J. L. Scott, *New J. Chem.*, **26**, 378 (2002).
   o) F. Toda, M. Senzaki, and R. Kuroda, *Chem. Commun.*, 1788 (2002).
   p) D. E. Lynch, G. Smith, K. A. Byriel, and C. H. Kennard, *J. Chem. Soc., Chem. Commun.*, 300 (1992).
5. N. Amanokura, T. Sahara, and R. Sato, *Anal. Sci.*, **11**, x273 (2006).
6. N. Amanokura, M. Kaneko, T. Sahara, and R. Sato, *Anal. Sci.*, in press.
7. The inclusion complex was expressed as a host·guest.
8. The **1a·2k** single crystal structure was prepared slowly from methanol.
9. Refer to the experimental section.
10. The case using **1a·2k** and **1a·2l** as catalysts indicated the most remarkable difference between only the imidazoles and the inclusion complexes in each experiment.
11. a) G. J. Buist, J. M. Barton, B. J. Howlin, J. R. Jones, and M. J. Parker, *J. Mater. Chem.*, **6**, 911 (1996).
    b) V. Spacek, J. Pouchly, and J. Biros, *Eur. Polym. J.*, **23**, 377 (1987).
    c) T. Kagurai and T. Noguchi, *Kougyou kagaku Zasshi*, **63**, 98 (1960).
    d) L. Shechter, J. Wynstra, and R. P. Kurkjy, *Ind. Eng. Chem.*, **48**, 94 (1956).
12. Refer to the experimental section.