

## Study of Epoxy Compounds. Part II. The Gelation Point of the Epoxy Resin–Acid Anhydride System

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### INTRODUCTION

In the quantitative treatment of the curing reaction of a thermosetting resin, it is important to study the relation of the gel point of the polyfunctional systems to the extent of reaction of the functional groups. The way in which the high polymeric substances are formed from the monomeric units may be classified<sup>1</sup> according to the number of the functional groups involved in the formation of an interunit junction, such as the polymerization by bi-, ter-, quadri-, . . . , multifunctional interunit junction. The polymerization by bifunctional interunit junctions, the simplest case, is most familiar, and almost all of the known polymerizations or polycondensations, such as vinyl polymerizations or the formation of polyesters and polyamides, belong to this group.

The theoretical treatment of the gel formation due to the bifunctional interunit junction has been established by Flory,<sup>2</sup> Stockmayer,<sup>3</sup> and many other workers.<sup>4,5</sup> Recently, Imoto<sup>6</sup> dealt with the gel formation of phenol-formaldehyde resin; Jonason<sup>7</sup> applied Flory's quantitative treatment to the polyesterification reaction that occurs in the making of oil-modified alkyd resins, and Kakurai and Noguchi<sup>8</sup> discussed theoretically the gelation of the epoxy resin–amine system.

It is the purpose of this paper to treat quantitatively the polyesterification that occurs in the curing of the epoxy resin–acid anhydride system and to deduce an expression for the gel point in this particular industrially important epoxy resin–acid anhydride system.

### EXPERIMENTAL

#### Reagents

Purification and physical constants of the epoxy resins, hexahydrophthalic anhydride (HHPA) and tertiary amines and alcohols used here have been reported previously.<sup>16</sup> Pyromellitic dianhydride, 1,2,4,5-benzenetetracarboxylic dianhydride (PMDA), and trimellitic anhydride, the anhydride of 1,2,4-benzenetricarboxylic acid (TMA), were obtained

from E. I. du Pont de Nemours & Co. and Amoco Chemicals Co., respectively. Their characteristics are shown in Table I.

TABLE I  
Characteristics of PMDA and TMA

| Anhydride | Appearance    | Melting point,<br>°C. |                      | Neutralization equivalent,<br>g./equiv. <sup>a</sup> |        |                      |       |
|-----------|---------------|-----------------------|----------------------|--|--------|----------------------|-------|
|           |               |                       |                      | Esterification<br>method                             |        | Hydrolysis<br>method |       |
|           |               | Obs.                  | lit.                 | Obs.   | Calc.  | Obs.                 | Calc. |
| PMDA      | White powder  | 283-284               | 286 <sup>b</sup>     | 109.9  | 109.06 | 54.02                | 54.53 |
| TMA       | <sup>11</sup> | 169-171               | 167-168 <sup>c</sup> | 191.6  | 192.12 | 64.37                | 64.04 |

<sup>a</sup> Method of Hammond.<sup>9</sup>

<sup>b</sup> Information from manufacturer.<sup>10</sup>

<sup>c</sup> Information from manufacturer.<sup>11</sup>

### Procedure

Carefully weighed quantities of the reagents were polymerized either in the presence of 0.5-1.0 wt.-% of triethanolamine or in the absence of the catalyst at 70-100°C.

The polymerization and analytical procedure have been adequately described previously.<sup>16</sup> From time to time during the reaction, viscosities were measured and samples were removed for titration of the unreacted epoxy groups and carboxyl groups. There is no difficulty in locating the gel point. Within an interval of about 2 min., in a reaction such as the one shown by Figure 2, the polymeric system loses completely its ability to flow in the viscometer and it becomes elastic.

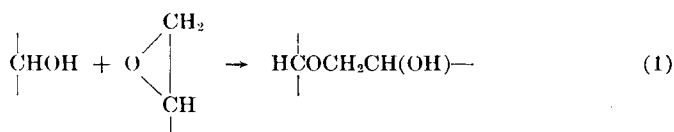
Samples removed just prior to gelation are completely soluble in MEK or dioxane, but those removed one or two minutes after gelation do not dissolve completely in such solvents.

## THEORETICAL

### The Extent of Reaction at Gel Point

We will deduce the gel point for the general case of the epoxy resin-acid anhydride system which may contain any or all of the different types of epoxide, polyhydric alcohol and acid anhydride, assuming that all functional groups of a material are equally reactive, and excluding intramolecular reaction.

As shown in the preceding paper<sup>16</sup> and Figures 1 and 2 in this paper, the etherification reaction shown in eq. 1



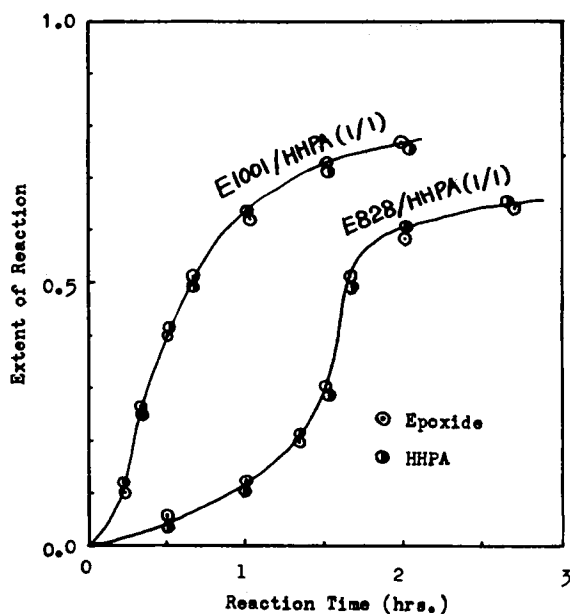


Fig. 1. Reaction of epoxy resins and HHPA with triethanolamine (ca. 0.5 wt.-%) at 100°C.

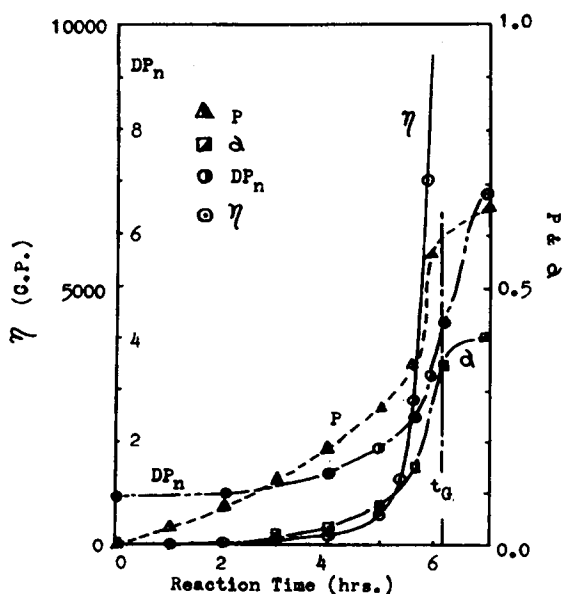






Fig. 2. Reaction of E-828/HHPA ( $r=1$ ,  $\pi=1$ ) system with triethanolamine (0.5 wt.-%) at 70°C.

did not occur or could be ignored even in the E-1001/HHPA system having an OH group in the molecular structure within the condition of this experiment. This result disagrees with the results of Fisch and Hofmann,<sup>12,13</sup> and Dearborn et al.,<sup>14</sup> but is consistent with the data of Fischer.<sup>15</sup> The functionality of an epoxide, monohydric alcohol and monoacid anhydride, therefore, may be represented as 2, 1, 2, respectively, and the monoepoxide is equivalent of 2 hydroxy groups. If the initial concentrations of epoxide and acid anhydride are  $C_A$  and  $C_B$ , respectively, and the extent of reaction of those reagents,  $P_A$  and  $P_B$ , respectively, the following relation may be obtained in the case of  $C_A = rC_B$

$$P_B = rP_A \quad (2)$$

Schematically, the monomeric units may be represented as shown in Table II.

TABLE II

|   | Monomer unit                            | Functionality |
|---|---|---------------|
| A   | Monohydric alcohol                      | $f_1 = 1$     |
| A—A   | Monoepoxide or dihydric alcohol         | $f_2 = 2$     |
|    | Trihydric alcohol or hydroxymonoepoxide | $f_3 = 3$     |
|    | Diepoxide or tetrahydric alcohol        | $f_4 = 4$     |
|   | Monohydroxy diepoxide                   | $f_5 = 5$     |
| B   | Monobasic acid                          | $g_1 = 1$     |
| B—B   | Acid anhydride                          | $g_2 = 2$     |
|  | Acid dianhydride                        | $g_4 = 4$     |

In these schemes, A = hydroxyl or 1/2 epoxide group, B = carboxyl group. The stoichiometry of the system is represented as shown by eqs. (3)–(8):

$$\rho = \text{A's belonging to A—A} / \text{total A's} \quad (3)$$

$$\theta = \text{A's belonging to } \begin{array}{c} \text{A} \\ \diagup \quad \diagdown \\ \text{A} \end{array} / \text{total A's} \quad (4)$$

$$\pi = \text{A's belonging to } \begin{array}{c} \text{A} \\ | \\ \text{A} - \text{C} - \text{A} \\ | \\ \text{A} \end{array} / \text{total A's} \quad (5)$$

$$\varphi = \text{A's belonging to } \begin{array}{c} \text{A} \\ | \\ \text{A} - \text{C} - \text{A} \\ / \quad \backslash \\ \text{A} \quad \text{A} \end{array} / \text{total A's} \quad (6)$$

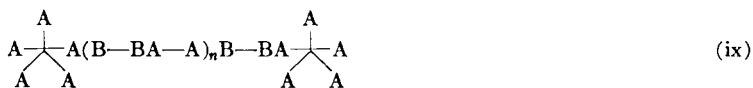
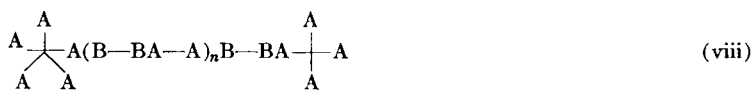
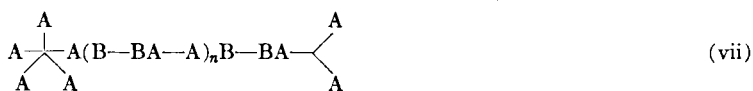
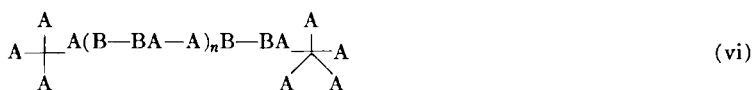
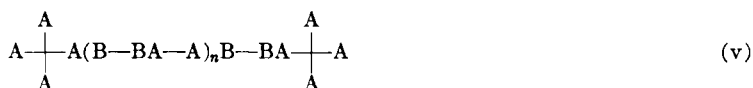
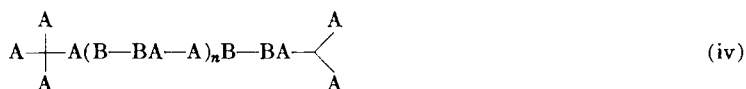
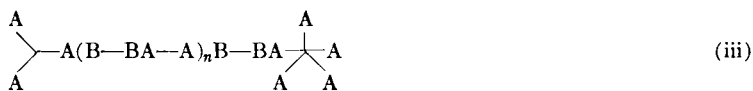
$$\lambda = \text{B's belonging to B/total B's} \quad (7)$$

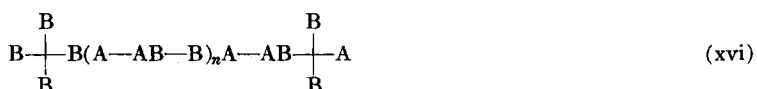
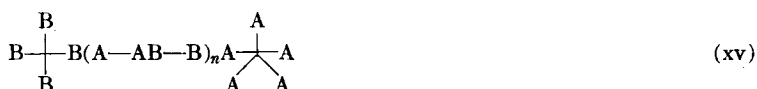
$$\mu = \text{B's belonging to } \begin{array}{c} \text{B} \\ | \\ \text{B} - \text{C} - \text{B} \\ | \\ \text{B} \end{array} / \text{total B's} \quad (8)$$

where

$$r = \text{total A's/total B's} \quad (9)$$

The probability  $\alpha$  that any A group belonging to a branch unit and selected at random is connected via a chain to another branch unit is obtained as follows. This state of affairs may come about in  $4\Pi_2 = 16$  possible ways shown in structures (i)–(xvi) below:





where  $n$  is any integer from 0 to  $\infty$ .

The probability  $\alpha$  is equal to the sum of the 16 individual probabilities of each of these 16 cases occurring in any selection taken at random, each case being equally valid for the purpose of evaluating  $\alpha$ . If the extent of reaction,  $P_A$  and  $P_B$ , are the fraction of A, B groups, respectively, that have reacted, then the 16 probabilities are given by eqs. (10):

$$\alpha_i = \sum_0^n P_A [\theta / (\theta + \pi + \varphi + \mu)] [(1 - \lambda - \mu) \rho P_A P_B]^n (1 - \lambda - \mu) P_B \theta$$

$$\alpha_{ii} = \sum_0^n P_A [\theta / (\theta + \pi + \varphi + \mu)] [(1 - \lambda - \mu) \rho P_A P_B]^n (1 - \lambda - \mu) P_B \pi$$

$$\alpha_{iii} = \sum_0^n P_A [\theta / (\theta + \pi + \varphi + \mu)] [(1 - \lambda - \mu) \rho P_A P_B]^n (1 - \lambda - \mu) P_B \varphi$$

$$\alpha_{iv} = \sum_0^n P_A [\pi / (\theta + \pi + \varphi + \mu)] [(1 - \lambda - \mu) \rho P_A P_B]^n (1 - \lambda - \mu) P_B \theta$$

$$\alpha_v = \sum_0^n P_A [\pi / (\theta + \pi + \varphi + \mu)] [(1 - \lambda - \mu) \rho P_A P_B]^n (1 - \lambda - \mu) P_B \pi$$

$$\alpha_{vi} = \sum_0^n P_A [\pi / (\theta + \pi + \varphi + \mu)] [(1 - \lambda - \mu) \rho P_A P_B]^n (1 - \lambda - \mu) P_B \varphi$$

$$\alpha_{vii} = \sum_0^n P_A [\varphi / (\theta + \pi + \varphi + \mu)] [(1 - \lambda - \mu) \rho P_A P_B]^n (1 - \lambda - \mu) P_B \theta$$

$$\begin{aligned}
\alpha_{viii} &= \sum_0^n P_A [\varphi/(\theta + \pi + \varphi + \mu)] [(1 - \lambda - \mu)\rho P_A P_B]^n (1 - \lambda - \mu) P_B \pi \\
\alpha_{ix} &= \sum_0^n P_A [\varphi/(\theta + \pi + \varphi + \mu)] [(1 - \lambda - \mu)\rho P_A P_B]^n (1 - \lambda - \mu) P_B \varphi \\
\alpha_x &= \sum_0^n P_A [\theta/(\theta + \pi + \varphi + \mu)] [(1 - \lambda - \mu)\rho P_A P_B]^n \mu \quad (10) \\
\alpha_{xi} &= \sum_0^n P_A [\pi/(\theta + \pi + \varphi + \mu)] [(1 - \lambda - \mu)\rho P_A P_B]^n \mu \\
\alpha_{xii} &= \sum_0^n P_A [\varphi/(\theta + \pi + \varphi + \mu)] [(1 - \lambda - \mu)\rho P_A P_B]^n \mu \\
\alpha_{xiii} &= \sum_0^n P_B [\mu/(\theta + \pi + \varphi + \mu)] [(1 - \lambda - \mu)\rho P_A P_B]^n \theta \\
\alpha_{xiv} &= \sum_0^n P_B [\mu/(\theta + \pi + \varphi + \mu)] [(1 - \lambda - \mu)\rho P_A P_B]^n \pi \\
\alpha_{xv} &= \sum_0^n P_B [\mu/(\theta + \pi + \varphi + \mu)] [(1 - \lambda - \mu)\rho P_A P_B]^n \varphi \\
\alpha_{xvi} &= \sum_0^n P_B [\mu/(\theta + \pi + \varphi + \mu)] [(1 - \lambda - \mu)\rho P_A P_B]^n \rho P_A \mu
\end{aligned}$$

and the sum of these 16 probabilities  $\alpha$  is:

$$\begin{aligned}
\alpha &= \sum_0^n P_A P_B \{ [(1 - \lambda - \mu)(\theta + \pi + \varphi)^2 + \rho\mu]^2 / (\theta + \pi + \varphi + \mu) \} [(1 - \lambda - \mu)\rho P_A P_B]^n + \sum_0^n [(P_A + P_B)(\theta + \pi + \varphi)\mu/(\theta + \pi + \varphi + \mu)] [(1 - \lambda - \mu)\rho P_A P_B]^n \quad (11)
\end{aligned}$$

Calculating the summation yields:

$$\begin{aligned}
\alpha &= P_A P_B [(1 - \lambda - \mu)(\theta + \pi + \varphi)^2 + \rho\mu^2] + (P_A + P_B)(\theta + \pi + \varphi)\mu/(\theta + \pi + \varphi + \mu) [1 - P_A P_B \rho (1 - \lambda - \mu)] \quad (12)
\end{aligned}$$

Now at the gel point,

$$\alpha_c = 1/(f - 1) \quad (13)$$

where  $f$  is the functionality of the branch unit. If there is more than one branch unit,  $f$  in eq. (13) must be replaced by the appropriate average. Thus, in this system where for each branch unit hydroxyl group, there is  $\theta/(\theta + \pi + \varphi + \mu)f_3$ -ol hydroxyl groups,  $\pi/(\theta + \pi + \varphi + \mu)f_4$ -ol hydroxyl groups, and  $\varphi/(\theta + \pi + \varphi + \mu)f_5$ -ol hydroxyl groups, and for each branch unit carboxyl group, there is  $\mu/(\theta + \pi + \varphi + \mu)g_4$ -carboxyl groups, the average value of  $f$  is

$$(\theta f_3 + \pi f_4 + \varphi f_5 + \mu g_4) / (\theta + \pi + \varphi + \mu)$$

so that, instead of eq. (13), we may write;

$$\alpha_e = (\theta + \pi + \varphi + \mu) / [\theta f_3 + \pi f_4 + \varphi f_5 + \mu g_4 - (\theta + \pi + \varphi + \mu)] \quad (14)$$

Thus the final gel point equation is

$$\begin{aligned} & (\theta + \pi + \varphi + \mu) / [(f_3 - 1)\theta + (f_4 - 1)\pi + (f_5 - 1)\varphi + (g_4 - 1)\mu] \\ & = P_A P_B [(1 - \lambda - \mu)(\theta + \pi + \varphi)^2 + \rho\mu^2] + (P_A + P_B)(\theta + \pi \\ & \quad + \varphi)\mu / (\theta + \pi + \varphi + \mu) [1 - P_A P_B \rho(1 - \lambda - \mu)] \end{aligned}$$

Rearranging, we have:

$$\begin{aligned} & P_A P_B \{ [(f_3 - 1)\theta + (f_4 - 1)\pi + (f_5 - 1)\varphi + (g_4 - 1)\mu] [(1 - \lambda - \mu) \\ & \quad \times (\theta + \pi + \varphi)^2 + \rho\mu^2] + \rho(1 - \lambda - \mu)(\theta + \pi + \varphi + \mu)^2 \} \\ & \quad + (P_A + P_B)\mu(\theta + \pi + \varphi)[(f_3 - 1)\theta + (f_4 - 1)\pi \\ & \quad + (f_5 - 1)\varphi + (g_4 - 1)\mu] - (\theta + \pi + \varphi + \mu)^2 = 0 \quad (15) \end{aligned}$$

In this equation,  $P_A$  is related to  $P_B$  by eq. (2), as shown before, so that the gel point equation can readily be expressed in terms either of  $P_A$  or  $P_B$  alone. Thus, for the general case,

$$\begin{aligned} & P_A^2 r \{ X[Z(Y - \mu)^2 + \rho\mu^2] + \rho ZY^2 \} \\ & \quad + \mu(1 + r)(Y - \mu)XP_A - Y^2 = 0 \quad (16) \end{aligned}$$

$$\begin{aligned} & P_B^2 \{ X[Z(Y - \mu)^2 + \rho\mu^2] + \rho ZY^2 \} \\ & \quad + \mu(1 + r)(Y - \mu)XP_B - rY^2 = 0 \quad (17) \end{aligned}$$

where  $X = (f_3 - 1)\theta + (f_4 - 1)\pi + (f_5 - 1)\varphi + (g_4 - 1)\mu$

$$Y = \theta + \pi + \varphi + \mu$$

and

$$Z = 1 - \lambda - \mu$$

When  $X[Z(Y - \mu)^2 + \rho\mu^2] + \rho ZY^2 \neq 0$ , therefore, we have

$$\begin{aligned} (P_A)_{gel} = & [-\mu(1 + r)(Y - \mu)X + \sqrt{\mu^2(1 + r)^2(Y - \mu)^2X^2 + 4r\{X[Z(Y - \mu)^2 + \rho\mu^2] + \rho ZY^2\}Y^2}] \\ & / 2r\{X[Z(Y - \mu)^2 + \rho\mu^2] + \rho ZY^2\} \quad (18) \end{aligned}$$

$$\begin{aligned} (P_B)_{gel} = & [-\mu(1 + r)(Y - \mu)X + \sqrt{[\mu(1 + r)(Y - \mu)X]^2 + 4r\{X[Z(Y - \mu)^2 + \rho\mu^2] + \rho ZY^2\}Y^2}] \\ & / 2\{X[Z(Y - \mu)^2 + \rho\mu^2] + \rho ZY^2\} \quad (19) \end{aligned}$$

and if

$$X[Z(Y - \mu)^2 + \rho\mu^2] + \rho ZY^2 = 0$$

$$(P_A)_{gel} = Y^2 / \mu(1 + r)(Y - \mu)X \quad (20)$$

$$(P_B)_{gel} = rY^2 / \mu(1 + r)(Y - \mu)X \quad (21)$$



where  $(P_A)_{\text{gel}}$  and  $(P_B)_{\text{gel}}$  signify that the particular values of  $P_A$  and  $P_B$  are those at the gelation point.

Equations (18)–(21) may be derived also by applying Stockmayer's generalized gel point equation for this system using the same symbols as defined above.

In practice, of course, it may be unlikely that four different epoxides are present at the same time. It is common, however, for the epoxide resin system to be made with a diepoxide and a monoepoxide, a diepoxide and a polyhydric alcohol of functionality of 2 or more, and a diepoxide and a monohydroxy diepoxide of functionality of 5.

For each of these special individual cases the general equations eqs. (12), (14), and (18)–(21) reduced to the following.

1. Epoxy resin/acid anhydride system from  $A \begin{array}{c} \text{A} \\ | \\ \text{---} \\ | \\ \text{A} \end{array} A$  with  $B-B$ .

$$\rho = \theta = \varphi = \lambda = \mu = 1 - \pi = 0 \text{ and } f_4 = 4.$$

$$(P_B)_{\text{gel}} = \sqrt{r/(f_4 - 1)} = \sqrt{r/3} \quad (22)$$

$$\alpha = P_A P_B = P_B^2/r \quad (23)$$

$$\alpha_c = 1/(f_4 - 1) = 1/3 \quad (24)$$

2. Epoxy resin/acid anhydride system from  $A-A$  and  $A \begin{array}{c} \text{A} \\ | \\ \text{---} \\ | \\ \text{A} \end{array} A$  with  $B-B$ .

$$\theta = \varphi = \lambda = \mu = 1 - \rho - \pi = 0 \text{ and } f_4 = 4.$$

$$(P_B)_{\text{gel}} = \sqrt{r/[(f_4 - 1)(1 - \rho) + \rho]} = \sqrt{r/(3 - 2\rho)} \quad (25)$$

$$\alpha = P_A P_B (1 - \rho)/(1 - P_A P_B \rho) = P_B^2 (1 - \rho)/(r - P_B^2 \rho) \quad (26)$$

$$\alpha_c = 1/(f_4 - 1) = 1/3 \quad (27)$$

3. Epoxy resin/acid anhydride system from  $A \begin{array}{c} \text{A} \\ \diagup \quad \diagdown \\ \text{A} \end{array}$  and  $A \begin{array}{c} \text{A} \\ | \\ \text{---} \\ | \\ \text{A} \end{array} A$  with  $B-B$ .

$$\rho = \varphi = \lambda = \mu = 1 - \theta - \pi = 0, f_3 = 3, \text{ and } f_4 = 4$$

$$(P_B)_{\text{gel}} = \sqrt{r/[(f_3 - f_4)\theta + (f_4 - 1)]} = \sqrt{r/(3 - \theta)} \quad (28)$$

$$\alpha = P_A P_B (\theta + \pi) = P_B^2/r \quad (29)$$

$$\alpha_c = 1/[(f_3 - f_4)\theta + (f_4 - 1)] = 1/(3 - \theta) \text{ or } 1/(2 + \pi) \quad (30)$$

4. Epoxy resin/acid anhydride system from  $A-A$ ,  $A \begin{array}{c} \text{A} \\ | \\ \text{---} \\ | \\ \text{A} \end{array} A$ , and  $A \begin{array}{c} \text{A} \\ \diagup \quad \diagdown \\ \text{A} \end{array} A$  with  $B-B$ .

$$\theta = \lambda = \mu = 1 - \pi - \varphi - \rho = 0, f_4 = 4, \text{ and } f_5 = 5$$

$$(P_B)_{\text{gel}} = \sqrt{r/(3\pi + 4\varphi + \rho)} \quad (31)$$

$$\alpha = P_A P_B (1 - \rho)/(1 - P_A P_B \rho) = P_B^2 (1 - \rho)/(r - P_B^2 \rho) \quad (32)$$

$$\alpha_c = (\pi + \varphi)/[(f_4 - 1)\pi + (f_5 - 1)\varphi] = (\pi + \varphi)/(3\pi + 4\varphi) \quad (33)$$

5. Epoxy resin/acid anhydride system from  $\begin{array}{c} \text{A} \\ | \\ \text{A} - \text{C} - \text{A} \\ | \quad | \\ \text{A} \quad \text{A} \end{array}$  with B—B.

$$\rho = \theta = \pi = \lambda = \mu = 1 - \varphi = 0 \text{ and } f_5 = 5$$

$$(P_B)_{\text{gel}} = \sqrt{r/(f_5 - 1)\varphi} = \sqrt{r/4} \quad (34)$$

$$\alpha = P_A P_B \varphi = P_B^2 / r \quad (35)$$

$$\alpha_c = 1/(f_5 - 1) = 1/4 \quad (36)$$

6. Epoxy resin/acid anhydride system from  $\begin{array}{c} \text{A} \\ | \\ \text{A} - \text{C} - \text{A} \\ | \\ \text{A} \end{array}$  with  $\begin{array}{c} \text{B} \\ | \\ \text{B} - \text{C} - \text{B} \\ | \\ \text{B} \end{array}$ .

$$\rho = \theta = \varphi = \lambda = 1 - \pi = 1 - \mu = 0, \text{ and } f_4 = g_4 = 4$$

$$(P_B)_{\text{gel}} = r(\pi + \mu)^2/(1 + r)[(f_4 - 1)\pi + (g_4 - 1)\mu] = 2r/3(1 + r) \quad (37)$$

$$\alpha = (P_A + P_B)/2 = P_B(1 + r)/2r \quad (38)$$

$$\alpha_c = (\pi + \mu)/[(f_4 - 1)\pi + (g_4 - 1)\mu] = 1/3 \quad (39)$$

7. Epoxy resin/acid anhydride system from A—A and  $\begin{array}{c} \text{A} \\ | \\ \text{A} - \text{C} - \text{A} \\ | \\ \text{A} \end{array}$  with B—B and  $\begin{array}{c} \text{B} \\ | \\ \text{B} - \text{C} - \text{B} \\ | \\ \text{B} \end{array}$ .

$$\theta = \varphi = \lambda = 1 - \rho - \pi = 0 \text{ and } 1 - \mu \neq 0$$

$$(P_B)_{\text{gel}} = \frac{-3\pi\mu(1 + r) + \sqrt{[3\pi\mu(1 + r)]^2 + 4r(\pi + \mu)\{(1 - \mu)[3\pi^2 + \rho(\pi + \mu)] + 3\rho\mu^2\}}}{2\{(1 - \mu)[3\pi^2 + \rho(\pi + \mu)] + 3\rho\mu^2\}} \quad (40)$$

$$\alpha = \frac{P_A P_B [(1 - \mu)\pi^2 + \rho\mu^2] + (P_A + P_B)\pi\mu}{(\pi + \mu)[1 - P_A P_B \rho(1 - \mu)]} \quad (41)$$

$$= \frac{P_B^2 [(1 - \mu)\pi^2 + \rho\mu^2] + P_B(1 + r)\pi\mu}{(\pi + \mu)[r - P_B^2 \rho(1 - \mu)]}$$

$$\alpha_c = (\pi + \mu)/[(f_4 - 1)\pi + (g_4 - 1)\mu] = 1/3 \quad (42)$$

8. Epoxy resin/acid anhydride system from A—A and  $\begin{array}{c} \text{A} \\ | \\ \text{A} - \text{C} - \text{A} \\ / \quad \backslash \\ \text{A} \quad \text{A} \end{array}$  with B—B.

$$\theta = \pi = \lambda = \mu = 1 - \rho - \varphi = 0 \text{ and } f_5 = 5$$

$$(P_B)_{\text{gel}} = \sqrt{r/[(f_5 - 1)\varphi + \rho]} = \sqrt{r/(4 - 3\rho)} \quad (43)$$

$$\alpha = P_A P_B (1 - \rho)/(1 - P_A P_B \rho) = P_B^2 \varphi/(r - P_B^2 \rho) \quad (44)$$

$$\alpha_c = 1/(f_5 - 1) = 1/4 \quad (45)$$

9. Epoxy resin/acid anhydride system from A and  $\begin{array}{c} \text{A} \\ | \\ \text{A} - \text{C} - \text{A} \\ | \\ \text{A} \end{array}$  with B—B.

$$\rho = \theta = \varphi = \lambda = \mu = 0 \text{ and } 1 - \pi \neq 0$$

$$(P_B)_{\text{gel}} = \sqrt{r/(f_4 - 1)\pi} = \sqrt{r/3\pi} \quad (46)$$

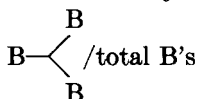
$$\alpha = P_A P_B \pi = P_B^2 \pi/r \quad (47)$$

$$\alpha_c = 1/(f_4 - 1) = 1/3 \quad (48)$$

10. Epoxy resin/acid anhydride system from  $\begin{array}{c} \text{A} \\ | \\ \text{A} - \text{C} - \text{A} \\ | \\ \text{A} \end{array}$  and  $\begin{array}{c} \text{B} \\ / \quad \backslash \\ \text{B} - \text{C} - \text{B} \\ | \quad | \\ \text{B} \quad \text{B} \end{array}$ .

$$\rho = \theta = \varphi = \lambda = 1 - \pi = 1 - \delta = 0 \text{ and } g_3 = 3$$

where  $\delta$  and  $g_3$  replace  $\mu$  and  $g_4$ , respectively, and  $\delta \equiv$  B's belonging to



$$(P_B)_{\text{gel}} = r(\pi + \delta)^2/\pi(1 + r) [(f_4 - 1)\pi + (g_3 - 1)\delta] = 4r/5(1 + r) \quad (49)$$

$$\alpha = (P_A + P_B)\pi\delta/(\pi + \delta) = P_B(1 + r)/2r \quad (50)$$

$$\alpha_c = (\pi + \delta)/(3\pi + 2\delta) = 2/5 \quad (51)$$

### The Number-Average Degree of Polymerization

The number-average number of units per molecule,  $DP_n$ , can be computed as Flory did. The number of A and B functional groups present initially will be represented by  $N_A$  and  $N_B$ , respectively, where the branch units of functionality  $f_i$  and  $g_j$  ( $i = 1, 2, \dots, 5$  and  $j = 1, 2, \dots, 4$ ) possess functional groups of the type A and B. The total number of units is then given by eq. (52):

Total no. of units

$$= 1/f_1 N_A (1 - \rho - \theta - \pi - \varphi) + 1/f_2 N_A \rho \\ + 1/f_3 N_A \theta + 1/f_4 N_A \pi + 1/f_5 N_A \varphi + 1/g_1 N_B \lambda \\ + 1/g_2 N_B (1 - \lambda - \delta - \mu) + 1/g_3 N_B \delta + 1/g_4 N_B \mu \quad (52)$$

and the total number of linkages is given by eq. (53):

$$\text{Total no. of linkages} = P_A N_A \quad (53)$$

Assuming as above that all linkages are intermolecular, the relation of eq. (54) may be obtained;

$$\text{Total no. of molecules} = (\text{no. of units}) - (\text{no. of linkages}) \quad (54)$$

Therefore, the number-average degree of polymerization can be shown as follows;

$$\text{DP}_n = (\text{no. of units})/(\text{no. of molecules}) = \\ \{1/f_1(1 - \rho - \theta - \pi - \varphi) + 1/f_2 \rho + 1/f_3 \theta + 1/f_4 \pi + 1/f_5 \varphi + 1/r [1/g_1 \lambda \\ + 1/g_2(1 - \lambda - \delta - \mu) + 1/g_3 \delta + 1/g_4 \mu]\} / \{1/f_1(1 \\ - \rho - \theta - \pi - \varphi) + 1/f_2 \rho + 1/f_3 \theta + 1/f_4 \pi + 1/f_5 \varphi + 1/r [1/g_1 \lambda \\ + 1/g_2(1 - \lambda - \delta - \mu) + 1/g_3 \delta + 1/g_4 \mu] - P_B/r\} \quad (55)$$

For each of the special individual cases the general equation, eq. (55) reduced to the form given in eqs. (56)–(65).

1. Epoxy resin/acid anhydride system from  $\text{A} \begin{array}{c} \text{A} \\ | \\ \text{---} \\ | \\ \text{A} \end{array} \text{A}$  with B—B.

$$\text{DP}_n = (1 + g_2/r)/(1 + g_2/r - f_4 P_B/r) \quad (56)$$

2. Epoxy resin/acid anhydride system from A—A and  $\text{A} \begin{array}{c} \text{A} \\ | \\ \text{---} \\ | \\ \text{A} \end{array} \text{A}$  with B—B.

$$\text{DP}_n = [f_4(\rho + 1/r) + f_2(1 - \rho)]/[f_4(\rho \\ + 1/r - f_2 P_B/r) + f_2(1 - \rho)] \quad (57)$$

3. Epoxy resin/acid anhydride system from  $\text{A} \begin{array}{c} \text{A} \\ \diagup \quad \diagdown \\ \text{A} \end{array}$  and  $\text{A} \begin{array}{c} \text{A} \\ | \\ \text{---} \\ | \\ \text{A} \end{array} \text{A}$  with B—B.

$$\text{DP}_n = \{f_4[\theta(1/f_3 - 1/f_4)] + 1 + g_2/r\} / \{f_4[\theta(1/f_3 \\ - 1/f_4) - P_B/r] + 1 + g_2/r\} \quad (58)$$

4. Epoxy resin/acid anhydride system from A—A,  $\text{A} \begin{array}{c} \text{A} \\ | \\ \text{---} \\ | \\ \text{A} \end{array} \text{A}$ , and  $\text{A} \begin{array}{c} \text{A} \\ \diagup \quad \diagdown \\ \text{A} \end{array} \text{A}$  with B—B.

$$\text{DP}_n = [f_2(f_5 - f_2)\rho + (f_5 - f_4)\pi + f_2(f_2 + f_5/r)]/[f_2(f_5 \\ - f_2)\rho + (f_5 - f_4)\pi - f_4 f_5 P_B/r + f_2(f_2 + f_5/r)] \quad (59)$$

5. Epoxy resin/acid anhydride system from  $A \begin{array}{c} \diagup A \\ | \\ A \end{array} \begin{array}{c} \diagdown A \\ | \\ A \end{array}$  with  $B-B$ .

$$DP_n = (g_2 + f_5/r)/(g_2 + f_5/r - f_5g_2P_B/r) \quad (60)$$

6. Epoxy resin/acid anhydride system from  $A \begin{array}{c} A \\ | \\ A \end{array} \begin{array}{c} B \\ | \\ B \end{array}$  with  $B \begin{array}{c} B \\ | \\ B \end{array} \begin{array}{c} B \\ | \\ B \end{array}$ .

$$DP_n = (\pi + \mu/r)/(\pi + \mu/r - P_B/r) = (1 + r)/(1 + r - P_B) \quad (61)$$

7. Epoxy resin/acid anhydride system from  $A-A$  and  $A \begin{array}{c} A \\ | \\ A \end{array} \begin{array}{c} A \\ | \\ A \end{array}$  with  $B-B$  and  $B \begin{array}{c} B \\ | \\ B \end{array} \begin{array}{c} B \\ | \\ B \end{array}$ .

$$DP_n = \{ (f_2 - 1)\rho + 1 + 1/r[f_2 - \mu(f_2 - 1)] \} / \{ (f_2 - 1)\rho + 1 + f_4P_B/r + 1/r[f_2 - \mu(f_2 - 1)] \} \quad (62)$$

8. Epoxy resin/acid anhydride system from  $A-A$  and  $A \begin{array}{c} A \\ | \\ A \end{array} \begin{array}{c} A \\ | \\ A \end{array}$  with  $B-B$ .

$$DP_n = [(f_5 - f_2)\rho + f_2 + f_5/r] / [(f_5 - f_2)\rho + f_2 + f_5/r - f_2f_5P_B/r] \quad (63)$$

9. Epoxy resin/acid anhydride system from  $A$  and  $A \begin{array}{c} A \\ | \\ A \end{array} \begin{array}{c} A \\ | \\ A \end{array}$  with  $B-B$ .

$$DP_n = [f_4 - (f_4 - 1)\pi + f_2/r] / [f_4 - (f_4 - 1)\pi + f_2/r - f_4P_B/r] \quad (64)$$

10. Epoxy resin/acid anhydride system from  $A \begin{array}{c} A \\ | \\ A \end{array} \begin{array}{c} A \\ | \\ A \end{array}$  with  $B \begin{array}{c} B \\ | \\ B \end{array} \begin{array}{c} B \\ | \\ B \end{array}$ .

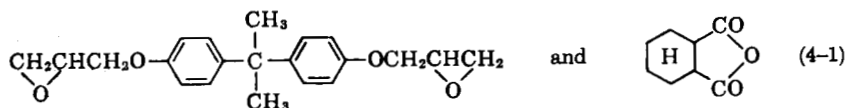
$$DP_n = g_3\pi + f_4\delta/r/g_3\pi + f_4\delta/r - g_3f_4P_B/r \quad (65)$$

It must be noted that eqs. (12) and (14)-(65) assume that all the reactants—diepoxide, monoepoxide, polyhydric alcohols and acid anhydrides—are present from the start of the reaction and are not added in stages.

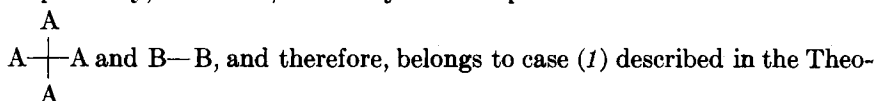
## RESULTS

### The E-828/HHPA System

Since the molecular structure of E-828<sup>17</sup> and HHPA are



respectively, the E-828/HHPA system is represented as a formulation from



retical section. The results from one of the experiments with E-828, HHPA, and triethanolamine are shown in Figure 2. By use of eqs. (22)–(24) and (55), the values of  $\alpha$  and  $\text{DP}_n$  shown in Figure 2 were calculated from  $P_A$  or  $P_B$ ,  $r$ , and  $\pi$  (in this case  $\pi = 1$ ). Also included in Figure 2 is the experimentally measured viscosity which increases slowly at first, but very rapidly when the gel point is approached. Data concerning gelation points obtained in this case are presented in Table III.

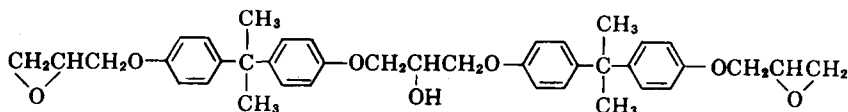
TABLE III  
Gel Point for System of E-828/HHPA at 100°C.  
( $\pi = 1$ , 0.5 wt.-% of Triethanolamine Added)

| E-828,<br>equiv. | HHPA,<br>equiv. | $r$  | $(P_B)_{\text{gel}}, \%$ |       | $(\alpha)_{\text{gel}}$ | $(\text{DP}_n)_{\text{gel}}$<br>calc. | $(\text{MW})_{\text{gel}}$<br>obs. |
|------------------|-----------------|------|--------------------------|-------|-------------------------|---------------------------------------|------------------------------------|
|                  |                 |      | Obs.                     | Calc. |                         |                                       |                                    |
| 2.54             | 2.54            | 1.00 | 55.0                     | 57.7  | 0.303                   | 3.75                                  | 820 $\pm$ 50                       |
| 2.10             | 2.63            | 0.80 | 50.0                     | 51.6  | 0.313                   | 3.50                                  | 850 $\pm$ 60                       |
| 2.54             | 1.78            | 1.43 | 68.0                     | 69.0  | 0.323                   | 2.41                                  | 530 $\pm$ 60                       |

The molecular weight at gelation point,  $(\text{MW})_{\text{gel}}$ , was determined by a cryoscopic method with the sample removed just prior to gelation. The solvent used was benzene.

### The E-1001/HHPA System

Since the molecular structure of E-1001<sup>17</sup> is



the E-1001/HHPA system is represented as a formulation from  $\begin{array}{c} \text{A} \\ | \\ \text{A}-\text{C}-\text{A} \\ | \\ \text{A} \end{array}$

and B—B and belongs to case 5 in the Theoretical section. One of the results of the experiments with E-1001, HHPA, and triethanolamine are shown in Figure 3. The values of  $\alpha$  and  $\text{DP}_n$  shown in Figure 3 were calculated from  $P_A$  or  $P_B$ ,  $r$ , and  $\varphi$  (in this case,  $\varphi = 1$ ), by use of eqs. (34)–(36) and (59). Data concerning gel points in this case are presented in Table IV.

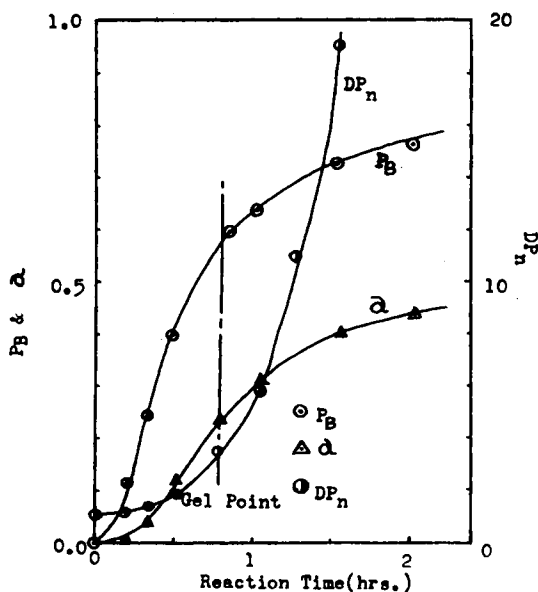


Fig. 3. Reaction of E-1001/HHPA ( $r = 1.350$ ,  $\varphi = 1$ ) system with triethanolamine (0.5 wt.-%) at 100°C.

TABLE IV  
Gel Point for E-1001/HHPA System at 100°C.  
( $\varphi = 1$ , 0.5 wt.-% of Triethanolamine Added and  $\alpha_c = 0.250$ )

| No.            | E-1001,<br>equiv. | HHPA,<br>equiv. | $r$  | $(P_B)_{gel}, \%$ |       | $(\alpha)_{gel}$ | $(DP_n)_{gel}$ | $(MW)_{gel}$<br>obs. |
|----------------|-------------------|-----------------|------|-------------------|-------|------------------|----------------|----------------------|
|                |                   |                 |      | Obs.              | Calc. |                  |                |                      |
| 1              | 1.368             | 1.011           | 1.35 | 59.7              | 58.1  | 0.264            | 4.56           | $1700 \pm 120$       |
| 2 <sup>a</sup> | "                 | "               | "    | 57.0              | "     | 0.240            | 3.85           | $1600 \pm 160$       |

<sup>a</sup> No catalyst.

### The E-828/Monoepoxide or Dihydric Alcohol/HHPA System

This system of E-828/monoepoxide/HHPA is represented as the  
 A  
 formulation from A—A and A— $\frac{A}{|}$ —A with B—B and belongs to case (2)  
 A

described in the Theoretical section. The result from one of the experiments with E-828, triethylene glycol, and HHPA are shown in Figure 5. Data obtained in this case are presented in the Table V. The values of  $\alpha$  and  $DP_n$  shown in Figure 5 and Table V were calculated from eqs. (22)–(24) and (56).

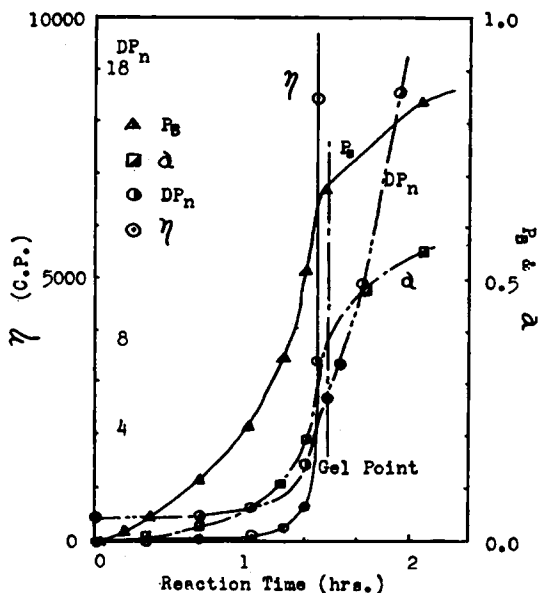


Fig. 4. Reaction of E-828/HHPA/octyl alcohol ( $r = 1.159$ ,  $\pi = 0.874$ ) system with triethanolamine (0.5 wt.-%) at 100°C.

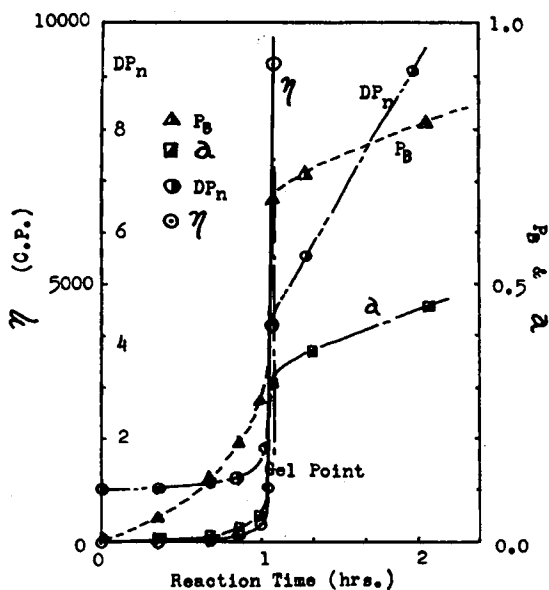


Fig. 5. Reaction of E-828/HHPA/triethyleneglycol ( $r = 1.215$ ,  $\pi = 0.725$ ) system with triethanolamine (0.5 wt.-%) at 100°C.



TABLE V  
Gel Point for E-828/A—A/H PA System at 100°C.  
( $\alpha_s = 1/3$ , 0.5 wt.-% of Triethanolamine Added)

| No.* | E-828, equiv. | A—A, equiv. | HHPA, equiv. | $r$   | $\pi$ | $\rho$ | $(P_B)_{gel}$ , % |       | $(\alpha)_{gel}$ | $(DP_n)_{gel}$ |
|------|---------------|-------------|--------------|-------|-------|--------|-------------------|-------|------------------|----------------|
|      |               |             |              |       |       |        | Obs.              | Calc. |                  |                |
| 1    | 2.54          | 0.47        | 3.01         | 1.00  | 0.844 | 0.156  | 63.6              | 61.0  | 0.364            | 5.16           |
| 2    | 2.10          | 0.38        | 3.11         | 0.80  | 0.847 | 0.153  | 57.2              | 54.5  | 0.368            | 4.60           |
| 3    | 5.26          | 2.00        | 5.97         | 1.215 | 0.725 | 0.275  | 72.0              | 70.4  | 0.358            | 5.60           |
| 4    | "             | "           | "            | "     | "     | "      | 70.6              | "     | 0.334            | 4.89           |
| 5    | "             | "           | "            | "     | "     | "      | 71.0              | "     | 0.342            | 5.00           |
| 6    | "             | "           | "            | "     | "     | "      | 70.8              | "     | 0.338            | 4.95           |
| 7    | "             | "           | "            | "     | "     | "      | 72.8              | "     | 0.357            | 5.57           |
| 8    | "             | "           | "            | "     | "     | "      | 71.6              | "     | 0.346            | 5.17           |

\* A—A used: 1 and 2, octylene oxide; 3, dodecene oxide; 4, allyl glycidyl ether; 5, phenyl glycidyl ether; 6, butyl glycidyl ether; 7, triethylene glycol; 8, ethylene glycol.

### The E-1001/Monoepoxide or Dihydric Alcohol/HHPA System

This system is represented as the formulation from A—A and  $\begin{array}{c} \text{A} \\ | \\ \text{A} \text{---} \text{C} \text{---} \text{A} \\ | \\ \text{A} \end{array}$  with B—B. Data obtained in this case are presented in Table VI, and the values of  $\alpha$  and  $DP_n$  were calculated from eqs. (43)–(45) and (62). In Table VI,  $(\alpha)_{gel}$  are the values of  $\alpha$  and  $DP_n$  respectively, at the gel point.

TABLE VI  
Gel Point for E-1001/A—A/HHPA at 100°C. System  
( $\alpha_s = 0.25$ , 0.5 wt.-% of Triethanolamine Added)

| No.* | E-1001, equiv. | A—A, equiv. | HHPA, equiv. | $r$   | $\rho$ | $\varphi$ | $(P_B)_{gel}$ , % |       | $(\alpha)_{gel}$ | $(DP_n)_{gel}$ |
|------|----------------|-------------|--------------|-------|--------|-----------|-------------------|-------|------------------|----------------|
|      |                |             |              |       |        |           | Obs.              | Calc. |                  |                |
| 1    | 0.695          | 0.203       | 1.039        | 0.864 | 0.226  | 0.774     | 53.8              | 51.0  | 0.281            | 3.82           |
| 2    | "              | "           | 0.898        | 1.000 | "      | "         | 56.8              | 54.9  | 0.268            | 3.85           |
| 3    | "              | "           | "            | "     | "      | "         | 55.6              | "     | 0.257            | 3.64           |
| 4    | "              | "           | "            | "     | "      | "         | 55.4              | "     | 0.255            | 3.60           |
| 5    | "              | "           | "            | "     | "      | "         | 56.0              | "     | 0.261            | 3.70           |
| 6    | "              | "           | "            | "     | "      | "         | 55.3              | "     | 0.254            | 3.58           |
| 7    | "              | "           | "            | "     | "      | "         | 56.2              | "     | 0.263            | 3.74           |


\* A—A used: 1, octylene oxide; 2, dodecene oxide; 3, phenyl glycidyl ether; 4, allyl glycidyl ether; 5, butyl glycidyl ether; 6, triethylene glycol; 7, ethylene glycol.

### The E-828/Monohydric Alcohol/HHPA System

The system in this case is represented as the formulation from A and A with B—B. Data concerning gel points obtained in this case are shown in Table VII, and the values of  $\alpha$  and  $DP_n$  were obtained from eqs. (46)–(48) and (64).

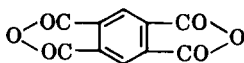
TABLE VII  
Gel Point for E-828/A/HHPA at 100°C. System  
( $\alpha_0 = 0.333$ , 0.5 wt.-% of Triethanolamine Added)

| No. <sup>a</sup> | E-828,<br>equiv. | A,<br>equiv. | HHPA,<br>equiv. | $r$   | $\pi$ | $1 - \pi$ | $(P_B)_{gel}$ , % |       | $(\alpha)_{gel}$ | $(DP_n)_{gel}$ |
|------------------|------------------|--------------|-----------------|-------|-------|-----------|-------------------|-------|------------------|----------------|
|                  |                  |              |                 |       |       |           | Obs.              | Calc. |                  |                |
| 1                | 5.26             | 0.768        | 5.20            | 1.159 | 0.874 | 0.126     | 68.6              | 66.4  | 0.355            | 4.19           |
| 2                | "                | "            | "               | "     | "     | "         | 69.0              | "     | 0.359            | 4.31           |
| 3                | "                | "            | "               | "     | "     | "         | 68.7              | "     | 0.356            | 4.19           |
| 4                | "                | "            | "               | "     | "     | "         | 67.4              | "     | 0.343            | 3.98           |
| 5                | "                | "            | "               | "     | "     | "         | 68.0              | "     | 0.348            | 4.08           |
| 6                | "                | "            | "               | "     | "     | "         | 67.5              | "     | 0.344            | 4.00           |

<sup>a</sup> A used: 1,  $C_6H_{17}OH$ ; 2,  $C_6H_9OCH_2CH_2OH$ ; 3,  $C_6H_5CH_2OH$ ; 4,  $(CH_3)_2CHCH_2CH_2OH$ ; 5,   $CH_2OH$ ; 6,  $(CH_3)_2C(CH_2OCH_3)OH$ .

### The E-828/PMDA System

The system of E-828/PMDA may be represented as the formulation from A with B—B and belongs to case 6, because the molecular structure of PMDA is:<sup>10</sup>



Data obtained are shown in Table VIII, and the values of  $(\alpha)_{gel}$  and  $(DP_n)_{gel}$ , which are the values of  $\alpha$  and  $DP_n$  respectively, at the gel point, were calculated from eqs. (37)–(39) and (61).

TABLE VIII  
Gel Point for E-828/PMDA System at 130°C.  
( $\alpha_0 = 0.333$ , 0.1 wt.-% of Triethanolamine Added)

| E-828,<br>equiv. | PMDA,<br>equiv. | $r$  | $\pi$ | $\mu$ | $(P_B)_{gel}$ , % |       | $(\alpha)_{gel}$ | $(DP_n)_{gel}$ |
|------------------|-----------------|------|-------|-------|-------------------|-------|------------------|----------------|
|                  |                 |      |       |       | Obs.              | Calc. |                  |                |
| 5.00             | 5.00            | 1.00 | 1.00  | 1.00  | 35.0              | 33.3  | 0.350            | 1.21           |
| "                | 6.25            | 0.80 | "     | "     | 30.5              | 29.7  | 0.342            | 1.20           |
| "                | 4.17            | 1.20 | "     | "     | 37.8              | 36.4  | 0.346            | 1.20           |

### The E-828/Monoepoxide or Dihydric Alcohol/HHPA/PMDA System

This system is represented as the formulation from A—A and  $\begin{array}{c} \text{A} \\ | \\ \text{A}-\text{A} \\ | \\ \text{A} \end{array}$  with B—B and  $\begin{array}{c} \text{B} \\ | \\ \text{B}-\text{B} \\ | \\ \text{B} \end{array}$ , and belongs to case 7 in the Theoretical section.

Data concerning gel points obtained in this case are shown in Table IX and the values of  $(\alpha)_{\text{gel}}$  were calculated from eqs. (40)–(42) and (62).

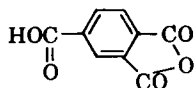
TABLE IX  
Gel Point for E-828/A—A/HHPA/PMDA System at 130°C.\*

| E-828,<br>equiv. | A—A,<br>equiv. | HHPA,<br>equiv. | PMDA,<br>equiv. | $r$ | $\pi$ | $\mu$ | $(P_B)_{\text{gel}}, \%$ |       | $(\alpha)_{\text{gel}}$ | $(DP_n)_{\text{gel}}$ |
|------------------|----------------|-----------------|-----------------|-----|-------|-------|--------------------------|-------|-------------------------|-----------------------|
|                  |                |                 |                 |     |       |       | Obs.                     | Calc. |                         |                       |
| 4.00             | 1.00           | 1.00            | 4.00            | 1.0 | 0.80  | 0.80  | 39.2                     | 38.5  | 0.341                   | 2.89                  |
| "                | "              | 3.00            | 2.00            | "   | "     | 0.40  | 48.4                     | 46.7  | "                       | 3.23                  |
| "                | "              | 1.60            | 2.40            | 0.8 | "     | 0.60  | 39.0                     | 37.4  | 0.351                   | 2.94                  |
| "                | "              | 2.40            | 3.60            | 1.2 | "     | "     | 47.3                     | 45.9  | 0.347                   | 3.00                  |

\* A—A used here was phenyl glycidyl ether.

### The E-828/TMA System

Since the molecular structure of TMA is<sup>11</sup>



this system is represented as the formulation from  $\begin{array}{c} \text{A} \\ | \\ \text{A}-\text{A} \\ | \\ \text{A} \end{array}$  with  $\begin{array}{c} \text{B} \\ \diagup \quad \diagdown \\ \text{B}-\text{B} \end{array}$ ,

and belongs to case 10 in the Theoretical section. Data obtained in this case are shown in Table X, and the values of  $\alpha$  and  $DP_n$  at gel point, which are represented as  $(\alpha)_{\text{gel}}$  and  $(DP_n)_{\text{gel}}$ , respectively, were calculated from eqs. (49)–(51) and (65).

TABLE X  
Gel Point for E-828/TMA System at 130°C.  
( $\alpha_o = 0.40$ , 0.5 wt.-% of Triethanolamine Added)

| E-828,<br>equiv. | TMA,<br>equiv. | $r$ | $\pi$ | $\delta$ | $(P_B)_{\text{gel}}, \%$ |       | $(\alpha)_{\text{gel}}$ | $(DP_n)_{\text{gel}}$ |
|------------------|----------------|-----|-------|----------|--------------------------|-------|-------------------------|-----------------------|
|                  |                |     |       |          | Obs.                     | Calc. |                         |                       |
| 3.00             | 3.00           | 1.0 | 1.0   | 1.0      | 41.1                     | 40.0  | 0.411                   | 3.40                  |
| "                | 2.40           | 0.8 | "     | "        | 36.9                     | 35.6  | 0.415                   | 2.27                  |
| "                | 3.60           | 1.2 | "     | "        | 45.1                     | 43.6  | 0.413                   | 3.49                  |

### The E-828/glycidol/HHPA System

Since the molecular structure of glycidol is



the system of E-828/glycidol/HHPA is represented as the formulation from

$\begin{array}{c} \text{A} \\ \diagup \quad \diagdown \\ \text{A} \end{array}$  and  $\begin{array}{c} \text{A} \\ | \\ \text{A}-\text{A} \end{array}$  with B—B, and belongs to case 3 described in

the Theoretical section. Data concerning gel points obtained in this case are shown in Table XI, and the values of  $(\alpha)_{\text{gel}}$  and  $(\text{DP}_n)_{\text{gel}}$  were calculated from eqs. (28)–(30) and (58).

TABLE XI  
Gel Point for A-828/glycidol/HHPA System at 100°C  
(0.5 wt.-% of Triethanolamine Added)

| E-828,<br>equiv. | Glycidol,<br>equiv. | HHPA,<br>equiv. | $r$ | $\theta$ | $\pi$ | $(P_B)_{\text{gel}}, \%$ |       | $(\alpha)_{\text{gel}}$ | $\alpha_0$ | $(\text{DP}_n)_{\text{gel}}$ |
|------------------|---------------------|-----------------|-----|----------|-------|--------------------------|-------|-------------------------|------------|------------------------------|
|                  |                     |                 |     |          |       | Obs.                     | Calc. |                         |            |                              |
| 4.00             | 0.45                | 4.45            | 1.0 | 0.10     | 0.90  | 60.4                     | 58.9  | 0.365                   | 0.345      | 4.92                         |
| "                | "                   | 5.57            | 0.8 | "        | "     | 54.1                     | 52.5  | 0.367                   | "          | 4.30                         |
| "                | "                   | 3.71            | 1.2 | "        | "     | 63.7                     | 64.3  | 0.339                   | "          | 4.71                         |
| "                | 1.00                | 5.00            | 1.0 | 0.20     | 0.80  | 58.0                     | 59.7  | 0.336                   | 0.357      | 4.11                         |

### The E-828/Monoepoxide or Dihydric Alcohol/E-1001/HHPA System

This system is represented as the formulation from A—A,  $\begin{array}{c} \text{A} \\ | \\ \text{A}-\text{A} \end{array}$  and  $\begin{array}{c} \text{A} \\ \diagup \quad \diagdown \\ \text{A} \end{array}$  with B—B and belongs to case 4 in the Theoretical section.

The results obtained in this case are presented in the Table XII, and the values of  $(\alpha)_{\text{gel}}$  and  $(\text{DP}_n)_{\text{gel}}$  were calculated from eqs. (31)–(33) and (59).

## DISCUSSION

### Comparison of Molecular Weight Found at Gelation Point with Calculated Value of $(\text{DP}_n)_{\text{gel}}$ from $(P_B)_{\text{gel}}$ or $(P_A)_{\text{gel}}$

The average molecular weights of the E-828/HHPA system at the gel point were calculated as 870 to 880 ( $r = 0.8$ – $1.0$ ) and 630 ( $r = 1.43$ ) for the values of  $(\text{DP}_n)_{\text{gel}}$  shown in the Table III. These results were consistent with the observed values of 820–850 and 530, respectively. The average molecular weights of 2080 and 1670, calculated for the system of E-1001/HHPA at the gel point using the values of  $(\text{DP}_n)_{\text{gel}}$  in the Table IV, were consistent with the observed results of 1700 and 1600, respectively.

TABLE XII  
Gel Point for E-828/E-1001/Monoepoxide or Dihydric Alcohol/HPHA System at 100°C.  
(0.5 wt.-% of Triethanolamine Added)<sup>a</sup>

| E-828,<br>equiv. | E-1001,<br>equiv. | A-A,<br>equiv. | HPHA,<br>equiv. | $\tau$ | $\rho$ | $\pi$ | $\varphi$ | $(P_n)_{gel}, \%$ |       | $(\alpha)_{gel}$ |       | Calc. | $(DP_n)_{gel}$ |
|------------------|-------------------|----------------|-----------------|--------|--------|-------|-----------|-------------------|-------|------------------|-------|-------|----------------|
|                  |                   |                |                 |        |        |       |           | Obs.              | Calc. | Obs.             | Calc. |       |                |
| 2.5              | 2.0               | 0.5            | 5.0             | 1.0    | 0.1    | 0.5   | 0.4       | 56.7              | 55.9  | 0.299            | 0.291 | 0.291 | 3.98           |
| "                | "                 | "              | 4.0             | 0.8    | "      | "     | "         | 48.3              | 50.0  | 0.270            | "     | "     | 3.13           |
| "                | "                 | "              | 6.0             | 1.2    | "      | "     | "         | 62.0              | 61.2  | 0.297            | "     | "     | 4.30           |
| 3.0              | "                 | 0.0            | 5.0             | 1.0    | 0.0    | 0.6   | "         | 52.6              | 54.3  | 0.277            | 0.295 | 0.295 | 3.57           |
| 2.0              | 3.0               | "              | "               | "      | "      | 0.4   | 0.6       | 53.8              | 52.7  | 0.289            | 0.278 | 0.278 | 4.06           |

<sup>a</sup> A-A used here is phenyl glycidyl ether.

### Effect of Resins on Values of $(P_B)_{\text{gel}}$

As shown in the Tables III and IV, the E-1001/HHPA system, having —OH groups in the molecular structure, has values of  $(P_B)_{\text{gel}}$  higher than the calculated ones and the E-828/HHPA system, having no —OH group in the molecular structure, has values lower than calculated. This seems to be due to the difference of the reactivity between the epoxide and hydroxyl groups, and is supported with the difference of the discrepancies,  $\Delta(P_B)_{\text{gel}}$ , between the cases with monoepoxides (alkylene oxides and glycidyl ethers) and with dihydric alcohols, as shown in Tables V and VI.

$$(\Delta P_B)_{\text{gel}} = [(P_B)_{\text{gel(obs.)}} - (P_B)_{\text{gel(calc.)}}] / (P_B)_{\text{gel(calc.)}} \times 100 \quad (66)$$

The discrepancy,  $\Delta(P_B)_{\text{gel}}$ , was calculated from eq. (66), where  $(P_B)_{\text{gel(obs.)}}$  and  $(P_B)_{\text{gel(calc.)}}$  are the observed and calculated values of  $P_B$  at the gel point, respectively.

### Effect of Functionality of Acid Anhydrides on Values of $(P_B)_{\text{gel}}$

The more the functionalities of acid anhydrides increase, the higher the observed values of  $(P_B)_{\text{gel}}$  become than the calculated ones, as shown in Tables III, VIII, and X. There were observed no effects of  $r$  within 0.8 to 1.43 of  $r$ , which is the equivalent ratio of A (the resins, monoepoxides and polyhydric alcohols) to B (acid anhydrides).

### Effect of Monohydric Alcohols on Values of $(P_B)_{\text{gel}}$

There are no effects of the kinds of monohydric alcohols within the condition of this experiment as shown in the Table VII.

### Effect of Monoepoxides on Values of $(P_B)_{\text{gel}}$

As shown in Table V and VI, the low reactive alkylene oxides having long carbon chains had higher values of  $(P_B)_{\text{gel}}$  than the alkylene oxides with short carbon chains and the glycidyl ethers, such as phenyl, allyl, and butyl glycidyl ether. This seems to be due to the difference of the reactivity between these alkylene oxides.

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### Synopsis

Equations are derived by means of Flory's original method for the gelation point of epoxy resin/acid anhydride/polyhydric alcohol systems containing various epoxy resins, acid anhydrides, and polyhydric alcohols. The resultant equations take no account of the reactivities of the various carboxyl, epoxy, and hydroxyl groups and are applied satisfactorily to epoxy resin/acid anhydride/polyhydric alcohol systems. The difference between the observed and calculated gelation point is about 2-3% when the acid anhydride used in HHPA and 4-5% when the acid anhydride used is tri- or tetrafunctional, such as TMA and PMDA. There is a little difference between resins E-828 and E-1001 for the gelation point. The discrepancy is believed to be due to the reactivity difference between epoxide and hydroxyl to carboxyl groups and to the occurrence of intramolecular condensation, and it is contended that the degree of intramolecular condensation in these branching systems obtained is a function of the branch unit functionality of reactant, in this case, acid anhydride or epoxide.

### Résumé

En employant la méthode originelle de Flory, on a dérivé des équations pour le point de gélation du système époxy résine/anhydride d'acide/alcool polyhydrique. Ce système contient plusieurs résines, époxy, anhydrides d'acides et alcools polyhydriques. Les équations déduites ne tiennent pas compte des réactivités des différents groupes carboxyliques, époxy et hydroxyliques et sont appliquées d'une manière satisfaisante aux systèmes d'époxy-résine/anhydride acide/alcool polyhydrique. La différence entre les points de gélation observés et calculés est environ 2 à 3% si l'anhydride utilisé est HHPA et 4 à 5% si l'anhydride utilisé est tri- ou tétrafonctionnel comme le TMA et le PMDA. Il y a une petite différence entre les résines E-828 et E-1001 quant au point de gélation. Le désaccord semble dû à la différence de réactivité entre époxyde et l'hydroxyle d'une part et les groupes carboxyliques de l'autre, et à l'occurrence d'une condensation intramoléculaire. On prétend que le degré d'une telle condensation intramoléculaire dans des systèmes branchés est obtenue comme une fonction de la fonctionnalité de l'unité d'embranchement, dans ce cas, l'anhydride d'acide ou époxyde.

### Zusammenfassung

Gleichungen für den Gelpunkt von Systemen mit verschiedenen Epoxidharzen, Säureanhydriden und mehrwertigen Alkoholen werden nach der ursprünglichen Methode von Flory abgeleitet. In den erhaltenen Gleichungen wird die Reaktivität der verschiedenen Karboxyl-, Epoxy- und Hydroxylgruppen nicht berücksichtigt; sie werden mit Erfolg auf die Systeme aus Epoxidharz, Säureanhydrid und mehrwertigem Alkohol angewendet. Bei Verwendung von HHPA als Säureanhydrid beträgt der Unterschied zwischen beobachtetem und berechnetem Gelpunkt etwa 2-3% und bei Verwendung eines tri- oder tetrafunktionellen Säureanhydrids, wie TMA und PMDA, 4-5%. Zwischen den Harzen aus E-828 und E-1001 besteht ein kleiner Unterschied im Gelpunkt. Der Unterschied wird dem Reaktivitätsunterschied zwischen Epoxid und Hydroxyl gegen Karboxylgruppen und dem Auftreten einer intramolekularen Kondensation zugeschrieben. Der Grad einer solchen intramolekularen in diesen Verzweigungssystemen wird als Funktion der Verzweigungsgruppenfunktionalität der Reaktionsteilnehmer, in diesem Fall Säureanhydrid oder Epoxid, betrachtet.

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