

Heat of Polymerization of Phenyl Glycidyl Ether and of an Epoxy Resin

C. H. KLUTE and W. VIEHMANN

Diamond Ordnance Fuze Laboratories, Washington, D. C.

INTRODUCTION

A search of the chemical literature has revealed no reliable value for the heat of polymerization of the epoxy resins or for their monofunctional analogue, phenyl glycidyl ether, despite the fact that this heat would be of scientific interest and of possible practical value. A variety of problems deriving principally from the low thermal conductivity of these materials when polymerized made the application of differential thermal analysis¹ to the determination of this quantity appear attractive. In the work reported below, a differential thermal analysis apparatus has been constructed which is specially suited to the measurement of heats of polymerization.

EXPERIMENTAL METHODS

Differential Thermal Analysis Apparatus

Figure 1 shows a cross section of the differential thermal analysis apparatus built for this work. The aluminum block which provides the thermal environment for the reaction rests upon a laboratory hot plate. In this block, cavities are machined to a size sufficient to allow a $\frac{1}{8}$ -in. air gap between their walls and the active and inactive sample holders or cells which are inserted therein. The cells which are $1\frac{1}{16}$ in. in diameter and $1\frac{1}{16}$ in. long are shown in Figure 2. They are cylinders of aluminum through each of which is bored an array of eight holes parallel to the cylinder axis and arranged symmetrically about it. These holes receive brass or aluminum cartridges $1\frac{1}{16}$ in. long and 0.224 in. in diameter in which the reacting mixture is placed in the performance of a determination. Actually the cartridges in only one of the two cells (i.e., the "active" cell) contain the reacting chemicals; the cartridges in the other cell contain epoxy resin already completely reacted. These cartridges are obtained in quantity from commercial sources and are very uniform in size. They press-fit tightly

into the holes, and the radial slots that pass diametrically through each of the holes distribute the stresses on the cartridges. Three desirable features of this design are (1) the heat transfer coefficient of the differential thermal analysis apparatus does not depend upon the physical state of the reactant because the thermocouples do not contact the resin; (2) by virtue of the expendable cartridges, the cells can be reused when the resin gells; and (3) the geometry of the reacting mass favors the prompt transfer of heat to the apparatus.

In an experiment using the apparatus just described, the resin and curing agent were mixed in known proportions at room temperature. The empty active cell was assembled with its cartridges in place and was then weighed on an analytical balance. The monomer-curing agent mixture was added to each of the eight cartridges by means of a syringe and the cell was then reweighed. The cell

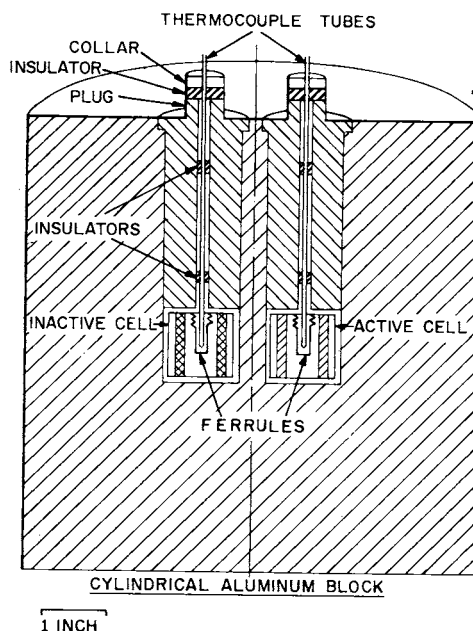


Fig. 1. Cross-sectional sketch of differential thermal analysis apparatus.

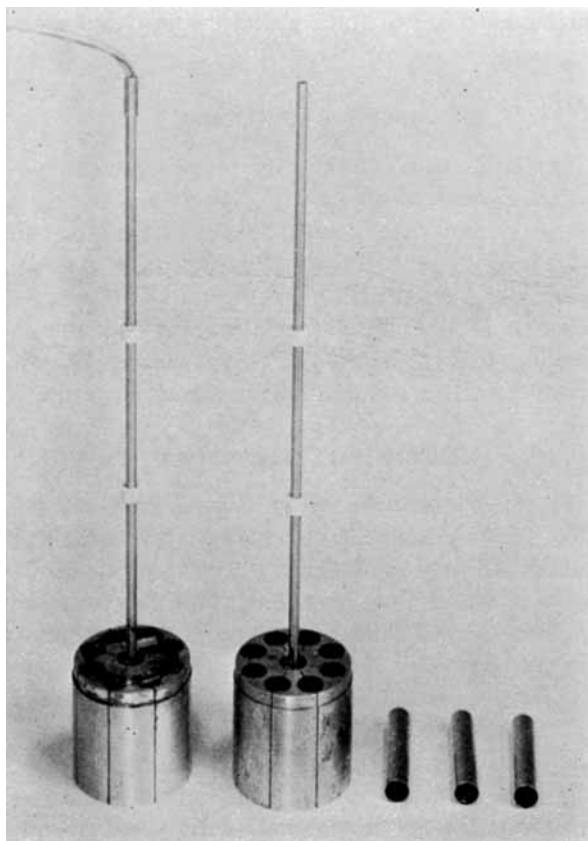


Fig 2. Cells for differentiation thermal analysis apparatus: left, calibration cell; center, active cell; right, cartridges for active cell.

was installed in its proper position within the block and the temperature of the block was raised at an arbitrary rate of about 1.5°C./min. Under ideal conditions, the monomer-curing agent mixture did not react until both cells were well above room temperature. When the temperature at which the reaction commenced was reached, a small temperature difference, θ , which rose to a maximum of about 5°C., appeared between the active and inactive cell. With very active catalysts, some reaction occurred at room temperature. In this event, a simple extrapolation of the θ vs. time curve back to the time of mixing was required.

The temperature difference between the active and inactive cells was measured by means of a single copper-Constantan differential thermocouple, with the two junctions located at the centers of the cylindrical aluminum cells. The thermocouple wires were introduced into the cells through metal conduits of hypodermic tubing 5½ in. long and 0.096 in. O.D. These conduits were coincident with the cell axes and attached to the cells by means of small threaded ferrules. The threaded ferrules

allowed the thermocouples to be detached from the cells so that the addition of the reactants to the active cell and the attendant weighings could be accomplished easily. As Figure 1 shows, the hypodermic tubing in conjunction with polytetrafluoroethylene spacers and adjustable collars also served to locate the cells precisely in the center of the cavities so that no other positioning equipment was necessary. The output emf from the differential thermocouple was fed to a high gain, breaker-type d.c. amplifier, and the amplified output from the latter was in turn connected to an attenuator and thence to one channel of a two-channel recording potentiometer. The attenuator was necessary to prevent overloading the input circuit of the recorder. The thermocouple at the center of the active cell also measured the temperature of this cell relative to an ice bath and the corresponding output was applied to the second channel of the recorder.

The total amount of heat released per mole of reaction in an experiment is given by the expression.^{2,3}

$$-\Delta H_{Meas} = (1/n) \int_0^{\infty} K(t)\theta(t)dt \quad (1)$$

where K = heat transfer coefficient for the apparatus, θ = temperature difference between cells, t = time, n = number of moles polymerized, and $-\Delta H_{Meas}$ = measured heat of polymerization.

The exact, numerical evaluation of the integral requires a knowledge of the variation of K with temperature, and hence with time. This will later be determined and shown to be slight. For most cases a suitable average value may be used. Where the curves of θ as a function of time are markedly unsymmetrical, a better approximation may be obtained by dividing the area into several segments and by using a value of K more suitable to each segment, as has been done in some cases reported below. In practice the output of the differential thermocouple was recorded before and after the reaction to locate a base line with respect to which the integration could be performed. These initial and final zero positions were only slightly separated.

In the work at hand it was convenient to determine K electrically. To this end, small resistance-wire heaters were encapsulated in place within the cartridges of an additional cell made as nearly like the active cell as possible. This cell was substituted for the active cell in calibration runs. The heater wires were led from the calibration cell to the outside of the apparatus through the hypodermic tube. To calibrate the apparatus, it was only

necessary to bring the apparatus to the desired temperature, apply a known voltage and current to the heater and record the steady-state value of the temperature difference on the chart paper. The results of this calibration are discussed in detail in a later section.

The arrangement described above worked excellently but was difficult to repair if the heater wire broke. A later version of the calibrating cell removed this difficulty in the following manner. The cell was assembled minus its heaters but with its cartridges filled with cured epoxy resin. A narrow cylindrical groove, coaxial with the cylinder was machined into the assembly passing diametrically through the cartridges over most of their length. A thin brass bobbin was prepared so that when the resistance-wire heater was wound on it, it would be snugly fitted into the cylindrical groove. If the heater wire broke, the bobbin could be removed, rewound, and reinserted in the active cell. This heater arrangement functioned perfectly and is the one shown in Figure 2 where the top of the brass bobbin appears at the top of the calibration cell. The small difference in heat capacity between the calibration cell, and the active and inactive cells, caused by the presence of the bobbin in the former, did not impair the performance of the apparatus.

At temperatures well above the polymerization temperatures, polymers generally decompose with the elimination or absorption of heat. In order to prevent the peaks in the θ -curve due to these processes from interfering with the evaluation of the heat of polymerization, it is necessary to use a slow rate of increase of reaction temperature and/or to terminate the run arbitrarily below the decomposition temperature.

Chemical Reagents

Commercial phenyl glycidyl ether was distilled under vacuum before use: b.p. = 112°C. at 5 mm. pressure; $n_D^{20} = 1.5287$. A commercial epoxy resin, primarily the diglycidyl ether of bisphenol-A, was used as supplied. The epoxy equivalent weight was determined to be 193 g. Benzylamine, pyridine, benzyl dimethyl amine, and piperidine were obtained as reagent grade chemicals and used without further purification. *m*-Phenylene diamine, 2,4,6-tris(dimethylaminomethyl) phenol, and its tri-2-ethyl hexoic acid salt, dimethyl amino propyl amine, boron trifluoride-monoethanol amine complex, and boron trifluoride-ether complex were ob-

tained as technical grade chemicals and used without purification.

Analytical Procedures

Determinations of the amount of epoxide consumed in each of the phenyl glycidyl ether-curing agent combinations were made by the method of Schechter et al.⁴ In this method the residual epoxide is reacted with a known amount of hydrochloric acid in dimethyl formamide and the unused chloride ion is determined by a potentiometric titration with a standard silver nitrate solution.

Theoretical Considerations

The elementary theory underlying the operation of the differential thermal analysis apparatus as embodied in eq. (1) has already been given in the experimental section, preceding. In this section the somewhat more fundamental problem of defining the relation between the molar heat of polymerization as measured in the equipment under discussion and its thermodynamic counterpart will be considered. In a polymerization reaction, the heat may be evolved over a very wide range of temperatures in a differential thermal analysis experiment, approaching 175°C. in some of the experiments reported subsequently. Under these circumstances it is by no means certain that the heat of polymerization measured in such experiments will correspond exactly to the thermodynamic heat of polymerization.

If a linear rate of rise of temperature prevails during the differential thermal analysis experiment, eq. (1) may be rewritten with the temperature of the apparatus, T , rather than the time as the independent variable:

$$-\Delta H_{Meas} = (1/n) \int_0^\infty K(T)\theta(T)dT \quad (2)$$

In the following derivation, n is taken to be unity for convenience. The idealized curve of θ as a function of T appears as the heavy solid line in Figure 3. It reaches its maximum value at temperature T_0 . In the neighborhood of this temperature most of the heat of the polymerization is liberated. It is therefore natural to identify T_0 with the mean reaction temperature, in analogy with the specified reaction temperature in the isothermal case. Each increment of heat that is liberated above and below T_0 must be corrected for the fact that it was not liberated at T_0 , but at some higher or lower temperature. Suppose that the T axis were divided up into equally small increments

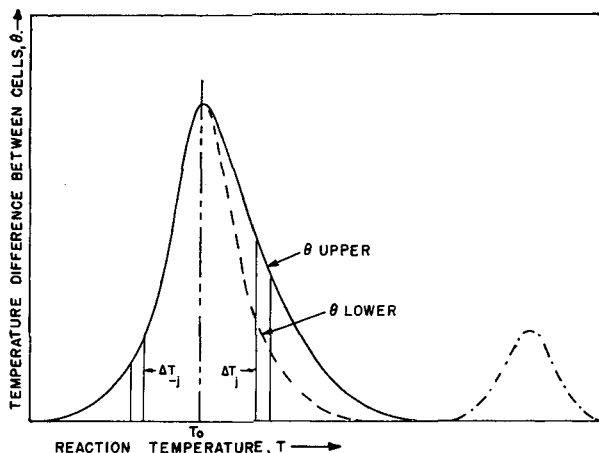


Fig. 3. Idealized curve of temperature difference between cells, θ , as a function of active cell temperature, T , for a polymerization reaction in a differential thermal analysis apparatus. Dashed curve is the reflection of the initial portion of the θ -curve about T_0 . Dotted-dashed curve in the right of the figure represents a secondary peak.

of length ΔT . Let the increments be numbered in the positive and negative direction starting at the point T_0 . Let the increment of the total heat released in the j th temperature interval, ΔT_j , be $(-\Delta h_j)$. If this same increment of heat had been released in the interval about T_0 , it would have had a different value, $(-\Delta h'_j)$. These two values are related by the Kirchhoff formula:⁵

$$(-\Delta h'_j) = (-\Delta h_j) + n_j \Delta C_p (T_j - T_0) \quad (3)$$

where T_j = temperature of the j th interval, n_j = number of moles of monomer polymerized in the j th interval, and ΔC_p = heat capacity of one mole of monomeric units in the polymer minus the molar heat capacity of the monomer, both at constant pressure in the reacting mixture.

The thermodynamic heat of reaction is given by:

$$-\Delta H_{Thermo} = \lim_{\Delta T_j \rightarrow 0} \sum_{j=-\infty}^{j=+\infty} (-\Delta h'_j) \quad (4)$$

By virtue of eq. (3), this can also be written:

$$-\Delta H_{Thermo} = \lim_{\Delta T_j \rightarrow 0} \sum_{j=-\infty}^{j=+\infty} (-\Delta h_j) + \lim_{\Delta T_j \rightarrow 0} \sum_{j=-\infty}^{j=+\infty} n_j \Delta C_p (T_j - T_0) \quad (5)$$

The first term on the right-hand side of eq. (5) is, of course, $-\Delta H_{Meas}$ and the second term is the correction term which must be applied to it to obtain the

thermodynamic heat of reaction. To evaluate the latter term one requires the relations.

$$n_j = (\Delta h'_j) / \Delta H_{Thermo} \cong (\Delta h_j) / \Delta H_{Meas} \quad (6)$$

This approximation is predicted upon the assumption that Δh_j and ΔH_{Meas} are, respectively, similar in magnitude to $\Delta h'_j$ and ΔH_{Thermo} . This will be shown to be the case shortly. Thus the expression obtained by eliminating n_j from eq. (5) is:

$$-\Delta H_{Thermo} = -\Delta H_{Meas} + (1/\Delta H_{Meas}) \lim_{\Delta T_j \rightarrow 0} \sum_{j=-\infty}^{j=+\infty} \Delta h_j \Delta C_p (T_j - T_0) \quad (7)$$

During the early part of the experiment, the small amount of polymer that is formed is swollen by the monomer. During the later stages of the run the temperature of the apparatus is well above the glass transition temperatures of most polymers. The reciprocity between diminishing swelling by monomer and rising reaction temperature characteristic of a differential thermal analysis experiment will in general keep the polymer above its glass transition temperature over the entire course of the run. For this reason the value of ΔC_p required in eq. (7) is that corresponding approximately to liquid polymer and liquid monomer, and this will be denoted $(\Delta C_p)_L$. Since $(\Delta C_p)_L$ would not be very sensitive to temperature, it may be factored from inside the summation sign. The remaining part of the sum may be handled in the following manner. For every index, $+j$, there exists an index, $-j$, reflected on the T axis about the point T_0 . If that part of the θ curve below T_0 were reflected about the line $T = T_0$ the indices j and $-(-j)$ would merge. This has been done in Figure 3 and the lower lying, dashed-line curve extending from the maximum in θ to higher values of T represents this reflection. The heat increments below T_0 may be similarly reflected and the differences between them and the heat increments above T_0 may be appropriately summed from $j = 1$ to $j = +\infty$. After this reflection, eq. (7) becomes:

$$-\Delta H_{Thermo} = -\Delta H_{Meas} + -[(\Delta C_p)_L / \Delta H_{Meas}] \lim_{\Delta T_j \rightarrow 0} \sum_{j=1}^{j=\infty} [(\Delta h_j)_{upper} - (\Delta h_j)_{lower}] (T_j - T_0) \quad (8)$$

where the subscripts upper and lower refer to heat increments above and below T_0 , respectively, and hence to the upper and lower lying branches of the θ - T curves above T_0 in Figure 3.

It remains now to take the limit of the sum in eq. (8). In the general case, the terms for the heat increments $(\Delta h_j)_{upper}$ and $(\Delta h_j)_{lower}$ are equal respectively to $[-K(T_j)_{upper}\theta(T_j)_{upper} \Delta T_j]$ and $[-K(T_j)_{lower}\theta(T_j)_{lower} \Delta T_j]$. Considerable simplification results in the case of practical interest in which the $K(T_j)$ may be replaced with the mean value $K(T_0)$. In this case $K(T_0)$ can be factored from the limit of the sum and from the denominator of the expression to obtain the final form of the equation:

$$-\Delta H_{Thermo} = -\Delta H_{Meas} + (\Delta C_p)_L \Gamma \quad (9)$$

where:

$$\Gamma = \frac{\int_{T_0}^{\infty} (\theta_{upper} - \theta_{lower}) (T - T_0) dT}{\int_0^{\infty} \theta dT}$$

The factor Γ is a fraction having the dimensions of degrees. Its numerator is the moment, about T_0 , of the excess of area enclosed by the θ -curve over that of a curve symmetrical with respect to T_0 . The denominator is the total area under the θ -curve. In the general case the factor Γ may be positive or negative depending on whether the θ -curve is skewed towards lower or higher temperatures. If the θ -curve is symmetrical, then $(\theta_{upper} - \theta_{lower})$ is zero and the correction term vanishes. In an extreme, opposite case, similar to the dotted dashed curve in Figure 3, a secondary peak could exist containing, for example, 33% of the total area concentrated at a point on the temperature axis 75°C. above T_0 . In this case, the factor Γ would only amount to about 25°C. Taking polystyrene as a typical example, $(\Delta C_p)_L$ is very nearly -4.0 cal./mole/°C.⁶ Thus the correction term $(\Delta C_p)_L \Gamma$ would be equal to -0.10 kcal./mole, if such a secondary peak were to exist which is actually not the case in the polymerization of styrene. Secondary peaks do, however, occur in some epoxide polymerizations. It will be shown in the following section that the heats of polymerization in this work ranged between 22 and 26 kcal./mole. Compared with this value $(\Delta C_p)_L \Gamma$ is small in the hypothetical case computed above. Not only would the hypothetical error be statistically insignificant compared with the experimental uncertainty of the differential thermal analysis measurements which will presently be shown to be ± 0.75 kcal./mole, but it is also well within the uncertainty quoted for the best isothermal heats in the literature, namely ± 0.16 kcal./mole.⁷ The calculation just given

is generally illustrative of the relative insignificance of the error under discussion.

It is apparent from the foregoing discussion that little difference will exist between Δh_j and $\Delta h'_j$ of eq. (3) because of the smallness of $(\Delta C_p)_L$, hence the approximation of eq. (6) is satisfactory. It should be mentioned that asymmetry of the primary peak in the θ -curve at temperatures near T_0 is far less damaging to the accuracy of the experimental heat measurement than one would suppose, because $(T - T_0)$ is small in this region.

RESULTS AND DISCUSSION

Calibration Experiments for Determining the Heat Transfer Coefficient of the Apparatus

The determination of the heat transfer coefficients were made in the manner described in the experimental section. The values of the heater current and voltage were measured with precision instruments so that bias from this source was less than the experimental uncertainty of the final results. It was also established that amplifier zero drift and gain instability did not make important contributions to this uncertainty.

At twelve temperatures distributed over the range from 22 to 150°C., determinations of the steady-state temperature difference were made corresponding to a known energy input. From these data, and the chart paper speed, the value of the

TABLE I

Evaluation of the Regression of the Heat Transfer Coefficient for the Differential Thermal Analysis Apparatus (\dot{K}) upon Reaction Temperature (T)

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- A. Number of determinations of $K = 12$.
 - B. Temperature range studied: 22 to 150°C.
 - C. Regression equation obtained: $K = 17.28 + 0.0243(T-76)$ where K has the units: calories per square inch of integrated area on recorder chart paper and T is in degrees centigrade.
 - D. Variance about the regression = 0.0205.
 - E. Variance of the regression coefficient = 0.827×10^{-6} .
 - F. Standard error of the regression coefficient = 0.909×10^{-3} .
 - G. Confidence limits for the regression coefficient = ± 0.02 (at 95% level).
 - H. Standard error of the regression estimates:
 - (1) at the point $K = 16.0$, $T = 22^\circ\text{C}$., S.E.(K) = 0.064.
 - (2) at the point $K = 17.3$, $T = 76^\circ\text{C}$., S.E.(K) = 0.041.
 - (3) at the point $K = 19.1$, $T = 150^\circ\text{C}$., S.E.(K) = 0.079.
 - I. Confidence limits for the regression estimates at the 95% level:
 - (1) at 22°C., $K = 16.0 \pm 0.14$.
 - (2) at 76°C., $K = 17.3 \pm 0.09$.
 - (3) at 150°C., $K = 19.1 \pm 0.18$.
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TABLE II

Measured (average) Values of the Heat of Polymerization of Phenyl Glycidyl Ether and of Epoxy Resin (193 g./epoxy equivalent)

Curing agent	Monomer	Moles curing agent per epoxy equivalent	Heat of polymerization — ΔH , kcal./mole		No. of determinations	Mean reaction temp., T_0 , °C.	Type of curve (see Figs. 4, 5, and 6)
			Mean value	Confidence limits, 95% level			
a. Primary Amine Curing Agents							
Benzylamine	Phenyl glycidyl ether	0.48	27.62	± 0.75	3	64	1
	Epoxy resin	0.53	26.83	± 0.75	3	84	1
<i>m</i> -Phenylene diamine	Phenyl glycidyl ether	0.52	26.26	± 0.75	3	77	2
	Epoxy resin	0.30	25.42	± 0.75	3	105	2
b. Tertiary Amine Curing Agents							
Pyridine	Phenyl glycidyl ether	0.19	26.17	± 0.75	3	101	2
	Epoxy resin	0.37	26.98	± 0.75	3	119	2
Benzyl dimethyl amine	Phenyl glycidyl ether	0.13	22.14	± 0.65	4	87	6
	Epoxy resin	0.19	22.44	± 0.75	3	98	6
2,4,6-Tris(dimethyl aminomethyl)phenol	Phenyl glycidyl ether	0.09	21.90	± 0.75	3	89	8
	Epoxy resin	0.10	22.31	± 0.75	3	81	8
2,4,6-Tris(dimethyl amino methyl)phenol tri-2-ethyl hexoate	Phenyl glycidyl ether	0.022	20.47	± 0.75	3	105	7
	Epoxy resin	0.028	19.88	± 0.75	3	103	7
c. Boron Trifluoride							
BF ₃ -diethyl ether complex	Phenyl glycidyl ether	0.34	22.15	± 0.75	3	58 and (141) ^a	4
d. Mixed-type Amine Curing Agents							
Dimethylaminopropylamine	Phenyl glycidyl ether	0.15	22.66	± 0.75	3	81	8
	Epoxy resin	0.19	22.78	± 0.75	3	74	8
Piperidine	Phenyl glycidyl ether	0.21	22.29	± 0.75	4	98	3
	Epoxy resin	0.29	21.43	± 0.92	2	106	3
BF ₃ -monoethanol amine complex	Phenyl glycidyl ether	0.15	25.39	± 0.92	2	(114) ^a and 167	5
	Epoxy resin	0.17	24.98	± 0.92	2	(110) ^a and 155	5

^a Secondary peak.

heat transfer coefficient, K , in cal./in.² of chart paper could be determined. The regression of these values of K upon the temperature of the active cell, T , was obtained by means of the usual least squares procedure. The results of this statistical treatment are summarized in Table I. It is apparent from the confidence limits of section I, Table I, that K is determined to better than 1% and that it varies only slightly with temperature. The smallness of the temperature variation makes unimportant the fact that the reaction temperature was determined only to the nearest degree.

Heats of Polymerization of Phenyl Glycidyl Ether and of an Epoxy Resin

In Table II, the average values of the heats of polymerization of phenyl glycidyl ether and of a

commercial epoxy resin cured with ten and nine different curing agents, respectively, are presented. The curing agents selected were predominantly amines including some used to cure the epoxy resins in industrial applications. Also included were two boron trifluoride complexes, one of which (i.e., BF₃-ethanol amine complex) finds industrial applications and the other of which is of scientific interest. Phenyl glycidyl ether should release the same heat per mole as does one equivalent of epoxide in the epoxy resin, but unlike the epoxy resin, it would form a polymer which is soluble in organic solvents. Thus it is possible to determine the completeness of the phenyl glycidyl ether polymerization by conventional chemical methods, and by a comparison of heat values determine the completeness of the epoxy resin polymerization as well.

TABLE III

Statistical Analysis of Measured Heats of Polymerization of Phenyl Glycidyl Ether and of Epoxy Resin

A. Variance within groups of determinations using the same curing agent when phenyl glycidyl ether was polymerized = 0.489

Degrees of freedom = 20 Standard Deviations = 0.699

B. Variance within groups of determinations using the same curing agent when epoxy resin was polymerized = 0.310

Degrees of freedom = 16 Standard Deviation = 0.557

C. Ratio of Standard Deviations = 1.26. Confidence limits for the ratio at the 95% level for 20 and 16 degrees of freedom respectively are: upper limit = 2.02, lower limit = 0.76

D. Variance overall. Because the lower limit is less than unity, it cannot be stated that the variance for either monomer differs from the other. Accordingly, the overall variance = 0.410. Corresponding standard deviation = 0.64 kcal./mole

Degrees of freedom = 36.

E. Confidence limits for replicate measurements:

Number of replicates	Confidence limits at 95% level
1	± 1.30 kcal./mole
2	± 0.92 kcal./mole
3	± 0.75 kcal./mole
4	± 0.65 kcal./mole
5	± 0.58 kcal./mole
6	± 0.53 kcal./mole
7	± 0.49 kcal./mole

F. Confidence limits for differences between means:

Number of replicates in first mean	Number of replicates in second mean	Confidence limits at the 95% level (in kcal./mole)
2	2	1.30
2	3	1.19
3	3	1.06
3	4	0.99
6	6	0.75
6	7	0.72

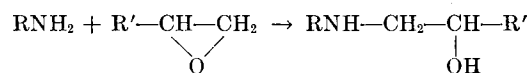
Pure phenyl glycidyl ether polymerizes very slowly and it is necessary to add a quantity of water or alcohol to it to secure rapid reaction. Accordingly, 20 parts by weight of ethylene glycol were added to 100 parts of phenyl glycidyl ether in these experiments. When this was done, chemical analysis showed that in every case the epoxide reacted completely under the conditions of continually rising temperature (but never rising above 200°C.) which prevailed in the differential thermal analysis apparatus.

In all, 55 experiments are summarized in Table II. The statistical analysis of these data is given in Table III. Certain differences between the

various groups of measurements are known *a priori* to be controlled by chemical effects. Differences within groups of determinations made with the same curing agent, however, should be random and should provide a valid estimate of the variance due to experimental error. When phenyl glycidyl ether is the monomer there is no reason to suppose that the error variance should be significantly different from that observed when the epoxy resin is used. This supposition is confirmed in sections A, B, and C of Table III and leads to a standard deviation of 0.64 kcal./mole for the individual experiments based on 36 degrees of freedom. This corresponds to a standard error of 0.37 kcal./mole for the mean of three determinations, the number most frequently used in work of this sort. Confidence limits at the 95% level are also given for the average values of the heats as well as for the differences between the various averages.

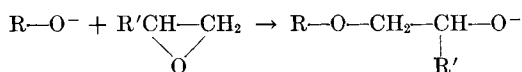
In Table II consider first the differences between the average heat values for each curing agent as determined for the phenyl glycidyl ether and for the epoxy resin. These differences are random and none of them are statistically significant. This confirms the earlier supposition that the epoxy resin reacts as completely as the phenyl glycidyl ether does and that it liberates the same amount of heat in so doing. This last statement should be qualified somewhat because the comparatively large amount of alcohol present in the phenyl glycidyl ether runs (approximately 0.98 equivalents of hydroxyl groups per equivalent of epoxide groups) causes a small amount of a side reaction to occur when tertiary amines are used to catalyze the reaction. However, it will shortly appear that, fortunately, this side reaction will not cause the values of the heats in Table II to differ significantly from their true values.

Consider next the primary amine type curing agents which form copolymers through the reaction:



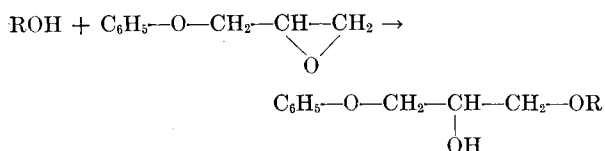
In this case, benzyl amine liberates on the average 27.23 kcal./mole for the epoxides used whereas *m*-phenylene diamine releases only 25.84 kcal./mole. The difference of 1.39 kcal./mole is statistically significant and reflects the chemical differences between the two amines. However, the difference is not very large and, apparently, reactions of this type can be expected to liberate about 26 kcal./mole.

The tertiary amine curing agents are true catalysts for the homopolymerization of epoxy compounds. Accordingly, with these curing agents the heat released should be predominantly due to the heat of the propagation reaction whereby a growing polymer chain adds another link, viz:



The heat of this reaction comes primarily from the release of the strain energy of the epoxide ring. For ethylene oxide this heat has been determined to be 19.4 kcal./mole from heats of combustion of monomer and polymer by Moureu and Dode.⁸ An additional contribution to this heat can be expected from the initiation and termination steps of the polymerization, in view of the fact that the molecular weight of the linear polymer is low⁹ and its crosslinked counterpart can be expected to have a corresponding number of chain ends. Accordingly, the values for the heats of polymerization obtained with benzyl dimethyl amine and with 2,4,6-tris-(dimethyl aminomethyl) phenol appear reasonable. The 2-ethyl-hexoic acid salt of the latter compound gives a heat which is significantly lower statistically. This is somewhat to be expected because some energy is required to separate the acid and amine components of this catalyst in order to promote the reaction. Pyridine gives an anomalously high heat and the reason for this is not presently apparent. Pyridine has been classed as a tertiary amine for the purposes of this paper because it has no active hydrogen attached to the nitrogen. It is, of course, recognized that in other respects pyridine differs in its general behavior from tertiary amines.

Chemical experiments which were performed after these thermal measurements were made indicated that when phenyl glycidyl ether was polymerized by the action of tertiary amines in an equimolar mixture of primary hydroxyl groups, almost exactly 20% of the ether forms a mono addition compound rather than the polymer being studied. This agrees with the findings of another laboratory which showed a similar side reaction when a secondary alcohol was present in an equimolar mixture with phenyl glycidyl ether.¹⁰ The addition reaction is the following:



In analogy with the corresponding reaction with ethylene oxide,⁸ this reaction should liberate only slightly more heat than the 19.4 kcal per mole quoted above. If 80% of the phenyl glycidyl ether polymerized with the evolution of approximately 22.4 kcal./mole, as apparently is the case, and if the remaining 20% formed the adduct, the reduction of the heat of polymerization relative to 100% polymerization would be less than 0.60 kcal./mole. This difference would be statistically insignificant in the present work. This point was examined in experiments in which phenyl glycidyl ether was polymerized with benzyl dimethyl amine in the presence of lesser amounts of alcohol, viz; 5 parts per hundred and 0 parts per hundred of ethylene glycol. In the latter case the reaction was much slower than when glycol was present and presumably was cocatalyzed by adventitious traces of moisture. The respective values of the heat of polymerization obtained were 21.85 ± 0.75 and 22.55 ± 0.75 kcal./mole. These heats are not significantly different statistically (i.e., at the 95% confidence limits) from that determined at 20 parts per hundred of ethylene glycol in Table II.

This side reaction would be potentially more serious where the reaction of epoxide groups with primary amines is concerned because the latter reaction evolves more heat than does the homopolymerization. However, data from another laboratory¹⁰ indicate that the side reaction does not occur in the presence of primary amines and this is confirmed by the good agreement between the heats of polymerization obtained with phenyl glycidyl ether in the presence of alcohol and with the epoxy resin when primary amines are used as comonomers.

The mixed-type amine curing agents are capable of reacting partly as comonomers but primarily as tertiary amine catalysts. Accordingly they can sometimes liberate heats intermediate between catalytic and copolymer types. The boron trifluoride-ether complex functions as a true catalyst and accordingly its heat release resembles that of a well behaved tertiary amine. The monoethanol amine complex also acts as a catalyst but a strong contribution to the heat of reaction is to be expected from the copolymerization of the amine portion with the epoxide. Thus this compound nearly equals the primary amine catalysts in its heat release.

One additional point should be discussed, namely the shape of θ vs. time curves for each curing agent-monomer system. In Figures 4, 5, and 6.

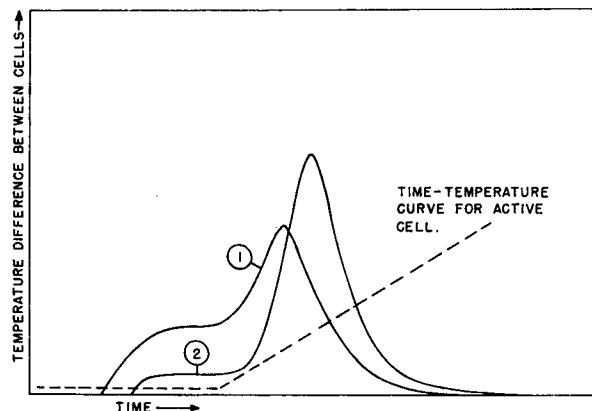


Fig. 4. Types of temperature difference-time curves for epoxy curing reactions in the differential thermal apparatus. The temperature difference between cells is amplified relative to the temperature excursion of the active cell.

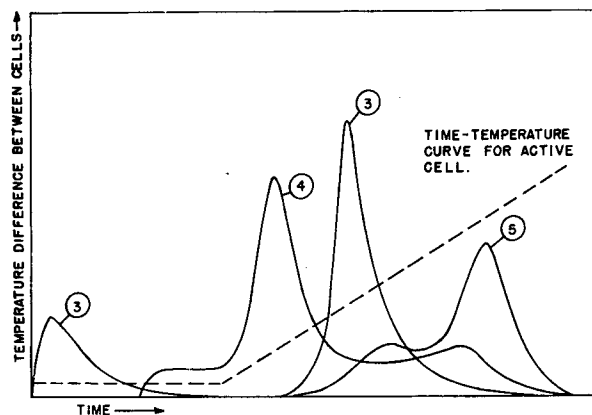


Fig. 5. Types of temperature difference-time curves for epoxy curing reactions in the differential thermal analysis apparatus.

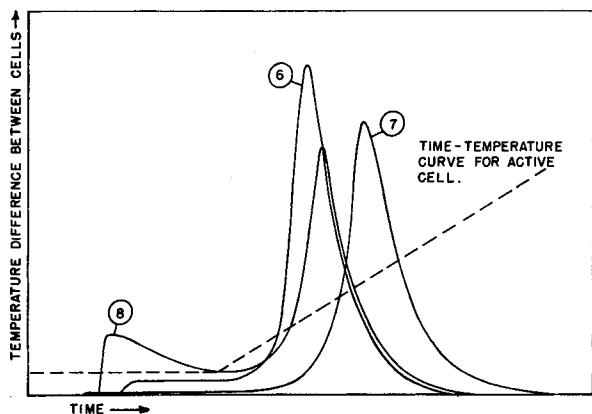


Fig. 6. Types of temperature difference-time curves for epoxy curing reactions in the differential thermal analysis apparatus.

the shapes of these curves for the various systems have been reproduced. Although the shapes of the curves are accurately reproduced, no attempt has been made to preserve the scales of the X (i.e., time) or the Y (i.e., θ) axes because the time scale varies so widely from one curing agent to another. The numbers from the curves identify them with the curing agents of Table II. The temperature at which the peak value of θ occurs will serve as a rough indication of the promptness of the reaction, the faster curing agents reaching the peak at a lower active cell temperature than the slower curing agents. These temperatures have been tabulated in Table II and they indicate significant differences in the rate of heat release between the various curing agents and apparently between the two monomers in some cases. In particular these curves show when the heat release occurs in two successive steps, as exemplified by curve types 4, and 5, or when appreciable reaction occurs at room temperature as in types 1, 3, and 8 (i.e., when heat is released before the active cell rises above room temperature).

CONCLUSIONS

From the results of the preceding section it can be concluded that the homopolymerization of the epoxy resin generally proceeded with the evolution of about 22 kcal./mole of epoxide reacted, and that a like amount of heat was liberated in the homopolymerization of phenyl glycidyl ether. When copolymers of either of these monomers were made by reacting them respectively with amines containing several active hydrogen atoms, approximately 26 kcal./mole of epoxide were liberated. It can be concluded also that the differential thermal analysis technique could be usefully applied to the study of the behavior of curing agents for epoxy resins and other casting resins in addition to those investigated here.

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Synopsis

A differential thermal analysis apparatus was constructed for the measurement of heats of polymerization. It featured an active cell in which the reacting mixture was contained in expendable thin-walled, narrow, cylindrical brass, or aluminum cartridges. The cartridges were tightly pressed into holes drilled into the body of the active cell and they, along with the solid reaction product, could be ejected therefrom at the completion of the reaction. A calibration cell was provided with small electric heaters which allowed known amounts of heat to be supplied to the apparatus in calibration runs. With this apparatus the mean value for three determinations of the heat of polymerization of epoxy resins, ca. 22 to 26 kcal./mole, could be measured to within a standard error of 0.37 kcal./mole (i.e., confidence limits of ± 0.75 kcal./mole at the 95% confidence level). The heats of polymerization of phenyl glycidyl ether and of an epoxy resin were measured with ten and nine different curing agents, respectively. Primary amine curing agents released about 26 kcal./mole of epoxide reacted, tertiary amines, and boron trifluoride-ether complex each released about 22 kcal./mole. Mixed-type curing agents, which could react in part as tertiary amines, or boron trifluoride, and in part as primary amines could liberate intermediate amounts of heat.

Résumé

Un appareil d'analyse thermique différentielle a été construit en vue de mesurer les chaleurs de polymérisation. La cellule de réaction (dans laquelle le mélange était introduit) contenait des cartouches cylindriques à parois minces et étroites en laiton d'aluminium. Ces cartouches étaient pressées dans des trous perforés dans le corps de la cellule même, et pouvaient être éjectés au dehors, en même

temps que le produit de réaction solide lorsque la réaction est achevée. Une cellule de calibrage était pourvue d'éléments chauffants électriques, permettant un apport d'une quantité connue de chaleur au cours du calibrage. Avec cet appareil la valeur moyenne de trois déterminations de la chaleur de polymérisation de résines époxyées, d'environ 22 à 26 Kcal par mole, pouvait être mesurée avec une erreur inférieure à 0,37 Kcal par mole (càd. $\pm 0,75$ Kcal par mole avec 95% de sécurité). Les chaleurs de polymérisation de l'éther phénylglycidique et d'une résine époxydique ont été mesurées avec dix et neuf agents de durcissement respectivement. L'action des amines primaires libéraient environ 26 Kcal par mole de groupe époxydé qui avait réagi; dans le cas des amines tertiaires et le complexe étheré du fluorure de bore on trouvait environ 22 Kcal par mole. Des mélanges de réactifs, qui pouvaient réagir en partie comme des amines tertiaires ou le trifluorure de bore, et en partie comme des amines primaires, libéraient des chaleurs de polymérisation intermédiaires.

Zusammenfassung

Ein Apparat zur Messung von Polymerisationswärmen durch differentielle, thermische Analyse wurde konstruiert. Er ist charakterisiert durch eine Zelle, in welcher die reagierende Mischung in expandierbaren, dünnwandigen, engen, zylindrischen Messing- oder Aluminiumpatronen enthalten ist. Die Patronen wurden dicht in Bohrungen im Zellkörper eingepresst und konnten daraus beim Reaktionsende zusammen mit dem festen Reaktionsprodukt ausgeworfen werden. Eine Eichzelle mit kleinen elektrischen Heizkörpern war vorhanden, mit welcher dem Apparat kleine, bekannte Wärmemengen zur Eichung zugeführt werden konnten. Mit diesem Apparat konnte der Mittelwert von drei Polymerisationswärmebestimmungen an Epoxyharzen, ca 22 bis 26 kcal pro Mol, mit einem Standardfehler von 0,37 kcal pro Mol (d.h. eine Sicherheitsgrenze von $\pm 0,75$ kcal pro Mol bei einer Sicherheitshöhe von 95%) gemessen werden. Die Polymerisationswärmen von Phénylglycidyläther und einem Epoxyharz wurden mit zehn bzw. neun verschiedenen Härtern gemessen. Primäre Amine als Härter setzten etwa 26 kcal pro Mol reagiertes Epoxyd frei, tertiäre Amine und der Bortrifluorid-Ätherkomplex jedes etwa 22 kcal pro Mol. Härter von gemischtem Typ, die zum Teil als tertiäre Amine oder Bortrifluorid, zum Teil als primäre Amine reagieren konnten, lieferten dazwischen liegende Wärmemengen.

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