Curing of Epoxy Resins with Diphenyliodonium Salts as Thermal Initiators

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Synopsis

The curing reaction of a thermally curable epoxy system containing diphenyliodonium hexafluoroarsenate was investigated by using the dynamic and isothermal techniques of differential scanning calorimetry (DSC). It was shown that the curing involved two consecutive reactions. The heat of the total curing reaction and overall kinetic parameters for the two reactions were obtained.

INTRODUCTION

Diaryliodonium salts with complex metal halide anions (such as PF_6^-, AsF_6^-, SbF_6^-, BF_4^-, etc.) have been reported as very effective photoinitiators of cationic polymerization.[1-3] One of the advantages of these salts is their apparent thermal stability allowing for long term storage under normal conditions in the absence of UV radiation. Thermally curable epoxy systems with a long pot life are attractive for more traditional uses. Recently, some investigations into the ability to break the latency of these initiators through the use of heat and using some single-function epoxides as monomers were reported,[4,5] but the detailed investigations of thermally curing commercial epoxy resin systems with diaryliodonium salts have not been carried out.

The mechanical and electrical properties of cured epoxy resins are strongly dependent upon the degree of cure. The curing reaction is a highly exothermic process, and the control of the rate of heat generation during the cure is often a key point to optimize properties. Calorimetric techniques have become one of the most effective methods to obtain complete quantitative information on the curing process of thermosets.[6,7] An important reason is that DSC may be used to determine the rate of polymerization directly, continuously, and even in a gel or solid state.

The primary objective of this work was to investigate the curing behavior of a bisphenol-A-type epoxy resin (Epon 828) with a diphenyliodonium salt by applying the principles of DSC and to compare the results obtained from two DSC techniques: method B of dynamic experiments and isothermal method 1 described by Prime.[8] Dynamic method B, which uses the dependence of the peak reaction temperature with heating rate, is quick and accurate, and is recommended by Prime especially for analyzing the curing kinetics of systems with multiple exotherms and in those cases where isothermal measurements are inaccurate or unreliable. Isothermal method 1 exploits the ability of DSC to monitor, simultaneously, the rate of reaction

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and the extent of reaction over the entire course of the reaction, allowing direct use of the derivative form of the rate equations.

EXPERIMENTAL

Materials

Epoxy Resin. A general-purpose DGEBA type epoxy resin Epon 828 (Shell) was used in this investigation.

Curing Agent. Several diphenyliodonium and triphenylsulfonium salts shown in Table I were synthesized using the procedures of Crivello and Lam,[9,10] but for the study of kinetics with the epoxy system only diphenyliodonium hexafluoroarsenate was used.

Catalyst. Cupric benzoate (K & K) was used as a catalyst in some cases.

Measurements of Epoxy Values

The epoxy value was measured by the hydrogen chloride–acetone method. The basic procedure is as follows: Place weighed samples (about 0.3 mgs) into flasks. Pipette 20 mL of hydrogen chloride–acetone solution into every one of the flasks and an empty flask (as a blank). Swirl the solution until the samples have been dissolved. After keeping at room temperature for 1 h all the solutions are titrated with a $0.1N$ aqueous NaOH solution, using methanolic methyl red as an indicator.

Calorimetric Measurements

The calorimetic measurements were carried out with a DuPont Thermal Analyzer Model 1090 equipped with a DSC cell. To make the data as accurate as possible, the systems were calibrated by measuring the heat of fusion of indium before every DSC run of both the temperature scanning and the isothermal techniques, using the same heating rate for the former and 0.5°C/min for the latter.

The heat of the curing reaction was measured by carrying the crosslinking reaction to completion at heating rates of 2, 5, 10, and 20°C/min.

The samples were prepared previously by mixing thoroughly Epon 828 with diphenyliodonium hexafluoroarsenate (4.88 phr, parts per hundred parts of resin by weight, being equal to the equivalent ratio of epoxy group to the iodonium salt of 1:0.02) to get a clear viscous liquid. (In catalyzed cases the amount of cupric benzoate was 0.25% of the total weight of epoxy resin and curing agent). The obtained liquids without catalysts were stored at room temperature and could be used for DSC runs for several months, because measurements of the epoxy value indicated that no curing reaction occurred during storage.

The required amount of samples were weighed into a hermetic pan and sealed just before each run. The weight of the pan with the sample was measured before and after the run to make sure that there was no weight loss during the DSC measurement.

TABLE I
Some Iodonium and Sulfonium Salts

	mp (°C)	Lit mp (°C)	T_d[a](°C), 5% loss in N_2		Elemental analysis				
					C	H	N	I or S	P
Ph$_2$I$^+$AsF$_6^-$	124.5-127	123-125[9]	258	Calcd:	30.67	2.13		27.01	
				Fnd:	30.76	2.07		27.14	
Ph$_2$I$^+$PF$_6^-$	139-142	138-140[9]	242	Calcd:	33.83	2.35		29.79	7.27
				Fnd:	33.65	2.29		30.09	6.98
Ph$_2$I$^+$BF$_4^-$	137-139	136[11]	185	Calcd:	39.18	2.72			
				Fnd:	39.49	2.70			
(NO$_2$PH)$_2$I$^+$PF$_6^-$	209-217[b]	—	256	Calcd:	27.93	1.55	5.43	24.59	6.00
				Fnd:	25.75	1.36	4.86	23.71	4.81
Ph$_3$S$^+$PF$_6^-$	203-204	—	370	Calcd:	52.96	3.67		7.85	7.59
				Fnd:	52.85	3.53		8.05	7.54

[a] The temperatures of decomposition were obtained by TGA analysis using a DuPont Thermal Analyzer Model 1090 equipped with 951 Thermogravimetric Analyzer, at a heating rate of 10°C/min.

[b] According to the IR spectrum the product is a mixture of meta- and para- isomers.

RESULTS AND DISCUSSION

Changes of Epoxy Value

Changes of EPV with time during storage at room temperature are shown in Figures 1 and 2, respectively, for the catalyzed and uncatalyzed systems. An equivalent ratio of epoxy group to curing agent of 1:0.02 was used. An apparent viscosity increase was simultaneously observed up to the vitrification of the samples as the EPV decreased for all the catalyzed systems. On the other hand, the fluidity did not change for the systems in which the EPV did not change.

Figure 2 indicates that systems A, B, and C have very good stability during storage under normal conditions, showing their value for practical applications. It was noted that the EPV of system D (containing dinitro-diphenyliodonium hexafluorophosphate) began to decrease gradually after 20 days and the material vitrified after 50 days' storage. This is because the electron withdrawing nitro groups on the benzene rings facilitated the reaction of the epoxy resin with the iodonium salt under ambient conditions.

Heats of Curing Reaction

The heat of polymerization of DGEBA with various curing agents varies from 20 to 27 kcal/mol.[12]

The heats of cure of Epon 828–Ph_2IAsF_6 system at different heating rates without or with catalyst are shown in Tables II and III, respectively. The same average values (25.0 and 25.6 kcal/mol) were observed for the uncatalyzed and catalyzed systems.

Also, almost the same amount of heat (24.33, 24.57, and 23.84 kcal/mol) evolved during the isothermal cure at 180, 190, and 200°C.
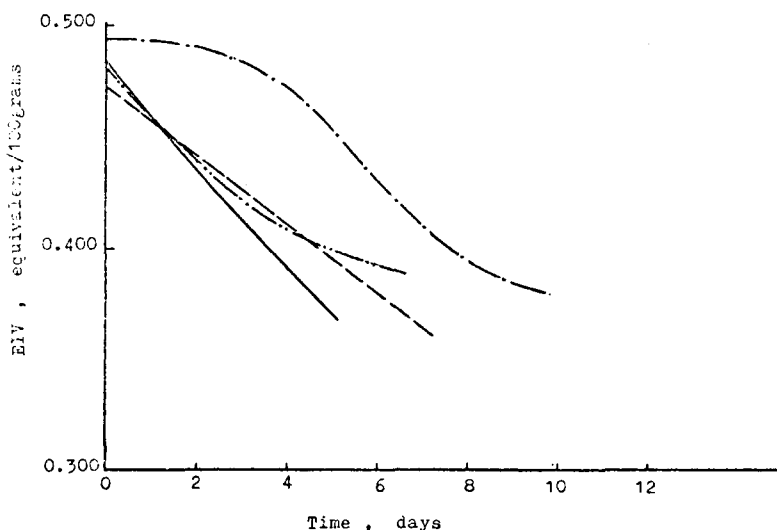

Fig. 1.   Changes of EPV of catalyzed epoxy systems: (—) Epon 828+Ph_2IAsF_6 (4.88 phr); (— · —) Epon 828+Ph_2IPF_6 (4.42 phr); (— —) Epon 828+Ph_2IBF_4 (3.82 phr); (— ·· —) Epon 828+$(NO_2Ph)_2IPF_6$ (5.03 phr).
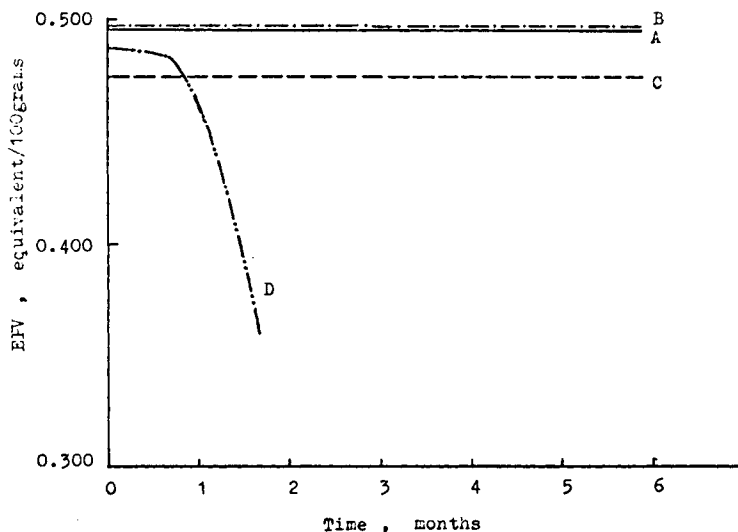
Fig. 2. Changes of EPV of uncatalyzed epoxy systems: (A) Epon 828+Ph$_2$IA$_s$F$_6$ (4.88 phr); (B) Epon 828+Ph$_2$IPF$_6$ (4.42 phr); (C) Epon 828+Ph$_2$IBF$_4$ (3.82 phr); (D) Epon 828+(NO$_2$Ph)$_2$IPF$_6$ (5.03 phr).

Reaction Mechanism

Figures 3–6 show the dynamic DSC traces, at different heating rates, of the cures of the uncatalyzed system. It is significant that there are two peaks on every curve. The cures appear to be due to two distinct curing reactions. Crivello et al.[4,5] and Pappas et al.[13] have investigated the reaction mechanism for some photoinitiating systems and also thermoinitiating systems with organocopper catalysts. Their results indicate that there are several possible modes to induce cationic polymerization of epoxides by using diaryl–iodonium salts. In the present case, it is suggested that the two different curing reactions proceed as follows:

The first step: Ph–I$^+$–Ph AsF$_6^-$ + R–OH $\overset{\Delta}{\rightarrow}$ Ph–OR + Ph–I + H$^+$AsF$_6^-$ (where ROH represents hydroxyl groups in the epoxy resin).

Formation of H$^+$AsF$_6^-$ in the first step starts the well known acid catalyzed ring opening polymerization of epoxides.[14]

The second step: Ph–I$^+$–Ph AsF$_6^-$ + M $\overset{\Delta}{\rightarrow}$ Ph–M$^+$ AsF$_6^-$ + Ph–I (where M is the epoxy group-containing monomer).

TABLE II
Heats of Cure, ΔH (Uncatalyzed)

Heating rate (°C/min)	ΔH (J/g)	ΔH[a] (kcal/mol)
2	538	25.97
5	513	24.76
10	514	24.86
20	508	24.52

[a] Calculated from ΔH (J/g) according to the formulation.

TABLE III
Heats of Cure, ΔH (Catalyzed)

Heating rate (°C/min)	ΔH (J/g)	ΔH^{a} (kcal/mol)
5	524	25.36
10	516	24.97
20	545	26.37

[a] Calculated from ΔH (J/g) according to the formulation.

Then the resultant carbenium ion becomes an active center for cationic polymerization of the epoxides.

The existence of the first reaction has been proven as follows: 2.02 g Benzyl alcohol and 0.44 g diphenyliodonium hexafluoroarsenate (under ratio 1:0.05) were heated at 200–210°C in a sealed tube for 30 min. The IR spectrum of the product showed the existence of Ph—O—C bond (1220 cm^{-1}) corresponding to the asymmetric stretching vibration. A band at 272 nm in the UV of the products corresponding to a phenyl ether end group[15] was also observed.

As evidence for the second reaction the following experiment was performed: Into a dry polymerization tube was placed a mixture of 4.08 g epichlorohydrin and 0.414 g diphenyliodonium hexafluoroarsenate (the ratio of moles was 1:0.02). Polymerization was induced by heating the mixture at 200–210°C for 30 min. A dark brown oil was obtained which was washed with methanol and dried at 80°C *in vacuo*. From the IR spectrum of the oligomer an absorption band at 1260 cm^{-1} was observed, indicating that the product contained the Ph—O—C bond.

In order to simplify the curing reaction studies it was decided to examine an epoxy system containing no hydroxyl groups. DSC runs of a system
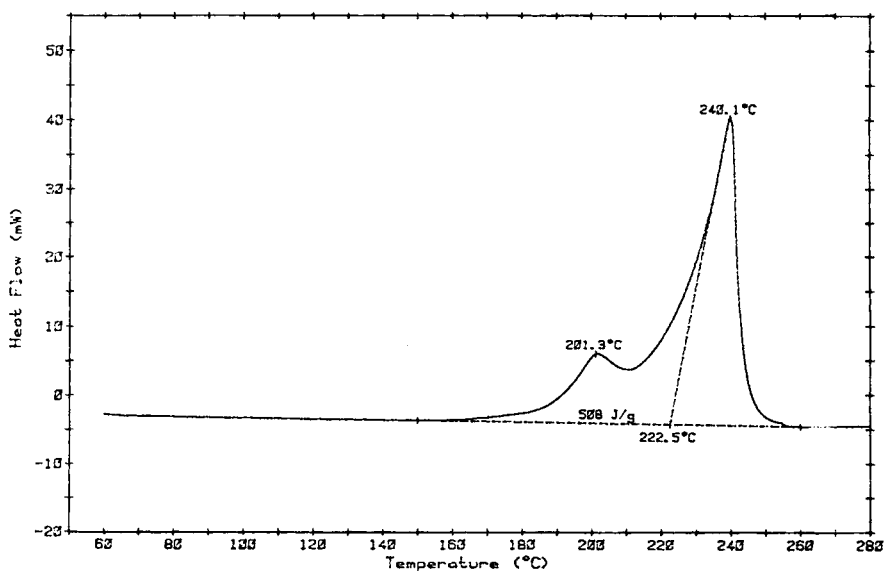

Fig. 3.   DSC trace of Epon 828–Ph$_2$I$^+$AsF$_6^-$ (20°C/min).
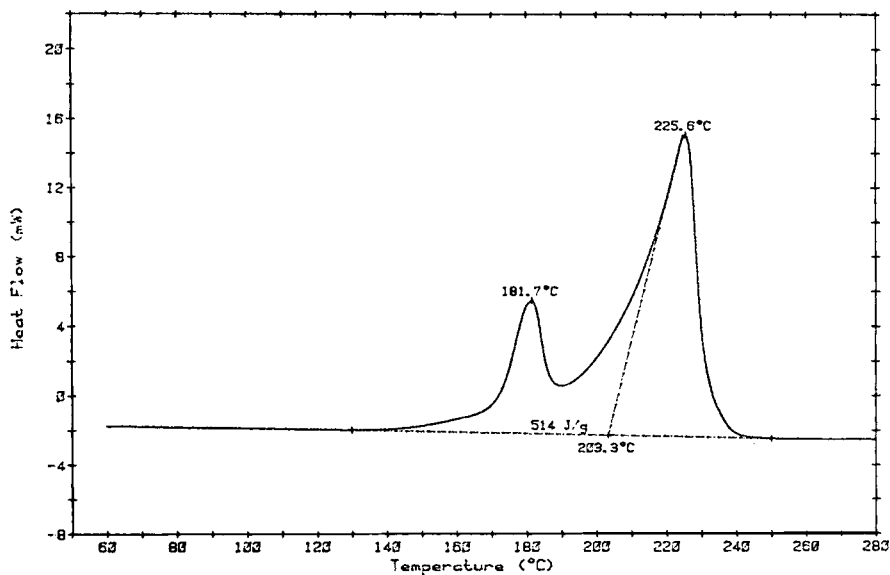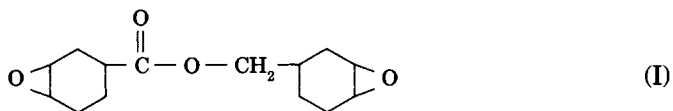
Fig. 4. DSC trace of Epon 828–Ph$_2$I$^+$AsF$_6^-$ (10°C/min).

consisting of a cycloaliphatic diepoxide (I) and diphenyliodonium hexafluo-roarsenate have been examined:

$$\text{(I)}$$

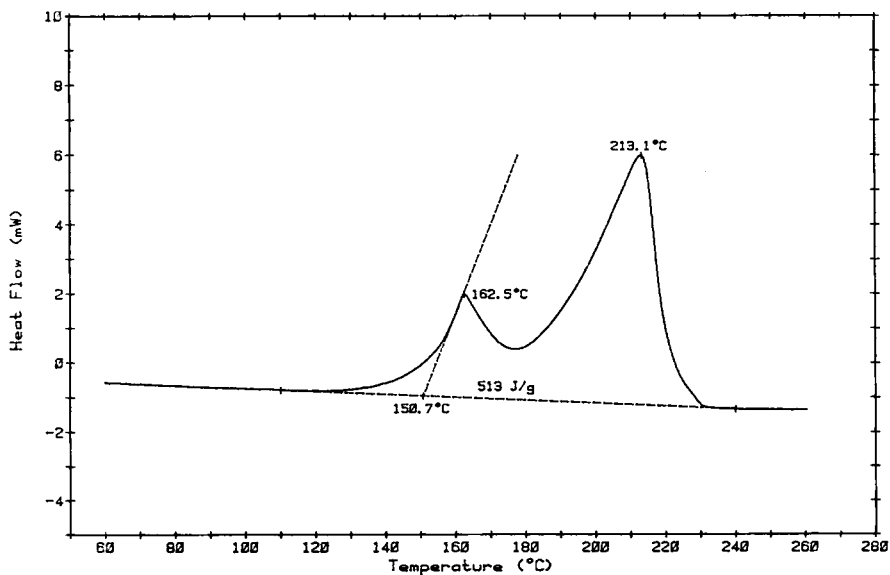As expected, both DSC traces from the scanning and isothermal methods

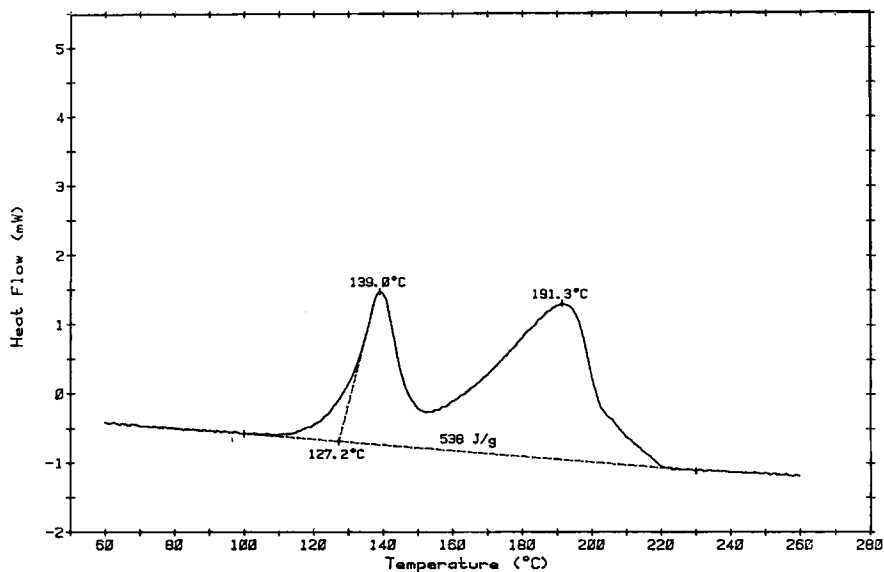Fig. 5. DSC trace of Epon 828–Ph$_2$I$^+$AsF$_6^-$ (5°C/min).

Fig. 6. DSC trace of Epon 828–$Ph_2I^+AsF_6^-$ (2°C/min).

gave exothermic curves with a single peak, indicating that some functional group other than epoxy groups in the Epon 828 system was responsible for one of the two peaks observed in that system.

By use of the dynamic DSC technique, which is mentioned later, the activation energy E of 24.2 kcal/mol for the reaction in the cycloaliphatic epoxy–diphenyliodonium hexafluoroarsenate system was obtained. Comparing this value with the two activation energies (13.5 and 20.1 kcal/mol) corresponding to the two consecutive reactions in the Epon system, which are also mentioned later, it is considered reasonable that the second reaction observed from the DSC traces of Epon 828 curing reaction corresponds to the reaction initiated by the phenylation of the monomer.

Kinetic Parameters

The data listed in Table IV were obtained from Figures 3–6, and were evaluated from a previously determined relationship between the DSC peak temperatures and the heating rates.[8]

The activation energies E_1 (13.5 kcal/mol) and E_2 (20.1 kcal/mol) were

TABLE IV
Heating Rates and Temperatures at Peaks

Heating rate (°C/min)	Temp at first peak, T_{p1} (°C)	$1/T_{p1} \times 10^3$ (K^{-1})	Temp at second peak, T_{p2} (°C)	$1/T_{p2} \times 10^3$ (K^{-1})
20	201.3	2.107	240.1	1.948
10	181.7	2.198	225.6	2.005
5	162.5	2.295	213.1	2.056
2	139.0	2.426	191.3	2.153

obtained after the above data were treated by regression analysis (with correlation coefficients of 0.998 and 0.982, respectively). Also, the frequency factors were calculated by Kissinger's equation.[8] So the overall rate constants k_1 and k_2 (for the first and second reactions, respectively) can be expressed as

$$k_1 \, (\text{s}^{-1}) = 1.77 \times 10^4 \exp(-13.5 \text{ kcal mol}^{-1}/RT)$$

$$k_2 \, (\text{s}^{-1}) = 4.38 \times 10^6 \exp(-20.1 \text{ kcal/mol}^{-1}/RT)$$

without assuming the kinetic order of the curing reaction.

A typical DSC trace of the same system by use of the isothermal technique is shown in Figure 7. The whole curing behavior seems rather complicated. It is obvious that the DSC trace consists of two sections indicating that two reactions occur consecutively. Figure 8 shows the degree of cure, α, as a function of time at different temperatures, and

$$\alpha = \Delta H(t)/\Delta H$$

where $\Delta H(t)$ is the heat evolved at time t and ΔH represents the total heat of cure.

Assuming that only the second reaction occurs as the degree of reaction, α, exceeds 35–40% (corresponding to 4, 6, and 10 min for 200, 190, and 180°C, respectively), a kinetic expression can be used to fit the isothermal experimental data:

$$d\alpha/dt = k_2(1 - \alpha)^n$$

where n is the order of reaction and k_2 is the rate constant of the second
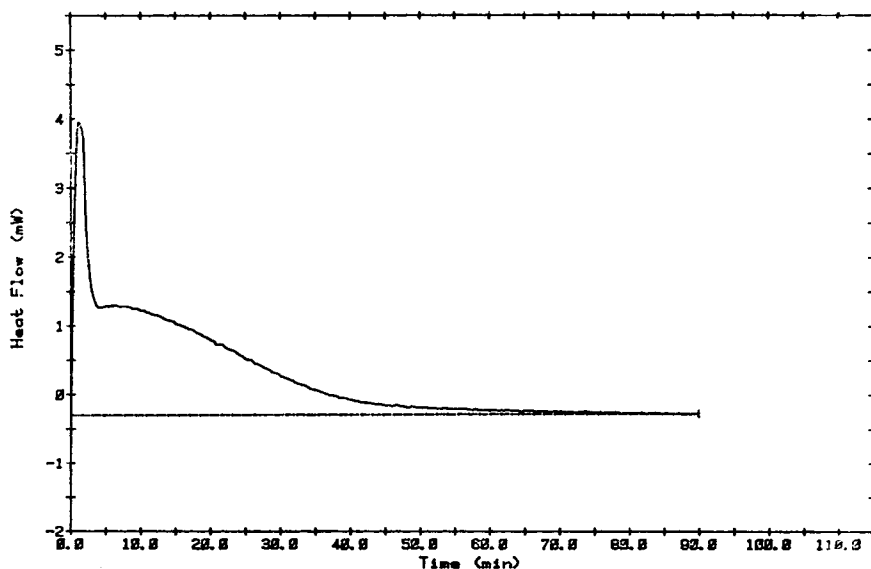

Fig. 7. DSC trace of Epon 828–Ph$_2$I$^+$AsF$_6^-$ (isothermal, 180°C).
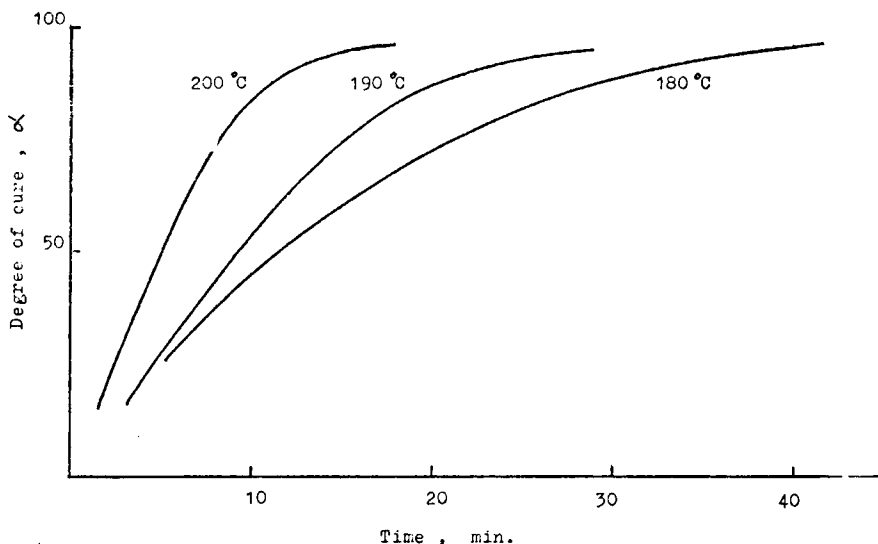
Fig. 8.   Degree of cure of Epon 828–Ph$_2$I$^+$AsF$_6^-$ vs. (time at different temperatures).

reaction. From the isothermal runs the results shown in Table V have been obtained using a linear regression technique.

The kinetic parameters for the second reaction were obtained (with correlation coefficient $r = 0.991$) as $A_2 = 4.23 \times 10^7$ s^{-1} and $E_2 = 22.2$ kcal/mol.

These results revealed good agreement with the above-mentioned kinetic parameters for the second reaction as characterized by the dynamic technique.

CONCLUSIONS

Expoxy systems consisting of diphenyliodonium salts with some complex metal halide anions and a DGEBA type resin (Epon 828) have a long storage life (at least 6 months) under ambient conditions. The heat of cure of Epon 828 with diphenyliodonium hexafluoroarsenate is 25.0 kcal/mol. The cure includes two consecutive reactions and the mechanisms have been investigated. The kinetic parameters for the two reactions have been obtained by the dynamic DSC technique.

The results for the second reaction using the isothermal DSC technique

TABLE V
k_2, n from the Different Temperatures

Temperature (°C)	180	190	200
$k_2 \times 10^4$ (s^{-1})	8.64	13.08	24.74
n	0.674	0.664	0.678

are in good agreement with the dynamic results, and the second reaction can be described as follows:

$$da/dt = 4.23 \times 10^7 \exp[-22.2 \text{ kcal mol}^{-1}/RT(1 - \alpha)^{0.67}]$$

indicating that the two techniques are effective.

References

1. J. V. Crivello, in *UV Curing: Science and Technology,* S. P. Pappas, Ed., Technology Marketing Corp. Norwalk, CT, 1978, p. 23.

2. William R. Watt, in *Epoxy Resin Chemistry,* R. S. Bauer, Ed., Am. Chem. Soc., Washington, DC, 1979, p. 17.

3. J. V. Crivello and J. H. W. Lam, in *Epoxy Resin Chemistry,* R. S. Bauer, Ed., Am. Chem. Soc., Washington, DC, 1979, p. 1.

4. J. V. Crivello, T. P. Lockhart, and J. L. Lee, *J. Polym. Sci., Polym. Chem. Ed.,* **21**, 97 (1983).

5. J. V. Crivello and J. L. Lee, *J. Polym. Sci., Polym. Chem. Ed.,* **21**, 1097 (1983).

6. K. Horie, I. Mita, and H. Kambe, *J. Polym. Sci., A-1,* **6**, 2663 (1968).

7. K. Horie, H. Hiura, M. Sawada, I. Mita, and H. Kambe, *J. Polym. Sci., A-1,* **8**, 1357 (1970).

8. R. B. Prime, in *Thermal Characterization of Polymeric Materials,* E. A. Turi, Ed., Academic, New York, 1981, pp. 540–545, 446–447.

9. J. V. Crivello and J. H. W. Lam, *J. Org. Chem.,* **43**, 3055 (1978).

10. J. V. Crivello and J. H. W. Lam, *J. Polym. Sci., Polym. Chem. Ed.,* **17**, 977 (1979).

11. J. V. Crivello and J. H. W. Lam, *J. Polym. Sci., Symp.* **56**, 383 (1976).

12. Henry Lee and Kris Neville, *Handbook of Epoxy Resins,* 1967, p. 63.

13. S. P. Pappas, B. C. Pappas, and L. R. Gatechair, *J. Polym. Sci., Polym. Chem. Ed.,* **22**, 69 (1984).

14. C. B. May and Y. Tanaka, *Epoxy Resin Chemistry and Technology,* 1975, pp. 199–205.

15. T. Saegusa and S. Matsumoto, *J. Polym. Sci., A-1,* **6**, 1559 (1968).