

## A Gel Point Method for the Estimation of Overall Apparent Activation Energies of Polymerization

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### INTRODUCTION

The gel time of a number of synthetic resin systems is an important technological property because of its bearing on the useful life of the system. Hitherto little fundamental significance has been attached to such measurements, in spite of the importance of the phenomenon of gelation in polymer science. In this paper we present evidence that kinetic information of a semiquantitative nature may be derived from gel point observations.

The critical degree of reaction in a polycondensation is calculable from the classical network theory of gelation, and, if allowance is made for ring formation, agreement between theory and experiment is good.<sup>1</sup> A recent series of papers by Gordon and Roe<sup>2</sup> has added much to our knowledge of this topic. They showed that, for model polyester systems, crosslinking in polyadditions is free from diffusion control up to the gel point. Thus the correct calculation of the gel point reverts to the simple theory of Flory and Stockmayer. It was shown that deviations in initial viscosity and gel points were consistent with internal cyclization of primary chains.

It follows from the preceding paragraph that, in any system in the process of forming a three-dimensional network, the degree of reaction at the gel point is an intrinsic property of the system and is not a function of the experimental conditions. We may therefore use the gel time as a measure of the overall rate of reaction, as long as only a single reaction mechanism is involved. If polymerization occurs by two or more simultaneous mechanisms having different activation energies, then this argument is not valid.

$$-dc/dt = kc^n \quad (1)$$

where  $c$  is the concentration of monomer,  $k$  is the overall rate constant, and  $n$  is the kinetic order

with respect to monomer. Integration of eq. (1) gives

$$kt = [1/(n-1)](c^{1-n} - c_0^{1-n}) \quad (2)$$

where  $c_0$  is the concentration of monomer when  $t = 0$ . Now let  $c_g$  be the concentration of monomer at gelation when  $t = G$ . Rearrangement of the resulting equation gives

$$k = (1/G) \{ [1/(n-1)] (c_g^{1-n} - c_0^{1-n}) \} \quad (3)$$

For a given system the term in braces is constant, and equals  $A$ , say; then combination with the Arrhenius equation gives,

$$A/G = Xe^{-E/RT}$$

or

$$\ln G = \ln(A/X) + E/RT \quad (4)$$

where  $X$  is the frequency factor,  $E$  is the overall apparent activation energy,  $R$  is the gas constant, and  $T$  is the absolute temperature. Hence a plot of  $\log G$  against  $1/T$  should give a straight line of slope  $E/2.303R$ . Thus in order to estimate  $E$  we must measure the gel point of the system under isothermal conditions.

The measurement of gel points presents certain difficulties. Gordon and Grieverson<sup>3</sup> have stated that although the gel point in polyfunctional systems is sharp, testing for the gel point always involves the application of a shearing force. Hence the sharpness of the gel point can be counteracted, in some cases, by the irreversible degradation of polymer molecules induced by flow. Gordon and Roe<sup>4</sup> observed a slight delay in gelation in a polyester, attributed to mechanical degradation induced by moving a magnetic probe. We conclude, therefore, that care is necessary in making gel point observations.

Some data are available in a paper by Warfield and Petree<sup>5</sup> which enable us to compare the use of

eq. (4) with results obtained by independent methods. These authors measured the overall activation energy of polymerization of diallyl phthalate by 1.96% of benzoyl peroxide. By following the change in electrical resistivity they obtained a value of 16 kcal./mole. From the other work cited in the same paper, it appears that  $16 \pm 1$  kcal./mole is the best value. The gel points were marked on the resistivity curves, and it was stated that gelation was sharp at the higher temperatures but indistinct at the lower temperatures studied. We have selected the gel times at the two highest temperatures as being the most reliable estimates, i.e., 26 min. at 110°C., and 49 min. at 100°C. These values have been substituted into eq. (4), which gives  $E = 17.7$  kcal./mole. This is regarded as reasonable agreement. We have now applied the gel point method to some epoxy resin-amine curing agent systems. In this case  $c$  and  $n$  in eqs. (1)-(3) refer to epoxide.

#### EXPERIMENTAL

The gel times were determined in the following manner. The side necks of a 250-ml. three-necked flask were fitted with corks carrying small sample tubes. These sample tubes were made by drawing out thin-walled 4 in.  $\times$  1/2 in. test tubes to a blunt point. The center neck of the flask was fitted with a reflux condenser and a thermometer to indicate the vapor temperature. The sample tubes were heated by the vapor of various liquids refluxed in the flask. The epoxy resin and curing agent were intimately mixed and the time noted. At recorded intervals one drop of the resin mixture was introduced into a sample tube. The gel point was estimated by slowly revolving a fine glass rod in the tube until the resin "climbed up" the rod. The gel times were plotted against time after mixing, and the graph extrapolated to  $t = 0$  to give  $G_0$ , the gel time at the instant of mixing;  $\log G_0$  was then plotted against  $1/T$ .

Since the samples were small (20-50 mg.) it was assumed that heat transfer was rapid and that polymerization occurred under essentially isothermal conditions. It was also assumed that the time required for the samples to reach the test temperature was negligible compared with the gel time. A low molecular weight epoxy resin was used throughout this work (Epikote 828, obtained from the Shell Chemical Co.). The curing agents used were an alkenyl-substituted heterocyclic polyamine (Synolide 960, obtained from Cray Valley Products Ltd.), triethylamine (British Drug Houses,

laboratory grade), and triethylamine in the presence of distilled water. Synolide 960 gave sharp gel points in these experiments, and triethylamine gave gel points estimated within  $\pm 2\%$ .

#### RESULTS

The Arrhenius plots are shown in Figure 1. The activation energies estimated from the slopes of the lines are given in Table I.

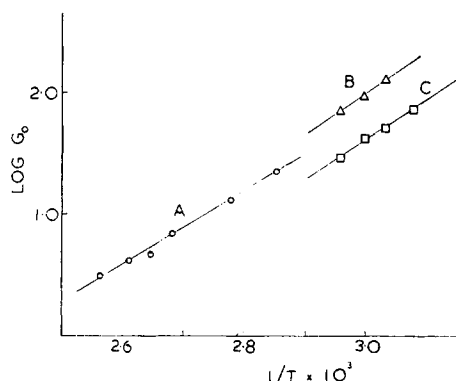


Fig. 1. Arrhenius plots for (A) Synolide 960-Epikote 828; (B) triethylamine-Epikote 828; (C) triethylamine-water-Epikote 828.

Overall activation energies of polymerization of epoxy resins by amine curing agents observed by other workers are shown in Table II.

TABLE I

System	$E$ , kcal./mole
40% Synolide 960/60% Epikote 828	$15.0 \pm 1$
10% Triethylamine/90% Epikote 828	$15.7 \pm 2$
9.8% Triethylamine/2.4% water/87.8% Epikote 828	$14.9 \pm 2$

TABLE II

Curing agent	$E$ , kcal./mole	Reference
Piperidine	12.9	6
<i>m</i> -Phenylenediamine	12	7
Diethylaminopropylamine	17	7
Versamid 125 (a polyamide resin)	11	7
Various amines	13-16	8

#### CONCLUSIONS

It is seen that the results obtained from the gel point method described above are in reasonable agreement with other measurements on similar systems. The advantages of the present method are found chiefly in its simplicity. Hence it should

prove a useful addition to the study of systems characterized by a sharp gel point. The accuracy attainable in any given case will depend mainly on the reliability of the gel point observations, and on the polymerization being carried out under isothermal conditions.

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### References

1. Flory, P. J., *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N. Y., 1953, pp. 354 et seq.
2. Gordon, M., and R.-J. Roe, *J. Polymer Sci.*, **21**, 27, 39, 57, 75 (1956).
3. Gordon, M., and B. M. Grieverson, *ibid.*, **17**, 114 (1955).
4. Ref. 2, p. 71.
5. Warfield, R. W. and M. C. Petree, *ibid.*, **37**, 305 (1959).
6. Belanger, W. J., and J. H. Denham, paper presented at the 134th Meeting of the American Chemical Society, Chicago, Ill., September 1958.
7. Warfield, R. W., and M. C. Petree, paper presented at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September 1959.
8. Warfield, R. W., and M. C. Petree, unpublished work (see ref. 7).

### Synopsis

The gel time, measured under isothermal conditions, may be taken as a measure of the overall rate of polymerization of

a given system under certain circumstances. This enables us to estimate the Arrhenius activation energy from such measurements. A simple piece of apparatus is described which has been used to measure the overall activation energy of some epoxy resin polymerizations. The agreement with previously published data is reasonable.

### Résumé

On peut considérer le temps de gélification, mesuré dans des conditions isothermiques, comme une mesure de la vitesse globale de polymérisation d'un système donné dans certaines circonstances. Ceci nous permet d'estimer l'énergie d'activation d'Arrhénius à partir de ces mesures. On décrit une simple partie de l'appareil qui nous a servi à mesurer l'énergie d'activation globale des polymérisations de certaines résines époxy. La concordance avec les résultats publiés antérieurement est raisonnable.

### Zusammenfassung

Die unter isothermen Bedingungen gemessene Gelbildungs-dauer kann unter gewissen Umständen als ein Mass der Bruttopolymerisationsgeschwindigkeit eines gegebenen Systems betrachtet werden. Dadurch ist man in der Lage aus solchen Messungen die Arrhenius-Aktivierungsenergie zu bestimmen. Eine einfache apparative Anordnung wird beschrieben, die zur Messung der Bruttoaktivierungsenergie einiger Polymerisationen von Epoxyharzen benützt wurde. Die Übereinstimmung mit früher veröffentlichten Ergebnissen ist annehmbar.

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