Investigation on the Polymerization of an Unsaturated Polyester System by a Resistivity Technique

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Synopsis

A continuous current monitoring technique has been used to follow the resistivity change during the early stages of the isothermal bulk polymerization of an unsaturated polyester resin.   The general form of the log (resistivity)–time curves is similar to the conversion–time curves of inhibited vinyl polymerization obtained by other techniques. An overall activation energy for the polymerization has been derived by using the post-gelation rate of resistivity change as a polymerization rate index.   An analysis of the data obtained from these experiments emphasizes the complexity of the reaction kinetics of the bulk polymerization.   There appears to be an unusual dependence of the rate of initiation upon initiator concentration and hence because of the short kinetic chain length, of the final rate of polymerization upon initiator concentration.

INTRODUCTION

Previous investigations have shown the potential use of resistivity techniques in kinetic studies of the curing of epoxide, unsaturated polyester, and polyurethane resins.   In these investigations resistivities ranging from 10^7 to 10^{16} ohm-cm. were measured by electrometer techniques.[1]

The constant slope of the log (resistivity)–time curves over a large part of the reaction indicated that measurements covering only the early stages should be sufficient to study many facets of the curing process.   A simple continuous current monitoring technique was developed to measure resistivity changes during the initial stages of cure and used to obtain information about the polymerization kinetics of unsaturated polyester resins.

EXPERIMENTAL

Polyester Resin Systems

Two commercial polyester resins, low viscosity Crystic 189 and Bakelite 17449, were used in this investigation.

The composition of these resins has not been disclosed but they are believed to be of the general type, i.e., an unsaturated polyester mixed with styrene as crosslinking monomer and containing a polymerization inhibitor to increase shelf life.[2]

Bulk polymerization of the resins was initiated by various concentrations of an organic peroxide catalyst (methyl ethyl ketone peroxide) and a organo-metallic accelerator (cobalt naphthenate). The MEK peroxide was added as a 60 wt.-% solution in dimethyl phthalate and the cobalt naphthenate as a solution in styrene containing the equivalent of 1% cobalt metal.

Resistivity Experiments

A polytetrafluoroethylene parallel plate cell and a resistance bridge described elsewhere[3] were used to determine the resistivity–time behavior of the low viscosity Crystic polyester resin. After filling the cell with a resin mix of 100 g. resin:5 ml. catalyst:5 ml. accelerator, and placing in an air circulating oven at 18°C., resistance measurements were made during polymerization. Volume resistivity values were calculated by using eq. (1):
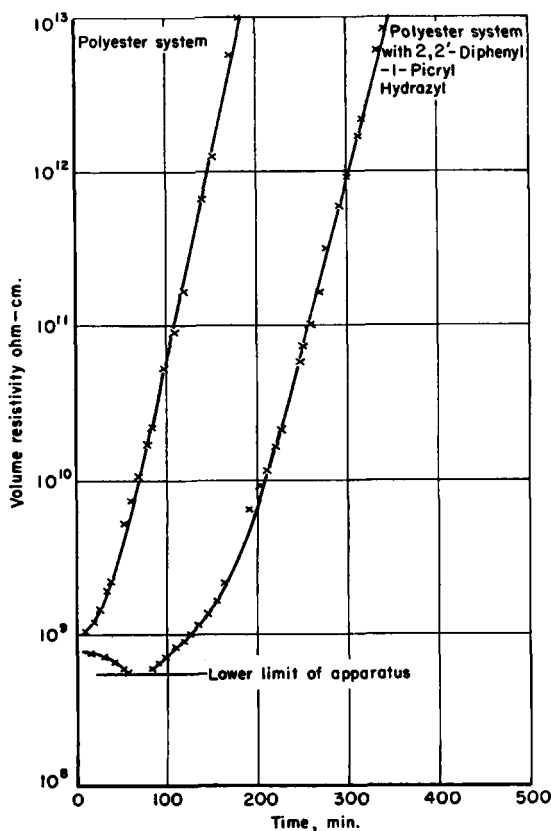
$$\rho = RA/L \tag{1}$$

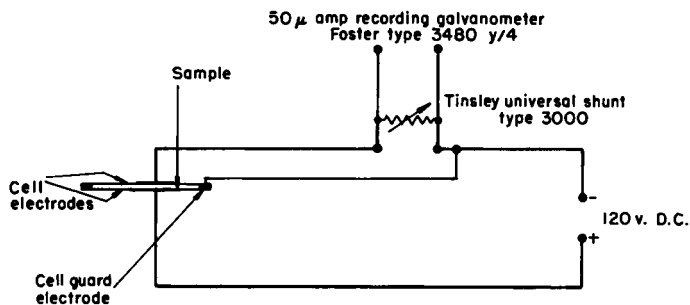Fig. 1. Resistivity–time behavior of an unsaturated polyester system with and without diphenyl picryl hydrazyl.

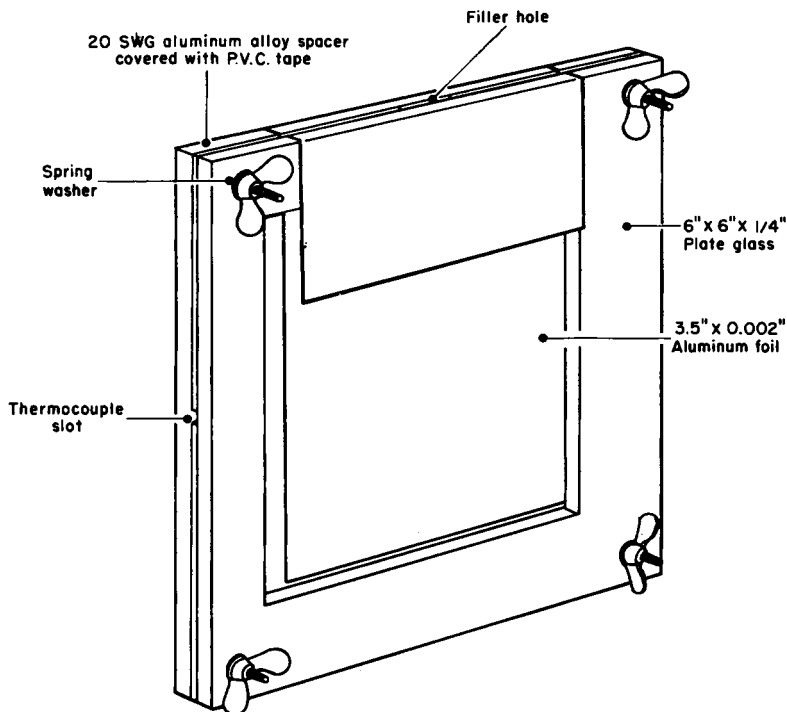Fig. 2. Circuit diagram for continuous current measurement.

Fig. 3. Parallel plate cell.

where ρ is volume resistivity (in ohm-centimeters), R is observed resistance (in ohms), A is the effective electrode area (in square centimeters), and L is the length of the conducting path (in centimeters). A curve log (resistivity) against time was constructed (Fig. 1). During the experiment a temperature rise of 6°C. was observed by means of a recorder attached to the cell. The temperature rise in the oven which was not thermostatically controlled was 3°C.

A similar experiment was conducted on the same polyester resin system with a 0.1 g. addition of 2,2′-diphenyl 1-picryl hydrazyl, a stable free

radical[4] (Fig. 1).   During this experiment the temperature of the cell also
rose 6°C.   The addition of diphenyl picryl hydrazyl produced behavior
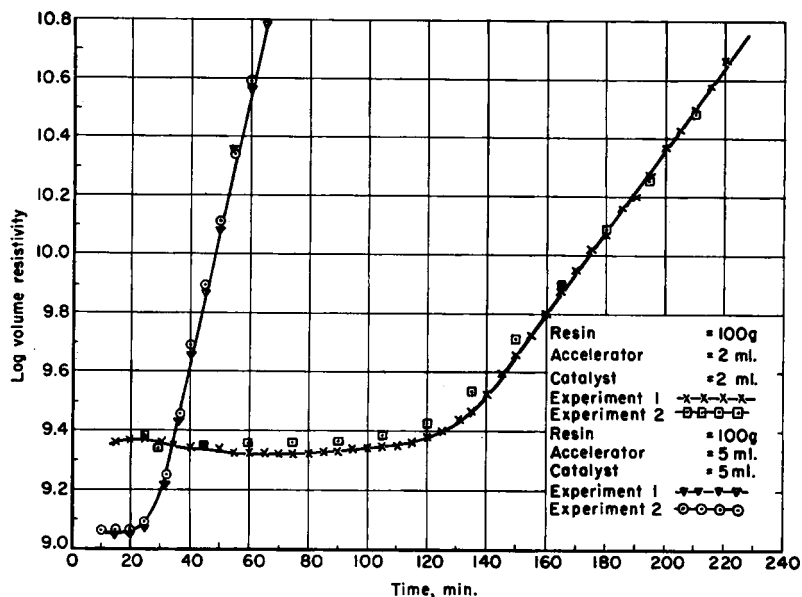similar to that observed in the conversion–time curves of inhibited vinyl

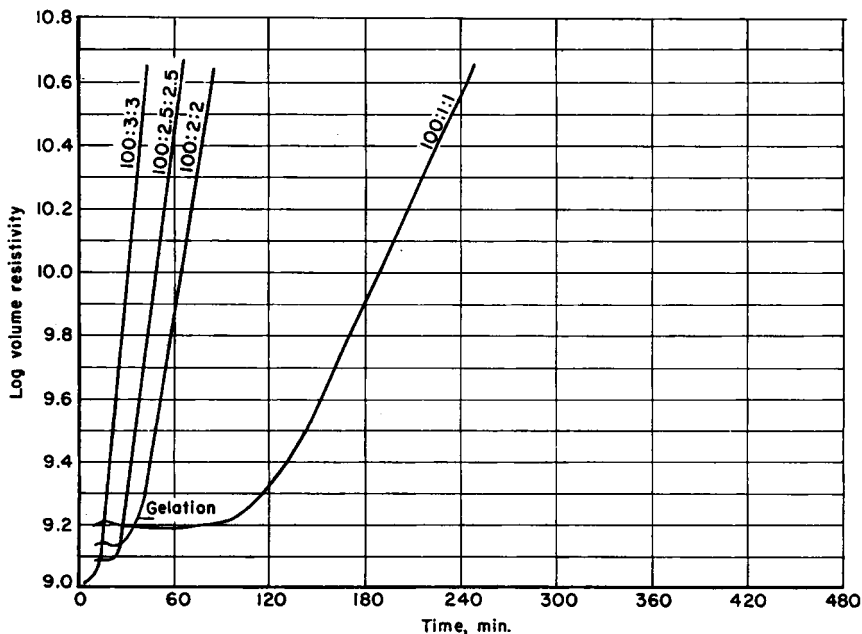Fig. 4. Resistivity–time behavior of several unsaturated polyester systems at 25°C.

Fig. 5. Resistivity–time behavior of an unsaturated polyester resin initiated with various
concentrations of methyl ethyl ketone peroxide and cobalt naphthenate at 39°C.

polymerizations.[5]   There was a pronounced induction period, followed by a gradual increase in the rate of log (resistivity) rise to a constant value, which was maintained at least over the range 10^{10}–10^{13} ohm-cm.   The constancy in this range in both the uninhibited and inhibited resin cases indicated that it was not necessary to follow the reactions to high degrees of conversion (and hence high resistivities) to obtain useful kinetic data. Resistivity measurements over the early stages of polymerization are simpler, because with suitable cell design large currents are involved and the need for ultrasensitive detectors eliminated.

The polymerization of a Bakelite polyester system was followed by applying a voltage and recording the current change through the sample maintained at constant temperature.   A circuit diagram is shown in Figure 2, and a parallel plate cell (Fig. 3) contained the sample both in the liquid and the solid state.

The parallel plate cell offers several advantages.   Polymerization exotherms are minimized by the use of thin sections, and styrene evaporation during polymerization is reduced by restricted exposure to atmosphere. Increasing the electrode area and decreasing the distance between electrodes allows larger currents to flow through the cell.   During the experiments the cell was contained in a chamber capable of temperature control within the limits $\pm 1°C$.

The cell was assembled with all exposed glass and the guard ring coated with a film of silicone grease.   Continuity between the guard ring contact

TABLE I
Results of Experiments with Continuous Current Monitoring Technique

Component ratio			Cure temperature, °C.	Electrode area, cm.[2]	Thickness of specimen, cm.	Induction period, min.	$d(\log \rho)/dt$
Resin, g.	Catalyst. ml.	Acceler- ator, ml.					
100	5.0	5.0	25	99.0	0.14	25	0.045
100	4.0	4.0	25	95.5	0.14	36	0.037
100	3.0	3.0	25	83.3	0.14	56	0.028
100	2.0	2.0	25	93.3	0.13	110	0.014
100	1.6	1.6	25	94.5	0.13	170	0.010
100	1.0	1.0	25	92.7	0.13	420	0.003
100	4.0	4.0	30	99.9	0.13	18	0.045
100	3.0	3.0	30	93.5	0.12	34	0.033
100	2.0	2.0	30	97.2	0.13	75	0.017
100	1.0	1.0	30	99.9	0.13	210	0.006
100	3.0	3.0	34	99.0	0.13	25	0.046
100	2.5	2.5	34	96.8	0.13	30	0.036
100	2.0	2.0	34	97.0	0.13	63	0.024
100	1.0	1.0	34	96.3	0.12	135	0.008
100	3.0	3.0	39	99	0.13	10	0.056
100	2.5	2.5	39	99.2	0.13	20	0.040
100	2.0	2.0	39	99	0.13	28	0.031
100	1.0	1.0	39	98.1	0.12	85	0.011

and the guard ring was checked, followed by a discontinuity test between electrodes.

The cell was connected into the circuit and the shunt adjusted to obtain maximum galvanometer sensitivity. Surface leakage currents were not measurable and therefore not significant for the purposes of the experiments.

A 100-g. portion of Bakelite polyester resin in a sealed container was placed in the chamber with the cell. When the cell temperature had stabilized, the requisite quantities of accelerator and catalyst were intimately dispersed in the resin and the cell was filled.

The introduction of the initiating system was taken as the time at which polymerization commenced. As polymerization proceeded the current range of the galvanometer was decreased as required. Frequent voltage measurements were made over the period of the experiment. When the experiment was complete, current–time data were obtained from the galvanometer trace and the corresponding resistances determined by Ohm's Law. Volume resistivities were then calculated as before.

Details of the experiments conducted in the above manner are given in Table I and typical curves of log (resistivity) against time are shown in Figures 4 and 5.

Gelation Experiments

A tray with the dimensions of the cell cavity was constructed. The tray and 100 g. of Bakelite polyester resin contained in a sealed container were placed in the constant temperature chamber. When temperature equilibrium had been attained, the requisite quantities of accelerator and catalyst were added to the resin and the mix poured into the tray to form a film. The onset of gelation was taken as the stage at which the resin mix did not flow after breaking the film with a glass rod.

The gelation time was measured from the introduction of the initiator. Values were obtained for several systems and the general position of the gelation point is indicated on a log (resistivity)–time curve in Figure 5.

RESULTS AND DISCUSSION

Polymerization exotherms as indicated on the recorder were reduced to 1°C. by the geometry of the system, and it was considered that the isothermal cure of thin plates was observed.

The curves log (resistivity) against time show the resistivity behavior during the early stages of cure. Reproducibility of the results is illustrated by the superposition of the curves obtained by duplicate experiments (Fig. 4).

All the curves exhibit the same pattern; a period (termed the induction period) is followed by a rapid increase in resistivity as polymerization proceeds. The induction period is taken as the time from the introduction of the initiator to that when the resistivity returned to its initial value. The slopes $[d(\log \rho)/dt]$ of the linear portions of the curves following the induction period were determined.

Both the induction period and $d(\log \rho)/dt$ vary with initiator concentration and temperature (Table I), and the slope may be taken as an index of polymerization rate.[1]

Reaction Kinetics of the Polyester System

The rate curves of the early stages of the bulk polymerization of a vinyl monomer, where viscosity and the degree of conversion are low, can be treated by simple mass law theories. In the later stages increased viscosity can lead to diffusion control of the termination reaction resulting in an increase in the rate of monomer consumption (Trommsdorff effect). Reactions in the final stages can be extremely complex as the whole process becomes diffusion-controlled.

Pre-gelation Period

The decrease in resistivity as the initiator concentration is increased indicates an increased concentration of current carriers. This may result from a reaction of the type.[6]

$$Co^{2+} + ROOH \rightarrow Co^{3+} + RO\cdot + OH^-$$

with conduction mechanisms possible through both hydroxyl ions and possibly free radicals.[7] The initial decrease in resistivity observed in practically all the experiment may arise from a temperature effect or an increase in the concentration of current carriers during the initiation reaction.

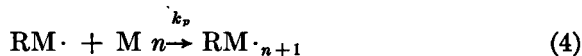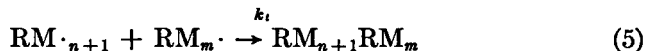The polymerization of a vinyl monomer can be expressed as shown in eqs. (2–5):

Initiation:

$$R\cdot + M \overset{k_i}{\rightarrow} RM\cdot \tag{2}$$

Inhibition:

$$R\cdot + I \overset{k_I}{\rightarrow} RI \tag{3}$$

Propagation:

$$RM\cdot + M \; n \overset{k_p}{\rightarrow} RM\cdot_{n+1} \tag{4}$$

Termination:

$$RM\cdot_{n+1} + RM_m\cdot \overset{k_t}{\rightarrow} RM_{n+1}RM_m \tag{5}$$

where $R\cdot$ is free radical derived from catalyst, M is monomer, and I is inhibitor.

Assuming the induction period can be attributed to the presence of added inhibitor, the concentration of this is constant for all the systems used. Assuming also that the rate of free radical production is directly proportional to the catalyst/accelerator concentration and that initially all the free
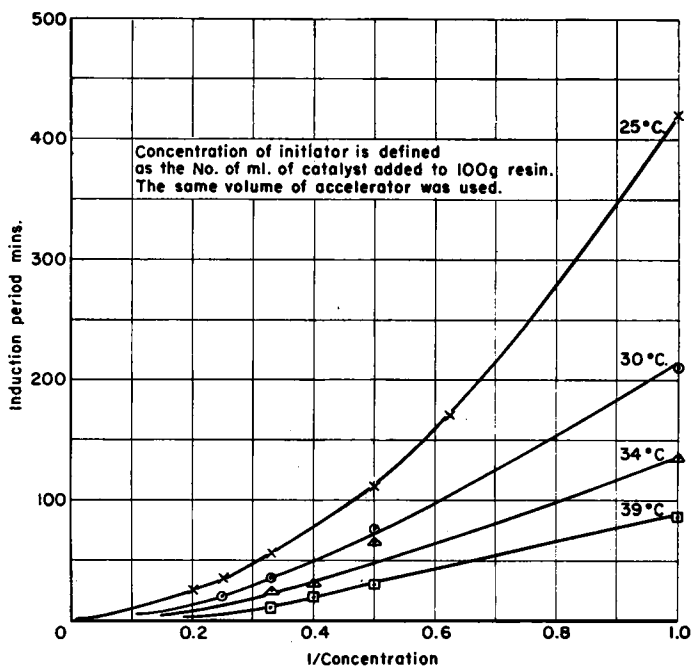
Fig. 6. Induction period vs. reciprocal concentration of initiator.

radicals are used up in removing the inhibitor, then a direct proportionality would be expected between the induction period and reciprocal catalyst/accelerator concentration. This relationship may be developed in the following manner.

By definition all the free radicals produced are deactivated by the inhibitor during the induction period. Ideally one molecular of inhibitor reacts with one free radical.

In a copolymerization reaction between monomers M_1 and M_2, the rate of production of free polymer radicals is $k_1[R\cdot][M_1]$ and $k_2[R\cdot][M_2]$, and the rate of removal of free radicals is $k_{I1}[R\cdot M\cdot_1][I]$ and $k_{I2}[RM\cdot_2][I]$. Then

Induction period (IP) =

   Concentration of inhibitor/rate of removal of inhibitor

Under steady-state conditions:

$$k_1[R\cdot][M_1] + k_2[R\cdot][M_2] = k_{I1}[RM\cdot_1][I] + k_{I2}[RM\cdot_2][I] \qquad (6)$$

Substituting yields

$$IP = [I]/k_1[R\cdot][M_1] + k_2[R\cdot][M_2] \qquad (7)$$

$$= [I]/[R\cdot](k_1[M_1] + k_2[M_2])$$

and since R· may be assumed to be proportional to initiator concentration [R·],

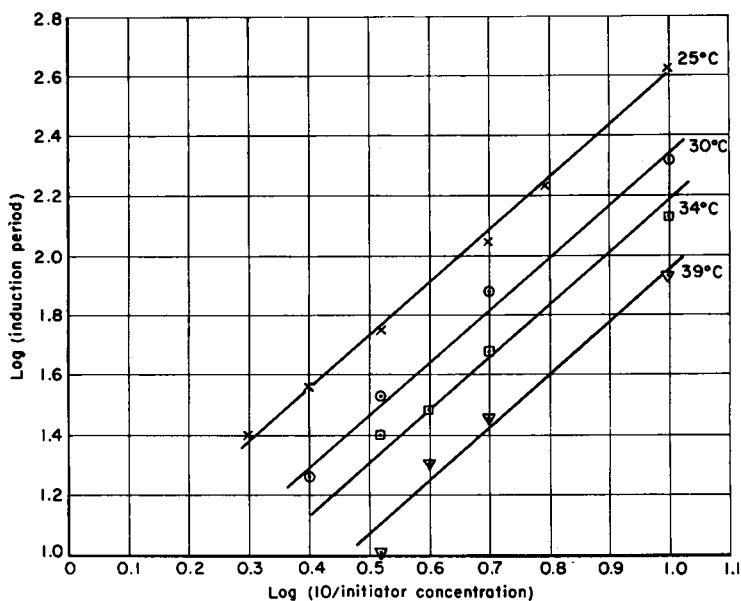$$IP \propto 1/[R] \qquad (8)$$

Fig. 7. Plot of log (induction period) vs. log (reciprocal initiator concentration).
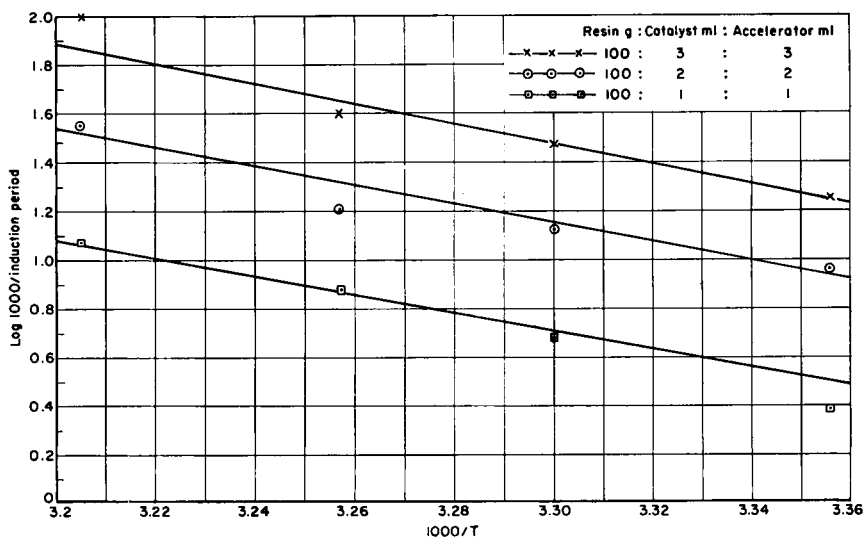

Fig. 8. Plot of log (reciprocal induction period) vs. reciprocal absolute temperature for several unsaturated polyester systems.

That this simple picture is not true is shown by Figure 6. A plot of log (induction period) against log (reciprocal catalyst concentration) (Fig. 7) gives four parallel straight lines, one for each temperature used, the slope of the lines being approximately 1.7–1.8. This dependency albeit an unusual one indicates that the reciprocal of the induction period can be used as an index of the rate of production of radicals. Arrhenius plots of this index are shown in Figure 8 for three different catalyst/accelerator concentrations. The slopes of the three lines are the same within experimental error and the activation energy for initiation calculated from them is 17 kcal./mole. This value compares with an estimate of 15 kcal./mole for the cobaltous–cobaltic oxidation reduction reaction.[10]

Post-Gelation Period

The constant slope of the log (resistivity)–time curves over a large part of their range indicates that the polymerization rate is constant. In some cases, specifically those with low rates of polymerization, some change in rate is observed in the gelation region, whereas in other cases there is no such change. The gelation point as measured in the current investigation is ill-defined and complicated by styrene evaporation. More refined gelation measurements on thin films in a closed system are required to clarify this issue.

Constancy of polymerization rate through the gelation stage has been observed in dilatometric studies of a polyester system,[8] indicating that the

TABLE II

Relationship between $R = d(\log \rho)dt$ and Various Initiator Concentration C Functions[a]

Temperature, °C.	R/C	$R/C^{1/2}$	$R/C^{3/2}$
25	9.0	20.1	4.2
	9.3	18.5	4.6
	9.3	16.2	5.6
	7.0	9.9	5.0
	6.3	7.9	5.0
	(3.0)[b]	(3.0)[b]	(3.0)[b]
30	11.3	22.5	5.6
	11.0	19.1	5.9
	8.5	12.1	6.0
	6.0	6.0	6.0
34	15.3	26.6	8.2
	14.4	22.8	9.1
	12.0	8.5	8.5
	8.0	8.0	8.0
39	18.7	32.4	10.0
	16.0	25.4	10.3
	15.5	22.0	11.0
	11.0	11.0	11.0

[a] $R = d(\log \rho)dt$; C = initiator concentration.
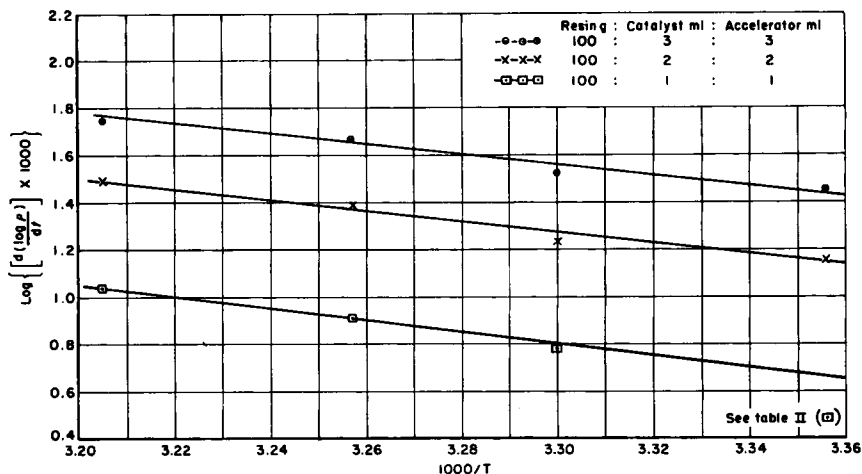[b] The final limiting rate may not have been attained in this experiment.

Fig. 9. Plot of log (rate of resistivity change) of several polyester systems vs. reciprocal absolute temperature.

onset of diffusion control of the rate processes does not necessarily occur on gelation.

In the copolymerization of vinyl monomers, if mutual termination of radicals occurs there is a dependency on the square root of initiator concentration, whereas if radicals disappear by a first-order reaction there is a direct dependency on initiator concentration.[9]

The values of $[d(\log \rho)]/dt$/initiator concentration and $[d(\log \rho)/dt]/$ (initiator concentration)$^{1/2}$ were calculated and are listed in Table II. It can be seen that neither of these functions is constant. A plot of log $[d(\log \rho)/dt]$ against log (initiator concentration) indicated that the dependence was much closer to a $^3/_2$ power and hence values of $[d(\log \rho)/dt]/$ (initiator concentration)$^{1/2}$ were also calculated and included in Table II.

At first sight this dependency seems strange, but it has been shown chemically[11] and kinetically[8] that on an average there are only one to two styrene molecules in the crosslinks between the polyester chains. This possibly means that in these systems the kinetic chain length is not great, and hence in the expression for rate of polymerization, the removal of monomer by the initiation step cannot be neglected as is normally done for long chains.

Therefore if kinetic chains are not long, however,

$$-d[\mathrm{M}]/dt = k_p[\mathrm{RM}\cdot_n][\mathrm{M}] + k_i[\mathrm{R}\cdot][\mathrm{M}] \qquad (9)$$

and a more complex dependence on [R·] results.

It has already been shown from the results in the pre-gelation period that there is an apparent dependence of rate of initiation on the 1.7–1.8 power of the initiator concentration. The inclusion of such a term in the expression for the rate of polymerization would help to account for the observed dependency. With the use of $d(\log \rho)/dt$ as an index of the rate of polymer-

ization, Arrhenius plots have been constructed for three different initiator concentrations (Fig. 9). The overall activation energy for polymerization calculated from the slope of these curves is approximately 11 kcal./mole.

CONCLUSIONS

The bulk polymerization of an unsaturated polyester resin can be followed by continuously monitoring its volume resistivity change during the conversion from the liquid to the solid state. An induction period can be identified on the log (resistivity)–time curves and is followed by a relatively rapid increase in resistivity. The induction period and the rate of resistivity change depend on polymerization temperature and the initiator concentration.

Analysis of the data emphasizes the complexity of the systems as used in practice. There is apparently an unusual dependence of rate of initiation upon initiator concentration and hence, because of the short kinetic chain length, of the final rate of polymerization upon the initiator concentration. The initiating system is a complex mixture of methyl ethyl ketone peroxide dissolved in dimethyl phthalate and cobalt naphthenate dissolved in styrene, and the absolute concentration of the initiating species is in doubt. Experiments are required using definite concentrations of a pure compound as an initiator to confirm the polymerization rate–initiator concentration relationship as measured by resistivity techniques. The reality of the induction period and its relationship to the rate of initiation should be examined further by adding definite amounts of an inhibitor such as diphenyl picryl hydrazyl to the system.

It would also be worthwhile to confirm whether or not there is a direct proportionality between the increase in resistivity and the degree of conversion by carrying out experiments on a simple system such as styrene or methyl methacrylate.

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Résumé

On a utilisé une technique de contrôle par courant continu, pour suivre le changement de résistivité au cours des stades préliminaires, de la polymérisation isothermique en bloc d'une résine de polyester non saturée. La forme générale des courbes du logarithme de la résistivité en fonction du temps est semblable aux courbes conversion–temps de la polymérisation vinylique inhibée, obtenues par d'autres techniques. On en a déduit une énergie d'activation totale de polymérisation en utilisant la vitesse de changement de résistivité, après formation de gel, comme mesure de la vitesse de polymérisation. L'analyse des données obtenues à partir de ces expériences montre la complexité des cinétiques de réaction des polymérisations en bloc. On trouve une dépendance inhabituelle de la vitesse d'initiation par rapport à la concentration en initiateur, du fait de la faible longueur de la chaîne cinétique; la vitesse de terminaison dépend de façon semblable de la concentration en initiateur.

Zusammenfassung

Ein kontinuierliches Stromaufzeichnungsverfahren wurde zur Verfolgung der Widerstandsänderung während des Frühstadiums der isothermen Polymerisation eines ungesättigten Polyesterharzes in Substanz verwendet. Die allgemeine Form der log (Widerstand)–Zeitkurven ist derjenigen der nach anderen Verfahren erhaltenen Umsatz-Zeitkurven der inhibierten Vinylpolymerisation ähnlich. Unter Verwendung der Geschwindigkeit der Widerstandsänderung nach der Gelbildung als Polymerisationsgeschwindigkeitsindex wurde eine Bruttoaktivierungsenergie für die Polymerisation abgeleitet. Eine Analyse der bei diesen Versuchen erhaltenen Daten lässt die komplexe Natur der Kinetik der Polymerisation in Substanz erkennen. Es scheint eine ungewöhnliche Abhängigkeit der Startgeschwindigkeit von der Starterkonzentration aufzutreten und infolge der geringen kinetischen Kettenlänge auch eine solche der Endgeschwindigkeit der Polymerisation von der Starterkonzentration.