

On the Curing Kinetics of Unsaturated Polyesters with Styrene

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Synopsis

The curing kinetics of a general purpose unsaturated polyester (UP) with styrene was studied by differential scanning calorimetry and dielectric capacitance measurements. Benzoyl peroxide was used as initiator. Results showed that there is a complete change in the phenomenological kinetics, in different temperature ranges. At low temperatures (70–90°C), the rate went through a maximum and then showed a first-order decay. At high temperatures (100–160°C) a second-order kinetics was suitable for all the conversion range. At $T > 160^\circ\text{C}$ another mechanism took place when the initiator amount was less than a critical value. From the changes in the dielectric capacitance it was inferred that the conversion rate of UP unsaturations followed a first-order decay after a certain conversion, with an activation energy close to values reported for diffusion of UP radicals. Possible free radical mechanisms accounting for experimental observations are discussed.

INTRODUCTION

Unsaturated polyesters are finding increasing markets in bulk, sheet, and thick molding compound applications. This has motivated a continuous interest in studies dealing with their bulk copolymerization with styrene.^{1–9} Regarding the kinetics of the curing reaction, Kamal and Sourour,² Kamal,³ and Pusatcioglu et al.⁶ have used an empirical model which takes into account the autoacceleration observed in isothermal differential scanning calorimetry (DSC) runs. On the other hand, Slupkowski et al.⁵ and Rojas et al.⁹ reported kinetic results for a system containing cobalt as an accelerator, using electron spin resonance⁵ and adiabatic temperature rise⁹ techniques. Recently, Stevenson⁷ developed a series of kinetic models for free radical copolymerization, based on the usually accepted mechanisms. Simplified versions were able to predict the general features of DSC runs over a range of compositions and temperatures.^{7,8}

One of the shortcomings of isothermal curing is the limited temperature range where useful kinetic information may be obtained.^{6,8} In this range, the copolymerization reaction presents an induction period; then the rate increases passing through a maximum and finally decreases till the final conversion is reached. Both empirical^{2,3,6} and more fundamental^{7,8} kinetic models take all these features into account. The induction period is related to the consumption of radicals by inhibitors present in commercial formulations.

The modeling of the industrial processing usually requires a knowledge of the

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curing kinetics in a broad temperature range. The extrapolation of kinetic expressions arising from isothermal runs to high temperatures is doubtful because changes in the free radical mechanism might take place. Also, at sufficiently high temperatures, thermal copolymerization may have a bearing on the overall kinetics. One of the aims of the present study is to discuss the validity of kinetic expressions in different temperature ranges, for the curing of a multipurpose unsaturated polyester with styrene.

On the other hand, it is accepted that homopolymerization of styrene monomer is significant relative to the copolymerization between styrene and unsaturated polyester,⁸ though no polystyrene is actually formed.⁴ Styrene is usually present in a 2:1 proportion with respect to polyester unsaturations. Because the heat of reaction of styrene homopolymerization is close to that of the reaction with UP,⁸ differential scanning calorimetry gives information related to the homopolymerization of unsaturations as a unique reaction. However, the structure and final properties of the resulting network will be dependent on the relative amount of both kinds of unsaturations which are reacted at any time. By using infrared spectroscopy, Horie et al.¹ showed that, for a given temperature, the final extent of conversion for styrene units was greater than the corresponding to the polyester unsaturations. In the present paper it will be shown that the measurement of the dielectric capacitance of the polymerizing mixture as a function of time gives useful information regarding this aspect of the reaction.

EXPERIMENTAL

Materials

The unsaturated polyester was a commercial general purpose formulation, prepared by the condensation of 1 mol phthalic anhydride, 1 mol maleic anhydride, and 2.2 mol propylene glycol, to give an acid number equal to 50–55 mg KOH/g (different batches had acid numbers in this range). It was available as a solution in styrene (71% resin, 29% styrene, by weight). It was cured with the addition of extra styrene (7.9 parts in 100 parts of commercial solution, by weight), giving a ratio of styrene to polyester unsaturations equal to 2.2:1. This high ratio is required to achieve a high conversion of reactive double bonds and to decrease the initial viscosity of the polyester resin.⁴ Benzoyl peroxide, BPO (Lucidol KL 50, with a 3.2% active oxygen), was used as initiator, in amounts ranging from 0% to 3.2% (g BPO/100 g polymerizing mixture).

Calorimetric Measurements

The calorimetric measurements were conducted in a DuPont 990 thermal analyzer, provided with a DSC pressure cell. A calibration curve in the temperature range 25–230°C and pressure range 10^5 – 4.5×10^6 Pa (14.7–650 psi) was obtained using known values of heat capacity of alumina and heat of fusion of indium. The upper temperature limit is fixed by the thermal decomposition of the polyester resin.⁴ When the curing reaction was carried out at atmospheric pressure, a loss of approximately 10% of the initial mass was always observed. At high pressures the loss of mass was negligible. All the DSC runs which will be reported were carried out at 4.5×10^6 Pa.

The thermal analyzer was operated both in the isothermal and scanning modes. The temperature range for isothermal runs was limited to 70–90°C. At lower temperatures there was a long induction period and a low intensity of the DSC signal. At higher temperatures a significant extent of reaction took place during the stabilization period of the device. The curing in the scanning mode was performed at heating rates of 5, 10, and 20°C/min. As the information arising from these runs did not depend on the heating rate, only results obtained at 10°C/min will be reported. The total heat of reaction was calculated from the area under the DSC curves in each case. The residual reactivity left in the isothermally cured samples was determined with a further scanning from room temperature to 230°C.

Dielectric Capacitance

An adequate device to measure changes in dielectric capacitance during the curing reaction was designed.¹⁰ Figure 1(a) shows the measuring cell, consisting of two copper plaques supported on teflon discs which are separated by a rubber o-ring. The gap for the sample has 2.5 mm thickness. Oil circulating from a

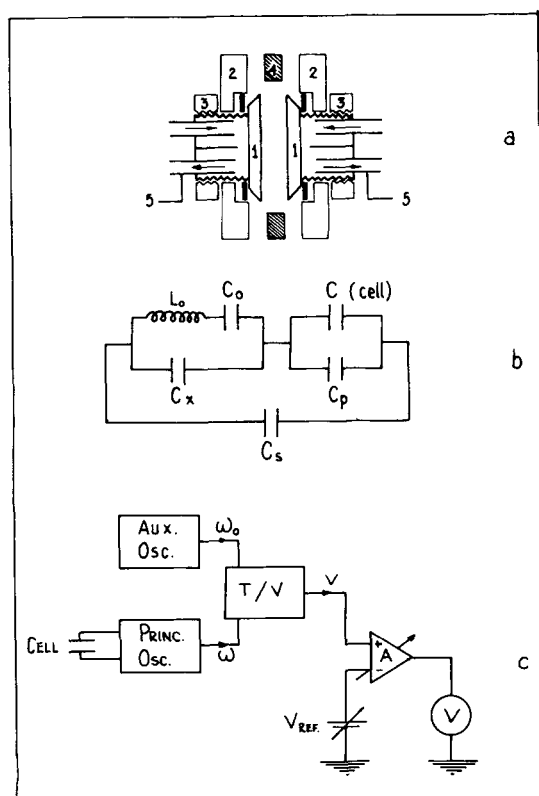


Fig. 1. Device for measuring the dielectric capacitance: (a) measuring cell [(1) copper plaques, 50 mm ϕ , 5 mm thickness; (2) teflon discs; (3) aluminum discs; (4) rubber o-ring; (5) electrical connexion]; (b) electronic oscillator (L_0 and c_0 = inductance and capacitance of the piezoelectric crystal; c_x = capacitance of the plaques bearing the crystal; c_s = coupling capacitance of high value; c_p = capacitance of the electrical connexion to the measuring cell; c = capacitance of the measuring cell); (c) block diagram of the complete device.

thermostat permitted us to keep a constant temperature during reaction. The cell was connected to an electronic oscillator controlled by a piezoelectric crystal and giving an oscillation frequency of 5×10^6 Hz [Fig. 1(b)]. The block diagram of the complete device is shown in Figure 1(c). To avoid the effect of temperature fluctuations on the measurements, an auxiliary oscillator with infinite capacitance and natural frequency w_0 was used. Both signals were mixed, filtered, and entered into an electronic circuit which acted as a linear transducer of periods (inverse of frequencies) into voltages. The resulting signal was compared with a reference voltage and measured, as a function of time, with a data logger (Fluke 2200 B).

The dielectric capacitance of the material contained in the measuring cell is given by¹⁰

$$\epsilon = (V - V_0)/(V_1 - V_0)$$

where V is the voltage associated with the period $\tau = (w - w_0)^{-1}$, V_0 with the period $\tau_0 = (w_1 - w_0)^{-1}$, and V_1 with $\tau_1 = (w_2 - w_0)^{-1}$. The reference voltage V_{ref} [Fig. 1(c)] was adjusted so that $V_{ref} = V_0$. w is the resonant frequency of the circuit indicated in Figure 1(b) when the cell is filled with the material; w_1 and w_2 are, respectively, the corresponding frequencies for the open circuit (nil capacitance) and for air filling the gap. The behavior of the device was checked by measuring the dielectric constants of reference substances. Benzene, chloroform, carbon tetrachloride, toluene, and dioxane were used. The resulting values were in a $\pm 4\%$ range with respect to literature values, showing a satisfactory performance.

RESULTS

Differential Scanning Calorimetry

Isothermal Runs: Figure 2 illustrates two isothermal runs for formulations containing 1.56% BPO. Major features are consistent with previously reported

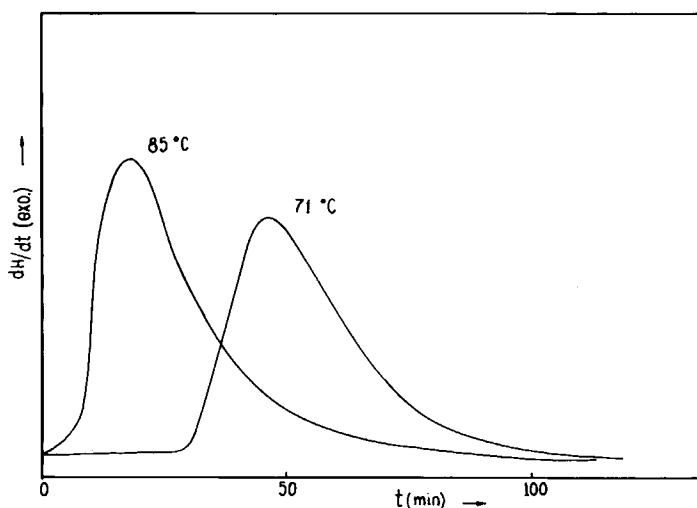


Fig. 2. Isothermal DSC runs for formulations containing 1.56% BPO.

results.^{1,2,6-8} The heat of reaction was 58 ± 3 cal/g (no variation with temperature could be detected within the experimental error). A distinctive behavior was the first-order decay after the maximum rate. Thus,

$$dx/dt = k(1 - x), \quad x > x_{\text{max rate}} \quad (1)$$

or

$$x = 1 - \exp[-k(t - t_0)] \quad (2)$$

The fitting of eq. (2) to experimental runs is shown in Figure 3. Both curves overlap from a conversion close to the one corresponding to the maximum reaction rate. This conversion decreases when temperature increases. For $T = 85^\circ\text{C}$ there is a very good agreement for most of the conversion range.

An Arrhenius plot for the first-order specific rate constant is shown in Figure 4, for two formulations (different batches of UP resin and amounts of BPO). The activation energy is $E \sim 15$ kcal/mol.

The influence of the initiator concentration of the first-order specific rate constant is shown in Figure 5. Results are correlated with an expression of the type

$$k = AI_0^{0.38} \exp(-15/RT) \quad (3)$$

The preexponential factor A may vary slightly from batch to batch of UP resin. However, the induction period varied significantly among different batches, due to the different concentration of inhibitors present in the commercial resins. This is a serious shortcoming for the design of the curing process. One way to avoid this difficulty is to increase the curing temperature shortening the induction time, but also introducing changes in the relevant steps of the free radical

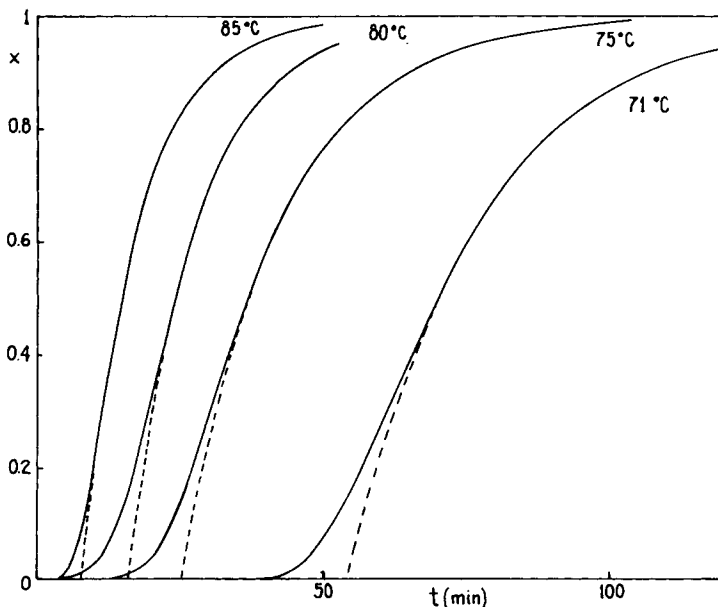


Fig. 3. Conversion-time curves arising from isothermal DSC information (—) (exptl) compared with a first-order rate expression [eq. (2)] (---).

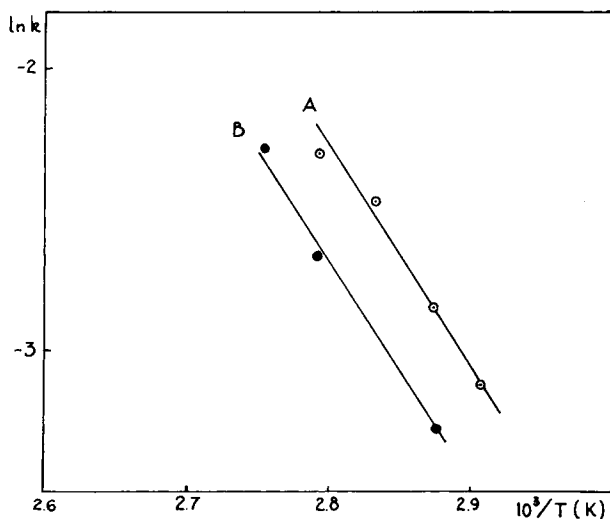


Fig. 4. Arrhenius plot for the first-order specific rate constant: (A) 1.56% BPO; (B) 0.67% BPO (both runs correspond to different batches of unsaturated polyester resin). $E \sim 15$ kcal/mol.

mechanism. In order to study the phenomenological kinetic expression at high temperatures, it is necessary to operate the DSC in the scanning mode.

Runs at a Constant Heating Rate: Figure 6 shows DSC runs at a constant heating rate of $10^\circ\text{C}/\text{min}$ and different % BPO. As reported by Kubota,⁴ two peaks appear. The first one, in the temperature range $100\text{--}160^\circ\text{C}$, may be associated with the copolymerization initiated by peroxide decomposition. The second one, in the temperature range $150\text{--}230^\circ\text{C}$, is related to the thermally in-

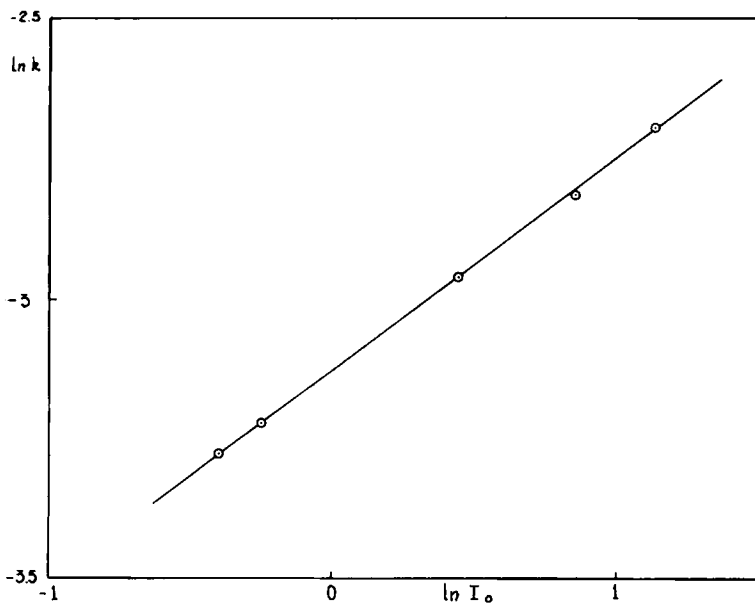


Fig. 5. Influence of the initiator concentration on the first-order specific rate constant ($T = 75^\circ\text{C}$, $k \sim I_0^{0.38}$).

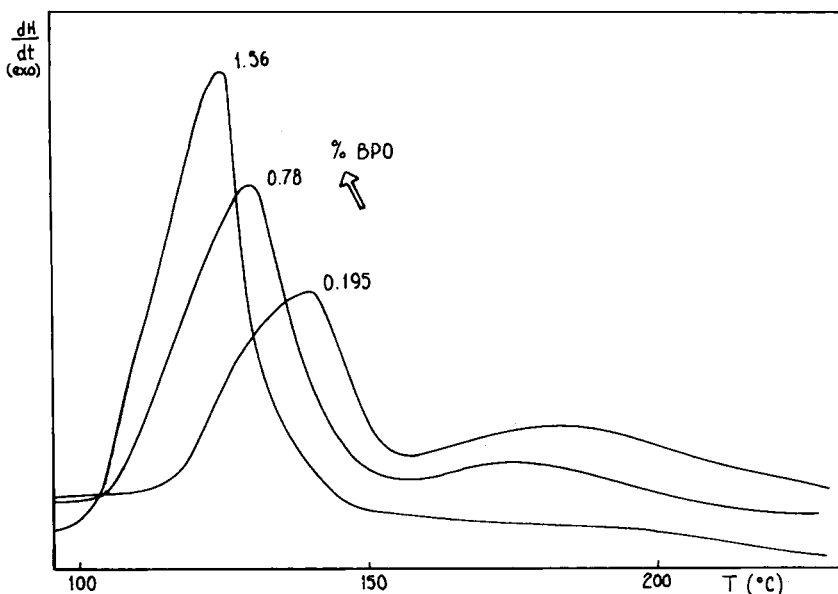


Fig. 6. DSC runs at a constant heating rate of $10^{\circ}C/min$ and different % BPO.

initiated copolymerization. Increasing the peroxide amount produces a corresponding increase in the fraction of area of the first peak. If no peroxide is added a broad peak with a maximum at $215^{\circ}C$ is obtained. In any case, the sum of both areas is constant, giving a heat of reaction equal to $(-\Delta H) = 70 \pm 3$ cal/g. Figure 6 also shows that there is a critical initiator concentration, near 1.5% BPO in our case, for which most of the cure is achieved by the initial peroxide decomposition (the second DSC peak is reduced to a small fraction of the first one). Moreover, the reaction rate clearly increases with the peroxide concentration. These aspects are relevant to the industrial curing in heated molds.

With the value of the total heat of reaction, the fractional conversion achieved in isothermal runs may be calculated. This amounts to $x_{iso} = 58/70 = 0.83$. This behavior was confirmed by measuring the residual reactivity in the scanning mode, for samples which had been isothermally cured. For example, an isothermal run carried out at $80^{\circ}C$ over one night gave $(-\Delta H) = 60$ cal/g. The residual reactivity was 8 cal/g, in rough agreement with what was expected.

The kinetics of the cure initiated by peroxide decomposition (first DSC peak) was obtained from the DSC information using Barrett's method.¹¹ If the kinetic equation is written as

$$dx/dt = Af(x) \exp(-E/RT) \quad (4)$$

then

$$\ln[(dx/dt)/f(x)] = \ln k = \ln A - E/RT \quad (5)$$

A plot of $\ln k$ vs. $1/T$ will be linear if $f(x)$ is correctly chosen. Figure 7 shows such a plot for $f(x) = (1-x)^2$ and three different peroxide concentrations. Values of the preexponential coefficient, activation energy, and correlation coefficient (CC) are shown in Table I, for different peroxide concentrations. If an average activation energy, $\bar{E} = 48.5$ kcal/mol, is chosen and the values of A giving the best

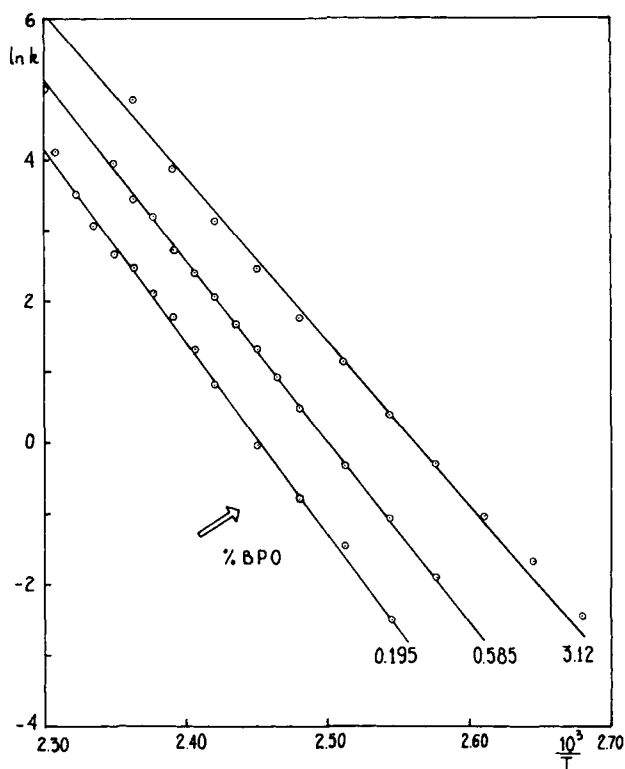


Fig. 7. Second-order regression corresponding to the first peak of nonisothermal DSC runs for samples containing different % BPO ($10^\circ\text{C}/\text{min}$).

correlation coefficient recalculated, the behavior plotted in Figure 8 results. A linear dependence of the specific rate constant on the initiator concentration is obtained. Then, the kinetics of the curing reaction in the high temperature range is given by

$$dx/dt = 5.2 \times 10^{26} (\text{min}^{-1}) I_0 (\% \text{ BPO}) \exp(-48.5/RT)(1-x)^2 \quad (6)$$

A complete change with respect to the curing in the low temperature range has resulted. At high temperatures one is no longer concerned with induction or rate-increasing periods. A simple phenomenological n th-order equation is adequate to describe the curing. When cobalt was used as accelerator, the kinetics also showed a first-order dependence with respect to the initiator, a low activation energy and an n th order ($2 \leq n \leq 4$) behavior with respect to conversion.⁹

TABLE I
Kinetic Parameters for the Second-Order Regression of Nonisothermal DSC Runs

% BPO	A (min^{-1})	E (kcal/mol)	CC
0.195	8.34×10^{28}	53.9	0.9986
0.585	4.78×10^{27}	50.6	0.9996
0.78	2.46×10^{26}	48.1	0.9965
0.78	1.10×10^{26}	47.7	0.9983
1.56	1.14×10^{23}	41.5	0.9909
3.12	4.27×10^{25}	45.7	0.9972

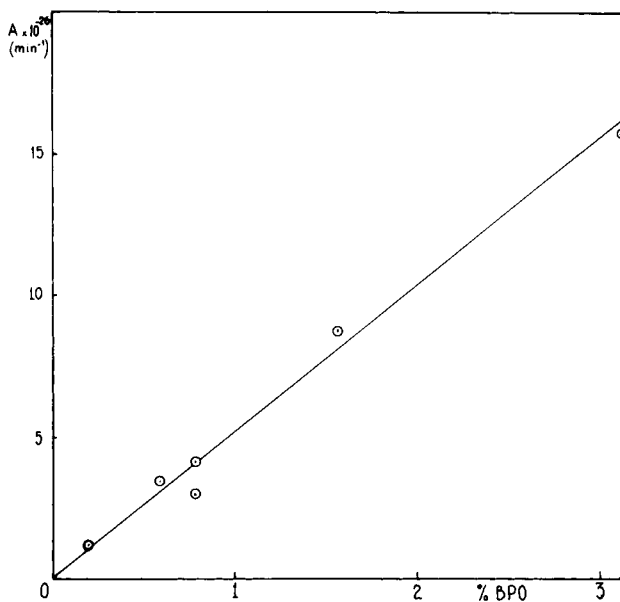


Fig. 8. Influence of the initiator concentration on the specific rate constant for an average activation energy, $\bar{E} = 48.5$ kcal/mol.

It is worth to point out that similar kinetic parameters were obtained at different heating rates or by processing the experimental information with the method of Freeman and Carroll.¹² Regarding the approaches to dynamic kinetics suggested by Draper¹³ and McCallum and Tanner¹⁴ and used by Prime^{15,16} for the curing of thermosetting polymers, they have been shown to be incorrect (i.e., see the discussion by Šesták¹⁷).

Dielectric Capacitance

All the results reported in this section were obtained in the device described in the experimental section, using a formulation containing 1.82% BPO and operating isothermally in the temperature range 69–101°C. Figure 9 shows the relative variation of the dielectric capacitance of the polymerizing mixture, for the curing at different temperatures. ϵ_0 and ϵ_∞ are, respectively, the initial and final values of the dielectric capacitance. There is an unsteady state, not shown in the figure, corresponding to the heating up of the resin to the desired curing temperature. ϵ decreases during the initial heating and then remains stable during the induction period; time 0 in the figure corresponds to the start of the reaction. A qualitative correlation between changes in dielectric capacitance and the kinetics of the isothermal curing process is observed.

The dielectric behavior of polar plastics is largely determined by dipole orientation.¹⁸ The decrease in the dielectric capacitance may be mainly associated with the partial immobilization of the permanent carbonyl dipoles belonging to the UP molecules when they are crosslinked through a free radical mechanism. That is to say, the change in dielectric capacitance will be strongly related to the crosslinking of an unsaturated polyester unit, rather than a styrene unit.

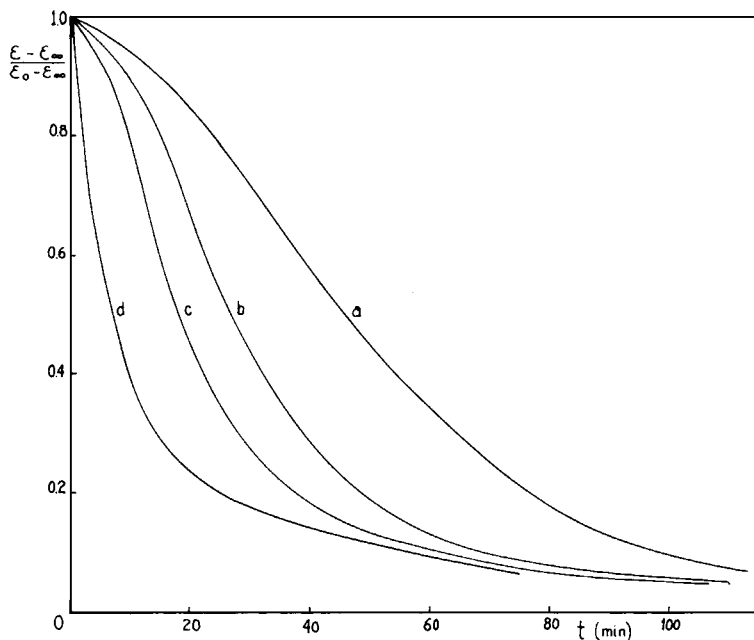


Fig. 9. Relative variation of the dielectric capacitance of the polymerizing mixture for the curing at different temperatures: (a) 69.3°C; (b) 79.0°C; (c) 84.4°C; (d) 101.0°C.

The conversion of UP units measured by the dielectric capacitance may be defined as

$$x_{UP} = (\epsilon_0 - \epsilon) / (\epsilon_0 - \epsilon_\infty) \quad (7)$$

If, similarly to the isothermal DSC runs, a first-order kinetics is proposed, it results

$$dx_{UP}/dt = k_{UP}(1 - x_{UP}) \quad (8)$$

or

$$\ln [1/(1 - x_{UP})] = k_{UP}(t - t_0) \quad (9)$$

Figure 10 shows such a plot for different curing temperatures, taking the actual induction periods into account. As in the isothermal DSC runs a good correlation is obtained after a certain conversion which varies with curing temperature. An Arrhenius plot of k_{UP} is shown in Figure 11. The dashed line corresponds to the first-order specific rate constant of the overall reaction, as measured by DSC, and for 1.82% BPO. The activation energy for k_{UP} is $E_{UP} = 8.8$ kcal/mol. The comparison of isothermal conversion–time curves arising from DSC (x) and dielectric capacitance measurements (x_{UP}) is shown in Figure 12, starting after the induction period.

DISCUSSION

One clue to understanding the phenomenological changes observed in the reaction kinetics in different temperature ranges is to analyze the initiator decomposition rate. Benzoyl peroxide has a 10-h half-life at 72°C and a 0.4-h half-life at 100°C.¹⁹ Its decomposition follows a first-order kinetics with an

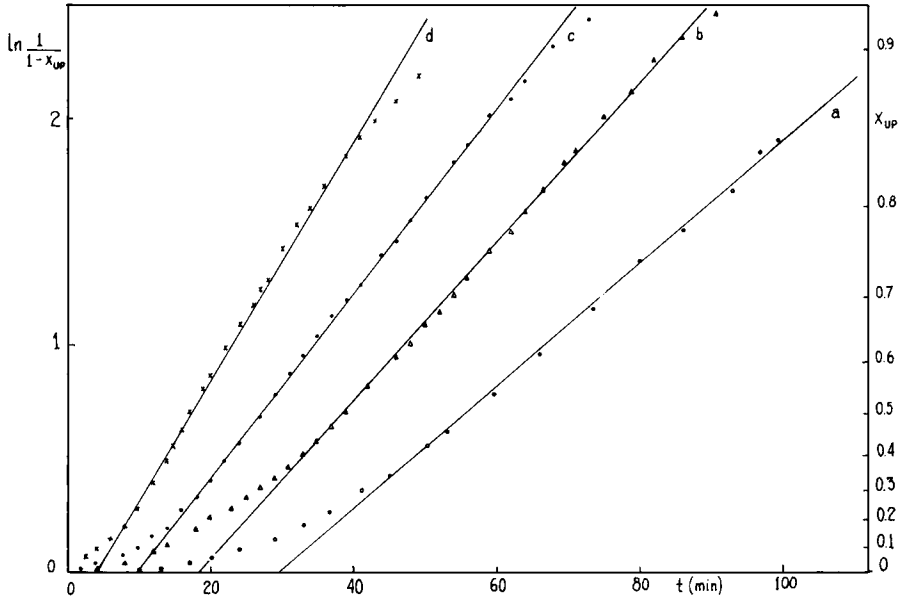


Fig. 10. First-order correlation of the relative changes in dielectric capacitance for different curing temperatures: (a) 69.3°C; (b) 74.2°C; (c) 79.0°C; (d) 89.0°C.

activation energy $E_i = 30 \text{ kcal/mol}$.^{1,20} By relating the half-life $t_{1/2}$ with the polymerization time t_p two limiting cases may be proposed. When $t_{1/2} \gg t_p$ (low temperatures), polymerization takes place at an almost constant initiator concentration. When $t_{1/2} \ll t_p$ (high temperatures), the initiator is almost com-

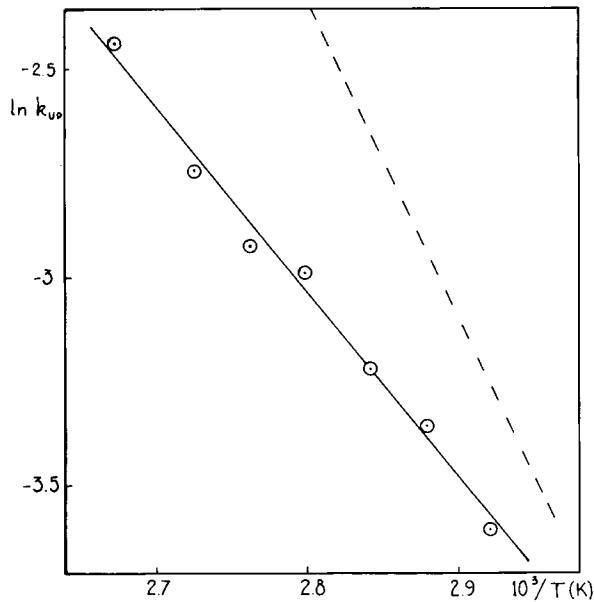


Fig. 11. Arrhenius plot for the first-order specific rate constant k_{UP} , arising from changes in the dielectric capacitance of the polymerizing mixture. The dashed line corresponds to the first-order specific rate constant of the overall reaction, as measured by DSC and for the same % BPO.

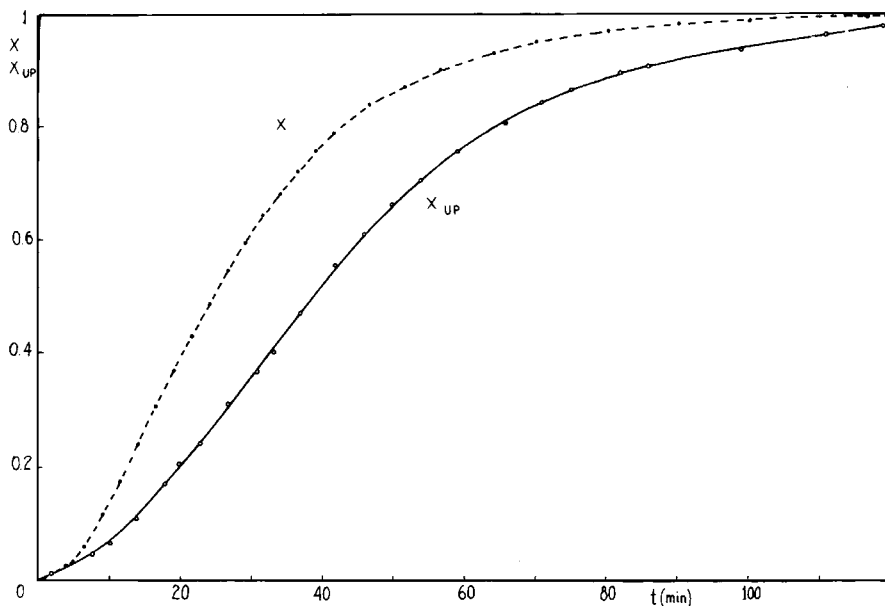
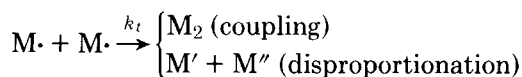
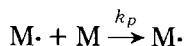
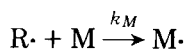
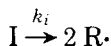


Fig. 12. Comparison of isothermal conversion-time curves arising from DSC (x) and dielectric capacitance measurements (x_{UP}) ($T = 74.2^\circ\text{C}$, BPO = 1.82%).

pletely depleted from the very beginning of the reaction, i.e., a flash initiation takes place. Both cases will be analyzed separately.

Low Temperatures

The classical free radical mechanism is assumed to hold:



I is an initiator molecule giving place to two radicals $R\cdot$; M is an unsaturation belonging to any one of the reactants. The reaction of $R\cdot$ with the inhibitor is assumed to be very much faster than the reaction with M . This last step does not take place until the inhibitor concentration has been sufficiently depleted. This occurs during the induction period.

With the usual assumptions [(i) the propagation reaction is the only consumer of unsaturation and (ii) a steady state is reached, where the radical population does not change rapidly with time], the following kinetic expression is obtained

$$-dM/dt = k_p(k_i/k_t)^{0.5}MI^{0.5} \quad (10)$$

The rate constant k_i includes the efficiency with which the initiator fragments successfully react with monomer.

Equation (10) gives a semiquantitative agreement with major experimental trends:

(a) The autoacceleration is explained by the increase in the ratio $k_p/k_t^{0.5}$ with the corresponding increase of the liquid viscosity and the subsequent production of a rubber phase after the gel conversion. Both propagation and termination steps are assumed to be controlled by diffusion of polymeric segments and monomer molecules over almost the whole range of conversion.¹ As shown in Figure 3, autoacceleration is more enhanced at lower reaction temperatures. This is consistent with previous reported results.¹

(b) When $k_p/k_t^{0.5}$ reaches a constant value, eq. (10) predicts a first-order dependence with respect to unsaturations and a 0.5-order dependence with respect to actual initiator concentration. The first-order kinetics is in agreement with experimental results (Fig. 3). If, on the other hand, the initiator decomposition rate is low and the initial inhibitor amount is much less than I_0 , actual initiator concentration $I \rightarrow I_0$. Thus, the theoretical 0.5-order is close to the experimental value, as shown in Figure 5.

(c) The apparent activation energy is given by

$$E = E_p + 1/2 (E_i - E_t)$$

The experimental result, shown in Figure 4, will agree with the model prediction if $E_p - E_t/2 = 0$. In fact, selected propagation and termination rate constants for chain polymerizations²¹ show this difference to account for 1–6 kcal/mol.

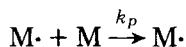
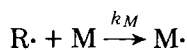
Regarding the change in the dielectric capacitance during the curing, it does only show a qualitative agreement with chemical kinetics, as measured by DSC. The decrease in the dielectric capacitance may be mainly associated with the increasing difficulty of the UP molecules, containing permanent dipoles, to migrate in the electric field. The apparent activation energy, shown in Figure 11, lies in the range 7–10 kcal/mol reported by Horie et al.¹ for the diffusion of unsaturated polyester radicals in the copolymerization with styrene. On the other hand, Figure 12 shows that the partial immobilization of UP fragments lags behind the overall chemical conversion. This result is consistent with infrared spectroscopy determinations carried out by Horie et al.,¹ showing that the fraction of UP incorporated into the network was less than the initial stoichiometric amount.

High Temperatures

It is assumed that the initiator decomposes so rapidly that, at $t = 0$, the free radical concentration is

$$R\cdot = 2 f I_0$$

where f is the efficiency of the decomposition reaction. The following mechanism is supposed to take place:



The termination step is a transfer reaction leading to an inactive radical (i.e., an intramolecular hydrogen abstraction). If k_M is sufficiently low, $R\cdot = 2fI_0$ is kept almost constant, and a steady state may be reached for the $M\cdot$ radicals,

$$M\cdot = (k_M/k_t)R\cdot M = (k_M/k_t) 2fI_0M$$

Accepting that the propagation reaction occurs so much more often than the others that it is effectively the only consumer of unsaturations, we get

$$-dM/dt = 2(k_M k_{pf}/k_t) I_0 M^2 \quad (11)$$

Equation (11) agrees with experimental observations: second order with respect to unsaturations and first order with respect to initiator concentration.

In conclusion, the bulk copolymerization of unsaturated polyester with styrene follows different kinetic laws depending on the initiator decomposition rate (k_i). At low k_i values a classical free radical mechanism allowing for a gel effect, explains most of the experimental observations. At high k_i values, a change in the nature of the termination step gives a mechanism accounting for the observed second-order kinetics. Of course, the suggested mechanism must be regarded as a mere possibility explaining the overall behavior. More research work is needed in this particular temperature range, which is precisely the most important for processing purposes. Another important point is the initial peroxide amount. It has a bearing not only on kinetics, but in the possibility of curing by thermal copolymerization when temperature goes over approximately 160°C. In order to avoid this second mechanism, thus curing at lower temperatures, the initiator concentration must exceed a certain critical value.

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