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# Unsaturated Polyester Resins: a Study of the Mechanism and Kinetics of the Curing Process by FTIR Spectroscopy

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The polymerization of a commercial grade polyester resin was investigated by Fourier Transform Infrared Spectroscopy. The conversion profiles of both the styrene and the polyester unsaturations were obtained in a temperature range from 336 K to 363 K. The kinetic data were interpreted in terms of the reaction mechanism and the molecular mobility of the reactants in the system. An attempt was made to describe the behavior of the system by using two different model equations. It was found that a model widely used in the literature did not describe satisfactorily the experimental data; better results were obtained by using a more general form of the same model equation.

Keywords: FTIR; Kinetics; Modelling; Unsaturated Polyester

## INTRODUCTION

Unsaturated polyester, UPE, resins are among the most widely used thermosetting materials due to their low cost and to the advantages they offer such as light weight and reasonably good mechanical properties.<sup>1</sup> They are employed in the fabrication of a broad range of products such as structural parts of automobiles, building materials, coating materials, and electrical parts. The development of bulk molding compound, BMC, and sheet molding compound, SMC, technology has given further impetus to the application of these resins into a variety of major areas. In general, unsaturated polyester resins are prepared by condensation of unsaturated and saturated dicarboxylic acids or anhydrides with glycols and dilution with unsaturated monomers (generally styrene, St). Variation in the type and in the relative ratios of each of these components allows an enormous flexibility in the design of resin formulations. However, the processing of these materials, as that of all thermosetting resins, requires an understanding of the reaction kinetics during cure, together with a basic understanding of their complex flow behavior. For such a reason a fairly large number of kinetic studies has been reported so far on UPE resins,<sup>2,3</sup> but only recently few contribution have concentrated on kinetic studies encompassing the whole conversion range.<sup>4,5,6</sup> This is because most of the research has been either product-oriented or engineering-oriented. In

the first case<sup>7,8</sup> attention was focused on the analysis of the final product in terms of conversion of styrene vinyls and polyester vinylenes with no attempt to follow the whole conversion profiles for the two reactive species.

The second approach<sup>2,3</sup> considered the curing reaction as a simple free radical homopolymerization, without differentiating between the reactivity of styrene and polyester double bonds. Although such a simplifying scheme can serve to empirically describe the kinetic behavior of the system by using techniques such as differential scanning calorimetry, DSC, it cannot provide detailed information regarding the reaction mechanism and how it is affected by parameters such as temperature, composition of the reactive mixture, and reactants conversion.

In the present contribution we have carried out a kinetic analysis on a commercial grade UPE resin in the temperature range from 336 to 363 K. The technique used to monitor in real time the consumption of the reactive species in the system was Fourier Transform Infrared Spectroscopy, which is known to be highly specific in detecting different functional groups and offer the additional advantages of sensitivity, optical stability, and high data collection rate. The kinetic data thus obtained have been discussed in terms of the currently accepted molecular mechanisms of the curing process as well as in terms of the reactants' molecular mobility.

Finally the kinetic behavior of the two reactive species was simulated by using two different models. It was found that a model widely used in the literature did not describe satisfactorily the experimental data; better results were obtained by using a more general form of the same model equation.

## EXPERIMENTAL SECTION

### MATERIALS

The UPE resin was an uncured, unsaturated polyester kindly supplied by Lonza S.p.A. The resin was available either as solution containing 33 wt% styrene, or in the form of the pure prepolymer. The acid number of the prepolymer, defined as the mg of KOH used for the titration of 1 g of prepolymer was 19.2. The OH number, obtained by titration of the excess acetic anhydride used to fully esterify the hydroxyl groups was 53.4. This cor-

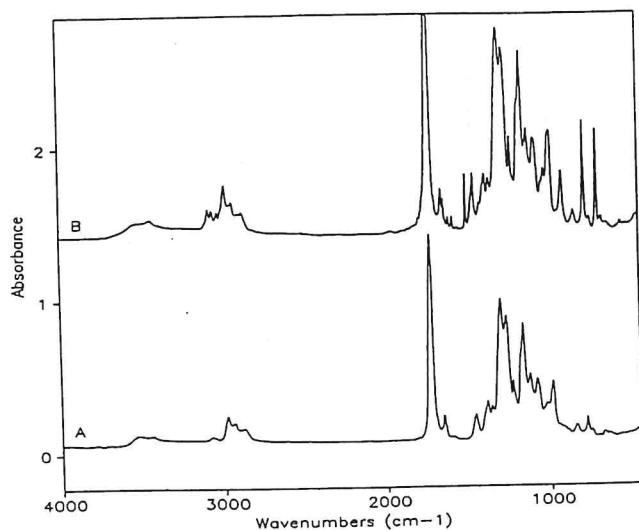


Figure 1. FTIR transmission spectra in the frequency range 4000-450  $\text{cm}^{-1}$  of: A) Polyester prepolymer; B) Uncured polyester/styrene mixture.

responds to 0.34 mmol of COOH groups and 0.95  $\mu\text{mol}$  of OH groups per gram of resin. The polyester prepolymer had a number average molecular weight,  $M_n$ , of  $2.4 \times 10^3$ , and a weight average molecular weight,  $M_w$ , of  $8.0 \times 10^3$ . It had an average number of double bonds per chain equal to 9.5, and the initial molar ratio between styrene and polyester unsaturations was 1.1.

In the resin formulation 0.1 wt% hydroquinone was used as inhibitor to prevent premature curing.

#### TECHNIQUES

FTIR spectra were collected on thin films (5-10  $\mu\text{m}$ ) of the uncured resin, obtained by sandwiching a drop of the reactive mixture between two KBr windows. A Nicolet 5DX-B spectrometer used was equipped with a deuterated triglycine sulfate detector, DTGS, and a Germanium on KBr beam splitter. The scanned wavenumber range was 4000-400  $\text{cm}^{-1}$ . The frequency scale was internally calibrated to an accuracy of 0.02  $\text{cm}^{-1}$  by a He/Ne reference laser. The interferograms were Fourier transformed using an Happ-Ganzel apodization function.

The temperature measurements were carried out in a SPECAC temperature chamber directly mounted in the spectrometer. This unit was driven by an Eurotherm 071 temperature controller to an accuracy of  $\pm 0.5^\circ\text{C}$ .

## RESULTS AND DISCUSSION

### BAND ASSIGNMENTS AND DATA ANALYSIS

The spectra of the polyester prepolymer, UPE, and of the St/UPE mixture used throughout this investigation are reported in Figures 1A and 1B respectively in the frequency range from 4000 to 400  $\text{cm}^{-1}$ .

Table 1: Peak positions and tentative assignments for the UPE prepolymer

Peak frequency, $\text{cm}^{-1}$	Tentative assignment
3534 w	VOH
3441 w	overtone VC=O
3081 w	aromatic VC-H
2985 w	$\nu\text{CH}_3$ asym.
2942 w	$\nu\text{CH}_2$ asym.
2882 w	$\nu\text{CH}_3$ sym.
1725 vs	VC=O
1645 w	VC=C
1454 w	$\delta\text{CH}_3$ asym.
1381 m	$\delta\text{CH}_3$ sym./ $\gamma\text{CH}_2$
1354 m	-
1296 s	VC-O
1261 s	VC-O
1225 m	-
1160 s	$\delta\text{CH}$ sym.
1119 m	Alkyl CH rock
1076 m	Alkyl CH rock
1018 w	$\nu\text{O-R}$ asym.
984 m	$\gamma=\text{CH}_2$ trans
841 w	VC-C sym.
775 w	VC-C asym.
746 w	$\gamma\text{C-H}$ , aromatic
673 w	$\gamma\text{C=O}$

s=strong; m=medium; w=weak; v=stretching;  
 $\delta$ =bending;  $\gamma$ =out of plane def.

Due to the complex and often ill defined molecular structure of the UPE molecule, normal coordinate analysis of UPE has yet to be reported. However, based on group frequency assignments<sup>9,10</sup> and on the IR analysis of low molecular weight analogs<sup>11,12</sup> the main peaks observed in the UPE spectrum can be assigned with sufficient degree of confidence. These tentative assignments are reported in Table 1.

As expected the most difficult region to assign is the 1300-1200  $\text{cm}^{-1}$  range, where strong, multiple absorptions due to C-O-C stretching modes are observed. The difficulty arises from the well-known conformational sensitivity of these modes.

For the purpose of the present investigation we are seeking for sufficiently well resolved peaks characteris-

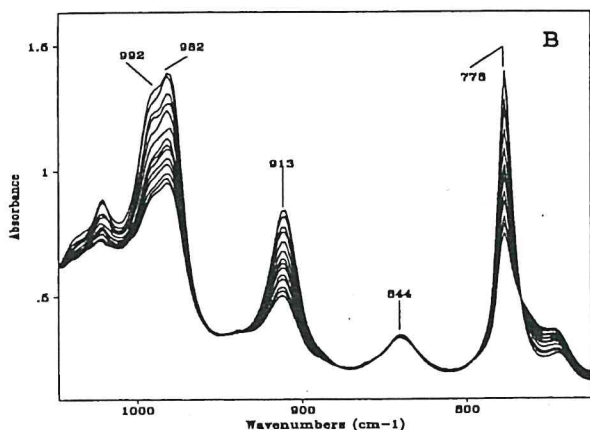
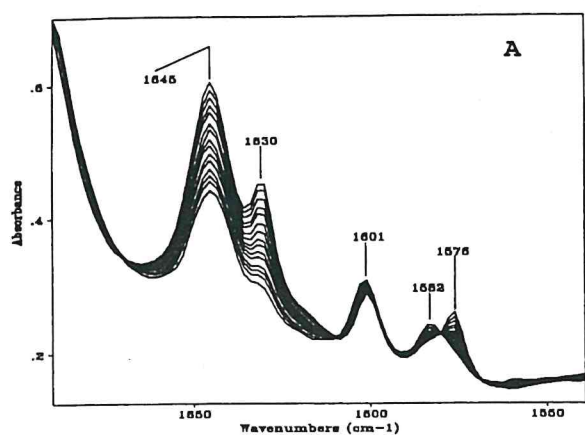


Figure 2. Real time spectroscopic monitoring of the curing reaction. The spectra were collected at different reaction times at 348 K. The two figures display the analytical frequency ranges: A) 1700-1500  $\text{cm}^{-1}$ ; B) 1100-1000  $\text{cm}^{-1}$ .

of the different types of unsaturations present in the system. The fumarate double bonds of UPE give rise to two such absorptions at 1645  $\text{cm}^{-1}$  (C=C stretching) and at 983  $\text{cm}^{-1}$  (trans -CH=CH- wagging). However, when St is present, a further peak is detected at 1630  $\text{cm}^{-1}$  (C=C stretching in St) which is only partially resolved from the fumarate absorption at 1645  $\text{cm}^{-1}$ . It should also be noted that both these peaks have low absorptivities. The styrene double bonds presents two characteristic modes in the =C-H wagging region. One is found at 992  $\text{cm}^{-1}$  and is due to a trans CH=CH- wagging and the other at 910  $\text{cm}^{-1}$  arises from a vinyl =CH<sub>2</sub> wagging. Both these peaks have high intensity but the former is completely overlapped with the already mentioned fumarate absorption at 980  $\text{cm}^{-1}$ , while the latter is completely free from any interfering absorption.

Several methods have been proposed in the literature to resolve the two components at 992 and 980  $\text{cm}^{-1}$  and,

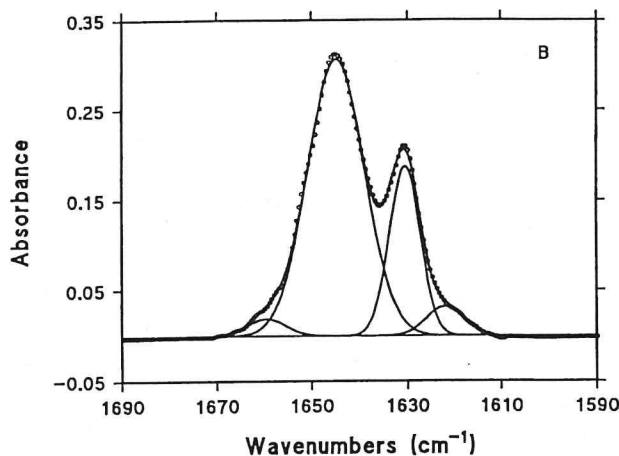
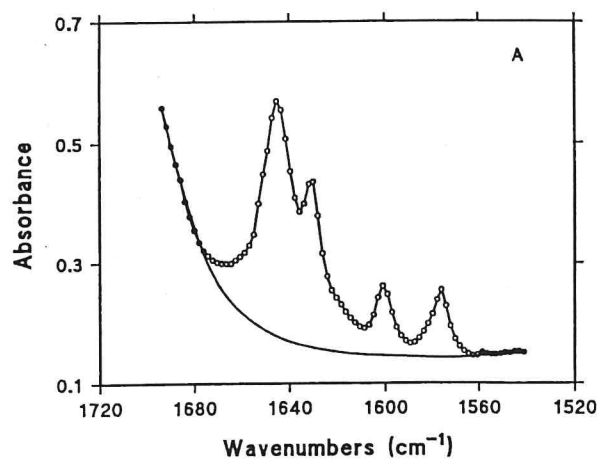


Figure 3. Curve fitting analysis in the 1700-1600  $\text{cm}^{-1}$  region: A) Experimental spectral profile with the evaluated pseudo-baseline. The solid circles represent the data points used to calculate the 4th order polynomial fit. B) The four gaussian components obtained by best fitting the experimental data points.

based on a series of simplifying assumptions, to provide quantitative kinetic information.<sup>4,5,13</sup> However, due to the complexity of the spectral profile in this region and especially to the difficulty in defining a reasonable base line, we preferred to turn our attention to the less severely overlapped region between 1700 and 1600  $\text{cm}^{-1}$ .

Our experimental data were analyzed by a two-step procedure: first a pseudo base line was found in the region of interest by using a 4th order polynomial regression (see Figure 2A). After subtraction of this baseline, the resulting spectral profile was separated into the individual components by applying an iterative curve fitting algorithm based on a least squares refinement procedure.<sup>14</sup>

To insure the uniqueness of the results, the peak shape (gaussian), the number of peaks and the peaks position (as evaluated by second derivative analysis), and the baseline were kept fixed, while the program was allowed to calculate, by best fitting the experimental data, the

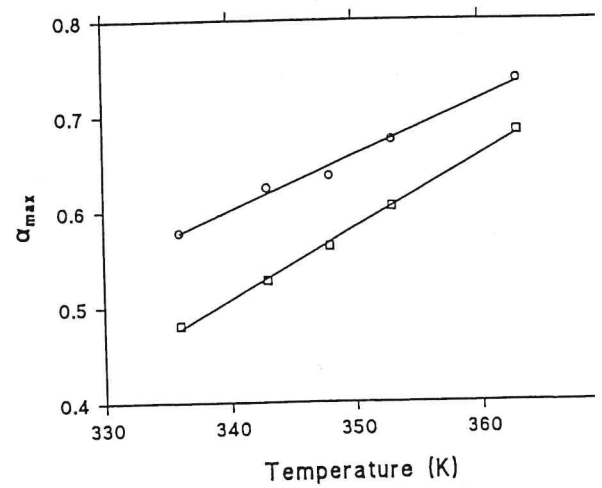
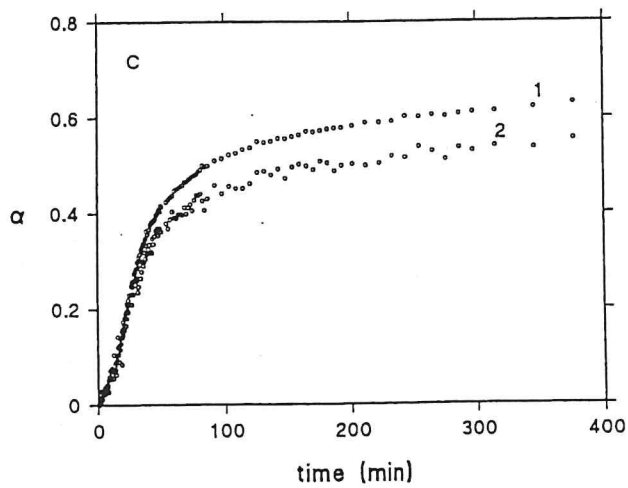
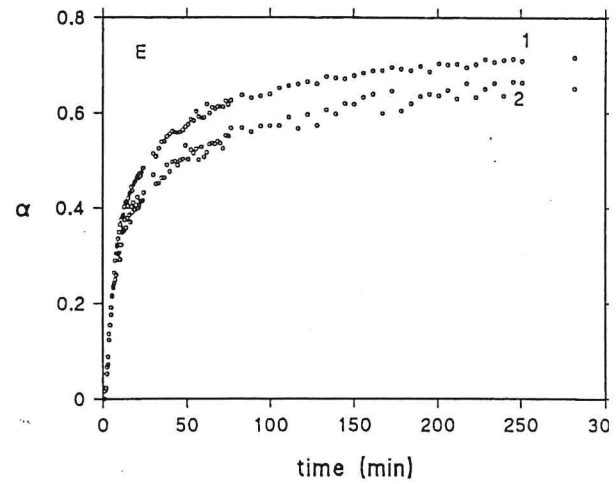
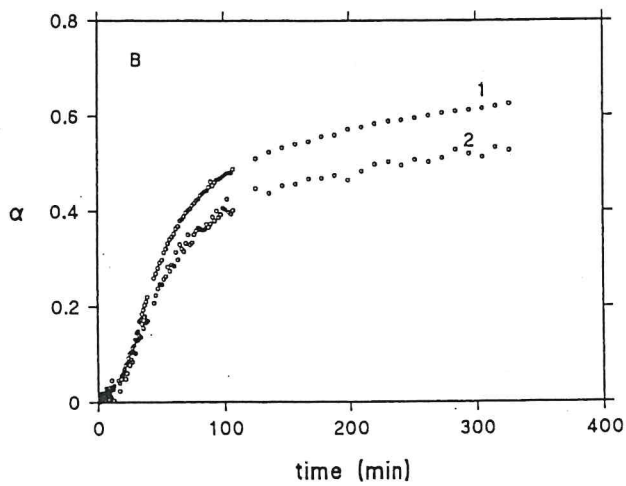
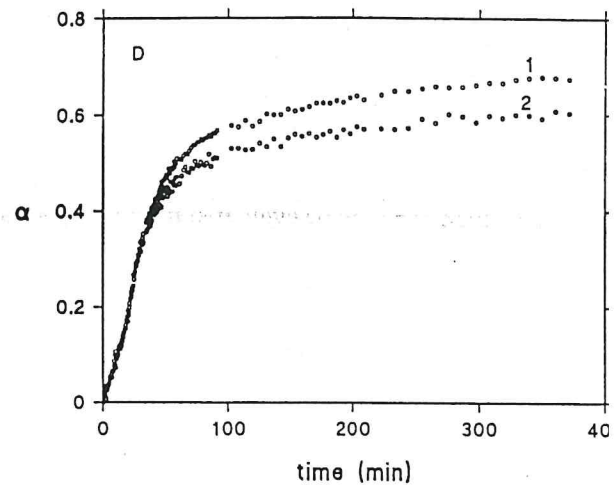
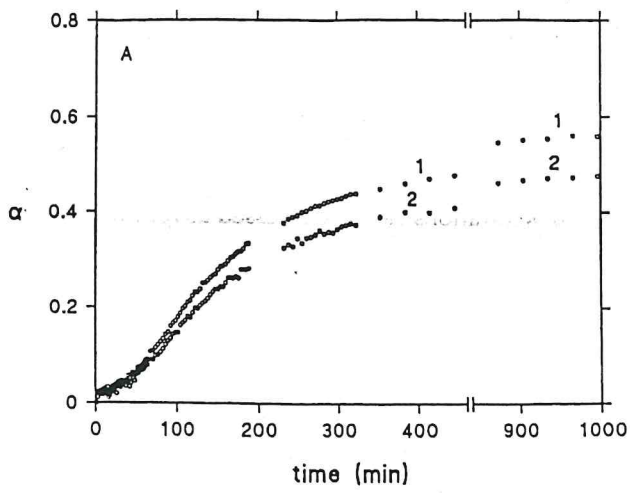


Figure 4. Conversion versus time curves for the styrene unsaturations (curves 1) and for the UPE double bonds (curves 2) at the various investigated temperatures: A) 336 K; B) 343 K; C) 348 K; D) 353 K; E) 363 K.

Figure 5. Final conversion values for the styrene unsaturations (O) and for the UPE unsaturations (□) as a function of the curing temperature.

height and the full width at half height, FWHH, of the components. Typical results from such an analysis are presented in Figure 2B. Note the presence of two unidentified low intensity absorptions along the wings of the two main components.

The relative conversion of the various reactive species participating in the curing process as a function of reaction time can now be evaluated from the spectral data:

$$\alpha = \frac{C_0 - C_t}{C_0} = 1 - \frac{C_t}{C_0}$$

and, from the Beer-Lambert law:

$$\alpha = 1 - \frac{A_t}{A_0}$$

where the symbols have the usual meaning and the subscripts 0 and t refer to times 0 and t respectively.

The parameter  $\alpha$  for the St unsaturations can be evaluated from both the peaks at  $1630 \text{ cm}^{-1}$  and at  $912 \text{ cm}^{-1}$ . As already noted the  $912 \text{ cm}^{-1}$  peak is free from any interfering absorption and yields "true"  $\alpha_{St}$  values, while the  $\alpha_{St}$  values from the  $1630 \text{ cm}^{-1}$  component can be used to cross-check the validity of the curve fitting analysis. It has been found that when the experimental absorbance of the  $1630 \text{ cm}^{-1}$  peak is used, the  $\alpha_{St}$  values are higher than those from the  $912 \text{ cm}^{-1}$  peak over the whole time scale. However, when the absorption of the  $1630 \text{ cm}^{-1}$  component obtained by curve fitting is considered, the  $\alpha_{St}$  values coincide with those from the  $912 \text{ cm}^{-1}$  peak. This effect is due to the interference of the absorption at  $1645 \text{ cm}^{-1}$  which, as clearly shown in Figure 2B, increases the apparent absorbance of the  $1630 \text{ cm}^{-1}$  component by about 10% of its true value. On the other hand, the same figure demonstrates that the latter peak is too low in intensity to influence appreciably the  $1645 \text{ cm}^{-1}$  component.

In summary to evaluate  $\alpha_{St}$  from the  $1630 \text{ cm}^{-1}$  peak, it is necessary to perform curve fitting analysis while  $\alpha_{UPE}$  can be directly evaluated from the experimental absorbance value at  $1645 \text{ cm}^{-1}$ .

#### THE KINETICS OF THE CURING PROCESS AS A FUNCTION OF TEMPERATURE

The conversion versus time curves for the UPE and for the St double bonds at various reaction temperatures are reported in Figures 4A to 4E. It is immediately apparent that, in the investigated temperature range (336 - 363 K), the initial reaction rate as well as the final conversion values increase with increasing the temperature. All the curves, except those at 363 K display an "s" shape which is evident at 336 K and becomes gradually less pronounced as the reaction temperature increases. As shown in Figure 5 the final conversion values for both the St and the UPE unsaturations increase linearly with the reaction temperature. To analyze the kinetic behavior of this com-

plex system we have to consider the reaction mechanism in detail. The peroxide initiated crosslinking of an unsaturated polyester resin in the presence of styrene is essentially a copolymerization reaction; three different reactions are possible: styrene-polyester, styrene-styrene and polyester-polyester. Accordingly, the reaction rates relative to the styrene monomer and to the polyester unsaturations can be expressed as follows:

$$-d[St]/dt = K_{St,St}[St\bullet][St] + K_{UPE,St}[UPE\bullet][St]$$

$$-d[PE]/dt = K_{St,UPE}[St\bullet][UPE] + K_{UPE,UPE}[UPE\bullet][UPE]$$

where  $[St]$  is the concentration of styrene monomer,  $[UPE]$  is the concentration of fumarate double bonds and  $[St\bullet]$  and  $[UPE\bullet]$  are the concentrations of the respective radical species.  $K_{St,St}$ ,  $K_{St,UPE}$  and  $K_{UPE,UPE}$  are rate constants.

Assuming a steady-state regime, if polyester-polyester reactions are neglected, the copolymerization equation becomes:

$$d[St]/d[UPE] = 1 + r_s [St]/[UPE]$$

where  $r_s = K_{St,St}/K_{St,UPE}$ . The copolymerization occurs under azeotropic conditions if  $[UPE]/[St] = 1 - r_s$ , which yields the relationship:

$$d[St]/d[UPE] = [St]/[UPE]$$

In such conditions the copolymer composition is exactly equal to the feed composition and the entire process occurs without a change in the feed composition.

Based on the above equations, if we plot  $\alpha_{St}$  as a function of  $\alpha_{UPE}$  a  $45^\circ$  line would characterize near azeotropic behavior. In Figures 6A to 6E such plots are presented for various investigated temperatures.

At 336 K a very high linear correlation among the data is found (correlation coefficient,  $r^2 = 0.999$ ); however the experimental straight-line lies above the  $45^\circ$  reference line in the whole conversion range, with a slope of 1.20. The linear behavior extending over the whole process indicates that the overall reaction mechanism is not appreciably affected by the reactants conversion and in particular by the bulk viscosity of the system which is known to increase as the cross-linking reaction proceeds. The fact that the experimental curve lies always above the reference line indicates that the styrene conversion is always higher than the polyester conversion, as can be readily noted also from the kinetic curve of Figure 4A.

The final values of  $\alpha_{St}$  and of  $\alpha_{UPE}$  are 0.56 and 0.48, respectively which means that, at the end of the process, 1.17 styrene vinyl groups have been consumed for every polyester vinylene reacted. This value represents the av-

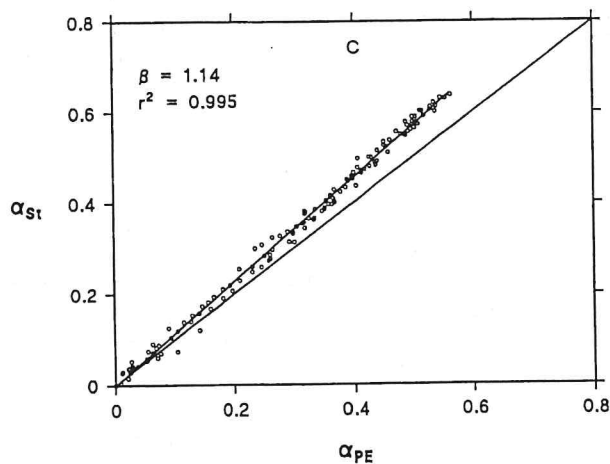
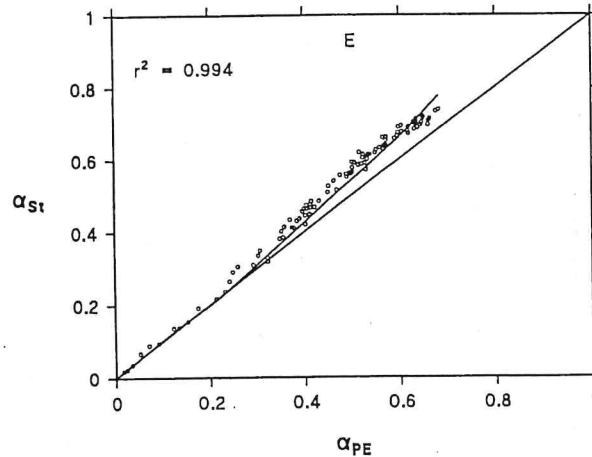
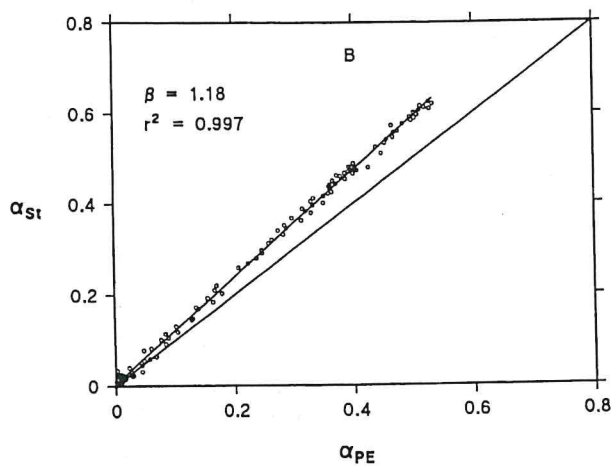
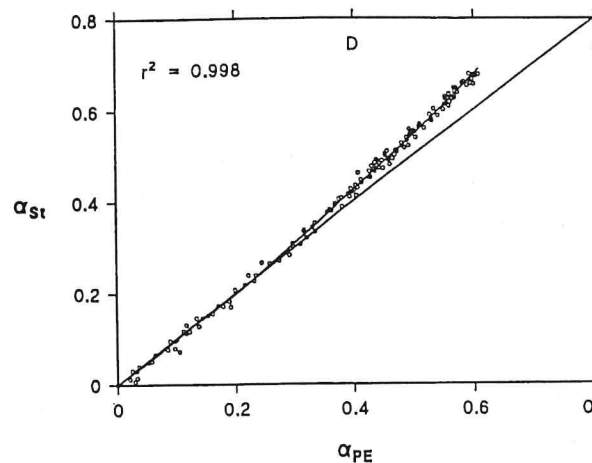
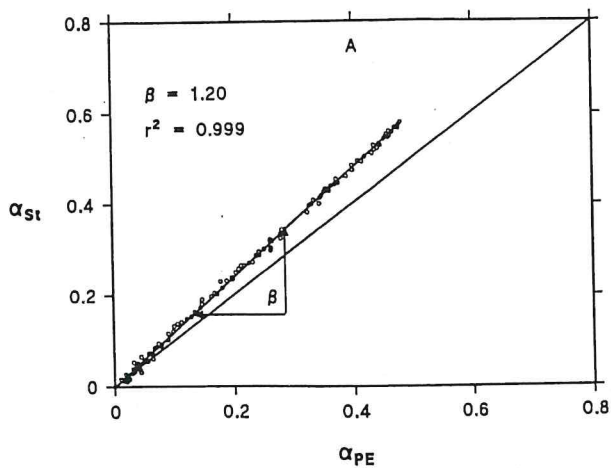


Figure 6. Styrene conversion versus UPE conversion at various investigated temperatures: A) 336 K; B) 343 K; C) 348 K; D) 353 K; E) 363 K. Slopes of linear least squares fit,  $\beta$ , and correlation coefficients,  $r^2$ , as indicated.

average crosslink length of styrene chains through which the vinylene groups of the adjacent UPE molecules (intermolecular crosslinks) or of the same UPE molecule (intramolecular crosslink) are connected. This value dif-

fers only slightly from the average crosslinking derived predicted by the near azeotropic copolymerization mechanism which is equal to 1.1 in the system under investigation owing to the initial stoichiometry of reactive mixture (see experimental section).

The observation that the styrene conversion is higher than the UPE conversion can be ascribed to a molecular mobility effect. The vinylene double bonds in the polyester molecules must have a proper orientation to react with the styrene vinyls. This orientation process may be slow at 336 K, owing to the reduced mobility of the long UPE chains at this temperature. Increasing temperature should increase the molecular mobility of UPE chains and, as a consequence the orientation of the UPE vinylenes. Thus a reduction of the average crosslink length of styrene in the network would be expected at higher temperatures. This effect is indeed observed. The experimental curves at 343 K and 348 K are still linear over the whole conversion range (correlation coefficients = 0.998 and 0.997, respectively) but they are both closer to the reference line relative to the near azeotropic behavior (the slopes calculated by a linear least squares fit of the data points are 1.18 and 1.14, respectively).



At 353 K and at 363 K the St-UPE conversion-conversion plots exhibit a slightly different behavior. Up to a value of  $\alpha_{\text{UPE}}$  equal to about 0.35 the data points fall onto the 45° reference line while, at higher UPE conversion, a gradual up bending of the curve is observed. As a matter of fact, in these two cases a second order polynomial fit gives a better correlation coefficient than a linear least squares fit.

Thus, at temperatures of 353 K or higher the copolymerization behavior seems to be more dependent on the reactants conversion than at lower temperatures. A possible explanation of this effect is the following: in the first stage the behavior is exactly azeotropic owing to a sufficient molecular mobility of the UPE molecules compared to the styrene monomer. At  $\alpha_{\text{UPE}}$  higher than 0.35 however, the UPE mobility becomes hindered by the formation of a three-dimensional network which, on the contrary does not affect appreciably the mobility of the low molecular weight styrene monomer.

To summarize we can state that at 336 K the UPE molecular mobility is always low with respect to styrene thus causing  $\alpha_{\text{St}}$  to be higher than  $\alpha_{\text{UPE}}$  in the whole conversion range. At 353 K or above the UPE molecular mobility is initially comparable with that of styrene but is gradually reduced by the network formation. In these conditions the crosslinking density of the resulting network at the end of the curing process is higher than that at lower temperatures.

#### MODELLING THE CURE KINETICS

As we have already noted in the previous paragraph the curing reaction of unsaturated polyester resins is a very complex process. A rigorous treatment of all the propagation and termination steps involved in such a process is a very difficult task. In addition, the effect of diffusion control on the kinetic constants of the process needs to be considered too in developing a useful kinetic model.

Owing to the inherent difficulty in developing such a model, a semi-empirical approach has been used by a number of investigators.

The starting point is invariably a general rate expression for an n-th order reaction, represented by:

$$d\alpha/dt = K(1 - \alpha)^n \quad [1]$$

where  $\alpha$  is the overall degree of cure (i.e., the extent of reaction),  $K$  is a rate constant which depends on the temperature according to the Arrhenius relationship and  $n$  is an empirical constant describing the order of reaction. This equation has been widely employed to describe the isothermal or non-isothermal curing kinetics of a variety of thermosetting systems.<sup>15,16,17</sup>

Later, Kamal and co-workers<sup>18,19</sup> pointed out that Eq 1 is not suitable to describe the process, since it does not account for the maximum observed in the DSC thermograms of some thermosets cured isothermally. They proposed an alternative form for the isothermal rate expression, namely:

$$d\alpha/dt = (K_1 + K_2\alpha^m)(1 - \alpha)^n \quad [2]$$

where  $K_1$  and  $K_2$  are rate constants following the Arrhenius relationship and  $m$  and  $n$  are constants describing the order of reaction. It is to be remarked that the form of Eq 2 is very close to that derived by Horie and co-workers<sup>20</sup> from an autocatalytic curing mechanism proposed for epoxy resins. For this reason, in the case of epoxies Eq 2 is regarded as "quasi-theoretically" justified. For unsaturated polyester resins no correspondence with the real reaction mechanism has been claimed; Eq 2 is applied in analogy with the kinetic behavior of other thermosetting systems. With the assumption of an over-all second order of reaction ( $m+n=2$ ), Eq 2 has been used successfully to describe the isothermal curing kinetics of a series of epoxy resins and later to model the behavior of UPE resins.<sup>2,3,16</sup> As the model become more and more popular, Ryan and Dutta<sup>21</sup> suggested a method for the rapid estimation of the kinetic parameters in Eq 2 from DSC data.

Near all of these kinetics studies have been carried out by differential scanning calorimetry, DSC, which has the considerable advantage of simplicity, few limitations, and the capability to yield at the same time information on the kinetics, energetics, and thermal properties. However DSC measures an overall heat of reaction and cannot differentiate between the single chemical reactions occurring in the system. In fact, the conversion  $\alpha$ , in DSC measurements is obtained from the following relation:

$$\frac{d\alpha}{dt} = \frac{d\Delta H_t}{dt} \frac{1}{\Delta H_T}$$

where  $d\alpha/dt$  and  $\alpha$  are the reaction rate and the conversion at a given time;  $d\Delta H_t/dt$  is the actual experimental value,  $\Delta H_t$  is the area of the exotherm from  $t=0$  to the given time and  $\Delta H_T$  is the total reaction exotherm. In addition this technique exhibits a decreasing sensitivity as the conversion increases owing to the fact that it relies on the heat generation of the process.<sup>22</sup>

It is to be noted that DSC gives the values of  $d\alpha/dt$ , i.e. the reaction rate as a function of time so that the process of best fitting the model equations in the experimental data is relatively straight forward.

FTIR spectroscopy is much more specific and, as discussed in the previous paragraphs, can monitor separately the kinetics of the various reacting species, thus giving information on the overall reaction mechanism. However this technique yields  $\alpha$  versus time curves and,

in order to fit the experimental data points with one of the proposed model equations, the time derivative curves have to be evaluated. This process is known to be critical since the random noise associated with the experimental determination of  $\alpha$  is strongly enhanced in the time derivative curves.

The  $\dot{\alpha}(t)$  versus  $\alpha$  experimental curves have been obtained by evaluating  $\dot{\alpha} = \Delta\alpha/\Delta t$  and choosing a suitable value of  $\Delta t$  in order to reduce to the minimum the dispersion of the data points. From these curves it was straight forward to obtain the  $\dot{\alpha}$  vs  $\alpha$  plots which formed the basis of the subsequent data analysis; examples of such curves are reported in Figures 7A, 7B, and 7C, relative to the reaction temperatures of 336 K, 343 K, and 363 K respectively.

Since the kinetic behavior of the two reactive species in the system is appreciably different at all temperatures, we attempted to apply the model separately to the conversion curves of styrene vinyls and UPE vinylenes instead of using an overall reaction conversion. This procedure would allow us to obtain kinetic parameters by which to describe the fate of both the unsaturations present in the system.

As a first attempt we used the widely applied assumption of an overall second order of reaction, i.e.,  $m+n=2$ . With such a condition the model equation becomes:

$$d\alpha/dt = [K_1 + K_2\alpha^{(2-n)}](1-\alpha)^n \quad [3]$$

and the number of parameters to be found is reduced by one with respect to a situation where  $m$  and  $n$  are only limited as to be positive. Moreover from Eq 2, we get

$$\left(\frac{d\alpha}{dt}\right)_0 = K_1$$

so that the value of  $K_1$  is easily obtained by a linear least squares fit of the initial part of the  $\alpha$  versus  $t$  curves. In summary the number of parameters to be found reduces to two, e.g.,  $K_2$  and  $n$ . The experimental data have been analyzed by both the method proposed by Ryan and Dutta<sup>21</sup> and by a non-linear least square curve fitting of the data points with Eq 3. The kinetic parameters obtained by the two approaches are found to be, to all purposes, coincident.

From the knowledge of  $K_1$ ,  $K_2$ , and  $n$ , the differential Eq 3 has been numerically integrated by using the Newton-Raphson method so as to provide the predicted  $\alpha$  vs time curves which can be compared with the original experimental data.

Such a comparison is shown in Figures 8A, 8B, and 8C which evidence that the model is able to describe suitably the kinetic behavior only over a very limited time range at the beginning of the process. At longer times, the calculated curves strongly deviate from the data points

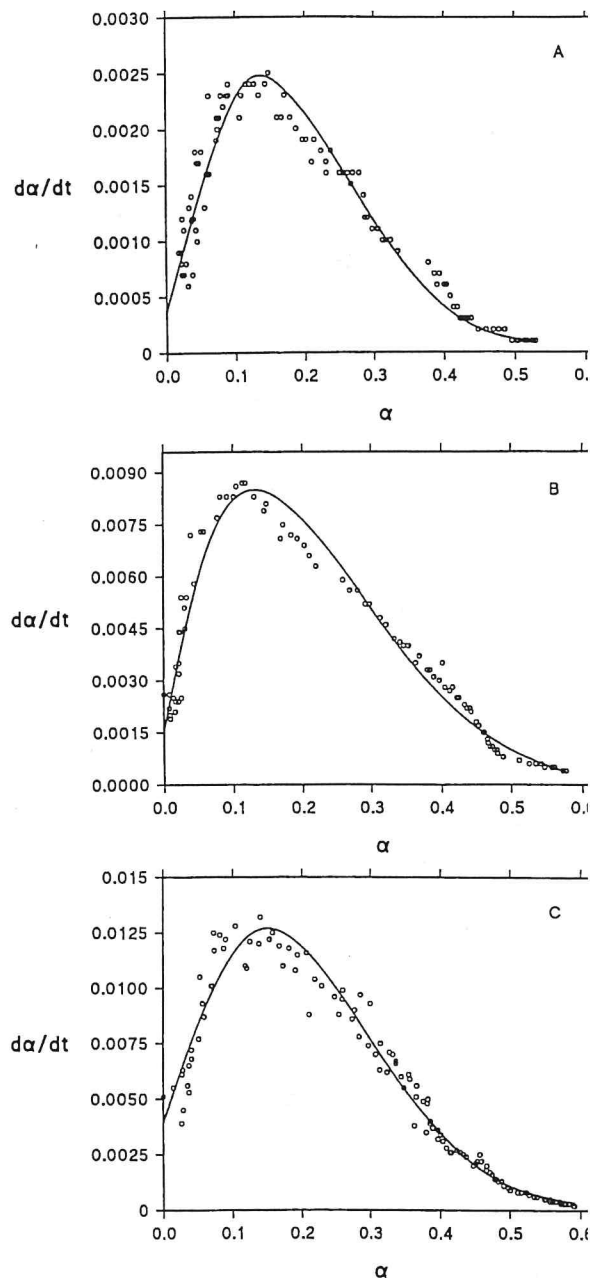


Figure 7. Experimental  $\dot{\alpha}$  versus  $\alpha$  curves (O) at three reaction temperatures: A) 336 K; B) 343 K; C) 363 K. The full lines represent the curves obtained by best-fitting the experimental data with Eq. 2.

and the conversion values predicted by the model are consistently higher than those experimentally measured.

The overall fit is unsatisfactory although it might be incidentally noted that, by increasing the temperature the fit seems to improve slightly.

A further attempt of data analysis was carried out by removing the condition  $m+n=2$ , with the only limitation on  $m$  and  $n$  to be positive. Here the  $\dot{\alpha}$  vs  $\alpha$  curves (see Figures 7A, 7B, and 7C) were subjected to a non-linear least square regression using Eq 2. It is immediate

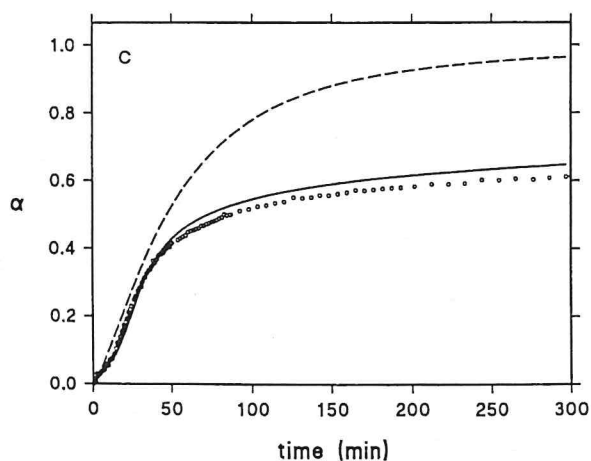
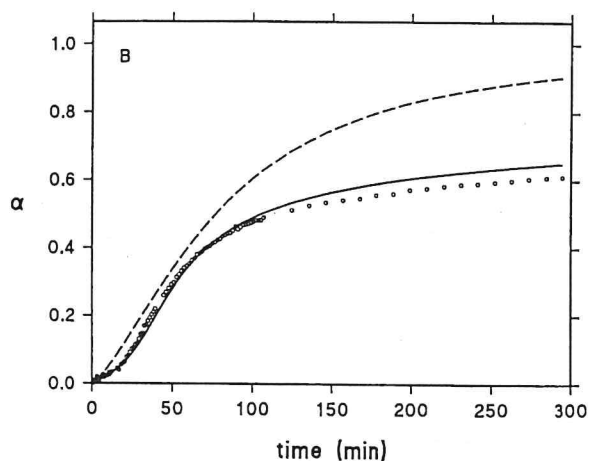
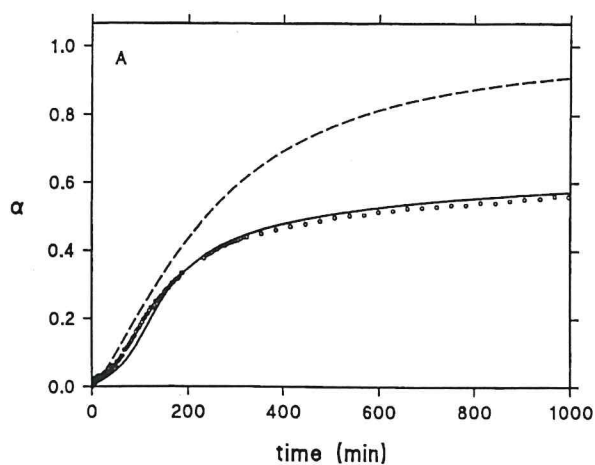


Figure 8. Conversion versus time curves for styrene unsaturations at three reaction temperatures compared with the predictions of the models used in the present study. The dotted lines are relative to the model Eq 3, the full lines refer to the model Eq 2 (see text). Figures A, B, and C are relative to reaction temperatures of 336 K, 343 K, and 348 K, respectively.

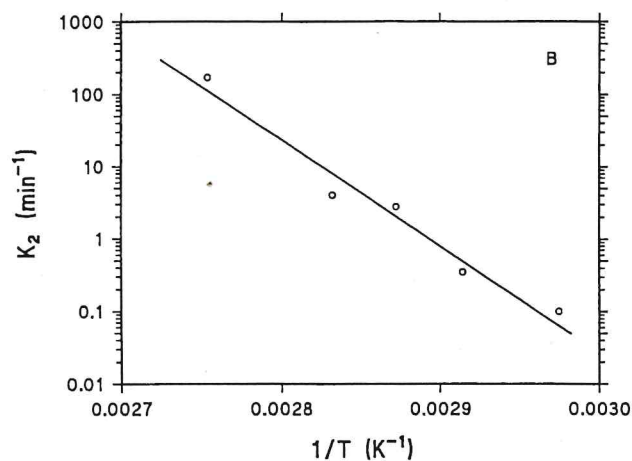
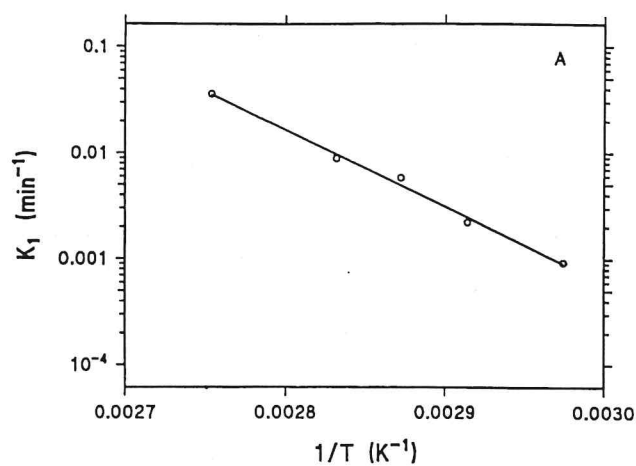


Figure 9. Arrhenius plots of  $K_1$  (A) and  $K_2$  (B) as evaluated using the model Eq 2 for the styrene conversion.

apparent that Eq 2 fits the data points much better than Eq 3. In fact, at 336 K, for instance, the Gauss coefficient obtained by fitting Eq 2 is 307 while it is  $26 \times 10^3$  if Eq 3 is considered in the best fitting procedure. Again the knowledge of  $K_1$ ,  $K_2$ ,  $m$ , and  $n$  allows to obtain, by numerical integration the predicted  $\alpha$  vs  $t$  curves which are represented as full lines in Figure 8. It appears that this alternative model is able to describe quite accurately the observed data over a wide range of conversions and in the whole temperature range investigated. In particular, it is found that even the "s" shape of the experimental curves is reproduced quite accurately, thus providing a useful approximation to the observed data even at the early stages of the process, at very low conversion. The kinetic parameters obtained with the above procedure are reported in Tables 2 and 3 and  $K_1$  and  $K_2$  are plotted according to the Arrhenius relationship in Figures 9 and 10.

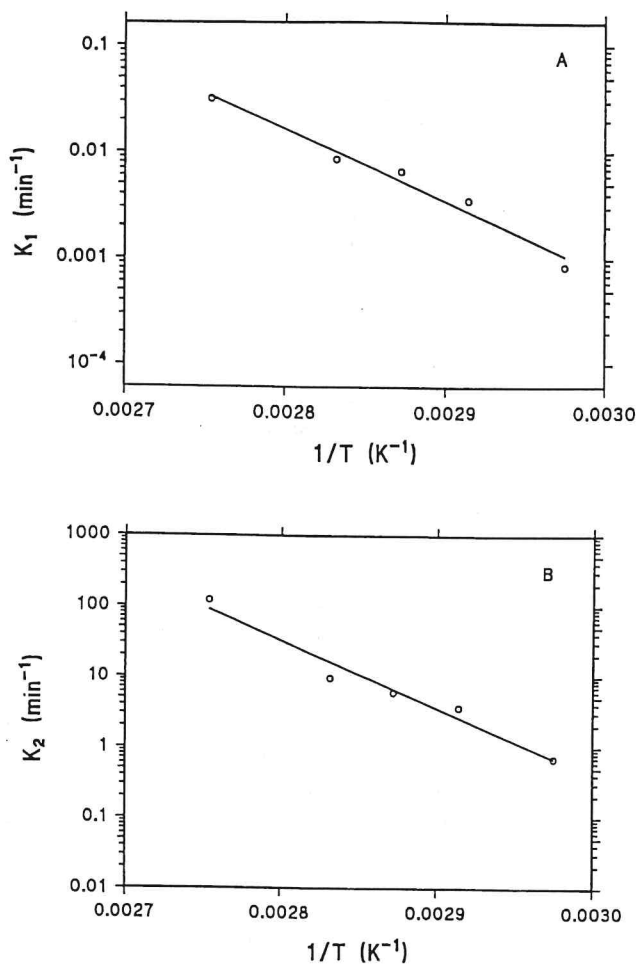


Figure 10. Arrhenius plots of  $K_1$  (A) and  $K_2$  (B) as evaluated using the model Eq 2 for the UPE conversion.

Both rate constants correlate linearly in an Arrhenius plot, giving apparent activation energies,  $E_a$ , of 60 KJ/mol for  $K_1$  and of 120 KJ/mol for  $K_2$  when the conversion of styrene is considered. For the UPE double bond conversion the apparent  $E_a$  values are 56 KJ/mol and 80 KJ/mol for  $K_1$  and  $K_2$ , respectively. It is noted that the overall activation energy for most chain polymerizations initiated by radical peroxides ranges from 80 to 100 KJ/mol.<sup>23</sup>

The absolute values of the  $K_1$  rate constant at various investigated temperatures compare favorably with those evaluated by Han and Lem,<sup>2,3</sup> while, in the present investigation, the  $K_2$  constants are consistently higher than those reported in Refs 2 and 3.

Furthermore, at all the temperatures investigated both the  $m$  and the  $n$  values are considerably higher than those reported in Refs. 2 and 3; in particular,  $n$  ranges from about 5 to 11.

The anomalous behavior of the parameter  $n$  is not easily explained. Clearly an autocatalytic second order

Table 2: Summary of the kinetic parameters obtained fitting the experimental data relative to the conversion of styrene unsaturations with the model equations 2 and 3.

T, °C	63	70	75	80	90
$K_1 \times 10^3, \text{min}^{-1}$	0.93	2.23	5.86	8.94	36
$^a K_2, \text{min}^{-1}$	0.10	0.35	2.76	4.00	18
$^b K_2, \text{min}^{-1}$	0.0051	0.0176	0.0252	0.0276	0.0
$^a m$	1.50	1.56	2.25	2.53	3.0
$^b m$	0.44	0.46	0.53	0.65	0.0
$^a n$	6.45	5.93	8.05	7.43	10
$^b n$	1.56	1.53	1.47	1.35	1.0
$^a \text{G.C.} \times 10^3$	0.362	0.353	0.466	0.505	1.6
$^b \text{G.C.} \times 10^3$	24	17	35	37	8

<sup>a</sup>kinetic parameters obtained by fitting model Eq 2

<sup>b</sup>kinetic parameters obtained by fitting model Eq 3 with the method of and Dutta

G.C. - Gauss coefficient, defined as:

$$\text{G.C.} = \frac{1}{p-q} \sum_{i=1}^p r_i^2 \quad \text{where: } r_i = \text{residuals; } q = \text{number of}$$

parameters of the model,  $p$  = number of data points

Table 3: Summary of the kinetic parameters obtained fitting the experimental data relative to the conversion of styrene unsaturations with the model equations 2 and 3.

T, °C	63	70	75	80	90
$K_1 \times 10^3, \text{min}^{-1}$	0.76	4.40	6.49	8.41	31
$^a K_2, \text{min}^{-1}$	0.692	3.65	5.98	8.96	121
$^b K_2, \text{min}^{-1}$	0.004	0.011	0.019	0.026	0.0
$^a m$	2.09	2.52	2.47	2.72	3.0
$^b m$	0.38	0.60	0.53	0.59	0.0
$^a n$	11.15	10.22	10.42	9.36	11
$^b n$	1.62	1.40	1.47	1.41	1.0
$^a \text{G.C.} \times 10^3$	0.307	0.374	0.422	0.290	1.6
$^b \text{G.C.} \times 10^3$	26	27	45	48	11

<sup>a</sup>kinetic parameters obtained by fitting model Eq 2

process is unrealistic for the temperature range and the particular composition investigated in the present work. On the other hand, it is difficult if not impossible to assign any mechanistic significance to reaction order values as high as 10 or above. Evidently in these cases of the model equation 2 is possible but on a purely empirical basis. It cannot provide any information regarding the mechanistic aspects of the process but can provide a useful approximation for predicting the kinetic

behavior of the various reactive species present in the system.

### CONCLUSIONS

In the present contribution we have carried out a kinetic analysis by FTIR spectroscopy on a commercial grade polyester resins in the temperature range from 336 to 363 K.

The spectroscopic technique employed for the real time monitoring of the process allowed to follow the conversion profiles of both the St and of the UPE unsaturations present in the system.

The kinetic data thus obtained have been discussed in terms of the currently accepted molecular mechanisms of the curing process as well as in terms of the reactants' molecular mobility.

Finally, an attempt was made to describe the kinetic behavior of the two reactive species in the system by using two different model equations. It was found that a model widely used in the literature, which gave satisfactory results in the case of epoxy resins, is not suitable to describe the experimental data discussed in the present contribution; however a drastic improvement in the accuracy of the model predictions was achieved by using a more general form of the same model equation. The kinetic constants obtained in this way were found to correlate well in an Arrhenius plot from which apparent activation energies were evaluated.

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