

Unsaturated Polyester Resins: Numerical Solution of a System of Equations Able to Describe Both Styrene and Unsaturation Consumption

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ABSTRACT: In this article, a numerical solution of a system of differential equations is proposed, able to describe the kinetic curing of a polyester resin in a temperature range between 336 K up to 363 K. The conversion degree of both styrene and polyester unsaturations were experimentally measured, in a preceding article, by Fourier Transform Infrared Spectroscopy; now we describe a more precise and correct theoretical calculation of the kinetic reactions relative to the experiments described in that previous article. This new calculation is based on the solution of the kinetic equations, based on free radicals polymerization reaction, instead of empirical formulas. The obtained results, relative to the conversion degree of both the components, show better agreement with the experimental values, both with respect to the usual kinetic model and also compared with a new empirical model that we proposed in the previous article, to fit the same set of experimental data. The comparison between the models was performed by hypothesis test. The parameters that characterize the propagation reactions were found to increase with increasing temperature, according to an Arrhenius law, leading to an activation energy between (98 ± 2) KJ/mol for the styrene and (110 ± 2) KJ/mol for polyester unsaturation, in the temperature range examined. We conjecture this system could be useful to monitor for each time, the consumption of the different species present in the kinetic reaction, and to refine the final thermo-mechanical properties of the resins. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 124–132, 2000

Key words: polyester; resin; curing; numerical; modeling

INTRODUCTION

In a preceding article¹ a kinetic analysis of a commercial grade unsaturated polyester (UPE) was carried out in the temperature range from 336 K up to 363 K. The experimental technique used to measure, in real time, the consumption of reactive species in the system, was Fourier Transform Infrared Spectroscopy (FTIR). The principal advantages of this technique are the ability to detect different

functional groups, resulting in the monitoring of both the styrene (ST) and the polyester unsaturations (PU) conversion. Moreover sensitivity, optical stability, and high data collection rate are other advantages of the FTIR technique.

Unsaturated polyesters (UPE) are one of the most used thermosetting materials, owing to their low cost and relatively good mechanical properties. They are employed in a broad range of products, such as the automotive industries and building industries. Generally, UPE are prepared by condensation reactions of saturated and unsaturated dicarboxylic acids (or anhydride) with gly-

col, and dilution with unsaturated monomers like styrene (ST); qualitative and quantitative variations in these components lead to a wide range of possibilities for the characteristics of the final products. This is one of the reasons why the UPE have so much success in many applications. Moreover, the development of injection techniques, like bulk molding compound (BMC) and sheet molding compound (SMC), has given more impulse to the commercial expansion of UPE, because of the well-known possibility, in realization of complex pieces, offered by these techniques.

From these arguments arises the need to control this enormous variability, by a better understanding of the reactions kinetics during cure, and their complex flow behavior during injection. Many articles address the final products from an engineering point of view, while a few articles²⁻⁴ studied the whole conversion process, step by step; they generally used the approach describing the curing reaction as a simple free radical homopolymerization,⁵⁻⁷ with no differentiation between the reactivity of ST and polyester double bonds. This simplified reaction scheme could be useful to describe the overall kinetic curing, monitored by Differential Scanning Calorimetry (DSC), with no possibility to distinguish the different species involved. It cannot give us detailed information on the reaction mechanism, i.e., cannot be useful to describe how the kinetics curing is affected by the parameters involved, and which of these parameters is really important. On the contrary, a differentiation of the involved species can be investigated by FTIR.

In this article we numerically solve a simplified form of a system of differentials equations, describing the evolution, with time and temperature, of the reactive species; particular attention was posed to describe the separate kinetics of styrene and polyester unsaturations. We find the solutions have general validity, but the materials parameters involved in the system were estimated to fit a set of experimental data in the temperature range from 336 K up to 363 K.

The final goal will result in a complete description for each time and temperature of the degree of consumption of the species PU, ST, and others species involved in the model of the kinetic reaction.

EXPERIMENTAL

Materials

As outlined in the Introduction, the experimental data used in the present article are the same as

from ref. 1, so the only work executed was a computational one. For any details regarding the uncured unsaturated polyester resin, see ref. 1.

Position of the Problem

This section describes a precise definition of the physical quantities needed to describe the kinetic reactions, with the simplified assumptions.

Under the hypothesis of free radicals reactions, the curing reaction of UPE requires chemical initiator, I, able to generate free radicals to start the polymerisation reaction. Afterwards, the reactions continue, characterized by reaction constant k_p . Moreover, according to the literature,¹⁰ the gelification phenomena lead to a diffusion controlled reaction. This last step cannot be taken into account by the usual equations to describe the degree of monomer conversion, α . One of the most used equation to describe the α evolution is:^{1,9,10}

$$\frac{d\alpha(t)}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n, \quad (1)$$

where α is the monomer degree of conversion defined by

$$\alpha(t) = \frac{1 - [M](t)}{[M]_0},$$

$[M]$ being the monomer concentration of initial value $[M]_0$; k_1 , k_2 , m , and n are empirical parameters. The square brackets have the meaning of a concentration, expressed in g/(mol · L).

In this case, there are two monomeric species, PU and ST, so we have two conversion factors, α_1 and α_2 :

$$\alpha_1(t) = \frac{1 - [PU](t)}{[PU]_0}$$

and

$$\alpha_2(t) = \frac{1 - [ST](t)}{[ST]_0}.$$

If we suppose that free radical polymerization can describe the reaction of the single component, we can simplify the reactions by the following scheme:

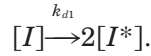
1. The initiator, I, decompose to a radical initiator I*.
2. The radical I* reacts with ST and PU to form a styrene radical ST* and UP*, respectively.

3. These radicals, ST^* and PU^* , can react with ST and PU monomers to form radicals of larger size by propagation and transferring reactions in which the reactivity is transferred.
4. When two radicals react, they link by covalent bond, and the resulting product cannot participate the reactions anymore; these are termination reactions.
5. The decrease of the number of free radicals has another cause: the presence of reactor inhibitor Z . The need of its presence lies in the necessity to prevent premature curing of the resins.

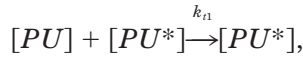
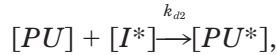
Each one of the chemical reactions described in step 1–5 can be schematized by a typical rate constant. These reactions can be collected in classes to describe the modality of the reaction, if we assume that their rates are not dependant on the molecular weight of the involved species.¹¹

So far, the dissociation reactions, characterized by the constants k_d , transferring reactions, k_t , propagation reactions, k_p , ending reactions, k_e , and inhibition reactions, k_z are distinguished.

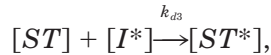
So we have four reactant species (I , Z , PU , ST) and their radicals (I^* , PU^* , ST^*) with the exception of the inhibitor Z . The five steps can be described by the following chemical formulas: for step 1:



For the PU , they are (steps 2 and 3):



The same reactions can be written for the ST , with different rate constants (steps 2 and 3).



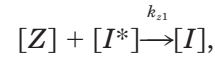
The termination reactions between the radicals: some radicals can terminate by coupled ter-

mination, with covalent bonds and loss of radical activity (step 4)



with loss of one radical activity.

Finally the inhibitor Z can react only with radicals (step 5).



This is the scheme of all the considered reactions. We outlined seven reactant species (I , Z , PU , ST , I^* , PU^* , ST^*), and 13 rate constants (k_{d1} , k_{d2} , k_{d3} , k_{t1} , k_{t2} , k_{t3} , k_{t4} , k_{e1} , k_{e2} , k_{e3} , k_{z1} , k_{z2} , k_{z3}). Note, once again, that we have assumed the rate constants do not depend on the molecular weight of each of the species to obtain a kinetic expression for the overall rate of polymerization.¹¹ So far, the rate of consumption of the monomer correspond to the growing rate of the building polymer.

By these assumptions, the following differential equations can be written to describe the reactions:

$$\frac{d[I]}{dt} = -\frac{1}{2}k_{d1}[I], \quad (2)$$

$$\begin{aligned} \frac{d[PU]}{dt} = & -k_{d2}[PU][I^*] - k_{t1}[PU][PU^*] \\ & - k_{t4}[ST][ST^*], \quad (3) \end{aligned}$$

$$\begin{aligned} \frac{d[ST]}{dt} = & -k_{d3}[ST][I^*] - k_{t2}[ST][ST^*] \\ & - k_{t3}[ST][PU^*], \quad (4) \end{aligned}$$

$$\frac{d[Z]}{dt} = -[Z](k_{z1}[I^*] + k_{z2}[ST^*] + k_{z3}[PU^*]), \quad (5)$$

$$\begin{aligned} \frac{d[I^*]}{dt} = & -\frac{1}{2}k_{d1}[I] - k_{d2}[PU][I^*] \\ & - k_{d3}[I^*][ST] - k_{z1}[I^*][Z], \quad (6) \end{aligned}$$

$$\begin{aligned} \frac{d[PU^*]}{dt} = & -\frac{1}{2}k_{d2}[I^*][PU] + k_{t4}[PU][ST^*] \\ & - k_{t3}[ST][PU^*] - k_{e2}[PU^*]^2 \\ & - k_{e3}[PU^*][ST^*] - k_{z2}[PU^*][Z], \quad (7) \end{aligned}$$

$$\begin{aligned} \frac{d[ST^*]}{dt} = & -\frac{1}{2}k_{d3}[I^*][ST] - k_{t4}[PU][ST^*] \\ & + k_{t3}[ST][PU^*] - k_{e1}[ST^*]^2 \\ & - k_{e3}[PU^*][ST^*] - k_{z3}[ST^*][Z]. \quad (8) \end{aligned}$$

This system is composed of seven equations in seven functions, together with 13 materials parameters. Looking at it from a statistical point of view, this system has too many degrees of freedom; in fact, we shall compare the system solutions with experiments, but only the experimental data that was collected are relative to the functions [ST] and [PU].

Moreover, the fits of the materials constants are calibrated to obtain the best agreement with only these two sets of experimental data: in such aspects, the use of so many parameters is meaningless from a statistical point of view. The intention, therefore, is to collect some constants, because we cannot distinguish between them in our preceding experiments.¹ So far, in eqs. (2)–(8), the following simplifying assumptions are made:

1. Do not take in account the single information on the radical species, but collect all together without distinction between them. The reason for this lies in the low concentration of the radicals with respect to monomer species; the radicals concentrations, generally, is about 10^{-4} times less than the initial monomer concentration. So:

$$[R^*] = [I^*] + [ST^*] + [PU^*].$$

2. Collect in one propagation constant, the diffusion and transferring reactions:

$$k_{p1} = k_{d2} = k_{t1} = k_{t4};$$

$$k_{p2} = k_{d3} = k_{t2} = k_{t3},$$

where the constants k_{p1} and k_{p2} are referred to the species PU and ST, respectively.

3. The action of Z is assumed to be the same for every species, so:

$$k_z = k_{z1} = k_{z2} = k_{z3}.$$

4. As further simplification, assume:

$$k_{e1} = k_{e2} = k_{e3} = 0,$$

neglecting the termination steps.

So far:

$$\frac{d[I]}{dt} = -\frac{1}{2}k_d[I], \quad (9)$$

$$\frac{d[PU]}{dt} = -k_{p1}[PU][R^*], \quad (10)$$

$$\frac{d[ST]}{dt} = -k_{p2}[ST][R^*], \quad (11)$$

$$\frac{d[Z]}{dt} = -k_z[Z][R^*], \quad (12)$$

$$\frac{d[R^*]}{dt} = -\frac{1}{2}f \cdot k_d[I] - k_z[Z][R^*]. \quad (13)$$

In eq. (13), f is a parameter to take in account the efficiency of the initiator, of initial value f_0 , and it decreases with increasing the polymer concentration. It can be expressed as:¹¹

$$\begin{aligned} f = & f_0^2 \frac{\left(\frac{[M] - [M]_\infty}{[M]_0 - [M]_\infty}\right)^2}{2(1 - f_0) \frac{[I]}{[I]_0}} \\ & \times \left(\left(1 + \frac{4(1 - f_0) \frac{[I]}{[I]_0}}{f_0^2 \left(\frac{[M] - [M]_\infty}{[M]_0 - [M]_\infty}\right)^2} \right)^{1/2} - 1 \right). \quad (14) \end{aligned}$$

The index $_0$ indicates the initial concentration of the species, while M_∞ is the residual monomer concentration after the cure.

As simplification for M , only in eq. (14), the expression

$$[M] = \frac{[PU] + [ST]}{2},$$

has the mean of an average value of the monomers concentration. Equations (9)–(13) are a system composed by five equations in five functions characterized by six materials constants, k_z , k_{p1} , k_{p2} , k_d , f_0 , and M_∞ .

To take into account the change to a diffusion controlled mechanism, assume a functional form for the propagation constants⁹

$$k_{p1} = k_{p01} \left(\frac{[PU] - [PU]_\infty}{[PU]_0 - [PU]_\infty} \right)^{m1}; \quad (15)$$

$$k_{p2} = k_{p02} \left(\frac{[ST] - [ST]_\infty}{[ST]_0 - [ST]_\infty} \right)^{m2}. \quad (16)$$

k_{p01} and k_{p02} are constants, depending on the temperature relative to PU and ST, respectively.

Note that the use of eqs. (14)–(16), to take in account the diffusion-controlled polymerization mechanism, introduce a new parameter, M_∞ ; in fact, when $M = M_\infty$, all the propagation constants are equal to 0, and the monomer conversion is stopped. This parameter takes an empirical one: the average value of the residual monomer concentration of the last 10% of our experimental data. The reason for this choice lie, once again, in the ratio between the number of parameters and the experimental curves at our disposal: if this ratio increases too much, estimation legitimacy decrease progressively.

It is well known that the curing cycle of resin is strongly influenced by the temperature. In eqs. (2)–(8), this dependence appear only in three objects. Explicitly in the k_d , where the activity of initiator is supposed to increase with increasing the temperature according to the equation:

$$k_d = k_{d0} e^{-E_d/RT}$$

Moreover, also k_{p0} and M_∞ are dependent on the temperature;⁹ this will be verified only when the estimation parameters is complete. f_0 was taken as 0.2;^{9,11} k_d was experimentally measured. So

far, estimated values of the five constants, k_z , k_{p01} , k_{p02} , m_1 , m_2 are used.

Procedure to Integrate Eqs. (2)–(8)

The procedure used to estimate the constants and to obtain the solution of eqs. (2)–(8) is explained.

The system is presented in normal form, as a typical Cauchy problem, with initial values. We integrate (2)–(8) by a standard Newton integrator supplied in Mathematica[®].

The accuracy of the method is limited by the machine precision, which, in single precision, is 10^{-8} . This precision is sufficient to catch the main features of the system.

A bisection technique was employed, based on arbitrary initial values of the parameters, moved to minimize the expression;

$$G = G_1 + G_2 \quad (17)$$

where

$$G_1 = \frac{1}{N - m} \sum_{i=1}^N (\alpha_1 - \bar{\alpha}_{1i})^2, \quad (18)$$

and

$$G_2 = \frac{1}{N - m} \sum_{i=1}^N (\alpha_2 - \bar{\alpha}_{2i})^2, \quad (19)$$

i.e., the measure of “error estimation” residuals between the experimental data, $\bar{\alpha}_{1i}$ $\bar{\alpha}_{2i}$ and the numerical models α_1 and α_2 . N is the number of experimental points, and m is the number of parameters employed in the model to fit the data.¹² In this model they are equal to the numbers of constants to determinate, 5. The constants were searched in the following range:

$$k_{z-\text{inf}} = 1,$$

$$k_{z-\text{sup}} = 10^6,$$

$$k_{p01-\text{inf}} = 1,$$

$$k_{p01-\text{sup}} = 10^6,$$

$$k_{p02-\text{inf}} = 1,$$

$$k_{p02-\text{sup}} = 10^6,$$

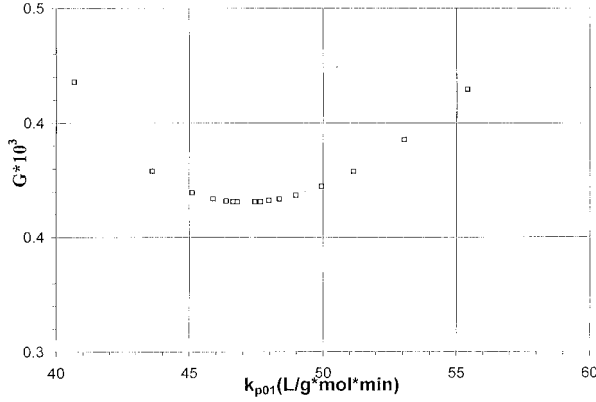


Figure 1 Gauss coefficient, G , vs. propagation constant k_{p01} in the optimization process; $T = 348$ K.

$$m_{1-\text{inf}} = 10^{-1},$$

$$m_{1-\text{sup}} = 10,$$

$$m_{2-\text{inf}} = 10^{-1},$$

$$m_{2-\text{sup}} = 10,$$

where inf and sup have the mean of the lower and upper limit, respectively. The k are expressed in $\text{L}/(\text{g} \cdot \text{mol} \cdot \text{min})$, while the m are dimensionless.

The set of constants whose corresponding solution obtain a lower G value, are fixed and the others changed. This procedure is repeated until the constant converges to a value. This method is known in the literature¹² under the name of bisection.

For an example of convergence, a plot of G as a function of the k_{p01} is showed in Figure 1; here, iteratively, the solution converges to a lower G , which has the mean of a best fit with the experimental data.

To test the validity of this procedure for each estimation we: (a) started it with many different initial values of constants; (b) changed the order of estimation between the constants in the program during the estimation; (c) the step of bisection was changed between 1/2 and 8/9; and (d) this procedure is repeated many times in all possible sorts of the chosen constants, always leading to the same value of the constants and G . Moreover, the fitted constant was changed between them to obtain a real absolute minimum of G .

The best fit set of constants were always the same. This is a necessary condition of stability of the program.

Initial Conditions for Eqs. (2)–(8)

The initial condition of the five functions, $[I]$, $[Z]$, $[ST]$, $[PU]$, $[R^*]$ were chosen as follow:

$$[I]_0 = I(t_0) = 4.53 \cdot 10^{-2},$$

$$[Z]_0 = Z(t_0) = 1.75 \cdot 10^{-4},$$

$$[\alpha_{PU}]_0 = \alpha(t_0) = 0,$$

$$[\alpha_{ST}]_0 = \alpha(t_0) = 0,$$

$$[R^*]_0 = R^*(t_0) = 0,$$

$$k_{d0} = 1.7467 \cdot 10^{-18} \text{ s}^{-1},$$

$$E_d = 0.823 \text{ J/mol},$$

$$f_0 = 0.2.$$

All the concentrations are expressed in $\text{g/mol} \cdot \text{L}$ and the values are the same as in ref. 1.

RESULTS

The monomers degree of conversion, α_1 and α_2 , together with the experimental data, $\bar{\alpha}_1$, and $\bar{\alpha}_2$, (measured in ref. 1) are shown in Figure 2(a)–(d). In Figure 2(a) and (b), the values of α_1 (PU) vs. time, as calculated from the numerical solutions of eqs. (2)–(8) are shown together with the experimental data, $\bar{\alpha}_1$ and $\bar{\alpha}_2$. The temperatures were 336 and 343 K [Fig. 2(a)], and 348, 353, and 363 K [Fig. 2(b)]. The same plot, for the ST monomer, are reported in Figure 2(c) and (d). The continuum curves represent the numerical solution.

These findings show that the agreement between experimental data and the theory is very good. The fit is still very good at high temperatures [Fig. 2(b) and (d)], where the approximations assumed in the model lead to a decreased agreement.

To perform a quantitative comparison between the models used to describe the kinetic cure reactions, as in the previously article, the Gauss coefficient as a hypothesis test was calculated. In Table I, they are shown for the five temperature and compared with that of ref. 1: the lowest coefficient always belongs to the method published in this article. This findings mean that despite its higher complexity, the method presented here leads to a fit of the experimental data significantly better than the other methods. In fact, by

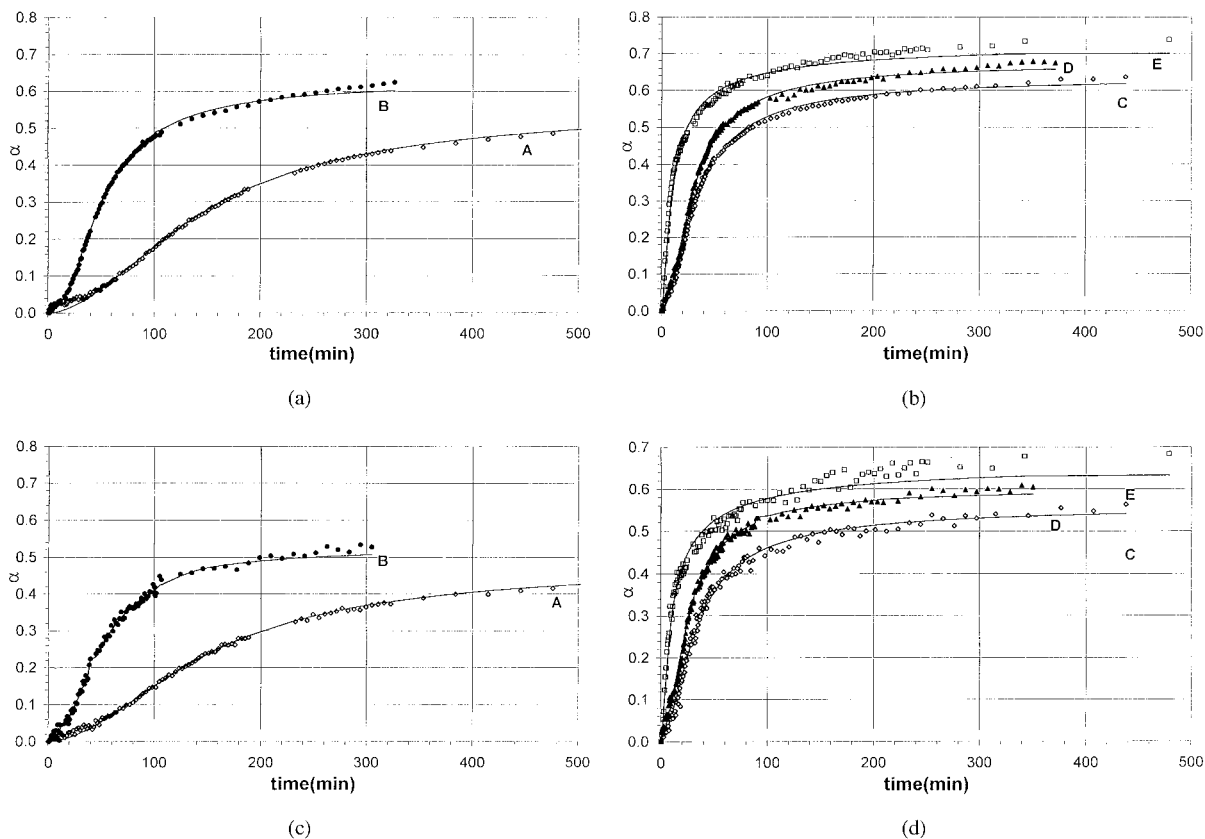


Figure 2 Conversion degree vs. time together with the numericals solutions for the investigated temperatures. (a) For styrene, ST, (A) 336 K, (B) 343 K; (b) (C) 348 K, (D) 353 K, (E) 363 K; (c) For polyester unsaturation, PU, (A) 336 K, (B) 343 K; (d) (C) 348 K, (D) 353 K, (E) 363 K.

definition, the Gauss hypothesis test was born to compare different methods taking in account the degree of freedom, i.e., the number of parameters to be fitted in the model. The kinetics of PU and ST were monitored separately.

In Figures 3–6, the functions $I(t)$, $Z(t)$, $R(t)$, $f(t)$ are plotted for the five temperatures.

As usual, no experimental monitoring was performed on these functions.

The solution for $I(t)$ [eq. (2), Fig. 3] is trivial and analytically solved; it represents the exponential decay of the initiator concentration.

From Figure 4, the decreasing concentration of inhibitor is very fast. Note that the reaction starts at a time when all the inhibitor is consumed.

The number of free radicals, R^* , is increased with increasing temperature (see Fig. 5) and is not going to zero with time, because the termina-

Table I Values of the Constants Fitted for the Five Temperatures

Temperature (K)	k_z (L/g · mol · min)	k_{p01} (L/g · mol · min)	k_{p02} (L/g · mol · min)	m_1	m_2	$G_a \cdot 10^3$ [1]	$G_b \cdot 10^3$ [1]	$G \cdot 10^3$
336	126.83	8.70	7.17	1.72	1.74	0.36	24.10	0.15
343	1881.04	46.64	35.77	1.61	1.64	0.35	17.09	0.16
348	704.52	68.97	65.28	1.95	2.16	0.47	35.05	0.30
353	1541.07	50.96	57.31	1.77	1.94	0.50	37.34	0.28
363	39.68	172.67	172.98	2.77	3.26	1.60	88.67	0.83

Gauss coefficient relative to this paper are showed in the last column. In columns 7 and 8 are shown the Gauss coefficients taken from ref. 1, for the model a and b (empirical equations), respectively.

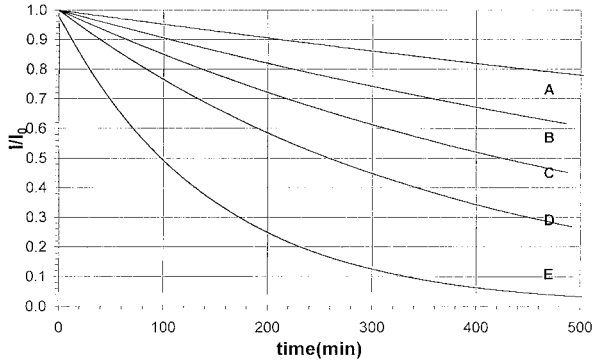


Figure 3 Analytical solutions of the initiator concentration for the investigated temperatures. (A) 336 K, (B) 343 K, (C) 348 K, (D) 353 K, (E) 363 K.

tion step is neglected. From eq. (13) it is understood that the radicals concentration reaches a plateau when $[Z]$ and $f^*[I]$ are very small. The efficiency of the initiator, f , is found to decrease with increasing time and temperature.

It can be pointed out, after 1/5 of the complete time of curing, that the presence of the inhibitor, Z , and initiator, I , no longer have importance, because their values, owing to the decreasing of f , are quite close to zero. At this point, the reaction is totally dominated by the free radicals concentration $[R^*]$, which is quite constant.

From Table 1 we can note that the k_{p01} and k_{p02} values increase with increasing temperature; Figure 7 shows these values can be fitted by an Arrhenius plot, according to the following equation:

$$k_{p01} = A_1 e^{-E_1/RT},$$

$$k_{p02} = A_2 e^{-E_2/RT};$$

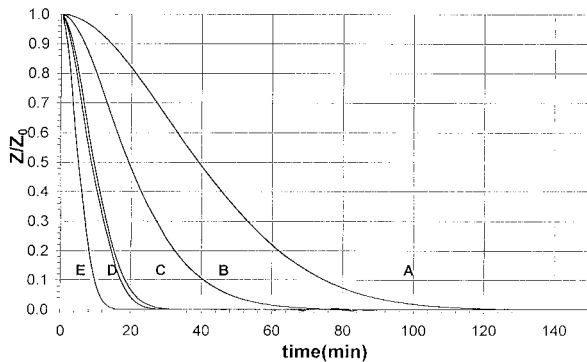


Figure 4 Numerical solutions of the inhibitor concentration, $[Z]$, for the investigated temperatures. (A) 336 K, (B) 343 K, (C) 348 K, (D) 353 K, (E) 363 K.

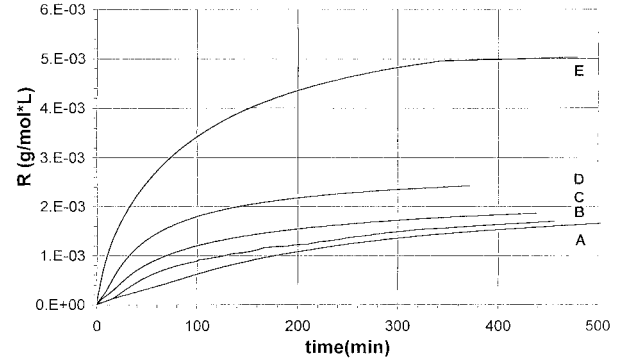


Figure 5 Numerical solutions of the radicals concentration, $[R^*]$, for the investigated temperatures. (A) 336 K, (B) 343 K, (C) 348 K, (D) 353 K, (E) 363 K.

where

$$A_1 = 1.1005 \cdot 10^{18} L \text{ (g mol min)},$$

$$A_2 = 2.6493 \cdot 10^{16} L \text{ (g mol min)},$$

The different slope corresponds to the activation energy of the propagation reactions. Their values were found:

$$E_1 = 98.1 \pm 2 \text{ KJ/mol}$$

$$E_2 = 110 \pm 2 \text{ KJ/mol}$$

The agreement of the fit is very good, as can be seen from Figure 7, and the values are in agreement with the literature.⁷

The constants m_1 , m_2 , seem to have a general increasing trend with increasing the reaction temperature (cfr. Table I), but no longer as the propagation constant. These results agree with Han and Lee.⁷

It could be noted as the model [eqs. (9)–(13)] can be reduced to the Han and Lee model just posing:

$$k_{p01} = k_{p02} \text{ and } [M] = [PU] + [ST].$$

CONCLUSION

The commercial unsaturated polyesters have large utilization, owing to their characteristics and the possibility to change them by modifying the kinetic parameters.

However, a complete description of the kinetic mechanism of styrene and polyester unsaturations, starting from the basic reactions, seem lacking in the literature. Many articles deal with techniques, like Differential Scanning Calorimetry, and are able to describe the overall kinetic process without distinguish between the different species involved.

Han and Lee⁷ proposed a more complete description of the kinetics, solving the model in the case of only one monomer species.

In this article, a complete solution of a system able to describe the kinetic of both styrene and polyester unsaturations is proposed.

This article measures and calculates the kinetics of ST and PU separately, instead of as one monomeric species. The advantage of this kinetic model, described by a system of differential equations, with respect to the empirical equations, lies in a better understanding of the kinetics mechanism, together with a better fit of the experimental data. Moreover, the method can be expanded if a more refined analysis is required. The equations were numerically solved, and the parameters fitted to the best fit of the experimental data, by the bisection method, to minimize the Gauss coefficient.

The solution show excellent agreement with the experimental data that was proposed in a previous article. The solutions show that the reaction, after a while, is totally regulated by the concentration of the free radicals; moreover, according to the literature, the reaction only starts after the inhibitor is quite totally consumed. The decreasing of the initiator concentration, together with its lost efficiency, enhanced this result.

The concentration of free radicals seems to reach a plateau, owing to the absence of a termination step, which was neglected to simplify the system.

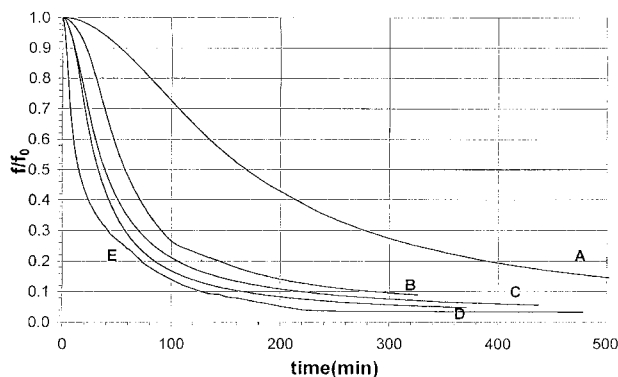


Figure 6 Numerical solutions of the initiator efficiency, f , for the investigated temperatures. A) 336°K; B) 343°K; C) 348°K; D) 353°K; E) 363°K.

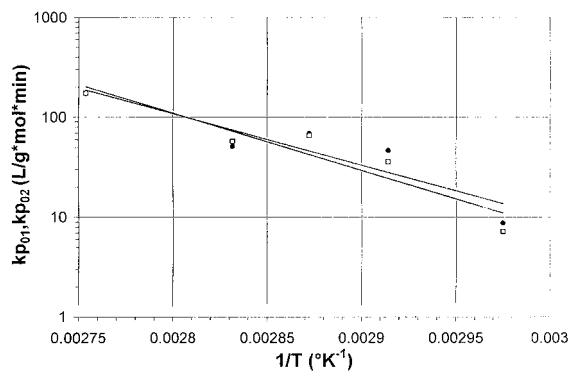


Figure 7 Arrhenius plots relative to the propagation constants, k_{p01} \square , and k_{p02} \bullet .

Finally, the calculation of the statistical parameters shows how, quantitatively, this solution obtains a better fit, when compared with both traditional empirical equations, and a new one that was proposed in a previous article.

This system can be reduced, by some simplifying, to the system proposed by Han and Lee by neglecting any distinction between the styrene monomers and the PU.

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