

# Kinetics of the Curing Reaction of Unsaturated Polyester Resins Catalyzed with New Initiators and a Promoter

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**ABSTRACT:** In this article, the curing of unsaturated polyester resins catalyzed with a promoter [cobalt(II) octoate] and free-radical initiators is presented. The new initiators were formed by the oxidation process of ethyl methyl ketone or cyclohexanone with hydrogen peroxide and the mixture of solvents containing hydroxyl groups. As a reference, a typical curing system containing ethyl methyl ketone hydroperoxide (Luperox) and the promoter was used. The differential scanning calorimetry runs were performed at different heating rates. The experimental data were fitted with the empirical kinetic model. First, the kinetic parameters (activation energy, frequency factor, and reaction order) were obtained with a single reactive process and with the  $n$ th-order reaction  $f(\alpha)$ , the  $n$ th-order

reaction  $f(\alpha)$  with autocatalysis, and the first-order reaction  $f(\alpha)$  with autocatalysis. Second, two or three different reactive processes with the  $n$ th-order reaction  $f(\alpha)$  for each step were used. The obtained values of the activation energies for the curing of the unsaturated polyester resins with the free radical initiator–cobalt(II) salt catalytic system were in the range 40–60 kJ/mol for the polymerization initiated by the redox decomposition of the initiators and 80–90 kJ/mol for the polymerization initiated by the thermal decomposition of the initiators at high temperatures. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1870–1876, 2006

**Key words:** differential scanning calorimetry (DSC); initiators; kinetics (polym.); resins

## INTRODUCTION

The curing of an unsaturated polyester resin is a free-radical polymerization in which the resin is transformed from the liquid state into a rigid crosslinked molecular structure. To induce the production of free radicals in the system, organic peroxides are commonly used. Free radicals can be formed by the thermal decomposition of peroxide or by chemical decomposition in ambient-temperature applications.<sup>1,2</sup> Cobalt(II) salts are usually required to cure polyester resins at low temperatures because they decompose the initiators rapidly under ambient conditions.

The curing reaction is highly exothermic and can be monitored by thermal analysis with differential scanning calorimetry (DSC). The DSC technique allows one to evaluate not only the heat of the reaction ( $\Delta H_R$ ) but also the reaction kinetics.<sup>3,4</sup> With this technique, it is assumed that the rate of evolution of exchanged heat is strictly proportional to the rate of the global chemical reactions at any instant as follows:<sup>5,6</sup>

$$dH/dt = \Delta H_R d\alpha/dt \quad (1)$$

where  $dH/dt$  is the heat generated by the time unit, or the heat flow (DSC ordinate);  $d\alpha/dt$  is the rate of the reaction; and  $\Delta H_R$  is the heat of the reaction obtained as the area of a DSC thermogram. Therefore, it is possible to evaluate  $d\alpha/dt$  at time  $t$  and the degree of conversion ( $\alpha$ ) reached at time  $t$  by means of the following expressions:

$$d\alpha/dt = 1/\Delta H_R dH/dt \quad (2)$$

$$\alpha = \Delta H_t/\Delta H_R \quad (3)$$

where  $\Delta H_t$  is the heat released up to time  $t$ ; it can be obtained by the integration of the calorimetric signal  $dH/dt$  up to time  $t$ .<sup>4</sup>

There are two possibilities for modeling the curing behavior of unsaturated polyester resins with the DSC technique: one using the concept of free-radical polymerization with its three steps, initiation, propagation, and termination,<sup>7–10</sup> and the other using an empirical kinetic model.<sup>11–13</sup>

In this study, we used an empirical method to obtain the kinetic parameters of the curing of the unsaturated polyester resins with the initiator–promoter catalytic system because, for practical purposes, it was more convenient. The empirical procedure relates  $d\alpha/dt$  to some function of  $\alpha$  and  $T$ . It is commonly accepted in the kinetic analysis of chemical reactions by thermal

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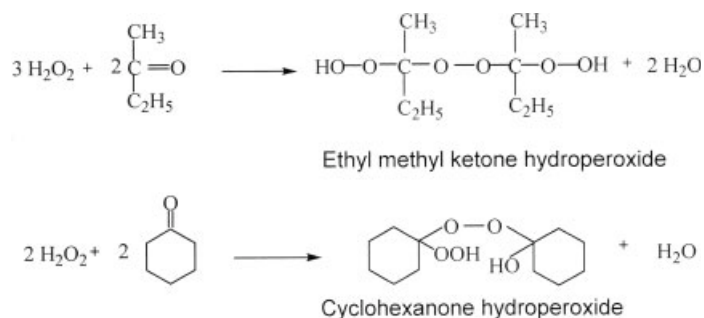


Figure 1 Exemplary synthesis of the hydroperoxide compounds.

analysis that any chemical process of reaction will obey a rate law of the form<sup>14,15</sup>

$$d\alpha/dt = k(T)f(\alpha) \quad (4)$$

where the dependence on  $\alpha$  from the dependence on  $T$  have been separated. Here,  $k(T)$  is the chemical rate constant, which is given by an Arrhenius-type equation dependence on the temperature:

$$k = A \cdot \exp(-E/RT) \quad (5)$$

where  $A$  is the frequency, or pre-exponential, factor and  $E$  is the activation energy of the reaction.<sup>2,4</sup> When the process is isothermal, the temperature is constant, but in nonisothermal processes, the temperature usually increases according to the constant heating rate ( $\beta$ ) =  $dT/dt$ . It is not necessary to know the equation for  $f(\alpha)$  in isothermal experiments, but in nonisothermal experiments, the function  $f(\alpha)$  has to be specified. In this study, the kinetic parameters of the unsaturated polyester resin curing with the free-radical initiator-promoter catalytic system were obtained at first with a single reactive process with the  $n$ th-order reaction  $f(\alpha)$  (Fn), the  $n$ th-order reaction  $f(\alpha)$  with autocatalysis (Cn), and the first-order reaction  $f(\alpha)$  with autocatalysis (C<sub>1</sub>). The functions used are given by the following expressions:

$$\text{Fn} : f(\alpha) = (1 - \alpha)^n \quad (6)$$

$$\text{Cn} : f(\alpha) = (1 - \alpha)^n(1 + J_{\text{katz}}) \quad (7)$$

$$\text{C}_1 : f(\alpha) = (1 - \alpha)(1 + J_{\text{katz}}) \quad (8)$$

where  $n$  is the order of the reaction.<sup>16</sup> Therefore, the experimental data was fit according to the next three expressions:

$$d\alpha/dt = Ae(-E/RT)(1 - \alpha)^n \quad (9)$$

$$d\alpha/dt = Ae(-E/RT)(1 - \alpha)^n(1 + J_{\text{katz}}) \quad (10)$$

$$d\alpha/dt = Ae(-E/RT)(1 - \alpha)(1 + J_{\text{katz}}) \quad (11)$$

The constants  $A$ ,  $E$ , and  $n$  are the kinetic parameters to be determined. The  $n$ th-order function for  $f(\alpha)$  reproduced curing better than the others so that the two different reactive processes [for the curing of the unsaturated polyester resin catalyzed with Luperox K1-cobalt(II) octoate] and three different reactive processes [for the curing of the unsaturated polyester resin catalyzed with new initiators cobalt(II) octoate] with the  $n$ th-order function  $f(\alpha)$  for each step were used. In the calculation procedure, the corresponding kinetic parameters were computed by the application of multivariate nonlinear regression (MULTIVAR-NLR), which applies a sixth-degree Runge-Kutta process in a modified Marquardt procedure to solve a system of differential equations, which are essentially based on differential equations relevant to different reaction types and their various combinations.<sup>16-18</sup>

TABLE I  
Chemical Composition of the Obtained Initiators

Initiator	Substrate (g)				
	Hydrogen peroxide	Ethyl methyl ketone	Cyclohexanone	Propano-1,2-diol	G 1000
1	60	25	—	20	20
2	60	—	53	20	20

**TABLE II**  
Concentration of Active Oxygen in the Studied Initiators

Initiator	Oxygen concentration (%)	
	Real	Calcd
1	13.51	13.08
2	11.15	10.50

## EXPERIMENTAL

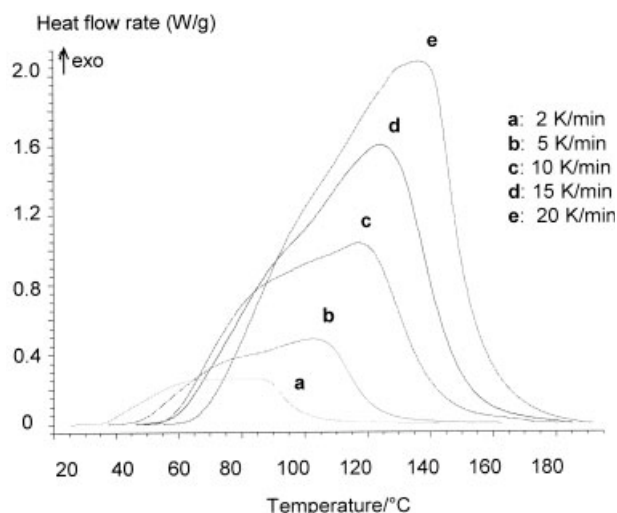
### Materials and calorimetric instrumentation

#### Chemicals

The commercially available orthophthalic unsaturated polyester resin Estromal 1454 was obtained from the Chemical Plant Erg (Pustków, Poland). Ethyl methyl ketone, cyclohexanone, and cobalt(II) octoate (a 1% solution in styrene) were delivered by POCh (Gliwice, Poland). Propano-1,2-diol and hydroxypolyether G 1000 (prepared from glycerin and propylene oxide with an average molecular weight of 1000 g/mol and three functionalities) were from the Chemical Plant Rokita (Brzeg Dolny, Poland). Hydrogen peroxide (60%) was bought from the Azoty Nitrogen Plant (Puławy, Poland). Luperox K1 (a 50% solution of ethyl methyl ketone hydroperoxide in dimethyl phthalate) was from the Luperox (Günzburg, Germany).

#### Preparation of the new liquid initiators

Hydrogen peroxide (60%) was dropped into the reactor containing ethyl methyl ketone or cyclohexanone, and the mixture of the solvents: propane-1,2-diol and hydroxypolyether G1000 while stirring. The

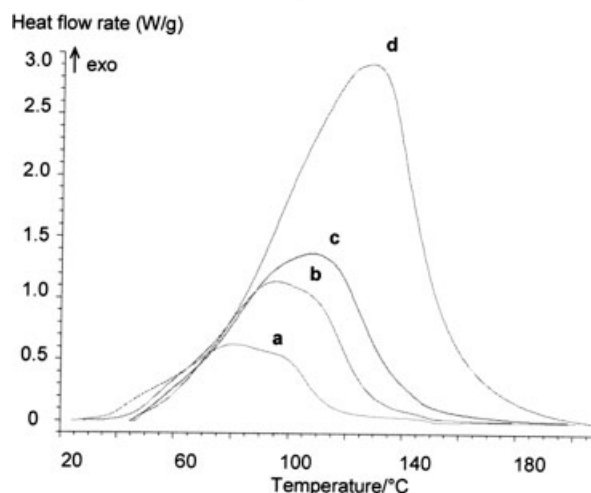
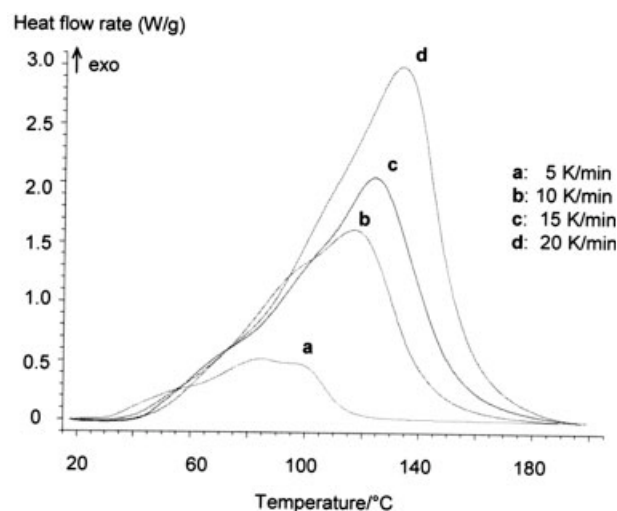


**Figure 2**  $dH/dt$  versus  $T_c$  ( $^{\circ}\text{C}$ ) for the resin cured with the Luperox K1-cobalt(II) octoate catalytic system at different  $\beta$ 's: 2, 5, 10, 15, and 20 K/min.

addition of hydrogen peroxide was done at such a rate that the temperature of the mixture content was  $35^{\circ}\text{C}$ . The homogeneous solution after the addition of the whole amount of hydrogen peroxide was stirred for 1 h. One day after the synthesis, the raw product was used as an initiator for the free-radical polymerization of the unsaturated polyester resin with promoter, a 1% solution of cobalt(II) octoate.<sup>19-21</sup> In this way, two initiators were prepared (Fig. 1).

The amounts of the substrates used for each synthesis are shown in Table I.

The concentrations of active oxygen in all of the initiators were determined by the titration of an initiator sample (dissolved in acetic acid) by a 0.1N solution of sodium thiosulfate in the presence of potassium iodine and starch according to Królikowski et al.<sup>22</sup> The concentrations of active oxygen in the studied initiators are given in Table II.



**Figure 3**  $dH/dt$  versus  $T_c$  ( $^{\circ}\text{C}$ ) for the resin cured with the initiator 1-cobalt(II) octoate and initiator 2-cobalt(II) octoate catalytic systems at different  $\beta$ 's: 5, 10, 15, and 20 K/min.

**TABLE III**  
 **$\Delta H_R$  and  $T_c$  at Different  $\beta$ 's for the Unsaturated Polyester Resin**

$\beta$ (K/min)	Luperox K1		Initiator 1		Initiator 2	
	$T_c$ (°C)	$\Delta H_R$ (J/g)	$T_c$ (°C)	$\Delta H_R$ (J/g)	$T_c$ (°C)	$\Delta H_R$ (J/g)
5	103.0	360.6	84.3	362.1	81.0	373.9
10	117.3	353.8	111.2	360.0	95.5	352.1
15	124.4	345.4	116.7	369.3	107.9	348.2
20	136.4	342.6	123.6	353.6	119.5	342.8
30	146.3	339.2	132.7	343.0	127.7	346.2

#### Curing procedure and calorimetric instrumentation

The obtained initiators (numbers 1 and 2) and Luperox K1 were used to cure the commercially available unsaturated polyester resin Estromal 1454. Cobalt(II) octoate (a 1% solution in styrene) was used as the accelerator.

The calorimetric measurements were carried out in a Netzsch DSC 204 calorimeter (Netzsch, Germany). All DSC measurements were made in aluminum pans with a pierced lid. The standard sample was prepared by the mixture of 10 g of unsaturated polyester resin with a fixed proportion of initiator and promoter (100 : 1 : 0.1) for approximately 1 min. The required amount of the sample (20 mg) was weighed into a previously weighed sample pan, sealed, and placed in the differential scanning calorimeter for each measurement. After each run, the weight of the sample was determined again to check any weight loss due to the evaporation of the styrene monomer. No significant weight loss was observed. The dynamic scans were performed from  $-10$  to  $250^\circ\text{C}$  with a nitrogen atmosphere and different  $\beta$ 's: 5, 10, 15, 20, and 30 K/min. All dynamic scans were analyzed with Netzsch Thermokinetics software (Netzsch-Gerätebau GmbH, Germany).

## RESULTS AND DISCUSSION

The DSC curves showed an asymmetrical peak, which could have been due to two different reactions taking place in the unsaturated polyester resin.<sup>23</sup> As shown in Figures 2 and 3, which present  $dH/dt$  versus the curing temperature [ $T_c$  (°C)], with  $\beta$  as the parameter for the resin cured with the Luperox K1–cobalt(II) octoate, initiator 1–cobalt(II) octoate, and initiator 2–cobalt(II) octoate catalytic systems, the temperature at which the reaction began and the exothermic DSC peak temperature (i.e.,  $T_c$ ) increased with  $\beta$ . The tem-

perature at which the completion of the cure reaction occurred increased with  $\beta$ , too.

$\Delta H_R$  estimated from the area under the DSC curve and  $T_c$  are given in Table III.

$\Delta H_R$  was due to a crosslinking reaction between the polyester double bonds and the styrene double bonds. However, the organic peroxide decomposition is a highly exothermic reaction, and different free-radical initiator systems can give different values for  $\Delta H_R$ .<sup>2,4,24</sup>

In the case of the resin polymerized in the presence of the new initiators (numbers 1 and 2) and cobalt(II) octoate in the range  $\beta = 10$ – $30$  K/min, slightly higher values of heat generated during the reaction were observed in comparison with the typical Luperox K1–cobalt(II) octoate redox system. Such behavior of the resin was probably due to the synergistic effect of the new initiators, which were richer in free radicals than the conventional organic peroxide<sup>25</sup> because free radicals were evolved by both hydrogen peroxide and ethyl methyl ketone peroxide or cyclohexanone peroxide formed during the oxidation process of ethyl methyl ketone or cyclohexanone with hydrogen peroxide. The heat generated during the curing reaction decreased with increasing  $\beta$ . Average values of 348.3 J/g for Luperox K1, 357.6 J/g for initiator 1, and 352.6 J/g for initiator 2 were assigned to the heat of polymerization of the unsaturated polyester resin. Other investigators<sup>26,27</sup> have reported a range of heat of polymerization from 292.6 to 426 J/g for unsaturated polyester resins. This range may be due to the different types of unsaturated polyester resins and free-radical initiator systems employed.<sup>23,27</sup>

#### Model-free estimation of E

Through the use of this method, the estimation of  $E$ , as the name points, could be made without the need to define a specific model for the function run. Therefore, the methods under consideration at first sight seem very enticing. However, it must be stressed that these methods only deliver correct results if the reaction processes to be investigated satisfy the required conditions. Within kinetic analysis, the model-free estimation of  $E$  is used as a powerful preliminary stage to solve the inverse reaction kinetics of complex reactions. The Friedman and/or Ozawa–Flynn–Wall methods are required to set up the reaction model in interaction with the original data.<sup>16</sup>

**TABLE IV**  
**Values of  $E$  (kJ/mol) and  $\log A$  Obtained by Friedman's Method for the Resin Cured with the Luperox K1–Cobalt(II) Octoate Catalytic System**

$\alpha$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$E$ (kJ/mol)	$46.12 \pm 1.96$	$43.22 \pm 1.43$	$42.81 \pm 0.96$	$44.18 \pm 1.32$	$45.73 \pm 1.45$	$46.64 \pm 1.60$	$46.81 \pm 1.37$	$43.85 \pm 1.62$	$43.21 \pm 2.46$
$\lg(A/s^{-1})$	4.12	3.69	3.62	3.81	4.03	4.18	4.24	3.88	3.80

TABLE V  
Values of  $E$  (kJ/mol) and  $\log A$  Obtained by Friedman's Method for the Resin Cured with the Initiator 1-Cobalt(II) Octoate Catalytic System

$\alpha$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$E$ (kJ/mol)	$39.46 \pm 0.93$	$44.85 \pm 2.60$	$44.57 \pm 2.37$	$43.68 \pm 2.80$	$45.37 \pm 2.78$	$48.59 \pm 2.37$	$48.89 \pm 2.85$	$44.36 \pm 4.22$	$42.03 \pm 5.66$
$\log A$ (s <sup>-1</sup> )	3.22	4.02	3.99	3.97	4.13	4.58	4.63	4.03	3.69

### Friedman analysis

Friedman proposed the application of the logarithm of the conversion rate  $d\alpha/dt$  (with  $\alpha_t$  given) as a function of reciprocal temperature:<sup>28,29</sup>

$$d\alpha/dt = A \exp(-E/RT)f(\alpha) \quad (12)$$

$$\ln(d\alpha/dt) = \ln[f(\alpha)] + \ln A - (E/RT) \quad (13)$$

As  $f(\alpha)$  is the constant for a given  $\alpha_t$ , the plot of dependence  $\ln(d\alpha/dt) = f(1/T)$  results in a straight line with a slope ( $m$ ) of  $-E/R$ . From  $m$  and the intercept of the straight line, the value of  $E$  and the logarithm of the pre-exponential factor ( $\log A$ ) can be obtained with a first-order reaction assumed.  $A$  is calculated as an average value over all dynamic  $\beta$ 's.

As shown from Tables IV–VI,  $E$  was not stable; it changed with  $\alpha$ . In the case of the resin polymerized with the Luperox K1-cobalt(II) octoate catalytic system, the maxima of  $E$  were observed at  $\alpha = 0.1$  and  $0.6$ , whereas for the initiator 1-cobalt(II) octoate and initiator 2-cobalt(II) octoate curing systems, the maxima of  $E$  were observed at  $\alpha = 0.2$  and  $0.7$  for each.  $E$  showed a clear dependence on  $\alpha$ ; this was an indication of the presence of a complex reaction path (a reaction with at least two steps).

### Ozawa–Flynn–Wall analysis

This method allows one to determine  $E$  (kJ/mol) and  $A$  for the  $n$ th-order reactions  $f(\alpha)$ . It is based on the variation of peak exotherm temperature with  $\beta$ , and the extent of reaction at the peak  $\alpha$  is constant and independent of  $\beta$ . In the Ozawa calculation procedure, the following equation is derived:

$$\ln \beta = \text{constant} - 1.052E/RT \quad (14)$$

As follows from this equation for a series of measurements at  $\beta$ 's for a fixed  $\alpha$ , the plot of  $\ln \beta = f(1/T)$  results in straight lines with

$$m = -1.052E/R \quad (15)$$

where  $T$  represents the temperatures at which  $\alpha$  is reached at  $\beta$ . The  $m$  values of the straight lines are directly proportional to  $E$ . A change in  $E$  with increasing  $\alpha$  indicates a complex reaction run, so that, in fact, the separation of variables as in the Ozawa–Flynn–Wall analysis is not recommended. These discrepancies are especially serious if the overall reaction is made up of competitive reactions.<sup>30,31</sup>

The average values of  $E$  and  $\log A$  for the resin cured with the Luperox K1-cobalt(II) octoate catalytic system were  $47.52 \pm 1.76$  and  $4.17$ , respectively. In the case of the resin polymerized with the new initiators cobalt(II) octoate redox systems, the following values of  $E$  and  $\log A$  were obtained:  $46.71 \pm 1.95$  and  $4.24$ , respectively, for the initiator 1-cobalt(II) octoate redox system and  $49.14 \pm 1.90$  and  $4.61$ , respectively for the resin cured with initiator 2-cobalt(II) octoate.

### Kinetic analysis with MULTIVAR-NLR

MULTIVAR-NLR applies a sixth-degree Runge–Kutta process in a modified Marquardt procedure to solve a system of differential equations, which are essentially based on the differential equations relevant to different reaction types and their various combinations. Fundamentally, multistep processes can only be analyzed with nonlinear regression. However, the nonlinear regression process can be advantageous for one-step processes as well because it provides a considerably better quality of fit compared to multiple linear regression.<sup>17,18</sup>

TABLE VI  
Values of  $E$  (kJ/mol) and  $\log A$  Obtained by Friedman's Method for the Resin Cured with the Initiator 2-Cobalt(II) Octoate Catalytic System

$\alpha$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$E$ (kJ/mol)	$46.52 \pm 0.94$	$47.68 \pm 1.94$	$46.03 \pm 2.22$	$45.70 \pm 2.16$	$47.01 \pm 2.25$	$48.76 \pm 2.48$	$48.42 \pm 2.89$	$44.31 \pm 3.14$	$42.00 \pm 4.22$
$\log A$ (s <sup>-1</sup> )	4.32	4.51	4.28	4.23	4.40	4.63	4.58	4.03	3.67

**TABLE VII**  
Kinetic Parameters of the Experimental Data Obtained with One Process and the Fn, Cn, and C<sub>1</sub> Functions  $f(\alpha)$  for the Unsaturated Polyester Resin Cured with the Luperox K1-Cobalt(II) Octoate Catalytic System

Type of reaction	ln A	log A	E (kJ/mol)	n	r
Fn	20.57	4.19	47.1	0.85	0.991
Cn	20.70	4.07	46.3	0.95	0.990
C <sub>1</sub>	20.07	3.98	45.8	—	0.991

The calculations of the kinetic parameters were performed in two steps: first, with the assumption of Fn, Cn, and C<sub>1</sub> and, second, with the assumption of a two-step process with the *n*th-order function  $f(\alpha)$  for the curing of the unsaturated polyester resin with the Luperox K1-cobalt(II) octoate catalytic system and a three-step process for curing of the unsaturated polyester resins with the new initiators cobalt(II) octoate catalytic systems.

**One single process**

In Tables VII-IX, we present the kinetic parameters determined for the unsaturated polyester resin cured with the Luperox K1-cobalt(II) octoate catalytic system (Table I) and the new initiators cobalt(II) octoate (Tables VIII and IX) with Fn, Cn, and C<sub>1</sub>.

In the examined range of  $\beta$ 's, 5-30 K/min, *E* varied insignificantly with the type of reaction model used. The calculated curves did not fit well with the experimental data at the beginning and the termination of the cure process, so the one-step models were unable to achieve a good description of this reaction.

**Two-step and three-step models**

In principle, the kinetic model should be as simple as possible. For the reasons already mentioned previously, for the curing process with the Luperox K1-cobalt(II) octoate catalytic system, an unbranched reaction process was assumed with the *n*th-order function  $f(\alpha)$  of reaction for each process (Fig. 4). In the examined range, 5-30 K/min, the received values of *E* were *E*<sub>1</sub> = 44.1 kJ/mol and *E*<sub>2</sub> = 80.7 kJ/mol for the Luperox K1-cobalt(II) octoate redox system. The logarithms of the frequency factor (ln *A*) was 13.8,

**TABLE VIII**  
Kinetic Parameters of the Experimental Data Obtained with One Process and the Fn, Cn, and C<sub>1</sub> Functions  $f(\alpha)$  for the Unsaturated Polyester Resin Cured with the Initiator 1-Cobalt(II) Octoate Catalytic System

Type of reaction	ln A	log A	E (kJ/mol)	n	r
Fn	15.45	4.63	49.1	0.99	0.995
Cn	15.51	4.35	47.4	1.09	0.996
C <sub>1</sub>	15.64	4.39	47.6	—	0.996

**TABLE IX**  
Kinetic Parameters of the Experimental Data Obtained with One Process and the Fn, Cn, and C<sub>1</sub> Functions  $f(\alpha)$  for the Unsaturated Polyester Resin Cured with the Initiator 2-Cobalt(II) Octoate Catalytic System

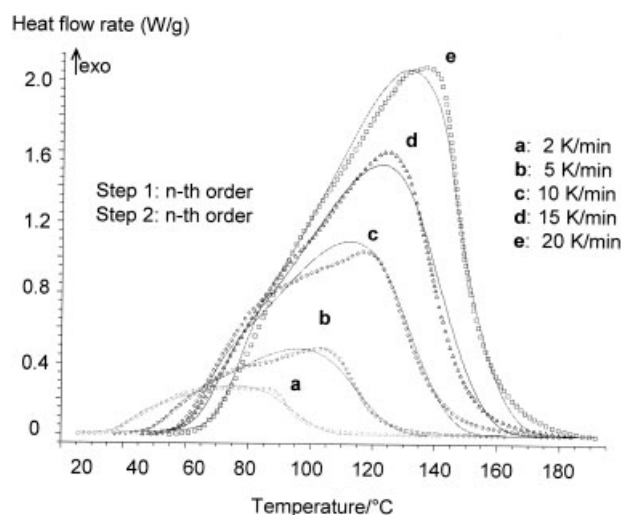
Type of reaction	ln A	log A	E (kJ/mol)	n	r
Fn	14.21	4.79	50.2	1.09	0.996
Cn	14.20	4.79	50.2	1.09	0.996
C <sub>1</sub>	15.34	4.50	48.2	—	0.995

and *n* was 0.81 for the first step and 1.77 for the second step with a correlation coefficient (*r*) of 0.997. *r*'s obtained with the *n*th-order function of reaction  $f(\alpha)$  and with two processes had higher values than those obtained with one single process of the reaction.

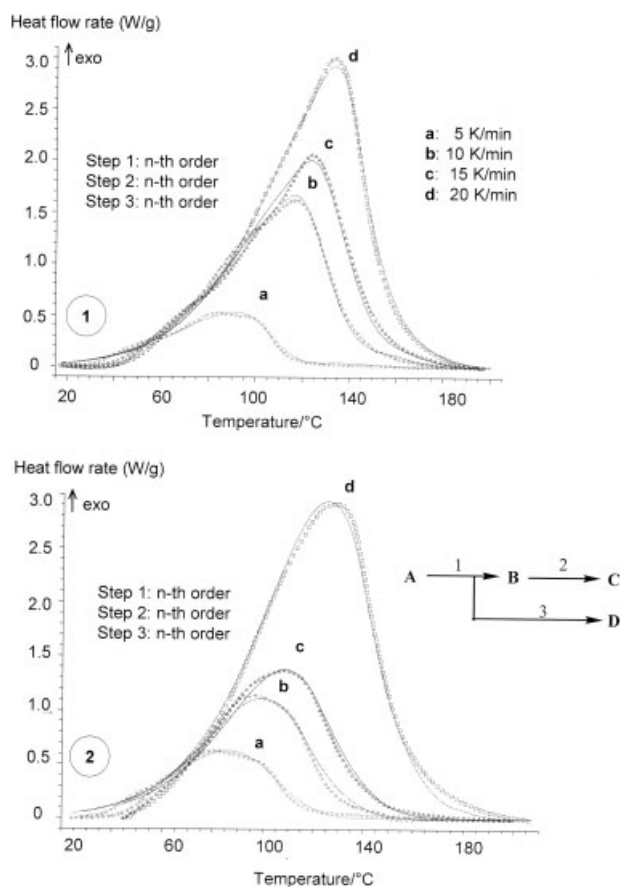
In the case of resins polymerized with the new initiators cobalt(II) octoate redox systems, a branched reaction process was assumed with three-step processes and with the *n*th-order function  $f(\alpha)$  for each process (Fig. 5).

The obtained *r* values were higher than those obtained with one single process of reaction with the values 0.998 for initiator 1 and 0.997 for initiator 2. The values of *E* of the third peak seemed to be constant with an average value of 89.2 kJ/mol for initiator 1 and 89.8 kJ/mol for initiator 2 with *n* = 0.97 and 0.68, respectively. For the first and second steps, the *E* and *n* values did not depend on the initiators: for initiator 1, *E*<sub>1</sub> = 45.2 kJ/mol, *n*<sub>1</sub> = 1.17, *E*<sub>2</sub> = 50.1 kJ/mol, and *n*<sub>2</sub> = 1.02 and, for initiator 2, *E*<sub>1</sub> = 45.3 kJ/mol, *n*<sub>1</sub> = 0.91, *E*<sub>2</sub> = 50.3 kJ/mol, and *n*<sub>2</sub> = 1.14.

As shown in Figure 5, the calculated curves fit well with the experimental data of the beginning and the termination of the cure process. This meant



**Figure 4** Kinetic analysis for the curing process with the Luperox K1-cobalt(II) octoate catalytic system with two processes and the *n*th-order function  $f(\alpha)$  of the reaction for each process ( $\beta$  = 5, 10, 15, and 20 K/min).



**Figure 5** Kinetic analysis for the curing process with the (1) initiator 1–cobalt(II) octoate and (2) initiator 2–cobalt(II) octoate catalytic systems with three processes and the  $n$ th-order function  $f(\alpha)$  of reaction for each process ( $\beta = 5, 10, 15,$  and  $20$  K/min).

that the two and three reactive processes better described the polymerization reaction than one single reactive process.

## CONCLUSIONS

The results presented here indicate that the new initiators based on 60% hydrogen peroxide and ethyl methyl ketone or cyclohexanone can be used in the polymerization of unsaturated polyester resins. The proposed branched reaction process for the resin polymerized with the new initiators and cobalt(II) octoate with three steps and with the  $n$ th-order function  $f(\alpha)$  for each step better described the polymerization process than one single process.  $r$  had higher values, above 0.997. The calculated values of  $E$  were in the range 45.2–50.3 and 89.2–89.8 kJ/mol for the curing process with cobalt(II) salt and initiators 1 and 2. They were comparable to those obtained when the typical initiating system composed of organic peroxide (Luperox) and cobalt(II) salt was used (44.1 and 80.7 kJ/mol, respectively).

The values of  $E$  obtained in the process of curing an unsaturated polyester resin with the free-radical initiators cobalt(II) octoate catalytic systems were in accordance with those tabulated in literature corresponding to a free-radical polymerization initiated by the redox decomposition of the initiator at low temperatures (the obtained values were located in the range 40–60 kJ/mol) and a free-radical polymerization initiated by the thermal decomposition of the initiator at high temperatures; the overall  $E$  values were approximately 80–90 kJ/mol.<sup>32</sup>

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