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THERMOSET CURE KINETICS BY ISOCONVERSIONAL METHODS

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Abstract

The curing kinetics of thermosets based on unsaturated polyester resin crosslinked with styrene was studied by differential scanning calorimetry (DSC). The isoconversional kinetic analysis was applied to non-isothermal data. The results obtained show a dependence of the activation energy (E_α) on conversion (α) that proves the existence of a multistep process and a complex kinetic scheme that must be interpreted in terms of chemical and physical mechanisms. The interrelationship of the Arrhenius parameters obtained from the isoconversional kinetic data has been used as a tool to investigate the production of free radicals by the action of a promoter (cobalt octoate) and the temperature on the initiator (methyl ethyl ketone peroxide). An optimum promoter/initiator ratio has been found.

Keywords: cure kinetics, isoconversional kinetics, thermosets

Introduction

Thermosets based on unsaturated polyester are crosslinked materials resulting from free-radical polymerisation of unsaturated polyester chains with a crosslinker agent, usually styrene. To induce the production of free radicals, organic peroxides are used that can be decomposed by temperature or by chemical promoters. The curing process is characterised by both chemical reactions and physical changes, namely gelation and vitrification [1, 2].

Kinetic studies of thermally induced reactions are usually performed by thermal analysis methods such as differential scanning calorimetry (DSC) that measure the heat flow of the reaction process in isothermal or dynamical (constant heating rate) experiments. It is generally assumed that at any given time or temperature the rate of exchanged heat is proportional to the overall fractional conversion rate, $d\alpha/dt$.

The main experimental problem encountered when performing kinetic studies of curing unsaturated polyester resins is the difficulty in finding a method that encompasses a wide experimental range of temperatures. If isothermal experiments are performed, it is impossible to work at very high temperatures since some of the reaction rate is lost during the stabilisation time, and so very low conversions cannot be studied. If work is done at very low temperatures some of the heat is likewise lost, since it is below the sensitivity threshold of the instrument. Dynamic experiments do not usually present these problems, since it is possible to reach high conversions, and al-

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though in some instances they are not equivalent to isothermal ones, it is possible to derive kinetic parameters that have been shown to agree with those obtained in isothermal experiments [3].

To apply the isoconversional kinetic analysis using multiheating rates (Ozawa's method [4]), it is not necessary to know the reaction model, $f(\alpha)$. It is possible to obtain, at each given conversion α, the activation energy E_α and another parameter that contains the pre-exponential factor k_0 and the integral form of the reaction model $g(\alpha)$. The main objective of the kinetic analysis is to obtain the kinetic triplet (E, k_0, $f(\alpha)$ or $g(\alpha)$) in order to predict reaction rates and the degree of conversion with time or temperature over the range of experimental chemical processes. In a previous work [3], it was shown that neither the explicit form of $f(\alpha)$ or $g(\alpha)$ nor the values of k_0 are necessary to simulate the isothermal behaviour from experimental results obtained with dynamical DSC runs. In fact, according to Vyazovkin [5, 6], the mere dependence of the activation energy on conversion is sufficient to reliably predict the kinetic behaviour.

The kinetic analysis is also expected to provide some information about the reaction mechanism, namely the steps which most contribute to the overall kinetic process. In the curing of unsaturated polyester resins, the chemical steps associated with a free radical polymerisation coexists with physical changes such as gelation and vitrification [7]. In the initiation stage, the production of initiation radicals by the decomposition of a peroxide can be induced by means of a promoter (chemical decomposition), although at some temperatures the peroxide decomposes spontaneously without the action of a promoter (thermal decomposition). As a result of all the above factors, the scanning DSC curves exhibited multiple peaks as shown in Fig. 1, revealing a multistep process. It is not easy from these experimental curves to account for the complexity of the process and identify individual kinetic steps.

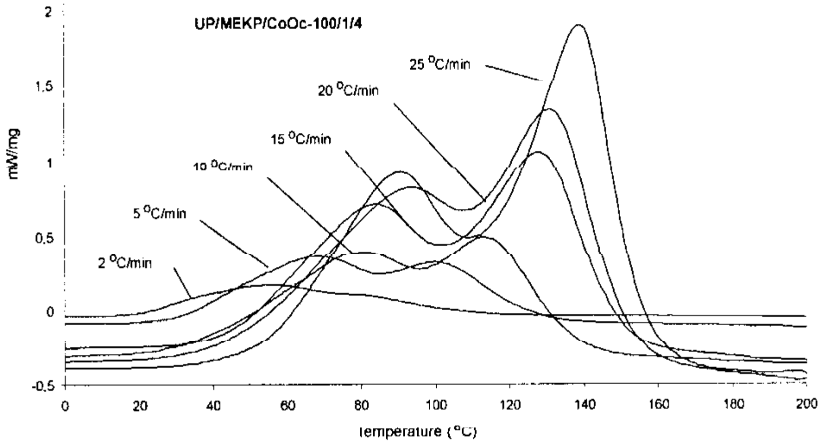

Fig. 1 Dynamic scans at different heating rates of the system 100/1/4 (polyester/initiator/promoter)

In isoconversional kinetic methods, it is accepted that the reaction rate at a constant conversion depends only on the temperature, and if there exists a single reaction mechanism, E_α is independent of α and may have the meaning of the intrinsic activation energy. The dependence of E_α on α proves the existence of several reaction steps. The study of this dependence may help to elucidate the different reaction mechanisms and possible interactions of the chemical and physical process [4, 8, 9].

Furthermore, from isoconversional kinetic data it is possible to generate the artificial isokinetic relationship (IKR) and investigate the existence of the actual IKR. An isokinetic relationship refers to the intersection point of the Arrhenius lines (i.e., $\ln k$ *vs.* $1/T$) of a series of reactions defining an isokinetic rate constant (k_{iso}) at an isokinetic temperature (T_{iso}) [10]. An isokinetic relationship is manifested as an interrelationship of Arrhenius parameters ($\ln k_{\mathrm{o,x}}=a+bE_{\mathrm{x}}$) where the subscript x refers to a factor producing a change in the Arrhenius parameters and can be used as a tool for understanding the reaction mechanism [11, 12].

In this paper we present the results obtained when the isoconversional kinetic analysis is applied to non-isothermal DSC data on the cure of an unsaturated polyester resin catalysed by the same amount of methyl ethyl ketone peroxide (MEKP) and different proportions of cobalt octoate as a promoter. The dependence of the activation energy (E_α) on conversion (α) is analysed in order to elucidate the kinetic scheme and the importance that the physical changes have in the curing kinetics. With the isoconversional data, we also investigate whether it is possible to assign a physical meaning to the isokinetic relationship between the Arrhenius parameters.

Some theoretical expressions

It is widely accepted that the rate equation of thermal transformations can be expressed as:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(t)\, f(\alpha) \tag{1}$$

where $f(\alpha)$ is the reaction model, a function of the conversion degree (α), $k(T)$ is the Arrhenius rate constant, T is the temperature and t is the time. For the kinetic analysis in dynamic heating experiments, the integral form of the rate equation $g(\alpha)$ is expressed as:

$$g(\alpha) = \int_{\mathrm{o}}^{\alpha} \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{k_{\mathrm{o}}}{\Phi} \int_{\mathrm{o}}^{\mathrm{T}} \mathrm{e}^{-\mathrm{E/RT}}\, \mathrm{d}T \tag{2}$$

where k_{o} is the pre-exponential factor, Φ is the heating rate, E is the activation energy, and R is the gas constant.

In order to determine kinetic parameters from DSC experiments, by expressing the right-hand side of Eq. (2) with a polynomial function proposed by Doyle [13] and rearranging the terms we obtain the well-known expression:

$$\log\Phi = \log\left(\frac{k_0 E}{g(\alpha)R}\right) - 2.315 - 0.4567\frac{E}{RT} \qquad (3)$$

As is usual, we suppose that E and k_0 do not depend on α or on T and Φ. According to Eq. (3), the activation energy E and the constant $A'=[\log(k_0E/g(\alpha)R)-2.315]$ can be determined from the slope and its intercept, respectively, of the linear relationship $\log\Phi$ *vs.* $1/T$ for a constant conversion α (Ozawa's method [4]). From the intercept, it is also possible to obtain the constant $A=\ln[k_0/g(\alpha)]$, which is only a function of the conversion degree (α).

From Eq. (1) with the only supposition that E and k_0 are independent of T and Φ it is also possible to obtain

$$\ln\left[\Phi\left(\frac{d\alpha}{dT}\right)\right] = \ln\left[k_0 f(\alpha)\right] - \frac{E}{RT} \qquad (4)$$

which in conjunction with DSC experimental data yields the activation energy E and the constant $\ln[k_0 f(\alpha)]$ of the linear relationship $\ln[\Phi\,(d\alpha/dT)]$ *vs.* $1/T$, for a constant conversion α.

Experimental

Materials

A commercially available general purpose UPE supplied by Reposa under the commercial name Estratil.-A228 was used in this study. It is an orthophthalic-type resin that contains phthalic anhydride, maleic anhydride and propylene glycol in a molar ratio of 3:2:5 determined by ^{1}H NMR. The average molecular mass of the UPE is 1696 g mol^{-1} and the equivalent molecular mass per mole C=C is 465 g mol^{-1}, with 35 wt% of styrene as a crosslinking agent (molar ratio of styrene to unsaturated polyester double bonds, S/E=2.4). As an initiator, a 50 wt% solution of methyl ethyl ketone peroxide (MEKP) in dimethyl phthalate supplied by AKZO (Butanox M-50) was used. Cobalt octoate (as a 6 wt% solution of cobalt) supplied by AKZO (NL51P) was used as a promoter.

Differential scanning calorimetry

The calorimetric measurements were made with a Mettler DSC 30 calorimeter coupled to a Mettler TA4000 thermoanalyser. The mass of the samples was 20 mg. A standard sample was prepared by mixing 10 g of UPE resin with fixed proportions of initiator (1% by mass of total resin) and different concentrations of cobalt octoate (ranging from 0 to 8% by mass of total resin) and rapidly stirring the mixture. Several dynamic curings were made from –100°C to 250°C and at heating rates of 2, 5, 10, 15, 20 and 25°C min^{-1} to determine the total reaction heat associated with the complete conversion of all reactive groups (ΔH_R). We assumed that in these conditions the material underwent complete curing. The reaction rate $d\alpha/dt$ and the degree of conversion α reached at time t were obtained by means of the following expressions:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=\frac{1}{\Delta H_{\mathrm{R}}}\frac{\mathrm{d}H}{\mathrm{d}t},\ \alpha=\frac{\Delta H_{\mathrm{T}}}{\Delta H_{\mathrm{R}}}$$

where ΔH_{T} is the heat flow released up to temperature T and ΔH_{R} is the total heat of the reaction, both obtained by integration of the calorimetric signal, $\mathrm{d}H/\mathrm{d}t$.

Results and discussion

Using Eq. (3), the isoconversional kinetic analysis was applied to the different degrees of conversion, for each composition used. For each degree of conversion the logarithm of the heating rate was correlated with the inverse of the temperature. Figure 2 shows the experimental curves $\log\Phi$ *vs.* T^{-1} for various degrees of conversion for the system with 4% cobalt octoate. The slope (E) and intercept (A') of the set of correlations shown in Fig. 2 were calculated for all the systems, which gave E_α and A_α for each formulation studied. $A_\alpha=\ln[k_o/g(\alpha)]$ was derived from the intercept $A'=\log(k_oE/g(\alpha)R)-2.315$ and E. Figure 3 shows the values of E_α for the different concentrations of cobalt octoate (ranging from 0 to 8%) used. Very similar curves are obtained when A *vs.* α is represented.

The actual dependence of E_α on α (Fig. 3) reveals a complex curing process formed by a multi-step mechanism in both cases, without and with promoter. It can be seen in Fig. 3 that the E_α does not only vary with the degree of conversion but it also varies strongly depending on whether the promoter is used or not, and varies slightly with the amount of promoter used. In a previous work [14] we explained the initial decreasing of E with α by the effect of autoacceleration. It is not possible to explain the increase of E with α, at $\alpha>0.5$, only in terms of chemical kinetic mechanisms and it is necessary to take into account the physical changes associated with the increase in viscosity and gelification. In a previous work we obtained $\alpha_{\mathrm{gel}}=0.45$ [13]. The presence of promoter softens the initial decrease and final increase of E with

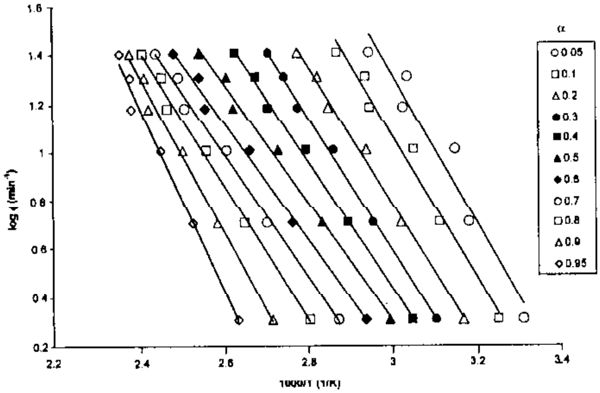

Fig. 2 Decimal logarithm of the heating rate *vs.* the reciprocal temperature at different conversion degrees for the system 100/1/4

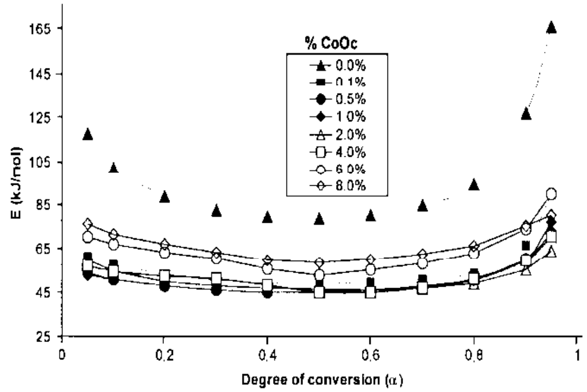

Fig. 3 Dependence of activation energy on the conversion degree for different proportions of promoter

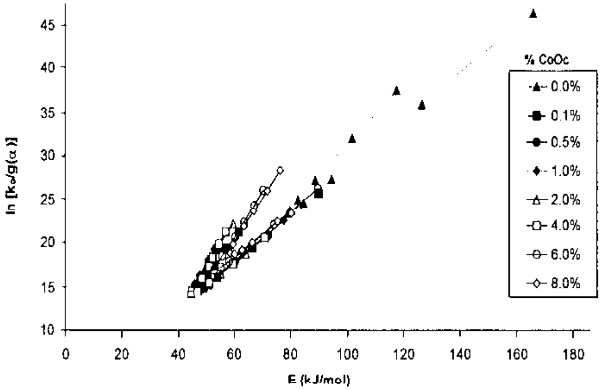

Fig. 4 $\ln[k_0/g(\alpha)]$ *vs.* activation energy at different proportions of promoter

α. The promoter appears to reduce the autocatalytic production of free radicals at the beginning of the reaction and facilitates the reaction process at high levels of conversion. In an early work [15] dealing with the appearance of multiple exothermic peaks (Fig. 1), we associated the lower temperature peak with polymerisation initiated by the cobalt octoate and the second, higher temperature peak with thermal decomposition of the MEKP. Recently Cook *et al.* [16] provided results that were also contrary to the above mechanism. Although we are still of the opinion that both processes (the chemical and thermal decomposition of the initiator) actually occur, it is clear that the physical environment and secondary reactions such as the homopolymerisation of the styrene [3] and the dual role of the cobalt octoate/MEKP redox system [16] have a great influence on the overall kinetics. Figure 3 shows that increasing the amount of promoter (above 2%) also increases the energy of activation, suggesting that the effectiveness of the promoter decreases. This result agrees with what was reported in [16]; at high concentrations, the cobalt species decomposes the initiator but also destroys the primary and polymeric radicals.

Table 1 Adjustment parameters of linear regression of the branches in Fig. 4

%CoOc	Branch I			Branch II		
	a	*b*	*R*	*a*	*b*	*R*
0.00	–4.84	0.360	1.000	2.052	0.267	1.000
0.10	–6.66	0.453	1.000	1.925	0.264	1.000
0.50	–9.09	0.527	0.999	2.750	0.250	1.000
1.00	–10.9	0.571	1.000	2.465	0.257	0.999
2.00	–8.53	0.516	0.999	3.550	0.235	0.997
4.00	–13.7	0.613	0.998	2.654	0.252	0.999
6.00	–10.4	0.517	0.999	2.472	0.264	0.999
8.00	–10.2	0.504	1.000	4.301	0.237	0.998

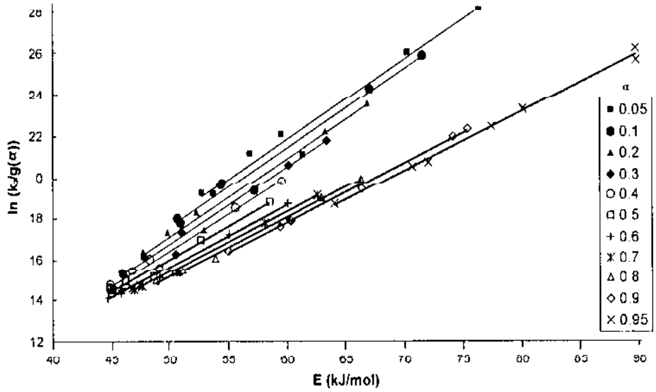

Fig. 5 $\ln[k_0/g(\alpha)]$ *vs.* activation energy at different conversion degrees

The representation of plots of $\ln[k_0/g(\alpha)]$ *vs.* E_α for each proportion of promoter, Fig. 4, shows one type of isokinetic relationship: $\ln[k_0/g(\alpha)]=a+bE_\alpha$. The figure suggests two very different processes at the beginning and at the end of the reaction (the two branches) and an intermediate process (the vertex) linking them. Table 1 shows the adjustment parameters of linear regression of all the branches. It can be seen that the slope of the branch associated with low conversion (branch I) varies significantly from 0 to 1% cobalt octoate, remaining constant or decreasing slightly

Table 2 Adjustment parameters of linear regression of the lines in Fig. 5

α	*a*	*b*	*R*
0.05	–1.387	0.387	0.985
0.10	–1.684	0.385	0.988
0.20	–1.919	0.380	0.992
0.30	–1.997	0.374	0.993
0.40	–1.368	0.355	0.992
0.50	–0.113	0.322	0.993
0.60	0.447	0.303	0.997
0.70	0.577	0.295	0.998
0.80	0.545	0.292	0.999
0.90	0.248	0.292	0.999
0.95	0.250	0.287	0.998

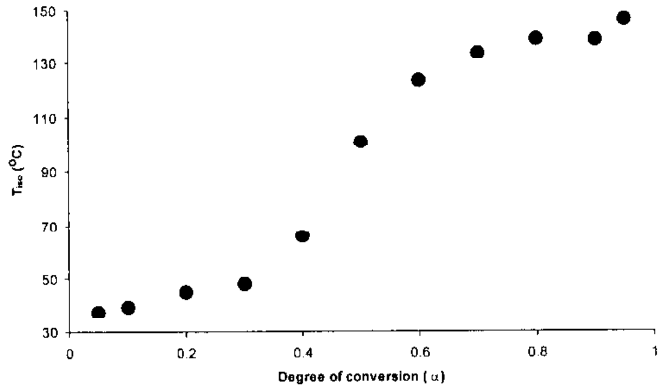

Fig. 6 T_{iso} obtained from the slopes of Fig. 5 *vs.* the conversion degree

at higher concentrations. However, the branch associated with a high level of conversion (branch II) has the same slope regardless of the amount of promoter, and it is also the same as the sample without promoter. If an actual IKR exists, the slope ($b=1/RT_{iso}$) of this relationship is inversely proportional to T_{iso}, which in turn is associated with the vibrational energy exchange between the reactants and their molecular environment [5, 10]. The T_{iso} derived from the low conversion and high conversion branches are too low and too high respectively to adopt a physical meaning, and thus no actual IKR exists. Another IKR was investigated by replacement of $\ln[k_0/g(\alpha)]_\alpha$ and E_α for reactions with varying amounts of promoter at constant α.

Figure 5 shows the linear relationships obtained and Table 2 the coefficient adjustment of linear regressions. Figure 6 shows the T_{iso} derived from the regression slope. It can be seen that two levels of T_{iso} were obtained, T_{iso}=140°C ($0.7<\alpha<1$) and T_{iso}=43°C ($0<\alpha<0.4$), which suggests that the reaction process takes place in three energy stages, one at low level, another at high level and the third at an intermediate stage that links the other two. When a promoter is used, the experimental curing process lies in a temperature interval of 40 to 150°C, depending on the temperature rate. Thus, it is now possible to assign some kind of physical meaning to the T_{iso} obtained.

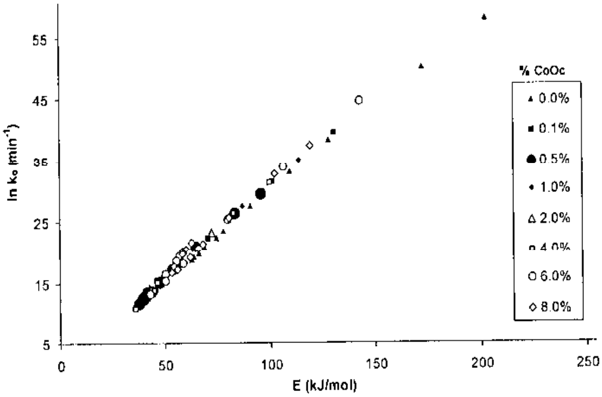

Fig. 7 lnk_0 *vs.* the activation energy for different proportions of promoter

In order to eliminate the influence of $g(\alpha)$ or $f(\alpha)$ on a possible IKR between k_0 and E, we accepted, for all the samples evaluated, an autocatalysed model $f(\alpha)=\alpha^m(1-\alpha)^n$ with m=0.428 and n=1.672, obtained from a previous work [17]. With DSC experimental data, from the slope of the linear relationship ln[Φ(dα/dT)] *vs.* 1/T we obtained the activation energy E_α and, from the intercept values [ln($k_0 f(\alpha)$)] and

Table 3 Adjustment parameters of linear regression of the lines in Fig. 7 and the values of T_{iso} obtained from the slopes

%CoOc	*a*	*b*	*R*	T_{iso}/°C
0.00	1.373	0.284	0.999	151.1
0.10	0.525	0.302	0.999	124.9
0.50	0.214	0.312	0.999	112.9
1.00	0.527	0.307	0.999	118.3
2.00	-0.011	0.321	0.999	101.1
4.00	0.200	0.316	0.998	107.8
6.00	0.882	0.308	0.997	117.9
8.00	1.048	0.307	0.992	118.9

using the preceding model, the constant $k_{0\alpha}$ for a constant conversion α. Figure 7 shows the IKR ($\ln k_0=a+bE$) that it is now possible to establish. Table 3 shows the coefficient adjustment of linear regressions with a regression coefficient near to 1 without the need to separate branches associated with low and high levels of conversion. Comparing Fig. 7 with Fig. 5 one can conclude that $g(\alpha)$ or $f(\alpha)$ varies strongly from low to high conversion owing to chemical and physical changes that take place with the advance of the reaction. The T_{iso} derived from the slope are also reported in Table 3. For a sample without promoter, T_{iso}=151°C; this falls to 101°C for a promoter content of 2% and then rises to 118°C for 8% octoate content. We found that the main thermal decomposition peak of MEKP appears in an 80–160°C interval [17]. The variation in T_{iso} is consistent with the explanations given above in that after an optimum concentration, the increase in cobalt octoate produces loss of effectiveness because it destroys primary and polymeric radicals.

Conclusions

Isoconversional kinetic analysis applied to the non-isothermal curing of an unsaturated polyester resin based thermoset shows an experimental dependence of the activation energy on the degree of conversion, which should be interpreted not only in terms of the reaction mechanism but also in terms of the change of physical properties with the degree of curing.

The isoconversional method makes it possible to study the overall kinetics without the need to separate or deconvolute the multiple peaks exhibited in DSC scanning curves, which should be interpreted as a general response of the DSC instrument to both chemical and physical changes.

From the isoconversional kinetic data it is possible to obtain the interrelationship of the Arrhenius parameters, called the isokinetic relationship. Although their physical meaning is questionable, they have been used as a tool to understand the effect produced by the variation of the amount of promoter with a constant initiator/resin ratio. The results show that the effectiveness of the promoter reaches a maximum at a low level of promoter (<2%) and decreases with higher proportions, probably owing to side reactions of the MEKP/octoate redox system. In terms of T_{iso} and vibrational energy, regardless of the amount of promoter, the reaction process takes place in three stages, one at low level ($0<\alpha<0.3$), another at high level ($0.7<\alpha<1$) and the intermediate stage that links the two.

When an autocatalytic model for $f(\alpha)$ is used to establish close relationships with $\ln(k_o)-E$, the separate branches of the $\ln[k_o/g(\alpha)]-E$ relationship are reduced to one for all α; thus, $f(\alpha)$ acts as a shape factor that varies strongly from low to high conversions. From this relationship, the same results are deduced as regards the effectiveness of promoter, resulting in an optimum MEKP/cobalt octoate ratio. Consequently, it is not necessary to know $f(\alpha)$ or $g(\alpha)$ to use IKR as a tool to investigate kinetics.

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