

Kinetic Study of Phenolic Resin Cure by IR Spectroscopy

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ABSTRACT: The cure reaction of a commercial phenolic resin (FRD-5002, Borden Chimie S.A.) has been studied by IR spectroscopy (Fourier transform IR). A phenomenological approach was used to characterize the kinetic of reaction. Various kinetic models, including homogeneous reactions, diffusion-controlled reactions, phase boundary movement, and nucleation and growth-type kinetic, have been tested. Kinetic analyses using integral procedures on isothermal data indicate that the cure reaction data can be described above 140°C using the homogeneous first-order reaction model. The activation energy has been found to be about 49.6 kJ mol⁻¹. At lower temperature, a diffusive mechanism was active, and the kinetic of reaction was well described by the Jander kinetic model. Because of the simple kinetic control active above 140°C, a mechanistic model for the resol cure at these temperatures has been also proposed.
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Key words: phenolic resin; resol; cure; kinetic; Fourier transform IR

INTRODUCTION

Phenol-formaldehyde (PF) resins are a class of materials having wide applications in many areas, largely due to their high temperature resistance, high char yield, and moderate flame resistance.^{1,2} PF is one of the few polymers whose production and developmental work have been steadily increasing, with continued interest sustained by active research over the past eight decades. The interest in and consequent growth of PF resins began with the early work of Von Bayer³ and the historic heat and pressure patents of Bakeland.^{4,5} Even today, PF resins continue to be an active field in both academics and industry. Academic interest is centred around (a) improvement of properties by chemical modifications,^{6–8} (b) understanding of cure mechanisms,^{9–11} and (c) decomposition mechanism studies.^{12–14}

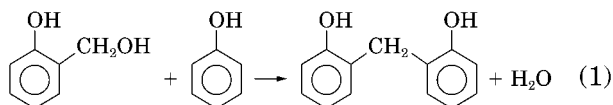
The kinetic investigation is probably the most active research field because, as in the case of other thermosetting materials, the cure of PF resins requires a careful control of processing conditions, in order to allow an adequate viscosity development, which is strictly dependent on temperature and polymer structure. In fact, the continuous change in the resin from a low-viscosity liquid monomer (at starting point) to a solid polymer (at process end) affects shrinkage, void content, residual stresses, and defines the final mechanical performance. Thus, the control of the cure of this material on a scientific basis requires an accurate knowledge of the polymerization kinetics as a function of the applied conditions. In recent years, it has been demonstrated that optimization and control procedures, based on the modeling of cure kinetics and fundamental transport phenomena associated with the specific process used, can be successfully applied to select the appropriate conditions of cure.

It has already been confirmed that the cure of PF resins is accomplished in a two-step process.^{15,16} The first step involves the addition of

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formaldehyde to phenol to form hydroxymethyl phenol, and the second one involves the condensation of hydroxymethyl phenols to form methylene and methylene-ether-bridged di- or high-molecular compounds. Eventually, the methylene ether bridge may lead to methylene-bridged phenol, water, and formaldehyde by disproportionation. However, the first reaction step does not occur in a commercial product because, to obtain a liquid material able to set by heating, the addition reaction has been mostly completed and the condensation reaction is usually stopped after an initial reaction stage by lowering the temperature. This intermediate product, called a resol, contains polymeric species at low degrees of polymerization, still soluble in alkaline solution, and just a low amount of formaldehyde. Branched polymer chains with a substantial amount of hydroxymethyl groups attached are contained in a commercial resol. This product needs for curing only to be heated sufficiently to continue the condensation reaction. In addition, the condensation of two hydroxymethyl groups to form a dibenzyl ether linkage can occur near neutral or acid pH values,¹⁷ but it is rare in the alkaline environment used to produce most of resols.^{18,19} Consequently, the most important reaction involved in the alkaline polymerization of a resol is the condensation of hydroxymethyl groups with unreacted active position of other phenolic rings:



Therefore, the knowledge of kinetic behavior of this reaction is required for the control and optimization of resol cure process. Different methodologies have been used in the literature for the evaluation of kinetic parameters.^{19–23} In general, kinetic expressions may be phenomenological or mechanistic. Phenomenological models are related to the main features of the reaction kinetic and do not take into account individual reactions, whereas mechanistic models are obtained from balances of species involved in the reaction. Unfortunately, a complete chemical characterization of the thermosetting reactions to provide a mechanistic kinetic model is frequently very difficult to perform, and, consequently, the phenomenological approach is preferred. The phenomenological reaction rate can be expressed either in the differential form,

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) \quad (2)$$

or in the integrated form,

$$g(\alpha) = \int \frac{d\alpha}{f(\alpha)} = \int k dt \quad (3)$$

where α is the fractional conversion at any time t , k the rate constant, and $f(\alpha)$ a functional form of α depending on the reaction mechanism. Functional forms of $f(\alpha)$ representing different reaction mechanisms have been described in the literature. Table I includes homogeneous reaction models, autocatalytic reaction models, phase boundary movement (or surface reaction) models, and nucleation and growth models. In addition to the form of $f(\alpha)$, the integrated form $g(\alpha)$ is also included in the table for each model. Applicability of a model can be tested using either derivative or the integral form of the rate expressions.

Here, the condensation reaction of hydroxymethyl groups with unreacted active phenolic ring positions, for a commercial resol (FRD-5002, Borden Chimie S.A.), has been studied by IR spectroscopy [Fourier transform IR (FTIR)], and the obtained isothermal conversion-time data has been tested using an integral method of analysis.

KINETIC MODELING

The kinetic modeling is carried out in a series of steps. As stated earlier, kinetic modeling can be performed using both derivative or integral procedures. If the derivative mode of analysis is used, then kinetic modeling starts with eq. (2). Instead, when the integral mode of analyses is used, then kinetic modeling starts with eq. (3). After choosing the mode of analysis, for the kinetic model to be tested, the functional form $f(\alpha)$ is selected from Table I. Then, the experimental conversion-time data are used to test the model. The testing criteria are (1) high regression coefficients, and (2) zero intercept value. A successful model should describe the experimental data irrespective of the mode of analysis. Procedures and results of the analyses are presented in the following sections. These procedures and computer software (KaleidaGraph, version 3.0.1, Synergy Software) have been all tested and verified with simulated conversion-time data for different models. In the de-

Table I Evaluated Kinetic Models

Model	$f(\alpha)$	$g(\alpha) = \int \frac{d\alpha}{f(\alpha)}$
Homogeneous reaction models		
First order	$(1 - \alpha)$	$-\ln(1 - \alpha)$
n th order	$(1 - \alpha)^n$	$\frac{[1 - (1 - \alpha)^{(1-n)}]}{(1 - n)}$
Autocatalytic reaction		
$m = 1, n = 1$	$\alpha^m(1 - \alpha)^n$	$\ln[\alpha/(1 - \alpha)]$
$m = 2, n = 1$		$\ln[\alpha/(1 - \alpha)] - 1/\alpha$
$m = 2, n = 2$		$\ln[\alpha/(1 - \alpha)] + 1/(1 - \alpha) - 1/\alpha$
Reaction interface models (phase boundary movement models)		
Diffusion controlling		
One-dimensional diffusion ($n = 1/4, 1/3, 1/2, 2$)	$\frac{1}{\alpha} \cdot \alpha^{(1-n)}$	α^n
Two-dimensional diffusion	$\frac{-1}{\ln(1 - \alpha)}$	$(1 - \alpha) \cdot \ln(1 - \alpha) + \alpha$
Gintsling–Brounshtein kinetics (3D diffusion)	$\frac{3(1 - \alpha)^{2/3}}{2[1 - (1 - \alpha)^{1/3}]}$	$[1 - (1 - \alpha)^{1/3}]^2$
Jander kinetics (3D diffusion)	$(3/2)[(1 - \alpha)^{-1/3} - 1]$	$1 - 2/3\alpha - (1 - \alpha)^{2/3}$
Surface reaction controlling		
Contracting geometry ($n = 2, 3$)	$n(1 - \alpha)^{\frac{(n-1)}{n}}$	$1 - (1 - \alpha)^{1/n}$
Nucleation and growth models		
Random nucleation	α	$\ln\alpha$
Avrami–Erofeev kinetic ($n = 1, 1.5, 2, 3, 4$)	$n(1 - \alpha)[- \ln(1 - \alpha)]^{1/n}$	$[- \ln(1 - \alpha)]^{1/n}$

rivative method of analysis, the computer program calculates $d\alpha/dt$ by finding the slope between two adjacent conversion points in the isothermal data. Then, for the selected model, it calculates the value of $f(\alpha)$ at each point and stores the results in an array. A plot of $d\alpha/dt$ vs $f(\alpha)$ should yield a straight line with zero intercept and a slope equal to the rate constant k . Instead, in the integral method of analysis, because the temperature is a constant in isothermal experiments, eq. (3) can be integrated to give

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = k \cdot \int_0^t dt \tag{4}$$

or

$$g(\alpha) - g(0) = k \cdot t \tag{5}$$

In the analysis of conversion-time isothermal data, the last method is more convenient because it does not require the evaluation of the $d\alpha/dt$ quantity. Since in isothermal experiments there is an initial dynamic portion, during which some reaction may take place, the start of the actual isothermal conditions corresponds to a nonzero value of conversion α_1 . With this consideration, eq. (5) becomes

$$g(\alpha) - g(\alpha_1) = k \cdot t_{\text{iso}} \tag{6}$$

where t_{iso} represents the time for the isothermal part of the experiment. A plot of $g(\alpha) - g(\alpha_1)$ vs t_{iso} should be a straight line with zero intercept and a slope equal to the rate constant k .

The models to be tested represent a wide variety of reaction mechanisms, the simplest being the homogeneous reaction model,²⁴ which assumes that the reaction is occurring simulta-

neously at the molecular level throughout the sample. This may be a rather simplistic assumption considering the complexity of cure reactions. However, it establishes a reference for comparative analyses. Also included in the homogeneous reaction mechanism category is the autocatalytic type of reactions, where the initial reaction product helps to catalyze the reaction process, thus accelerating the reaction rate. Autocatalytic reaction models are often used to describe the cure kinetics in epoxy systems.^{25,26}

When the reaction starts at a phase boundary and advances into the unreacted zone of the sample, the kinetic characteristics of the overall rate process are determined by the geometrical mode of advance of the reaction interface from these boundaries toward the centers of the unreacted zone. Two- and three-dimensional phase boundary rate expressions are available.

In diffusion-limited reaction, the overall rate is determined by the movement of reactant species (or a product from) toward a reaction interface. Diffusion can be envisioned to take place in one, two, or three dimensions. The rate expressions include these differences in the mode of diffusion. One of the three-dimensional diffusion models tested in this study is the Gintsling–Brounshtein model, which assumes the Fick's law of diffusion, while the other tested model is the Jander model, which assumes that thickness (x) of the diffusion layer increases according to $dx/dt = D/x$, where D is the diffusivity and t denotes the time.

The nucleation process involves conversion of a small volume of reactant into a stable particle of product and continued reaction (growth) occurs preferentially at the interfacial zone of contact between these two phases. Initial nucleation and growth expressions, like the power law expression, which assumes that the growth rate increases continually, were developed to describe crystallization processes, and fail to describe actual chemical reaction processes for which such an assumption would be unrealistic. However, modifications by Avrami, Erofeev, and Mitskevich, and by Mampel, yield a more general form of the equation that is found to describe many reactive systems over the entire conversion range.

EXPERIMENTAL

The analyzed material was a monocomponent commercial phenol/formaldehyde resin system, FRD-5002, developed by Borden Chimie S.A. The

Table II Methylolated Phenol IR Absorption Bands

Functional Group	Absorption	Wavenumber (cm ⁻¹)
H—O	Stretching	3330
Ar—H	Stretching	3100
—CH ₂ —	Stretching	2900
C—C	Stretching	1612
C—C	Stretching	1598
C—C	Stretching	1480
—CH ₂ —	Bending	1450
H—O	Bending	1359
Ar—O ⁻	Stretching	1200
CH ₂ —OH	Stretching	1100
Ar—H	Out-of-plane bending	770–740

resin was stored in a refrigerator at a temperature of -6°C, to prevent room temperature polymerization.

A Nicolet 5PC FTIR spectrometer at a resolution of 4 cm⁻¹ was employed in the transmission mode for both resin characterization and kinetic study. To follow the reaction courses, the chamber was first heated to the desired temperature before any measurement. A small drop of resin was placed on a sodium chloride (NaCl) plate and it was mounted in the chamber. Three consecutive scans were taken at each sampling time, and their average was stored for the later data analysis. All the IR spectra for the kinetic studies were shown in the absorbance mode.

IR analysis is based on the fact that each chemical group in a sample absorbs IR radiation of some characteristic frequencies. The use of the Lambert–Beer law allows the determination of the concentration of an absorbing species in the reaction medium, if there is an absorption peak that obeys the Lambert–Beer law. The Lambert–Beer law can be expressed as follows:

$$A = \varepsilon_T^\lambda \cdot b \cdot c \quad (7)$$

where A is the absorbance, ε_T^λ is the molar extinction coefficient at T temperature and λ wavelength, b is the thickness of the test sample, and c is the concentration of the absorbing molecule. The principal IR absorption bands of a methylolated phenol molecule are reported in Table II. According to the correlation described in the literature,²⁷ the deformation vibrations of C—H bond in benzene rings give absorption bands in

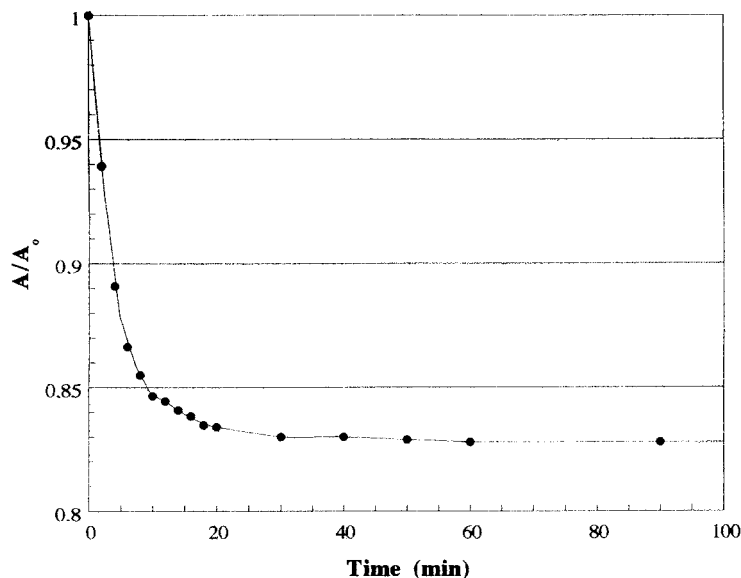


Figure 1 Relative IR absorption of the reference peak vs time at 85°C.

the 770–740 cm^{-1} range. This group disappears during the polymerization and, therefore, its concentration can be used as an index of the polymerization conversion. The deformation vibrations of C—C bonds in phenolic groups absorb in the region 1500–1400 cm^{-1} . This group does not participate in any chemical reaction during the polymerization; however, the peak showed a gradual decrease as the polymerization proceeded (see Fig. 1), because when the reaction takes place, the volume of the system contracts. Such volume contraction changes the sample thickness and induce an error in the measured absorbances. The absorption peak of C—C bond at 1480 cm^{-1} can be chosen as internal standard in order to eliminate this error. In particular, the absorbances at maximum of the absorption, i.e., at 740 and 1480 cm^{-1} , have been followed and scanned in the study of the reaction kinetic. The absorption peaks at 740 and 1480 cm^{-1} are named sample peak (SP) and reference peak (RP), respectively.

The relationship between the conversion ratio (α) and the concentration of the reactive group can be expressed as

$$\alpha = \frac{n_1^0 - n_1}{n_1^0} = 1 - \frac{n_1}{n_1^0} = 1 - \frac{C_1}{C_1^0} \quad (8)$$

where n_1^0 and C_1^0 are respectively the initial number of moles and concentration of reactive group, and n_1 and C_1 are the number of moles and con-

centration of reactive group at t time. Using the Lambert–Beer law eq. (7), the relationship between α and the reactive group absorbance can be written as

$$\alpha = 1 - \frac{b_1^0}{b_1} \cdot \frac{A_1}{A_1^0} \quad (9)$$

where b_1^0 and b_1 are the specimen thickness at initial and t time, respectively. The b_1^0/b_1 quantity can be obtained from the absorbance of the reference group, whose concentration does not change during the polymerization. Finally, eq. (9) becomes

$$\alpha = 1 - \frac{A_1/A_2}{A_1^0/A_2^0} = 1 - \frac{\bar{A}}{\bar{A}^0} \quad (10)$$

where A_1^0 , A_1 , A_2^0 , and A_2 are the initial absorbance and the absorbance at t time of the reactive and reference groups, respectively, and the synthetic quantity \bar{A} is named reduced absorbance.

If the absorbances of reactive and reference groups can be measured at different times, the reaction conversion can be calculated from changes in the reduced absorbance by eq. (10). The comparative conversion behavior obtained from isothermal analysis at different temperatures is shown in Figure 2.

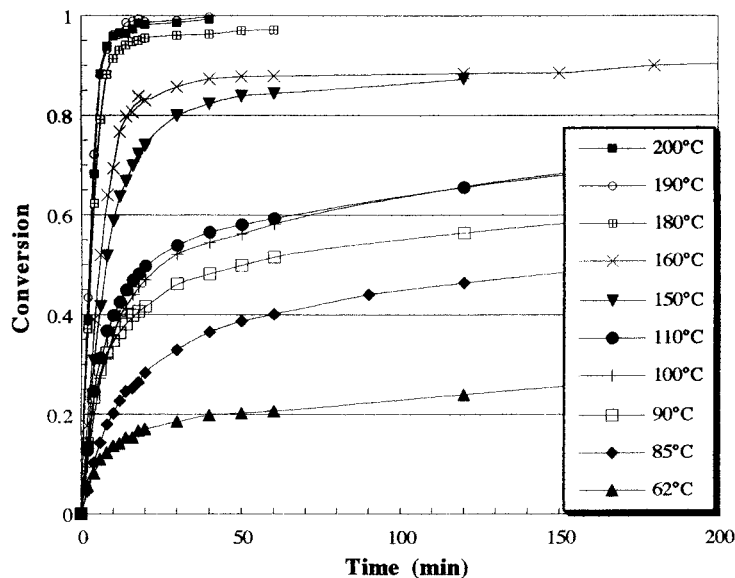


Figure 2 Conversion behaviors obtained by isothermal FTIR analyses performed at different temperatures.

RESULTS AND DISCUSSION

Data obtained from isothermal experiments performed at temperatures ranging from 60 to 200°C were analysed by the integral method of analysis.

Figure 3 shows a plot of $g(\alpha) - g(\alpha_1)$ [i.e., $-\ln(1 - \alpha)$] vs the isothermal hold time (t_{iso}) for the homogeneous first-order model. The dots represent the values of the integrated function at different times and the straight line is the linear regression curve. This graphic representation is very useful because it allows an easy visual analysis of the model fitting capacity. A very good linear correlation, characterized by a high regression coefficient and a low intercept value, was observed at temperatures higher than 140°C. Homogeneous zero-order, second-order, and higher-order kinetic models cannot be used to describe the experimental data. The values of the kinetic constants (k) at different temperatures have been obtained from the slope of $-\ln(1 - \alpha)$ vs isothermal time curves and these values were used to plot the relative conversion-time expressions. In particular, the analytical expression for the conversion is

$$\alpha = 1 - \exp(-k \cdot t) \quad (11a)$$

However, this expression is not able to fit the experimental data in the full conversion range because at high conversion it always predicts a

maximum value equal to 1. Therefore, to improve the data fitting on the full range of conversion, the conversion-time equations have been modified by introducing the maximum conversion value (α_{max}):

$$\alpha = \alpha_{\text{max}} - \exp(-k \cdot t) \quad (11b)$$

The simulated behaviors obtained using eqs. (11b) are shown in Figures 4. As it can be seen such a semiempirical function has a better ability to fit the full set of data than the expression (11a). Figure 5 shows the behavior of the maximum conversion with polymerization temperature. The regression analysis of max-conversion data gives

$$\alpha_{\text{max}}^{T < 150^\circ\text{C}} = 0.042 + 0.0041 \cdot T(^{\circ}\text{C})$$

$$\alpha_{\text{max}}^{T > 150^\circ\text{C}} = 0.68$$

where T is the polymerization temperature. Other models were also tested using the same conversion data. Some of the results are shown Table III and IV. Table III shows the rate constants as well as the corresponding regression coefficients and the intercepts obtained from the integral analyses using the models given in Table I. The one-dimension diffusion and random nucleation models are not able to fit the data in any range of conversion. The performed analysis

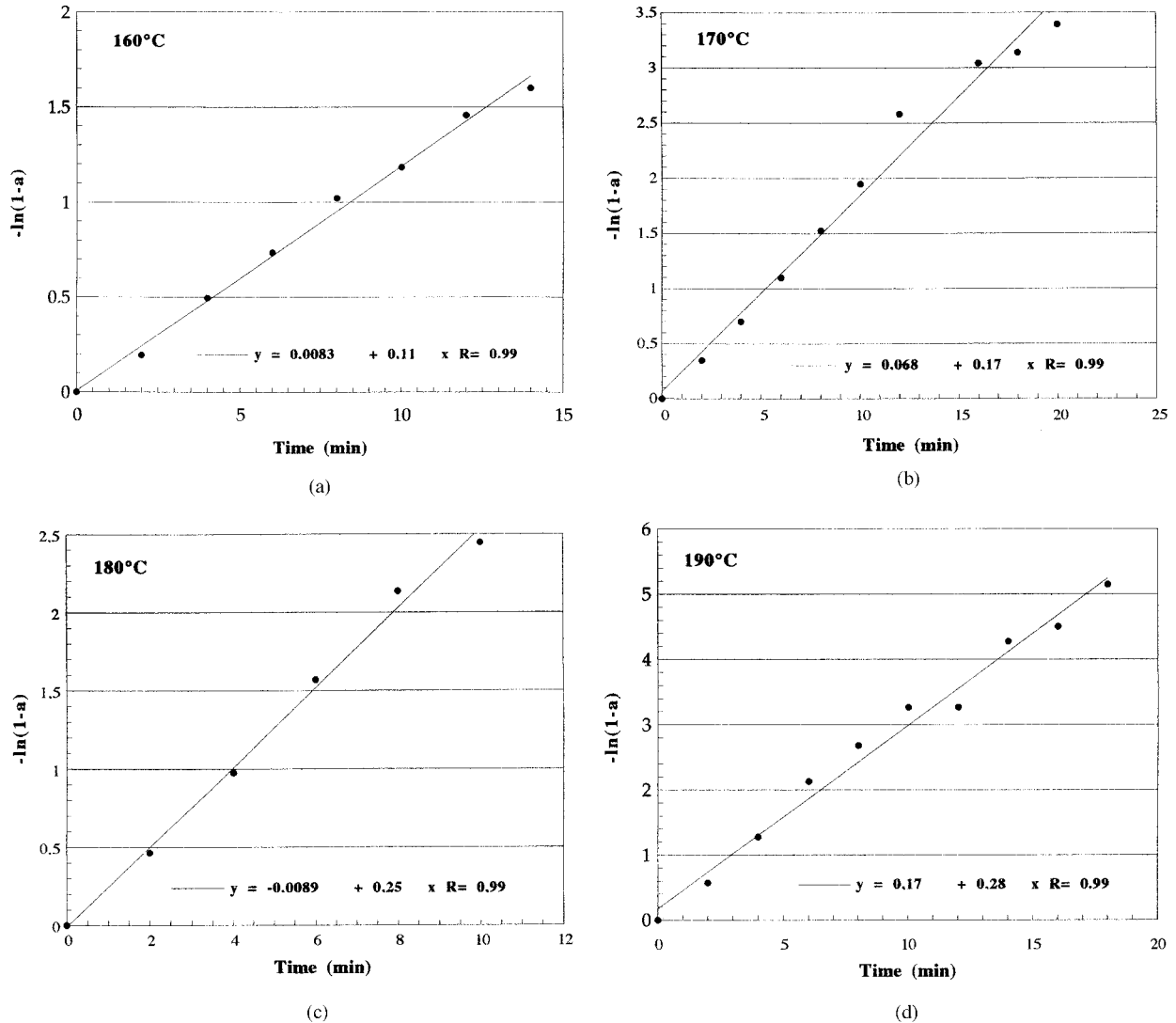


Figure 3 The $g(\alpha) - g(\alpha_1)$ vs isothermal hold time for the homogeneous first-order model.

shows that the integral method has a very good ability to discriminate among the different models, allowing a fast identification of the functional form more convenient to use.

To obtain the activation energy from isothermal experiments, a plot of the rate constant, obtained by integral analysis of isothermal data with the first-order homogeneous model, vs. $1/T(k^{-1})$ has been drawn (see Figure 6). The pre-exponential factor and activation energy for the homogeneous first-order reaction model have been obtained by linear regression analysis of data.

$$E_a = 49.6 \text{ kJ mol}^{-1}$$

At low temperatures, i.e., less than 90°C, the polymerization kinetic seems to follow a mechanism controlled by diffusion. All three-dimensional diffusion models are able to fit the experimental data (see Figures 7 and 8), except at very low conversion values. The data fit by Jander kinetic model has shown the highest regression coefficient and an intercept value closest to zero in a wide range of temperatures.

Some of the elementary reactions involved in the mechanism of phenolic resin cure are well understood and described in the literature. In particular, the addition step of formaldehyde to phenol to form hydroxymethyl resorcinol has been investigated by several authors using different

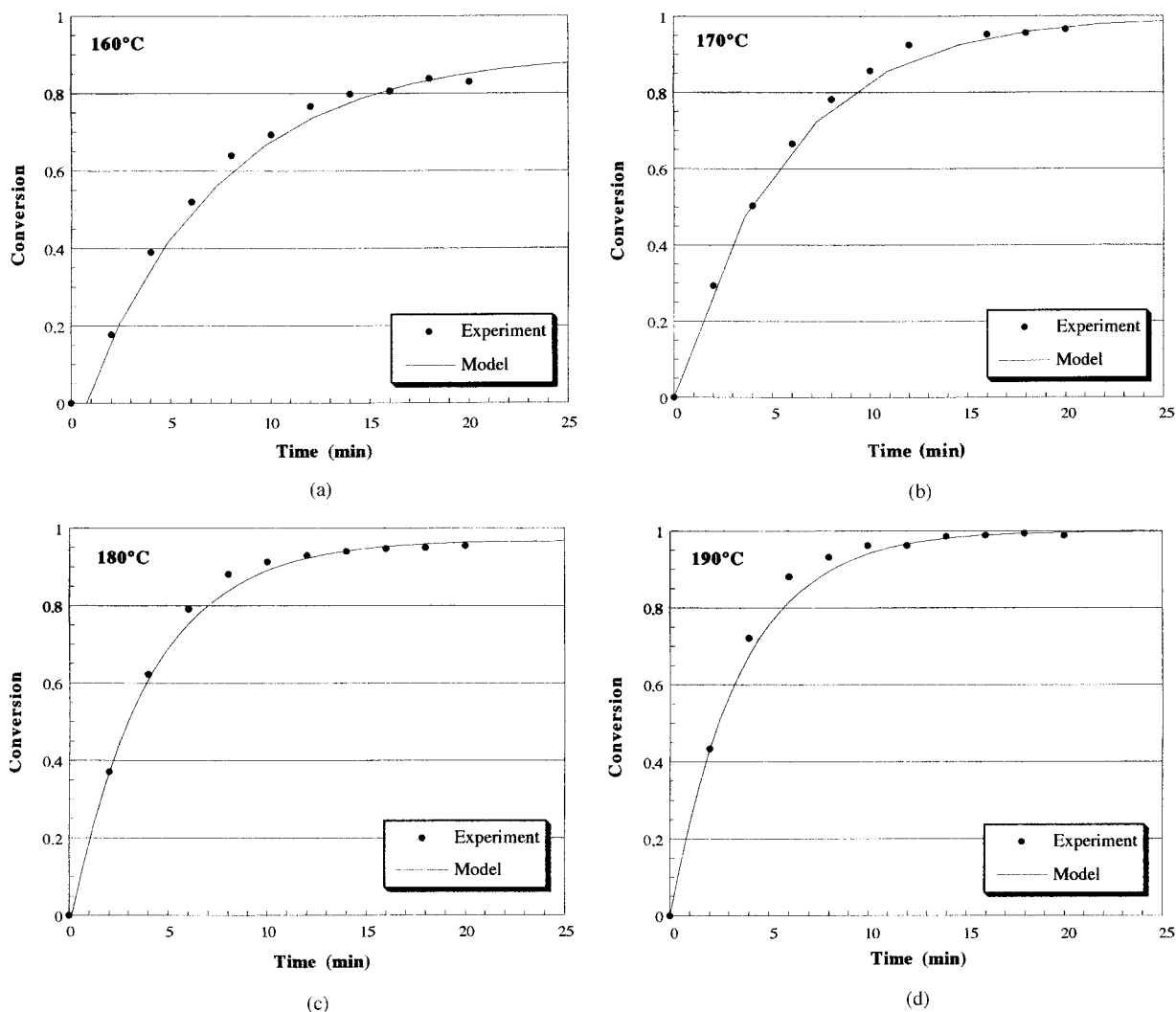


Figure 4 Simulated conversion behaviors for a homogeneous first-order model.

analytical approaches (from the pioneering work of Freeman,²⁸ based on chromatographic techniques, to the more recent experiments of Zavittas^{29,30}). This process has been widely investigated because it is involved in the large-scale preparation of commercial resol products. However, still little is known about the elementary reactions involved in the mechanism of the resol polymerization—especially for commercial products to be polymerized by alkaline catalysts. Also, a simple phenomenological kinetic descriptions of resol polymerization is still not available for most commercial products. Such information is very important for the resins users, because in many practical applications the times required for curing under the different experimental conditions can be a relevant factor. The kinetic approach

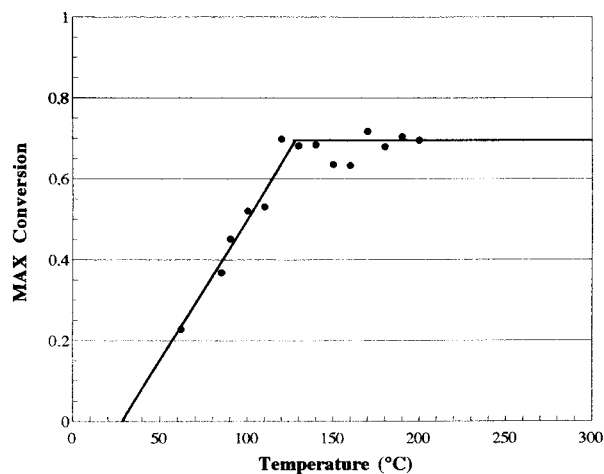


Figure 5 Maximum-conversion vs. temperature.

Table IIIa Rate Constants, Regression Coefficients, and Intercepts for the Nucleation and Growth Model (170°C, 0–100% Conversion Range)^a

<i>n</i>	<i>i</i>	<i>k</i>	<i>R</i>
1	0.34	0.14	0.99
1.5	0.31	0.089	0.99
2	0.23	0.067	0.99
3	0.15	0.044	0.99
4	0.12	0.033	0.99

^a Variables: *i* is the intercept; *k* is the rate constant; *R* is the linear regression coefficient; *T* is the temperature (°C); and *m*, *n* are model parameters.

used in this work to analyze the cure of the FRD-5002 resin can be easily applied to the study of other resols, in order to make available a complete description of their cure behavior. In addition, because of the simple kinetic control operative above 140°C, a mechanistic model for the resol cure can be also proposed.

The industrial preparation of a commercial alkaline catalyzed resol starts with the chemical reaction between phenol and formaldehyde in alkaline aqueous solution (pH above 8) at moderate temperature. When a mixture of one mole of phenol and one or more moles of formaldehyde is reacted in presence of a base, the initial polymerization reaction involves the formation of a single-ring phenol alcohol (methylolated phenol). These molecules represent the initial addition product; however, their condensation to yield various dimers begins soon after the first phenol alcohol molecules have been formed, particularly at commercial operating temperatures. The phenol has a functionality of three, and it reacts at *para* and *ortho* positions to the hydroxyl. The two *meta* positions will react only under severe conditions,³¹ generally not found in resin reactions,

Table IIIb Rate Constants, Regression Coefficients, and Intercepts for the Autocatalytic Reaction Model (170°C, 0–100% Conversion Range)^a

<i>m</i>	<i>n</i>	<i>i</i>	<i>k</i>	<i>R</i>
1	1	0.076	0.14	0.98
2	1	−0.054	0.12	0.99
2	2	−11	2.2	0.99

^a See Table IIIa footnote.

Table IIIc Rate Constants, Regression Coefficients, and Intercepts for the Surface Reaction Controlling Model (170°C, 0–100% Conversion Range)^a

<i>n</i>	<i>i</i>	<i>k</i>	<i>R</i>
2	0.64	0.021	0.89
3	0.76	0.014	0.89

^a See Table IIIa footnote.

and consequently, they are considered as inactive. In addition to the simple methylol addition, there is increasing evidence of hemiformal formation.^{32,33} The produced molecules can continue to react with further heating and the average molecular weight of the resin will increase. If the reaction is not stopped it will proceed with crosslinking to produce a gelled structure. However, by cooling, the rate of the various reactions may be practically stopped. Thus, a very low-molecular-weight resin may be prepared that is water soluble at room temperature and useful for impregnation or saturation of a number of substrates. The RFD-5002 resin is an example of this class of resols. Alternatively, the reaction may be carried further until the resin is a semisolid, which may be dissolved in an organic solvent such as alcohol and used as a varnish or coating or applied to sheets for subsequent lamination. The reaction may be carried still further, until after careful dehydration a truly solid grindable resin is recovered that is soluble in organic solvents and fusible. This product may be ground to a powder and used as a binder for fibrous or particulate substrates. In the three states the resin is heat reactive; therefore, when heat is applied, the resol polymerization continues until the final infusible, insoluble, crosslinked state is reached.

The hardening of a resol, i.e., the reaction of the phenol alcohols (methylolated phenols and derived compounds), as heating is continued

Table IIId Rate Constants, Regression Coefficients, and Intercepts for the Two-Dimensional Diffusion Model (170°C, 0–100% Conversion Range)^a

<i>i</i>	<i>k</i>	<i>R</i>
−0.057	0.063	0.99

^a See Table IIIa footnote.

Table III Rate Constants, Regression Coefficients, and Intercepts for the Jander Kinetics (Conversion Range: $\alpha > 0.87$)^a

<i>T</i>	<i>i</i>	<i>k</i>	<i>R</i>
160	0.91	9.710^{-5}	0.96
170	0.19	0.013	0.99
180	0.37	0.0020	0.98
190	0.99	0.00030	0.91

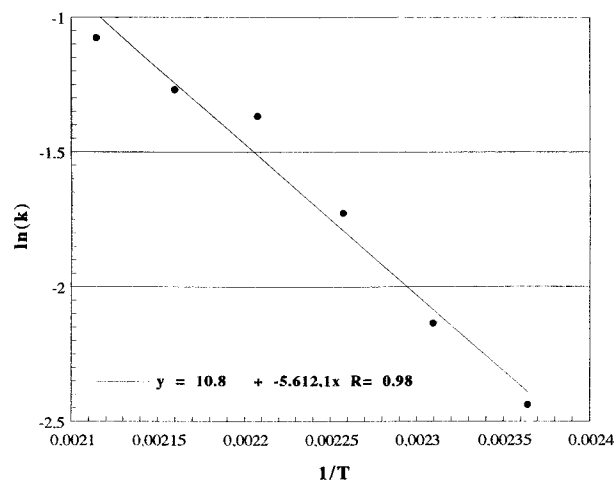
^a See Table IIIa footnote.

leads to two possibilities: (a) formation of the methylene ether, and (b) independent or subsequent formation of the diarylmethane. In particular, the methylene ether compound may lead to diarylmethane by disproportionation, producing water and formaldehyde as by-products. The condensation of two hydroxymethyl groups to form a dibenzyl ether linkage is a reaction possible in acid environment, but rare in the presence of the alkaline catalysts used to produce commercial resols.^{19,20} Such a point has been experimentally confirmed by the observation that only little variations characterize the methylene absorption (2900 cm^{-1}) in the FTIR spectra of FRD-5002 resin during polymerization. Consequently, the most important reaction involved in the alkaline polymerization of a commercial resol is the condensation of hydroxymethyl groups with unreacted active position of other phenolic rings. This reaction has already been studied by Hultzs³⁴ working on FP model systems in presence of acid catalysts, but little is known about the reaction behavior in alkaline environments.

The kinetic analysis of isothermal conversion-time data has shown that at temperatures higher than 140°C the RFD-5002 cure reaction can be

Table IV Rate Constants, Regression Coefficients, and Intercepts for the Nucleation and Growth Model (180°C , Conversion Range: $\alpha > 0.94$)^a

<i>n</i>	<i>i</i>	<i>s</i>	<i>R</i>
1	2.8	0.013	0.98
1.5	2.0	0.0060	0.98
2	1.7	0.0041	0.96
3	1.4	0.0022	0.96
4	1.3	0.0015	0.96

^a See Table III footnote.**Figure 6** Calculation of Arrhenius parameters from experimental data.

conveniently described by a homogeneous first-order kinetic model. Although a phenomenological approach has been used to investigate the kinetics of reaction on the full range of cure temperatures, the simple kinetic control operative above 140°C allows the formulation of some hypotheses on the mechanism involved in the reaction at these temperatures. In particular, it can be supposed that, above this temperature, most of elementary reactions involved in the mechanism of condensation of hydroxymethyl group with an unreacted active position of the phenolic ring become so fast that their contribution to the full process rate is negligible. Only one elementary reaction, involving a single reactive molecule, should have a reaction rate so low to be able to define the rate of the full reaction process.

The simplest reaction path that can be supposed to justify the observed experimental behavior involves two steps: (1) formation of a high-reactive quinoid molecule, and (2) its addition to the active position of another phenolic ring. The quinoid molecule is a highly reactive species and consequently the activation energy required for its formation is high. Therefore, the first elementary reaction is a low-rate reaction step. The unstable quinoid molecule gives a fast addition with the *ortho* or *para* positions of an activated phenolic ring (ionic state) and consequently this elementary reaction constitutes the high-rate reaction step. Probably, the difference in the activation energies of the two steps is not enough to simplify the rate equation of the full process at low temperatures, but with increasing temperature, the second step becomes so fast as to give just a negligible contribution.

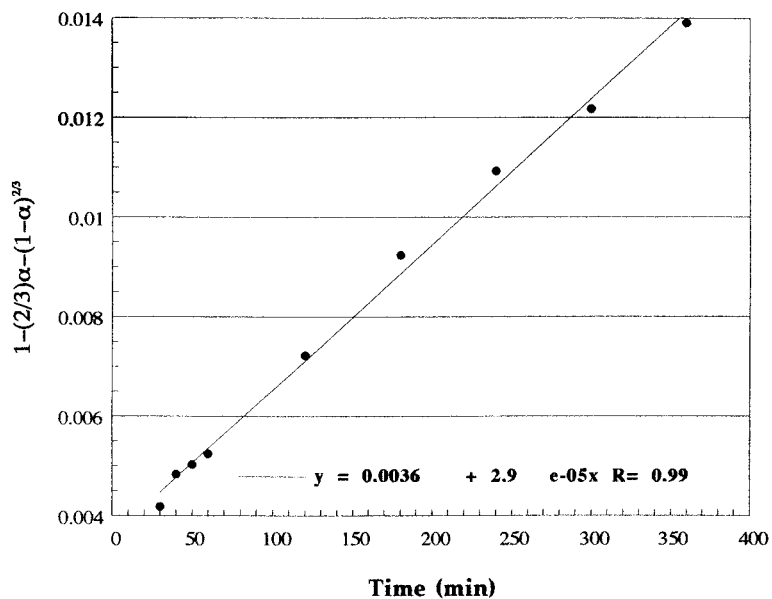
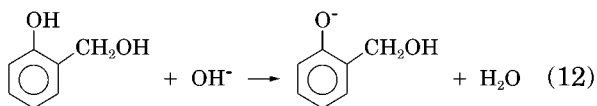


Figure 7 The $g(\alpha) - g(\alpha_1)$ vs isothermal hold time for the Gintsling-Brounshtein kinetic model (65°C).

In particular, in presence of an alkaline catalyst (e.g., sodium hydroxide), the hydroxymethyl phenolic derivative assumes the anion form:



This ionic form is in equilibrium with the alcohol, but it can also lose a hydroxyl ion from the hydroxymethyl group, producing an unstable quinoid structure. Both *para* or *ortho* quinoid structures can be generated, according with hydroxymethyl group position. Such a carbon ion can immediately react with the free *ortho* or *para*

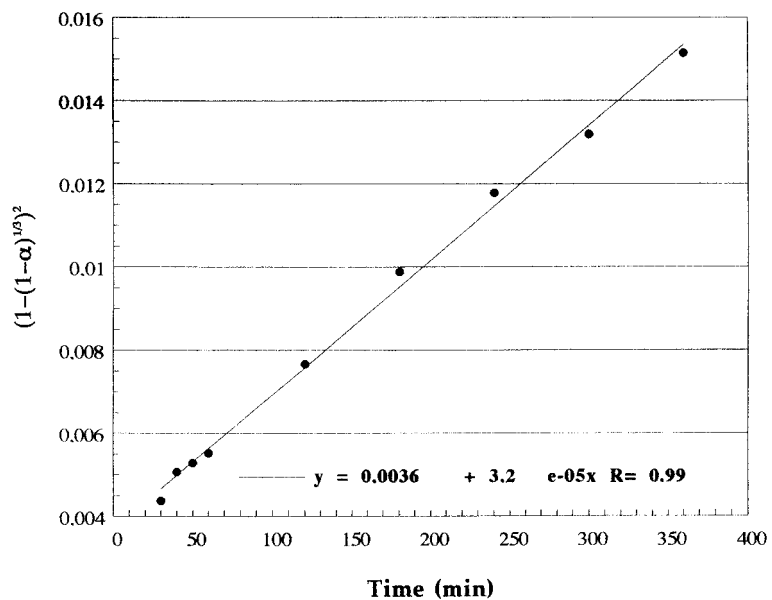
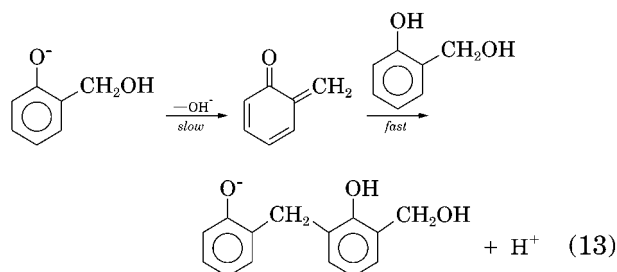


Figure 8 $g(\alpha) - g(\alpha_1)$ vs isothermal hold time for the Jander kinetic model (65°C).

position on a phenolic ring, regenerating a proton and producing the dihydroxydiphenylmethane compound (electrophilic addition to the aromatic ring).



The mechanism proposed for the polymerization of the FRD-5002 resin at temperatures higher than 140°C is probably valid for the polymerization of most resols in an alkaline environment. Such a mechanistic scheme is similar to the mechanism based on the formation of dehydrated carbon ion already proposed by Hultzsich for the acid-catalyzed FP polymerization.³³ In particular, Hultzsich suggested that the intermediate form in the acid-catalyzed polymerization may be the quinone methide, which he investigated in detail particularly to explain the reaction of phenol alcohol.

CONCLUSIONS

The kinetics of the condensation reaction of hydroxymethyl groups with unreacted active positions of phenolic rings, primarily involved in the resol cure, has been studied by FTIR spectroscopy for a commercial product (FRD-5002, Borden Chimie S.A.). In particular, the changes in absorbance of the IR band produced by the deformation of C—H bonding in benzene rings has been monitored. From the integral analysis of data obtained by isothermal experiments, it can be concluded that the cure reaction of the FRD-5002 resin can be represented above 140°C by a first-order homogeneous reaction mechanism. Several additional phenomenological models have been tested (higher order homogeneous reactions, diffusion-controlled reactions, surface reactions, and nucleation and growth-type reaction); however, none is able to represent the kinetic behavior over the entire conversion range of reaction. This simple kinetic control offers the possibility to formulate hypotheses on the resol cure mechanism in this range of temperatures.

Finally, a diffusive kinetic mechanism was operative at lower temperature, and at these temperatures the experimental data can be conveniently described by the Jander kinetic model.

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