

Cure Kinetics of the Cardanyl Acrylate–Styrene System Using Isothermal Differential Scanning Calorimetry

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ABSTRACT: The curing kinetics of styrene (30 wt %) and cardanyl acrylate (70 wt %), which was synthesized from cardanol and acryloyl chloride, was investigated by differential scanning calorimetry under isothermal condition. The method allows determination of the most suitable kinetic model and corresponding parameters. All kinetic parameters including the reaction order, activation energy E_a and kinetic rate constant were evaluated. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2034–2039, 2002

Key words: crosslinking; curing of polymers; differential scanning calorimetry; kinetics (polym.); radical polymerization; thermosets

INTRODUCTION

Cardanyl acrylate (CA), obtained by modification of cardanol and acryloyl chloride has received considerable attention in the last ten years.^{1,2} Due to the presence of the acrylic group and the unsaturation in the long alkyl side chain (C₁₅), CA (Scheme 1) can be a potential vinyl monomer material providing improved flexibility for many products of the vinyl polymerization reactions.

The copolymers, which were obtained from cardanyl acrylate with vinyl monomers such as styrene, methyl methacrylate, and acrylonitrile, were also studied by several authors.^{1,2} Many studies have been done to clarify the reaction between CA and styrene but until now, kinetic investigations of CA in free radical copolymerization reactions have not been carried out. One reason is the complexity of the system in which

cardanyl acrylate provides two different types of double bonds and results in a “pseudo” ternary system with styrene as a comonomer.

Interest in the kinetics and mechanism of the curing of the CA–styrene system using free radical initiator derives from the potential usage of CA in crosslinking reactions for vinyl ester resin (VER) systems on the basis of phenylacrylate. The kinetics of curing CA–styrene using a free radical initiator system is rather complex as CA contains double bonds, which differ in their reactivity in the radical copolymerization. Copolymerization of CA with styrene is a thermosetting reaction that was shown in a previous study.³ The understanding of the mechanism and kinetics of this special type of copolymerization is therefore an essential step to evaluate the crosslinking ability of CA for phenacrylate VER systems.

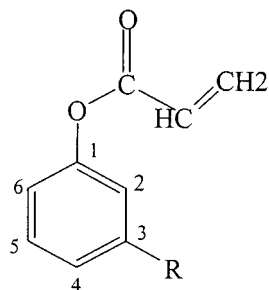
A variety of experimental techniques have been employed to study the kinetics of thermosetting reactions. Differential scanning calorimetry (DSC) has been the most commonly used experimental technique for curing studies. DSC is used to determine the amount of heat, which is generated during the curing reaction. Isothermal studies were used effectively to determine the rate of

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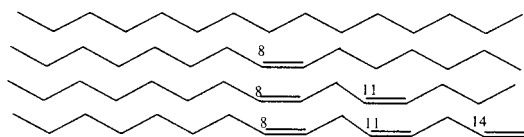
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where $R = C_{15}H_{31-n}$, which is a composition of differently unsaturated components as follows:



Scheme 1 Chemical structure of CA.

heat generation as a function of time, which is needed for kinetic calculations. The degree of reaction vs time can be estimated directly by assuming that it is proportional to the exothermic heat evolved during cure. In most cases, the reaction rate has been described by means of a simple n th-order kinetic expression governed by a single Arrhenius rate constant. However, since the cure of the CA-styrene system has been found to be autocatalytic, a simple n th-order kinetic expression is inadequate to provide an accurate quantitative description of the entire curing process. The detailed descriptions of a kinetic isothermal model that was used in this work is given.

KINETIC MODEL

In the use of DSC for studying the isothermal curing kinetics of the CA-S system, the conversion of the reaction as a function of time can be calculated directly by using the values of heat generated during the reaction.

The reaction conversion a can be expressed as

$$a = H/H_{ult} \quad (1)$$

where H_{ult} is the ultimate heat of cure, which would have been generated if the complete cure (i.e., $a = 1$) had been achieved. H_{ult} is determined by

$$H_{ult} = H_t + H_r \quad (2)$$

where H and H_t are an instantaneous heat of reaction at time t and a total heat of reaction during isothermal cure at a given temperature, respectively. H_r is a residual heat of reaction obtained from a dynamic scan, which is performed after the isothermal cure.

The isothermal heat of cure, H_t , was determined from the total area under the exothermic curve, based on the extrapolated baseline at the end of the reaction.

The rate of curing reaction, da/dt , can be estimated:

$$\frac{da}{dt} = \frac{1}{H_{ult}} \left(\frac{dH}{dt} \right) \quad (3)$$

In most cases, the reaction rate has been described by means of a simple n th order expression governed by a single rate constant as follows^{4,5}:

$$da/dt = k(1 - a)^n \quad (4)$$

where n is the order of the reaction. The reaction systems that obey this simple n th order law will obviously have the maximum reaction rate at $t = 0$.

If the plot da/dt vs time shows a maximum reaction rate at a time greater than zero, then the simple n th-order kinetic model may not be recommended in this case.

For thermosets following an autocatalytic cure reaction kinetic, in which their isothermal thermograms normally show a maximum of the reaction at some point other than the reaction start (at $t = 0$, $a = 0$), a generalized kinetic model was proposed by Kamal⁶:

$$da/dt = (k_1 + k_2 a^m) (1 - a)^n \quad (5)$$

where m, n are reaction orders.

When $t = 0$, $a = 0$, and eq. (5) reduces to $(da/dt)_{t=0} = k_1$, k_1 can be directly obtained from isothermal reaction rate curves (plot da/dt vs t).

If $k_1 = 0$, then eq. (5) can be rewritten:

$$da/dt = k a^m (1 - a)^n \quad (6)$$

Using a rapid estimation technique proposed by Ryan and Dutta,⁷ the relationship between m and n may be readily determined if there is a maximum in the isothermal reaction rate and time curve (plot da/dt vs t). Because $d^2a/dt^2 = 0$ at this maximum, one obtains⁷⁻⁹:

$$m/(m+n) = a_p \quad (7)$$

where a_p is the value of conversion at the peak.

From (6) and (7), eq. (8) can be received:

$$\ln(da/dt) = \ln k + m\{\ln a + [(1 - a_p)/a_p] \times \ln(1 - a)\} \quad (8)$$

Plotting eq. (8) with the representation of $\ln(da/dt)$ as a function of $\{\ln a + [(1 - a_p)/a_p] \times \ln(1 - a)\}$, the reaction order m and the rate constant k can be obtained from the value of the slope and intercept of the straight portion of the graphic representation.

EXPERIMENTAL

Materials

Cardanol was obtained by direct vacuum distillation (at a pressure of 5–6 mbar at 190–210°C under nitrogen) of cashew nut shell liquid, which was received from Vietnam (Tai Loi Company). Acryloyl Chloride was supplied by Fluka (Buchs, Switzerland). Styrene (Fluka) was freed from inhibitor by extraction with diluted alkali solution and subsequent vacuum distillation before using in the copolymerization investigation. Hydroquinone, sodium hydroxide, methyl ethyl ketone peroxide (MEKP, 35 wt % solution in a mixture of diisobutylphthalate and diacetone alcohol), and the solvents were supplied by Merck (Darmstadt, Germany). Cobalt naphthenate (Co^{2+} , 1 wt % solution in toluene) was supplied by Vianova Resins Company (Graz, Austria).

Monomer Preparation

CA was synthesized according to ref. 10. The density of the purified CA was measured with a pycnometer at 20°C giving a value of $d_{20} = 0.94 \text{ g/cm}^3$. The refractive index measured is $n_D^{20} = 1.509$.

Equipment and Procedure

Before isothermal experiments were carried out, thermogravimetric and Fourier transform infrared (FTIR) measurements on the different mixtures under investigation were carried out under curing conditions. We conclude from these results that the occurrence of side reactions, such as decomposition of monomers is negligible with the

applied experimental procedure. The results are consistent with our findings from a further study that uses a different comonomer to investigate the network formation in a ternary system (submitted to this journal).

One gram of the reaction mixture of CA with styrene with a content of 30 wt % styrene was first weighed into a small glass vessel with a tight lid and was then put in a liquid nitrogen bath. Forty milligrams of MEKP solution and 40 mg of cobalt naphthenate solution was added under stirring for about 30 s. A small fraction of this reaction mixture (15–20 mg) was quickly weighed into a stainless steel high-pressure pan. This pan was then placed in the DSC cell at room temperature. The DSC was then started with a temperature jump routine (190 K/min) to reach quickly the temperature chosen for the isothermal run.

Isothermal curing was performed on a Perkin-Elmer DSC-7 calorimeter in a temperature range of 120–240°C. The curing times were 240 min for the run at 120°C and 180 min for the runs at 140–240°C. After the isothermal run, samples were cooled down to room temperature and then a dynamic scan was carried out from 50 to 300°C at a heating rate of 20°C/min to determine any residual heat of reaction. The observed weight losses were negligible in all cases.

The heat of reaction was determined from the isothermal DSC curves at different temperatures 120, 140, 160, 180, 200, and 240°C and the corresponding dynamic DSC curves. The degree and rate of reaction were then determined as described above.

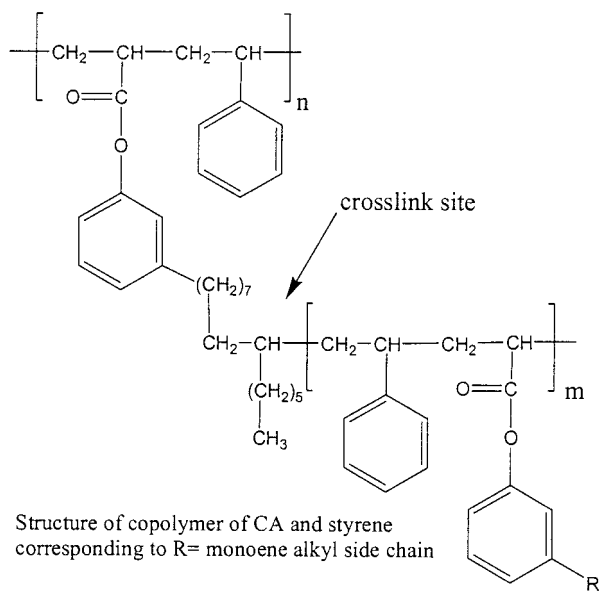
RESULTS AND DISCUSSION

Scheme 2 describes one possible structure of a copolymer crosslinked via a side-group double bond.

Figures 1 and 2 show the experimental results of isothermal DSC for the conversion and rate of reaction as a function of time at different temperatures.

In all isothermal DSC thermograms, the rate of reaction (da/dt) was found to exhibit a maximum at times greater than zero. On the other hand, the da/dt curve started at $t = 0$ with $(da/dt)_{t=0} = 0$. Therefore, the kinetic model, which is applied for the present study, is expressed by eq. (6).

From the isothermal experimental values of a_p , which were obtained from the value of conversion at the peak of the DSC curves at different tem-



Scheme 2 One possible structure of a copolymer crosslinked via a side-group double bond.

peratures, the ratio $m/(m+n)$, may be determined on the basis of eq. (7) by the plot shown in Figure 3. The straight line obtained in Figure 3 corresponds to the following equation:

$$a_p = m/(m+n) = 4.57143 \times 10^{-4} \times T - 0.16027 \quad (9)$$

As shown above [cf. eq. (8)] $\ln(da/dt)$ was plotted as a function of $X = \{\ln a + [(1 - a_p)/a_p] \times \ln(1 - a)\}$ for different temperatures as is shown in Figures 4–6.

By using a nonlinear least-squares regression technique, it can be seen that the reaction order m

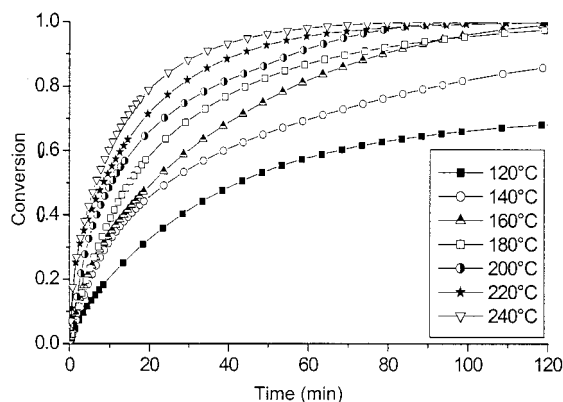


Figure 1 Degree of reaction vs time (min).

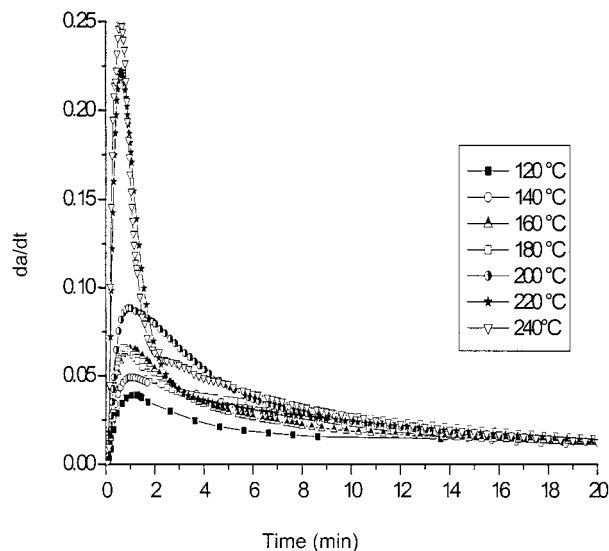


Figure 2 Isothermal reaction rate (da/dt) vs time (min).

and the rate constant k can be obtained from the slope and intercept of the straight portion of the plots.

From plots shown in Figures 4–6, the values of reaction order m and $\ln k$ at different cure temperatures were calculated and the dependence of rate constant k and order m on temperature are plotted in Figures 7 and 8, respectively.

Plotting $\ln k$ vs $1/T$ and using the linear least-square method a straight line was obtained with a slope = $-E/R$ and an intercept of $\ln A$. The Arrhenius equation expressing the relationship

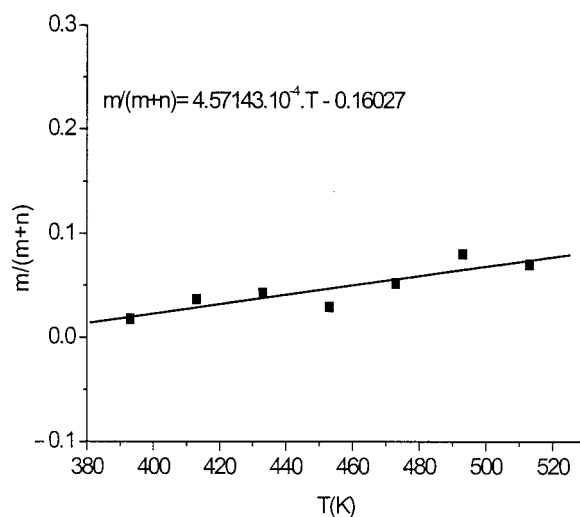


Figure 3 Temperature dependence of the ratio of reaction orders.

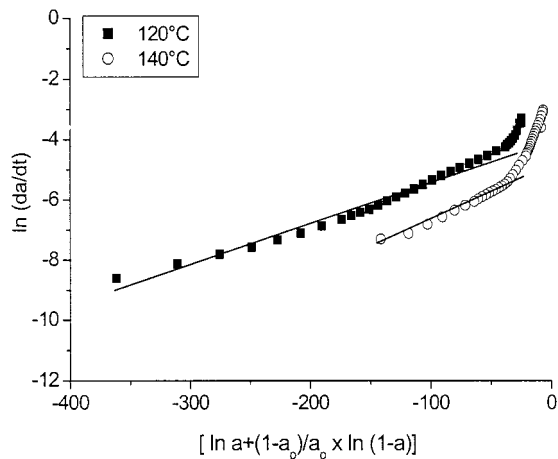


Figure 4 Variation of parameters m and k with temperature: 120 and 140°C.

between rate constant k and reaction temperature was obtained as follows:

$$\ln k = 10.15 - 6005.38 \times (1/T) \quad (10)$$

The activation energy (E) of the reaction system was found to be $E = 49.9$ kJ/mol and the frequency factor $A = 0.256 \times 10^5$ (s⁻¹).

Equation (10) can be rewritten as follows:

$$k = 0.256 \times 10^5 \times \exp[(-49.9/R) \times (1/T)] \quad (11)$$

with $R = 8.31 \times 10^{-3}$ Pa L K⁻¹ mol⁻¹.

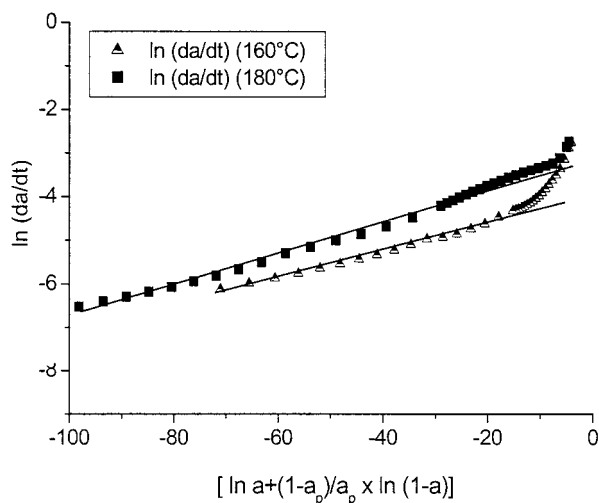


Figure 5 Variation of parameters m and k with temperature: 160 and 180°C.

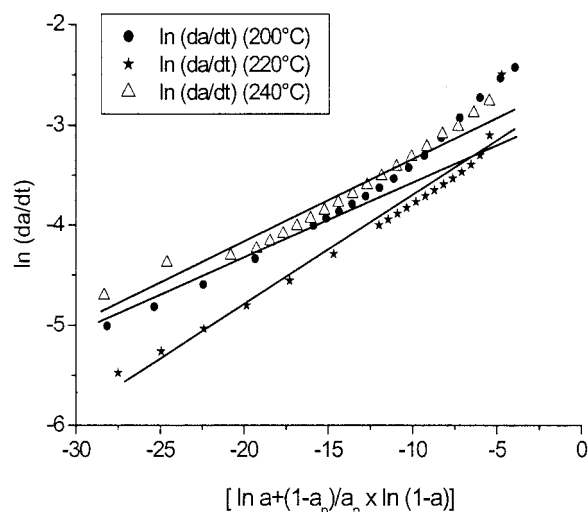


Figure 6 Variation of parameters m and k with temperature: 200, 220, and 240°C.

By plotting m vs the temperature, the equation describing the dependency of m on temperature was obtained. The best data fit for m is

$$m = 0.0014 \times T - 0.5318 \quad (12)$$

From eqs. (9) and (12), the values of reaction orders m and n at different temperatures were calculated, and are shown in Table I.

The variation of reaction orders with temperature indicates that the reaction mechanism changes due to several different reactions that may happen as expected for the complex CA-styrene-initiator-accelerator system. The pres-

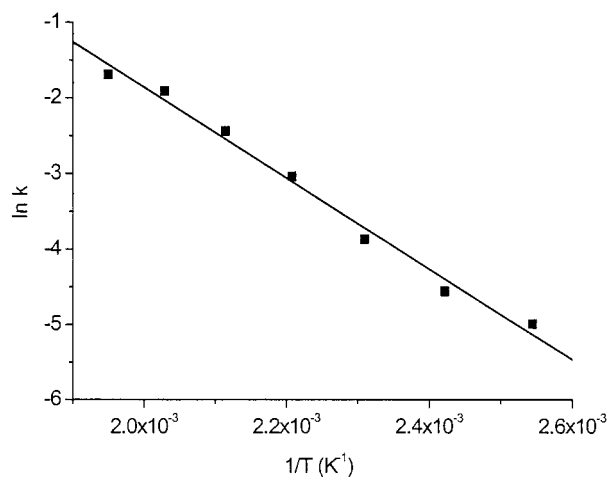


Figure 7 Logarithm of k as a function of reciprocal absolute temperature.

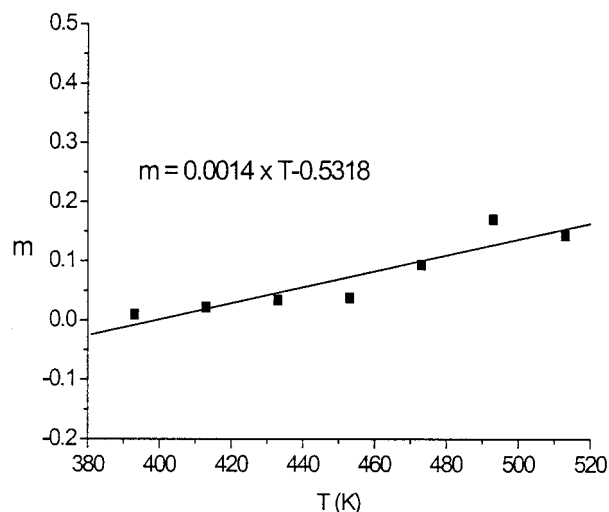


Figure 8 Plot of reaction order m vs temperature (K).

ence of three different kinds of double bonds in the long alkyl side chain adds to this complexity. The relatively small value of the activation energy demonstrates the high reactivity of this CA-styrene-initiator system even at lower temperature.

CONCLUSIONS

Despite the complexity of this system, the kinetic model represented by eq. (5) and eq. (6) has been successfully applied to the autocatalytic polymerization reaction with 30 wt % of styrene. The introduction of three parameters (k , m , n) leads to

Table I Variation of Reaction Orders m and n with Temperature

T (°C)	T (K)	$m/(m+n)$	m	$m+n$	n
120	393	0.0194	0.011	0.568	0.557
140	413	0.0285	0.039	1.368	1.329
160	433	0.0377	0.067	1.779	1.712
180	453	0.0468	0.095	2.03	1.935
200	473	0.05596	0.123	2.198	2.075
220	493	0.0651	0.151	2.3198	2.169
240	513	0.0742	0.179	2.411	2.232

a good fit to the experimental data. The rate constant k_1 was found to be zero in all cases. The temperature dependence of the predominant rate constant k_2 gives an excellent Arrhenius fit (cf. Figure 8). Therefore, it can be concluded that the applied kinetic model is valid for to the CA-styrene system at other ratios of styrene, CA, and initiator to evaluate and predict the ability of crosslinking reaction and its mechanism in VER systems. The rate of cure defines the shelf life of the curing resin product. Hence, based on the model and the method presented here, the kinetic parameters such as rate constant, activation energy, and reaction order that were obtained are very important and are useful information to design, optimize and control the curing process of thermosetting systems and therefore control their properties.

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