Gel Point Determination for the Copolymerization System of Cardanyl Acrylate and Styrene and Its Critical Conversion

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ABSTRACT: The copolymerization of cardanyl acrylate (CA) and styrene (S) with methyl ethyl ketone peroxide (MEKP) and cobalt salt as the initiator was studied by means of rheometry and isothermal DSC. The gel point of the CA-S reaction system was determined by rheological measurements at 50 and 70°C. In addition, rheological measurements provide very useful information on the evolution of the physical properties of the system during curing, such as viscosity and shear modulus. We demonstrate that isothermal DSC experiments, using the Avrami model, can be used to obtain a more detailed description of the curing process. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2385–2390, 2003

Key words: gelation; curing of polymers; rheology; differential scanning calorimetry (DSC); radical polymerization

INTRODUCTION

Recently, there has been an increasing interest in the development of polymers based on cardanol extracted from cashew nut shell liquid (CNSL), which is a mixture of natural alkyl phenols with C_{15} at the *meta*-position. It has been especially considered as an excellent monomer with an advantageous long-chain substituent for thermosetting polymer production, and has been used in a variety of applications.[1]

Cardanyl acrylate (CA), which can be obtained by modification of cardanol and acryloyl chloride, has received considerable attention due to the presence of the acrylic group and the unsaturation in the long alkyl side chain (C_{15}), CA (Scheme 1). This potential vinyl monomer provides improved flexibility for many products of the vinyl polymerization reactions.

Interest in the kinetics and mechanism of the curing of the CA–styrene system using a 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 the curing reaction of CA–styrene using a free radical initiator system is rather complex because CA contains several types of double bonds that differ in their reactivity in the radical copolymerization. The understanding of the mechanism and kinetics of this copolymerization is therefore an essential step to evaluate the crosslinking ability of CA for phenacrylate VER systems. We therefore investigated the curing kinetics of the CA–styrene system using isothermal DSC. All kinetic parameters including the reaction order, activation energy E_a (E = 49.9 kJ/mol) and kinetic rate constant (k = $0.256 \times 10^5 \times \exp[(-49.9/R) \times (1/T)]$) were evaluated for the CA–styrene system with 30 wt % styrene and reported details in ref. 2. The reactivity of each type of double bond in CA with styrene was also evaluated using time-resolved FTIR via the determination of the reactivity ratios in the (co)polymerizations.[3]

The presence of two kinds of double bonds in CA allows the formation of a regular network by crosslinking with styrene. By addition of a radical, the different unsaturated C_{15} alkyl side chains in cardanol and its derivatives form in most cases allyl radicals [cf. eqs. (b)–(i)], which are hardly capable of chain propagation. Only the reaction shown in eq. (a) leads to a highly reactive secondary alkyl radical. It is to be expected that the radical, which is formed by eq. (a), will be the most active one in homopolymerization or copolymerisation (Scheme 3).

The gel point is an important parameter for the chemistry of crosslinked polymers due to several reasons that relate to polymer processing such as shaping, which has to occur before the gel point while the polymer is still able to flow and stress can relax to zero. Exact knowledge of the gel point may allow for
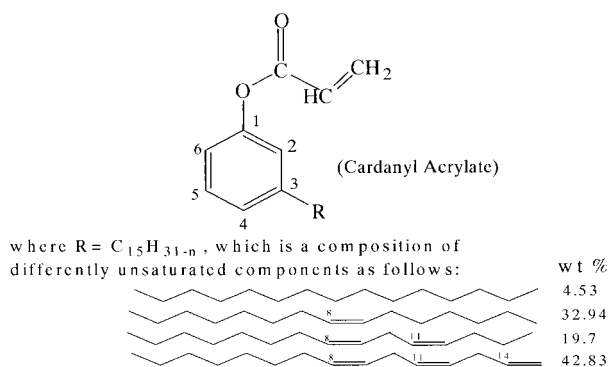
Scheme 1 Chemical structure of cardanyl acrylate (CA).

processing in the critical gel stage, and novel techniques of gel processing can be developed.

The gel point is usually determined experimentally at the time when the reaction mixture suddenly loses fluidity.[4] The gel point can be detected by monitoring the degree of branching and waiting until it has reached the theoretical critical value α_c. However, the degree of branching is difficult to measure with sufficient accuracy.

Determination of the gel point has been studied and reported by many authors. According to the literature, the gel point can be determined using the following methods: sol fraction, ball drop method,[5] thermomechanical analysis[6] (TMA), and differential scanning calorimetry (DSC).[6,7] Winter[8–10] studied the formation of the gel point by rheological methods, which will be also applied in this work. Additionally, the use of the Avrami model to forecast the gel point was performed in this study by DSC measurements, a simple and effective method.

Detection of gel point by rheological experiment

Rheological methods have been used to determine the gel point of crosslinking polymers. Dynamic mechanical measurements allow direct determination of the point at which a network polymer gels. The network at gel point was shown to be governed by a power law stress relaxation of dynamic moduli over the entire experimental range. At a critical extent of reaction necessary for gelation, a power law stress relaxation of the modulus is observed to follow: $G(t) = St^{-n}$ where strength S depends on the flexibility of molecular chains and crosslinks; n $(0 < n < 1)$ is relaxation exponent. In such an experiment, the evolution of storage G' (t, ω) and loss G'' (t, ω) moduli is measured in small amplitude oscillatory shear as a function of crosslinking time t. The frequency ω is kept constant throughout.

According to Winter, near the gel point both G' and G'' obey the common power law, G' $(\omega) \sim G''$ $(\omega) \sim \omega^n$.

Chambon and Winter observed a critical extent of reaction when $G' = G''$.

Hence, the gel point can be determined by a crossover between the G' and the G'' curves when G' and G'' are proportional $\omega^{1/2}$ for stoichiometrically balanced network polymers and networks with excess crosslinker.

Avrami model using isothermal calorimetric data[11–13]

Recently, the Avrami model has not only been used to analyze polymer crystallization, but also used to investigate the curing behavior of unsaturated polyester systems[11] and that of epoxy resins.[12]

The kinetics of curing the CA–styrene system is as complex as that of curing polyester resin or vinyl ester resin because many reactions occur, such as decomposition of an initiator, release of free radicals, styrene–CA copolymerization, styrene homopolymerization, and CA homopolymerization. During the curing, microgels are formed and developed, resulting in an increased number of microgels and microgel diameter. This phenomenon resembles the situation of polymer crystallization. Therefore, the Avrami theory, based on phase changes, which has been often used to analyze polymer crystallization kinetics, can be applied for the CA–styrene copolymerization process via the growth of microgels.

The Avrami equation using calorimetric data:

$$1 - \alpha = \exp(-kt^n) \qquad (1)$$

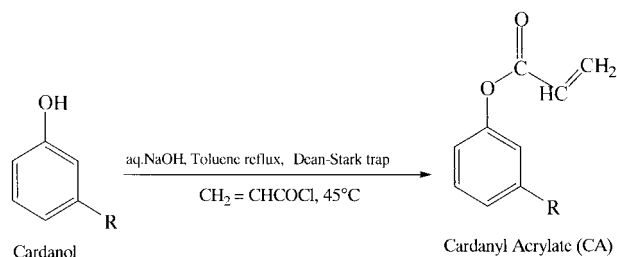where α is the corrected degree of cure, which is determined from isothermal DSC.

k is the rate constant and n is the avrami exponent.

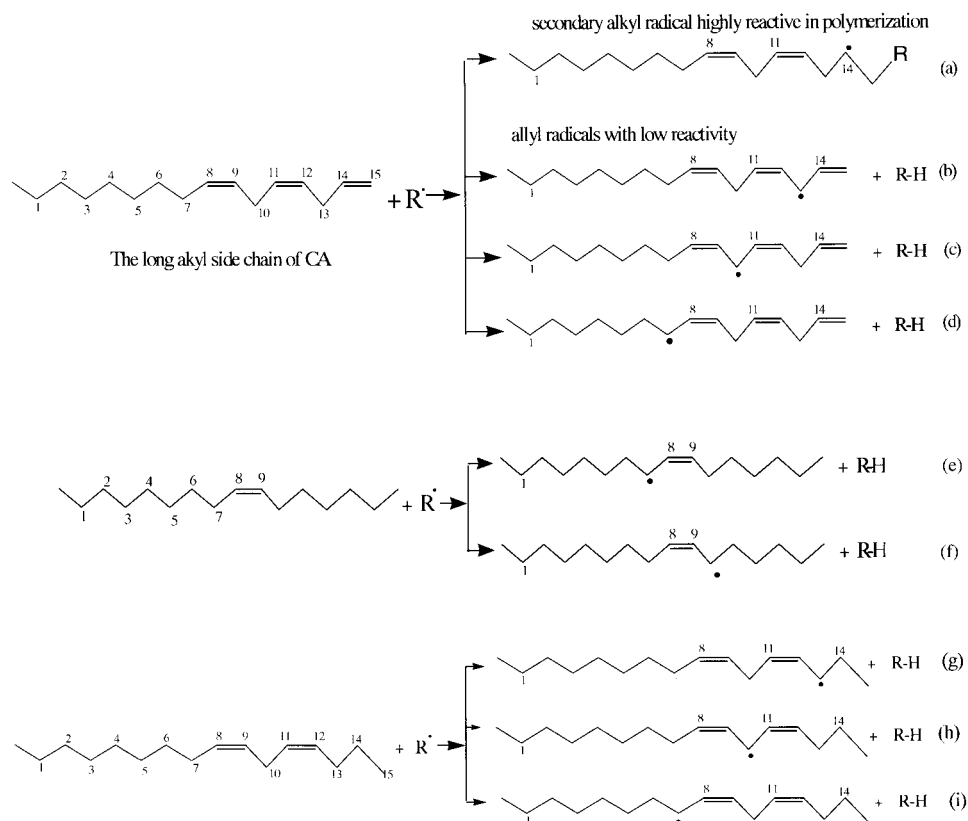The reaction conversion α can be expressed as:

$$\alpha = H/H_{ult} \qquad (2)$$

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

$$H_{ult} = H_t + H_r \qquad (3)$$

Scheme 2 Reaction of cardanol and acryloyl chloride to form cardanyl acrylate.

Scheme 3 Qualitative considerations on the reactions of the unsaturated C_{15} alkyl side chains in cardanol and its derivatives with radicals.

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 exothermal curve, based on the extrapolated baseline at the end of the reaction.

Equation (1) can be rewritten:

$$\ln\left[-\ln\left(1 - \alpha\right)\right] = \ln k + n \times \ln t \qquad (4)$$

Plotting the left-hand side of eq. (4) vs. ln (time), the Avrami plot is obtained in which the slope of the curve is the value of the Avrami exponent n.

EXPERIMENTAL

Materials

Cardanol was obtained by direct vacuum distillation (at a reduced pressure of 5–6 mbar at 190–210°C under nitrogen) of cashew nut shell liquid that was received from Tai Loi Company (Vietnam). 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 copolymerisation investigation. Hydroquinone, sodium hydroxide, methyl ethyl ketone peroxide (MEKP, 35 wt % solution in a mixture of diisobutylphtalate 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

Cardanyl acrylate (CA) was synthesized according to reaction Scheme 2. The synthesis was carried out as described in ref. 14. The density of the obtained CA was measured with a pyknometer at 20°C giving a value of $d_{20} = 0.94$ g/cm^3. The refractive index measured is $n^{20}_D = 1.509$.

Copolymerization procedure

Two different mixtures of cardanyl acrylate (CA) and styrene were prepared with a ratio of 30 and 50% styrene by weight, named CA-S30-I and CA-S50-I, respectively. The experimental condition is listed in Table I. The copolymerization reactions were started by catalyzing with 4 wt % MEKP solution and 4 wt %

TABLE I
Reactive Mixtures for Rheological Measurements

Sample name	Reaction system	Temperature of measurement (°C)	Gelation time measured by rheology (min)	Gelation time measured by DSC (min)
CA-S30-Ia	CA-30 wt % styrene-initiator	50	170	—
CA-S30-Ib	CA-30 wt % styrene-initiator	70	138	129
CA-S50-Ia	CA-50 wt % styrene-initiator	50	195	—
CA-S50-Ib	CA-50 wt % styrene-initiator	70	160	—

Co^{2+}. After mixing, the reaction sample was placed into the equipment immediately for the rheometric measurement. An isothermal DSC measurement for the sample CA-S30-I was also performed additionally at 70°C for 300 min for the confirmation of the result that was obtained from rheological measurements.

Rheological measurements

Dynamic rheological data, i.e., storage modulus (G') and loss modulus (G''), were recorded during copolymerization using a Rheometrics mechanical spectrometer RMS-800. The sample of reaction mixtures (less then 1 g), CA-S30-I and CA-S50-I, were subjected to dynamic shear between two parallel plates at a constant frequency (6.28 rad · s^{-1}) and were reacted isothermally at 50 and 70°C during 420 min. The diameter of the plates was 25 mm, and the gap between the plates was less then 0.3 mm. Because the gap was very small, it is assumed that, in the analysis of the experimental data any temperature variation during cure, due to the exothermic reaction, had only a negligible effect on the accuracy of measurements.

DSC measurement

One gram of the reaction mixture of CA 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 were 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 (No. B018-2901, Perkin-Elmer). This pan was then placed in the DSC cell at room temperature. The DSC was then started with its temperature jump routine (190 K/min) to quickly reach the temperature chosen (70°C) for the isothermal run. Isothermal curing was performed on a Perkin-Elmer DSC-7 calorimeter.

RESULTS AND DISCUSSION

Determination of gel point using rheology

The presence of two different kinds of double bonds, acrylic double bonds and the double bonds in the

alkyl side chain C_{15}, in CA allows the formation of a regular network by reactions with styrene.

The gel point in this study is determined experimentally as a function of time using rheological methods. The reactions of CA with styrene were carried out isothermally under dynamic shear between parallel plates at a constant frequency ω_o as described above. Plots of viscosity, log (G') and log (G'') vs. time were recorded for the examined reaction mixtures, CA-S30-I and CA-S50-I. Typical plots that present rheological behavior of the isothermal curing of CA-S30-I and CA-S50-I systems at two different temperatures of 50 and 70°C are shown in Figures 1–4.

It is seen that both storage (G') and loss (G'') moduli increase during the cure as a result of the increasing molecular weight by the polymerization. The beginning of the curves increases slowly due to the increase of the fraction consisting of a prepolymer (oligomer). Later, the curves increase dramatically, indicating that there is a sudden increase in molecular weight by crosslinking reactions. The crossover of log (G') and log (G'') can be considered as a transition point from a linear polymer to a crosslinked polymer. After this
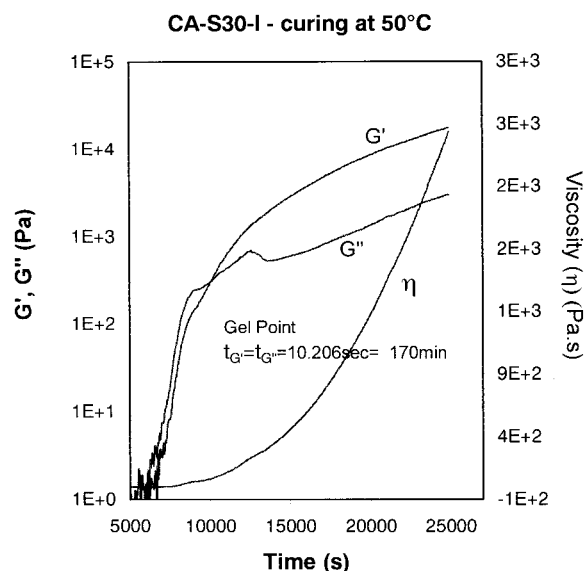

Figure 1 Storage and loss dynamic shear moduli (G' and G'') and viscosity (η) for the reaction sytem of CA-S30-1a (at 50°C).

CA-S30-I - curing at 70°C

Figure 2 Storage and loss dynamic shear moduli (G' and G'') and viscosity (η) for the reaction sytem of CA-S30-Ib (at 70°C).
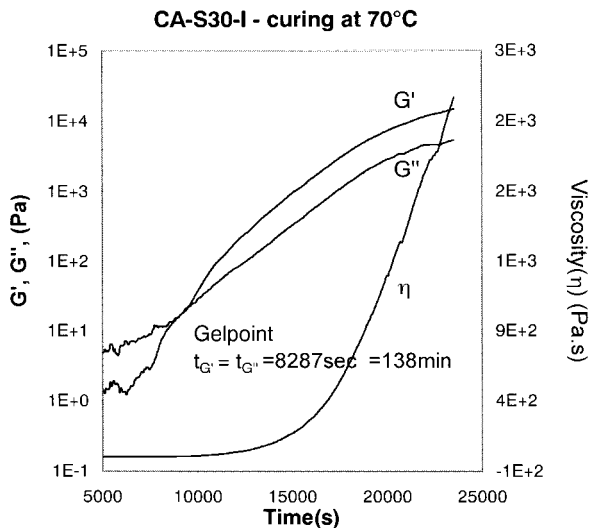
CA-S50-I - curing at 70°C

Figure 4 Storage and loss dynamic shear moduli (G' and G'') and viscosity (η) for the reaction sytem of CA-S50-Ib (at 70°C).

point the molecular weight increased dramatically due to the increasing formation of crosslinks in the system CA-S.

The gel time determined from the crossover between log (G') and log (G'')[7–9,15,16] was found to be 170 and 138 min for the system CA-S30-I and 195 and 160 min for the CA-S50-I system at 50 and 70°C, respectively. In addition, Figures 1–4 also show that at an early stage of curing, the complex viscosity increases slowly, but beyond gel point the viscosity exhibits a substantial increase with time as a result of the formation of crosslinks. This can be explained by the assumption that in the early stage before the gel point reactions are mainly due to the formation of a pre-
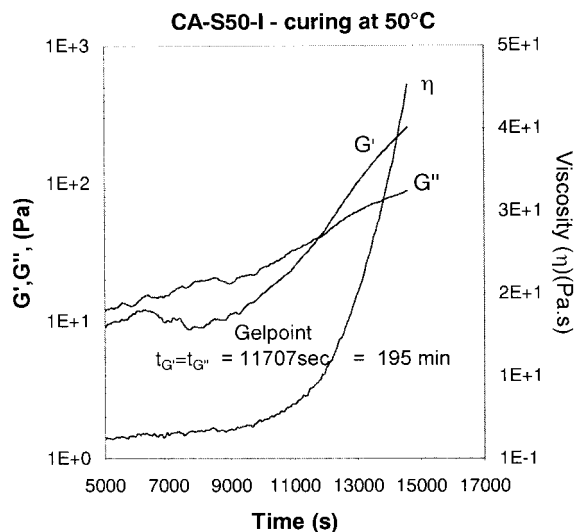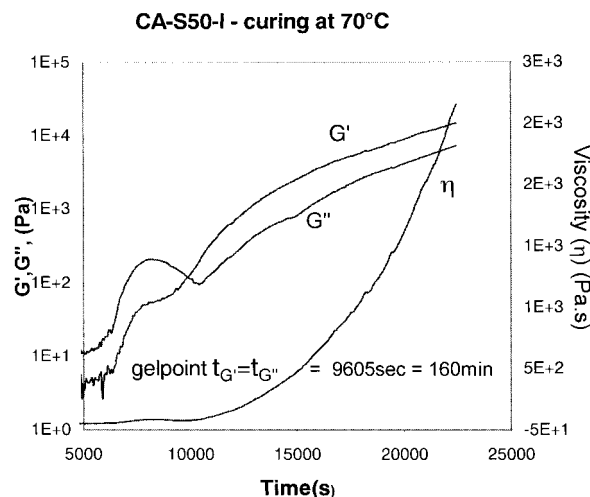
polymer (oligomer), which contains mainly linear chains. As the crosslink network starts to form, the increase of molecular weight becomes significant, and therefore its viscosity as well as the moduli increase, resulting in this sudden change. In addition, in the early stage the fraction with the higher molecular weight increases unnoticeably because the reactions lead only to linear chains. But as these chains are connected to form crosslinks, the molecular weight increases dramatically. The copolymerisation of the CA-S system can be considered to occur as follows: first styrene reacts with acrylic double bonds to form main chains; afterwards, styrene might react with cardanol double bonds in oligomers to form crosslinks.

It can be seen that as the temperature rises the gel time decreases for both systems of CA-S30-I and CA-S50-I. This fact can be explained by the increase of reaction rate, as a result of increasing reaction temperature.

At higher content of styrene, the difference in the initial reaction rate can be predominantly attributed to the styrene dilution effect. Increasing the amount styrene reduces the probability of a crosslink formation. The molecular weight increases more slowly. As a result, the gel point appears later; in other words, the gel time increases.

CA-S50-I - curing at 50°C

Figure 3 Storage and loss dynamic shear moduli (G' and G'') and viscosity (η) for the reaction sytem of CA-S50-Ia (at 50°C).

Avrami model

To confirm the gel point determined by rheological measurements, the Avrami model using calorimetric isothermal data is applied on CA-S30-Ib (curing at a temperature of 70°C).

Figure 5 shows the conversion as a function of time for the representative CA-S30-Ib sample using calorimetric isothermal data.

Figure 6 shows the Avrami plot of the CA-S30-Ib system. It can be seen that the curve is nonlinear, and shows a remarkable change in the slope. A change of the slope in the Avrami curve, in other words a change of n during the cure, indicates a change in the poly-merisation mechanism. Two distinct regions can be seen on the curve with a transition between them occurring at about 129 min. It is interesting to see that this value is very close to the gel point determined by rheological measurements (Fig. 2). The critical extent of the reaction, which corresponds to this gel point is about $\alpha_c \sim 0.4$ (Fig. 5). An explanation for this obser-vation can be made as follows.

The early stage of the curing relates to the reaction of low molecular weight molecules that is chemically controlled. As the curing proceeds, the size of molec-ular chains increases and at the gel point the reaction mixture suddenly loses fluidity; therefore, the mobil-ity of molecules (or radicals) becomes limited. As a result the reaction transfers from chemically con-trolled to diffusion controlled. This change in the po-lymerization mechanism gives a change in the slope of the Avrami curve.

CONCLUSION

Generally, rheological measurements provide very useful information on the evolution of the physical properties of the system during curing, like viscosity, shear modulus, and gel time. In addition, we were able to show that the Avrami model is also helpful to determine the gel time. The results from the two dif-ferent methods are in very good agreement. As shown in this study, a change of the Avrami exponent be-
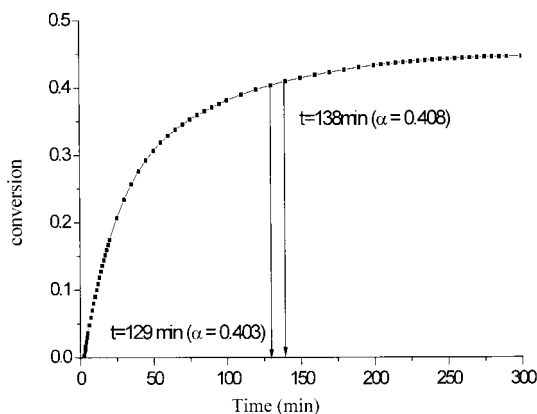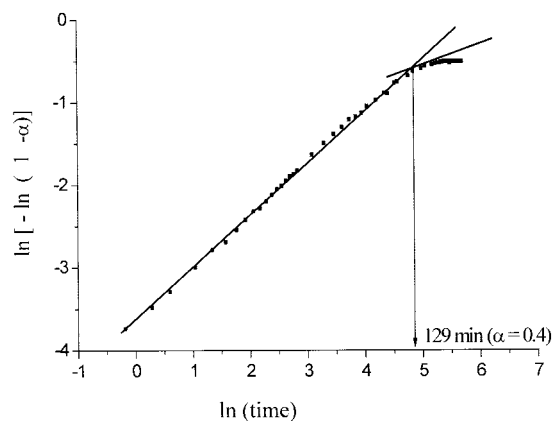

Figure 6 Avrami plot for the CA-S30-Ib system cured at 70°C.

tween the first and second sections of the curve (Fig. 6) indicates a change in the polymerization mechanism. Hence, the Avrami model may be additionally used to describe the curing that involves the formation of microgels.

A combination of both methods gives an easy pow-erful way to determine the critical conversion of a reaction, gel time, as well as to understand the curing process and a change of its mechanism.

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Figure 5 Conversion vs. time of the CA-S30-Ib system us-ing isothermal DSC at 70°C.