

Cyclization Reaction in Poly(acrylonitrile/Itaconic Acid) Copolymer: An Isothermal Differential Scanning Calorimetry Kinetic Study

Renjith Devasia, C. P. Reghunadhan, Nair, P. Sivadasan, B. K. Katherine, K. N. Ninan

Propellant and Special Chemicals Group, Vikram Sarabhai Space Centre, Trivandrum-695 022, India

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ABSTRACT: The kinetics of the cyclization reaction in the poly(acrylonitrile/itaconic acid) (PAN) copolymer in the temperature range 175–200°C was studied by isothermal differential scanning calorimetry (DSC). The reaction conforms to an n^{th} -order autocatalytic model, with an overall order of 2. The kinetic parameters were derived by multiple regression analysis. The activation energy is 110.3 kJ/mol for the acid-catalyzed reaction and 153.2 kJ/mol for the

autocatalytic part. The autocatalysis indicates the catalysis of the nitrile group cyclization by the initially formed pyrimidine groups. The kinetic parameters were used to predict the reaction profile at a given temperature. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 915–920, 2003

Key words: calorimetry; kinetics (polym.); catalysis; polyacrylonitrile

INTRODUCTION

The use of carbon fibers as reinforcements in composites has gained wide acceptability because of the ability of these fibers to withstand high temperature and environmental effects.^{1–4} Carbon-fiber-reinforced composites are used in products ranging from sporting goods to hi-tech items for various industries like aerospace and defense. Among all the precursors available, polyacrylonitrile (PAN) fibers remain one of the best materials for making carbon fibers.^{2–13} The PAN precursor is modified to improve its properties by incorporation of a small concentration of suitable acidic co-monomers, like itaconic acid (IA). This modification not only increases the hydrophilicity of the PAN precursor but also catalyzes the cyclization of nitrile groups during heat treatment.^{4–8} The conversion of PAN precursor fibers to carbon fibers involves an intermediate step, a ‘stabilization reaction,’ to yield a cyclized ladder structure.^{3–5,9–13} This stabilization reaction is normally performed in the temperature range 180–300°C. The acid plays a catalytic role in the cyclization process, which is an important step during pre-oxidation that stabilizes the polymer backbone prior to carbonization. The major reaction involved in the process of stabilization is the cyclization of nitrile groups to form a ladder polymer. Since the

low-temperature stabilization reaction is the rate-determining step, its efficiency determines, to a great extent, the quality of the carbon fiber formed during pyrolysis. The cyclization reaction is seen as a relatively strong exotherm in differential scanning calorimetry (DSC) results, as reported by previous authors.^{9–17} It has been noted that IA initiates the cyclization via an ionic mechanism,^{4,17} and lowering the temperature of initiation of cyclization reaction to 180–200°C, which thereby makes the exotherm broader.

Various authors have reported the cyclization kinetics of PAN in different co-monomers in varying concentrations. Fitzer and Muller⁵ reported the cyclization to be a first-order reaction with an activation energy (E) of 126 kJ/mol in nitrogen and 142 kJ/mol in air for a copolymer of AN containing 5% methylacrylate (MA). Ko et al.^{11,12} reported an E of 100 kJ/mol for pretreated fibers containing 93% AN, 6% MA, and 1% IA. Bajaj et al. reported an E of 121 kJ/mol for copolymer P(AN/IA) containing 3.2 mol% IA and variation of E in the presence of different co-monomers and different co-monomer concentrations.¹⁷ The previous works analyze the cyclization kinetics with the n^{th} -order concept by distinct techniques, taking into consideration the peak maximum at different heating rates. The conclusions could be erroneous if the entire reaction does not follow uniform kinetics. To generate a better insight in to the cyclization kinetics, the cyclization reaction was analyzed by an isothermal DSC technique in the present work. The kinetics of the cyclization reaction for a PAN precursor for carbon fiber containing ~1.5 mol% IA was studied.

Correspondence to: C. P. Reghunadhan Nair (cprnair@eth.net).

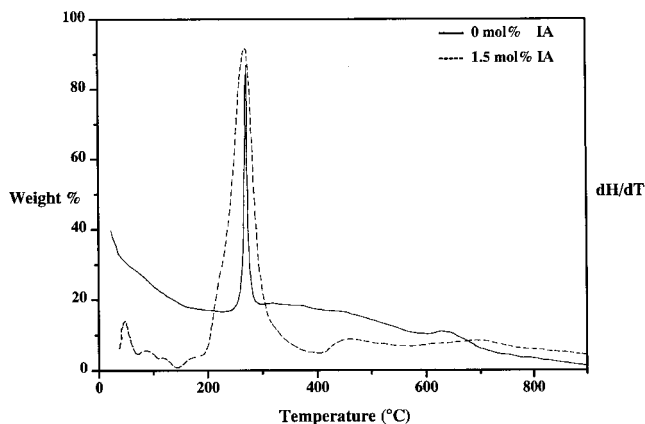


Figure 1 Nonisothermal DSC thermograms of PAN homopolymer and its copolymer with IA (heating rate, 10°C/min).

EXPERIMENTAL

Materials

Acrylonitrile (AN; Ottokemi, Mumbai, India) was purified by alkali washing followed by distillation. Itaconic acid (IA; Spectrochem, Mumbai, India) was re-

crystallized from acetone. Dimethylformamide (DMF; Ranbaxy, New Delhi, India) was dried over phosphorous pentoxide and distilled under vacuum. α, α' -Azo-bisisobutyronitrile (AIBN; Spectrochem, Mumbai, India) was recrystallized from methanol.

Sample preparation

The PAN precursor was synthesized by a process developed in-house. The polymer has a viscosity average molecular weight of $\sim 3 \times 10^5$ and contains 1.5 mol% IA. Dry powdered and pelletized samples were used for measurements.

DSC measurements

DSC measurements were performed using a TA Instruments differential scanning calorimeter (Model TA 2920). Isothermal experiments were conducted under a nitrogen flow of 50 mL/min at 200, 195, 185, 180, and 175°C. The time conversion data were obtained using TA Instruments "Universal Analyzer" software.

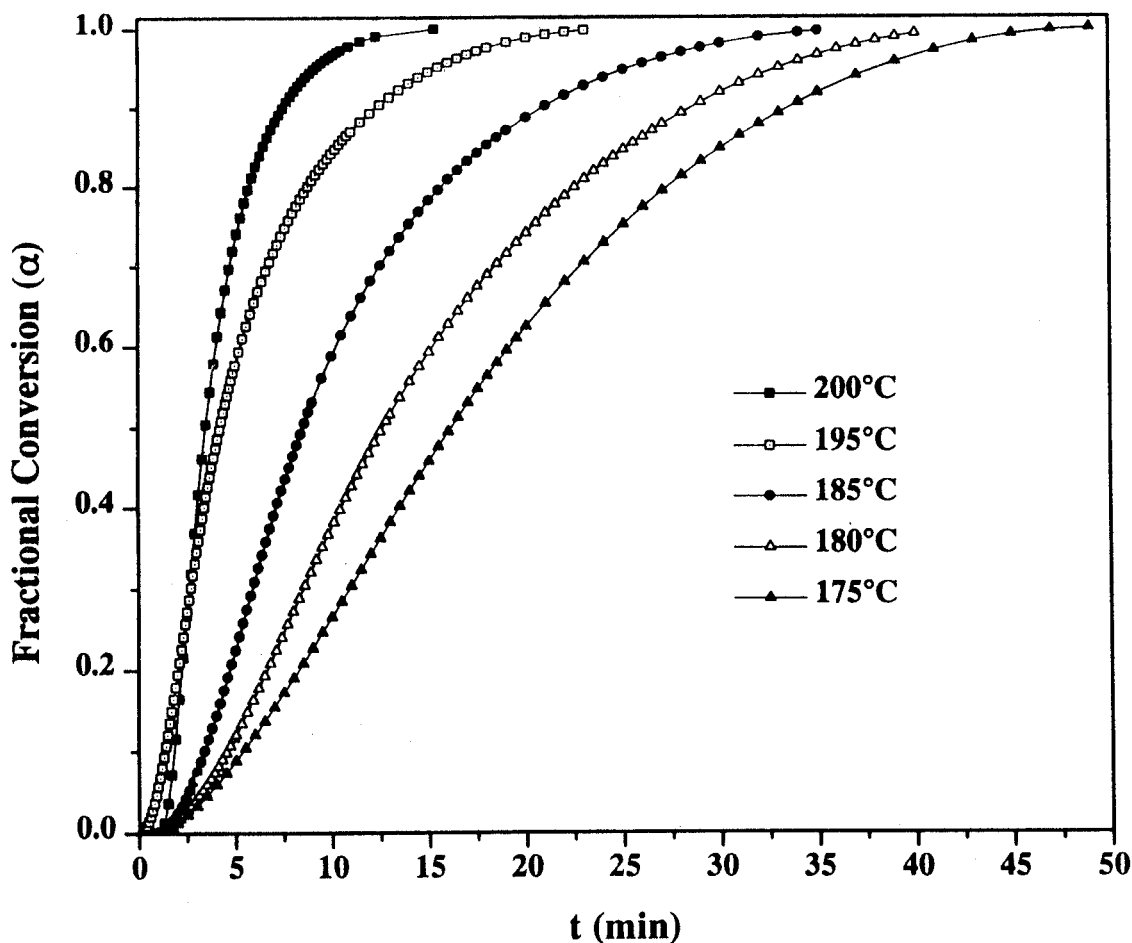


Figure 2 Conversion-time plots at different temperatures.

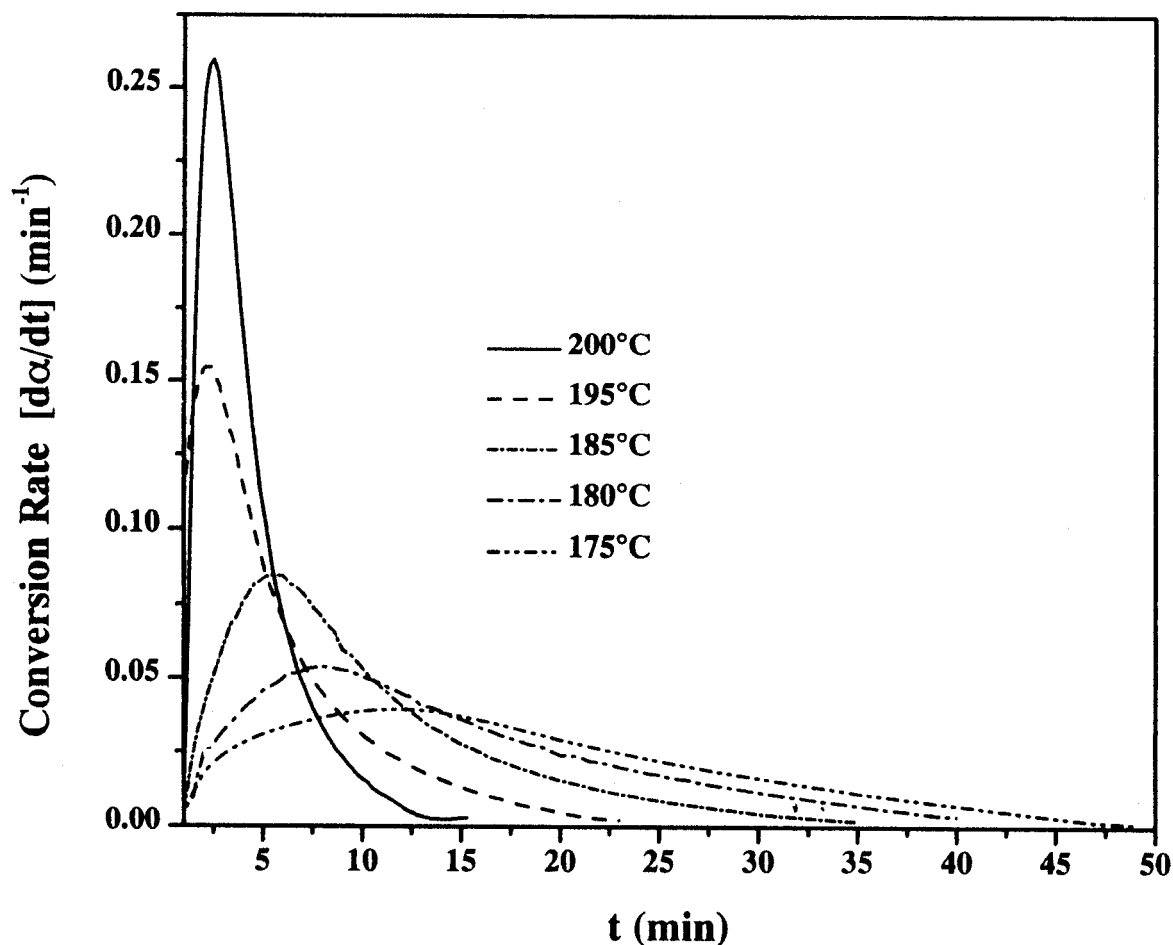


Figure 3 Conversion rate–time plots at different temperatures.

RESULTS AND DISCUSSION

The PAN homopolymer undergoes nitrile cyclization, initiated at a temperature of $\sim 250^{\circ}\text{C}$ and higher. Incorporation of a small concentration of IA lowers the initiation temperature to the $180\text{--}200^{\circ}\text{C}$ region, with a consequent increase in the char yield. The cyclization reaction is reported to be initiated through a radical mechanism in the case of PAN homopolymer and an ionic mechanism in the presence of IA.^{4,17}

The cyclization reaction is shown as a strong exotherm in DSC analysis. The difference in dynamic DSC thermograms of PAN homopolymer and its copolymer incorporating 1.5 mol% IA is shown in Figure 1. The PAN copolymer shows the initiation of cyclization reaction at $\sim 180\text{--}200^{\circ}\text{C}$, with a consequent broadening of the exotherm.

DSC analyses were performed at five different temperatures. The conversion (α) at any time (t) was obtained from the relation:

$$\alpha = \frac{\Delta H_f}{\Delta H} \quad (1)$$

where ΔH_f is the fractional heat of reaction and ΔH is the total enthalpy. The resultant conversion–time profiles are shown in Figure 2. On increasing the temperature, the reaction shows a systematic shift towards the shorter time regime, implying a faster rate.

The isothermal conversion rate curves as a function of time for different temperatures are shown in Figure 3. With the increase in temperature, there is a shift in the peak value of the reaction rate to the shorter time.

The conversion rate was plotted as a function of conversion in Figure 4. The maximum conversion rate was observed in the 15–30% conversion region. The results in Figure 4 imply that the reaction does not follow a simple n^{th} order model. For a general ' n^{th} ' order reaction, the kinetic expression is:

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (2)$$

where α is the conversion at time t and n is the reaction order.

An initial increase in the conversion rate was indicative of an autocatalytic process. On fitting the exper-

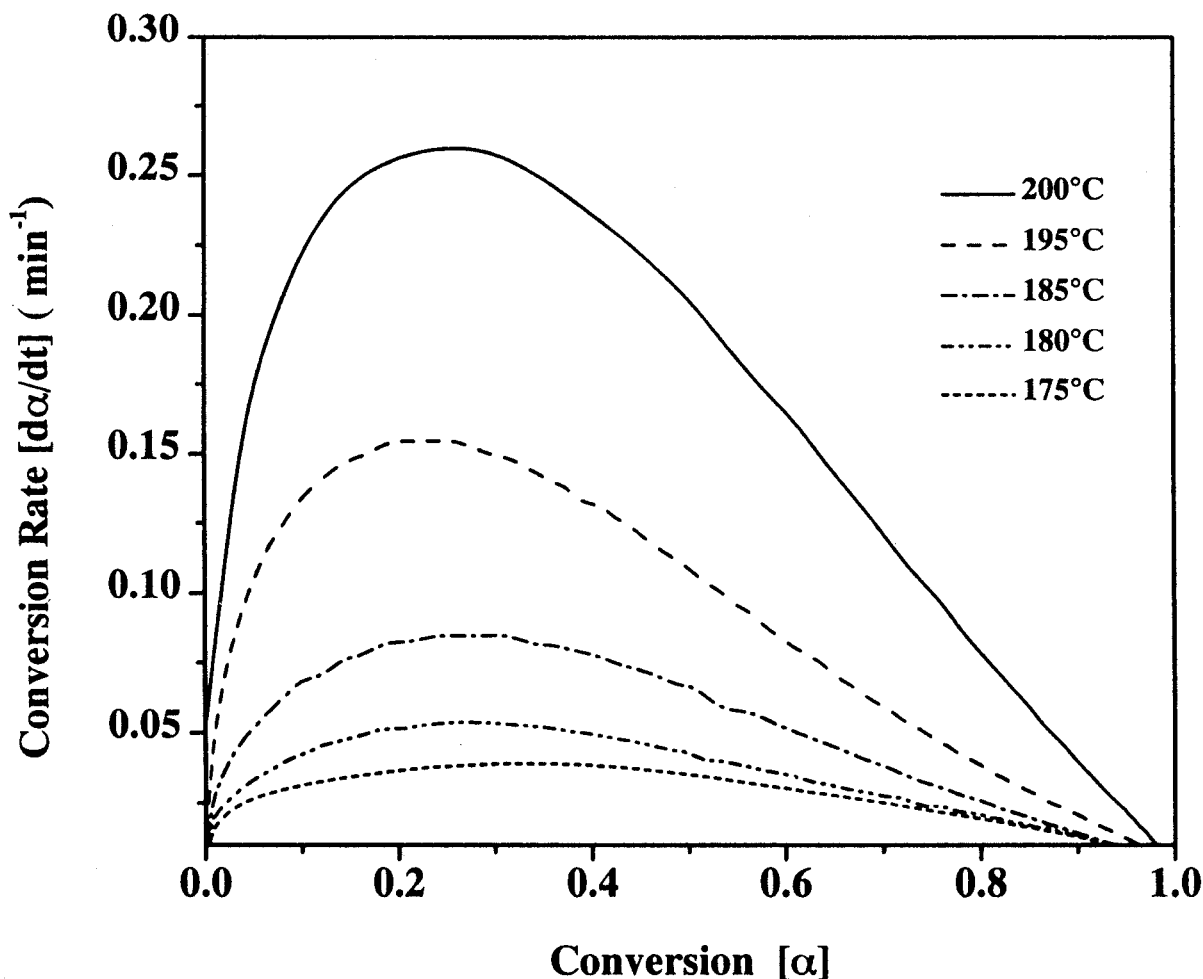


Figure 4 Dependency of conversion rate on conversion.

imental data to different models using multiple regression analysis, the autocatalytic n^{th} order was found to be the most appropriate one. For an autocatalytic reaction, where the initial reaction rate is not zero, the generalized expression proposed by Yoon et al.¹⁸ is as follows:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (3)$$

where m and n are the reaction orders and k_1 and k_2 the kinetic rate constants. The kinetic rate constants are assumed to be constant at a given temperature and to follow an Arrhenius temperature dependence, which can be expressed mathematically as follows:

$$k_i = A_i \exp\left(\frac{-E_i}{RT}\right) \quad (4)$$

$$i = 1, 2$$

where A_i is the pre-exponential factor, E_i is the activation energy, R is the gas constant, and T is the absolute temperature.

In the present study, k_1 was graphically calculated as the initial conversion rate at the point where the curve meets the y -axis in the $d\alpha/dt$ versus α plot shown in Figure 4. The other kinetic parameters, k_2 , m , and n , were calculated by fitting the experimental data to eq. 3 for each temperature. Typical curve-fitting plots for the two cases are shown in Figure 5. Similar acceptable curve fits were obtained in all cases, implying that the reaction conformed to an n^{th} -order autocatalytic model. The kinetic parameters obtained by this method are given in Table I. Temperature dependence of the kinetic rate constants is shown in Figure 6.

The reaction orders were obtained as $m = 0.6$ and $n = 1.27$ by averaging the values of m and n from all the experiments. The overall reaction order ($m + n$) converged nearly to 2. The rate constants, k_1 and k_2 , increased with increasing temperature. The activation energies for the catalyzed step and the autocatalytic

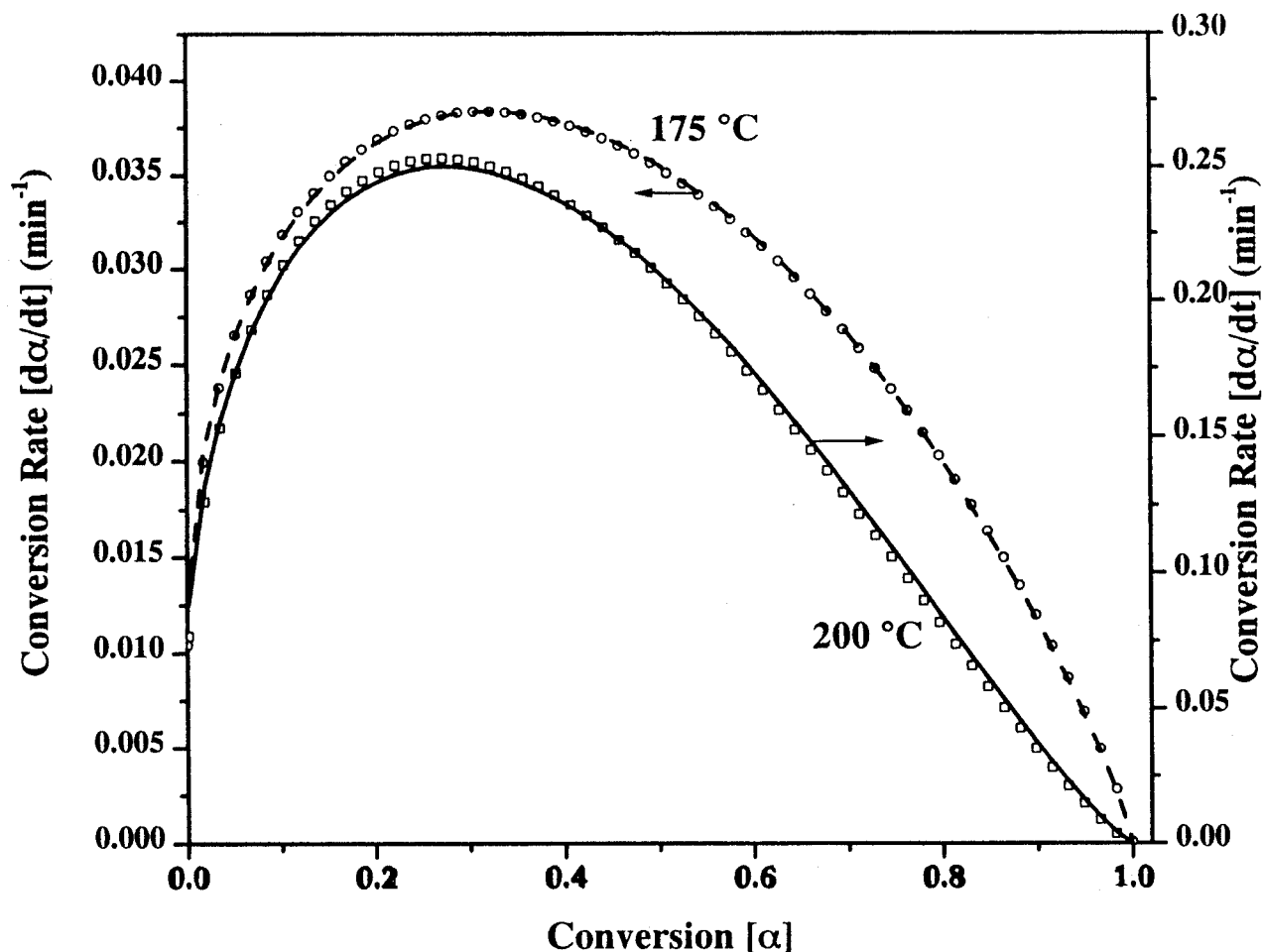


Figure 5 Multiple regression curve-fitting for calculating kinetic parameters.

steps from the Arrhenius relationship were calculated as 110.3 and 153.2 kJ/mol, respectively. The E and A values for the catalytic step are close to the values reported by Bajaj et al.,¹⁷ wherein the calculations were based on the heating rate dependence of the DSC peak maxima, assuming a uniform mechanism for the entire process. The present study shows that an autocatalytic model is more befitting.

It is reported that the cyclization process proceeds through an ionic process initiated by the $-\text{COOH}$ group.¹⁷ The autocatalytic mechanism can be explained by the fact that the basic pyrimidine groups formed from nitrile groups can catalyze the cyclization

reaction further, by way of intramolecular anionic interaction between the imine and the remaining nitrile groups, as shown in Scheme 1.

Prediction of cyclization reaction profile

The kinetic data were useful for predicting the isothermal cyclization reaction profile at a given temperature. Typical comparisons between the experimental and the predicted reaction profiles are shown in Figure 7. These comparisons were made with a computer-aided numerical integration of the following general differential equation:

TABLE I
Kinetic Parameters for Cyclization of Nitrile Group

Temperature, °C	k_1 ($\times 10^{-4}$), s^{-1}	k_2 ($\times 10^{-3}$), s^{-1}	m	n	A_1 ($\times 10^9$), s^{-1}	A_2 ($\times 10^{15}$), s^{-1}	E_1 (kJ/mol)	E_2 (kJ/mol)
175	1.83	1.25	0.51	0.85	—	—	—	—
180	3.00	2.10	0.64	1.15	—	—	—	—
185	3.66	4.36	0.68	1.45	1.45	1.03	110.3	153.2
195	6.50	7.81	0.62	1.60	—	—	—	—
200	10.00	11.38	0.57	1.31	—	—	—	—

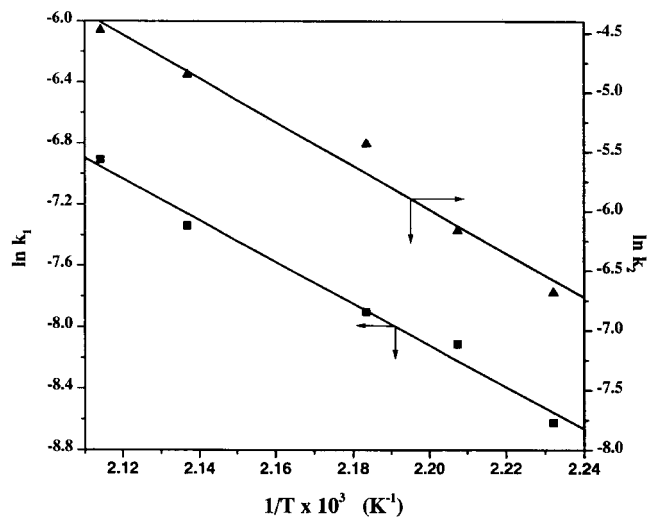


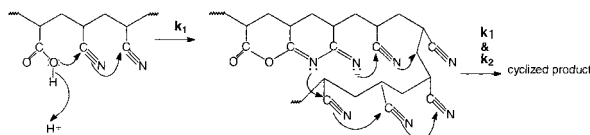
Figure 6 Temperature dependence of k_1 and k_2 .

$$\frac{d\alpha}{dt} = A_1 e^{\frac{-E_1}{RT}} (1 - \alpha)^n + A_2 e^{\frac{-E_2}{RT}} \alpha^m (1 - \alpha)^n \quad (5)$$

The predicted profiles conform to the experimental data within error limits for typical cases, as shown in Figure 7.

CONCLUSIONS

Isothermal DSC studies show that the nitrile cyclization reaction in PAN is best explained by an n^{th} -order autocatalytic model. The overall reaction conformed to second-order parameters. The kinetic constants k_1 and k_2 increased with temperature. The activation energies for the catalytic and autocatalytic steps were evaluated and were useful for predicting the reaction profile at a given temperature. The autocatalysis is explained



Scheme 1 Probable mechanism of autocatalysis of cyclization reaction in PAN.

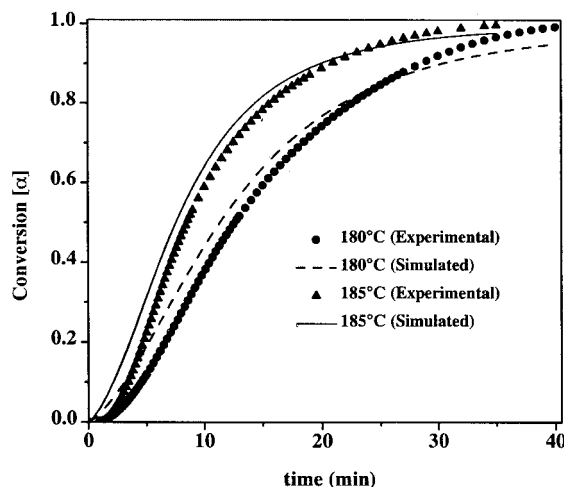


Figure 7 Prediction of isothermal reaction profiles.

based on the participation of initially formed pyrimidine group in catalyzing the nitrile cyclization.

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