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Polyamides from lactams via anionic ring-opening polymerization: 3. Rheology*

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This paper summarizes a study on the time-dependent growth of complex viscosity during the anionic ring-opening polymerization of caprolactam employing isophthaloyl-bis-caprolactam and caprolactam–magnesium-bromide as initiator and catalyst. The complex viscosity of the system—nylon 6 polymerizing in its monomer—has been defined over the temperature range of 120–160°C by *in situ* mixing and polymerizing two caprolactam streams, one containing initiator, the other containing catalyst, between oscillating platens of a Rheometrics rheometer. Isothermal rheometry at five temperatures was accomplished for one initiator/catalyst combination. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: anionic polymerization; rheology; complex viscosity)

INTRODUCTION

This paper is the last of the three-part series on polyamides from lactams via anionic ring-opening polymerization[1,2]. This study was undertaken primarily in support of a reaction injection pultrusion project. Anionic ring-opening polymerization of caprolactam to nylon 6 is uniquely suited to form a thermoplastic matrix for pultruded composites. Besides the fast reaction kinetics, low viscosity of the monomer affords superior wetting of the reinforcing fibres leading to improved adhesion between the fibres and the matrix, as compared to the conventional thermoplastic composite processes where the melt viscosity of the thermoplastic polymers are too high to afford good wetting of the fibres.

In order to understand the time-dependent growth of complex viscosity, $|\eta^*|$, during the anionic polymerization of caprolactam, we have developed a concurrent polymerization and concurrent rheological test methodology. In this test, two monomer streams—one containing catalyst and the other containing initiator—are mixed essentially instantaneously as they enter the gap between the parallel plates in a Rheometrics Mechanical Spectrometer. The polymerization is thus carried out under isothermal conditions, over the range of 120–160°C, while rheological measurements are made. The complex viscosity $|\eta^*|$ was monitored with an end toward defining the rheo-kinetics of the anionic ring-opening homopolymerization of caprolactam using isophthaloyl-bis-caprolactam and caprolactam–magnesium-bromide as initiator and catalyst. Isothermal rheometry at five temperatures was accomplished for one initiator/catalyst concentration. The objectives of this paper are: (1) to define the rheology of nylon 6 anionically polymerizing by ring-opening polymerization in caprolactam; (2) to correlate this rheology with the kinetics of polymerization.

EXPERIMENTAL

Complex viscosity growth during anionic polymerization of caprolactam was measured under isothermal conditions using a Rheometics Dynamic Mechanical Analyser (DMA), RMS-800. *Figure 1* shows a schematic diagram of the delivery method for simultaneously injecting two streams through a static mixer into the rheometer platen gap where the polymerization reaction and oscillatory complex viscosity measurement occur simultaneously. Prior to injection of a sample, the instrument was first equilibrated at the desired temperature and the gap was set. The details of the instrument and run conditions are given below.

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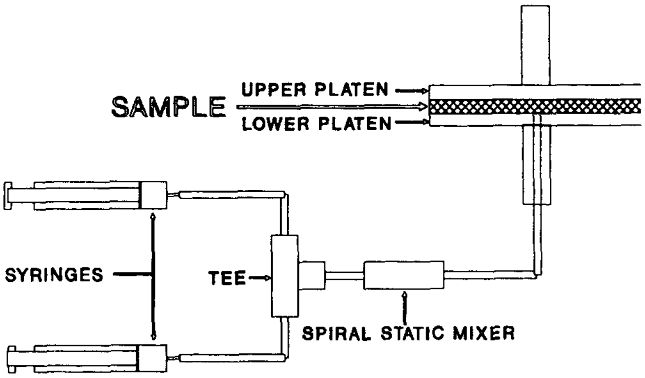

Figure 1 Dual stream injection system for *in situ* rheo-kinetic study of anionic ring-opening polymerization of caprolactam

Instrument and run conditions

The instrument used was a Rheometrics Mechanical Spectrometer (RMS-800EH). The run conditions were as follows. (1) Test geometry: disposable aluminium parallel plates of 50 mm diameter × 0.5 mm gap. (2) Shear mode: sinusoidal oscillatory shear rate of $\omega = 100\,\mathrm{rad\,s^{-1}}$ (this high frequency was chosen in order to maximize the data acquisition in minimum time). (3) Strain amplitude: 10% programmed, but 4–10 percent actually applied depending on run. (4) Options: one cycle correlation with no time or correlation delay (i.e. minimum cycle time was allowed). (5) Time/measurement: set time equalled 1 s but actual time was about 1.5 s after the first 6 s. (6) Surface/volume ratio: *in situ* sample surface to volume ratio was $40\,\mathrm{cm^{-1}}$. Measurements were automatically terminated when the instrument sensed overload on the torque load cell.

Caprolactam monomer feeds

The monomer feeds were prepared fresh daily, kept in sealed vials in an oven at 100°C, and never used after more than 6 h because some 'gel' formation was apparent in the monomer–catalyst solution after 6 h at 100°C. In order to keep the caprolactam monomer in the liquid state (m.p. about 70°C), the disposable aluminium platens were preheated to the isothermal run temperature at the start of each injection. The small gap and the large platen area ensured isothermal conditions despite the exothermic nature of the reaction. The temperature of the feed was monitored by means of a thin wire thermocouple inserted in one of the Teflon tubes connecting the syringes to the platens. Moisture was minimized by drying all parts in contact with the monomer before use. Syringes were pre-heated to 100°C before use.

Injection and mixing system

In order to inject two monomer streams—one containing catalyst and the other containing initiator—it was necessary to provide for a dual monomer stream feed system. This was accomplished by injecting one stream each, monomer–catalyst and monomer–initiator, from two syringes connected to the opposing side ports of a 1/8" stainless steel tee (Swagelok stainless steel 1/8" tee, part #SS-200-3, Hartford Valve & Fitting, Avon, CT 06001). The outlet port of this tee, at a 90° angle to the inlet ports, was connected to a static mixer with 12 mixing elements (Series 85 spiral static mixer, 3/16" o.d. × 1.5" long, part #084-312, TAH Industries, Robbinsville, NJ) and subsequently to the lower platen of the parallel plate assembly (a hole was drilled through the centre of the lower disposable aluminium platen). All connections and tubing were made of Teflon, and all materials in contact with the monomer streams, until the monomer was actually introduced between the aluminium platens, were made of stainless steel, glass or Teflon.

Post-run sample removal and handling

At the end of data acquisition, the oven surrounding the parallel plates of the rheometer was cooled rapidly with cold nitrogen gas to below the glass transition temperature (T_g) of the polymer. The oven was then opened, the platen set screws loosened, and the upper platen raised to separate the platens from the platen fixtures. The platen/polymer/platen 'sandwich' thus removed was immediately immersed in liquid nitrogen to stop any further polymerization and to freeze the sample. The additional time to accomplish cooling, removal and freezing was about 1–2 min. Inspection of the sample after freezing and separation of the platens allowed for the determination of the percent fill of the gap.

Feed composition

The single feed composition investigated consisted of $133\,\mathrm{mmol\,l^{-1}}$ of caprolactam–magnesium-bromide and $45\,\mathrm{mmol\,l^{-1}}$ of the difunctional isophthaloyl-bis-caprolactam. Note that $45\,\mathrm{mmol\,l^{-1}}$ of the difunctional isophthaloyl-bis-caprolactam contain $90\,\mathrm{mmol\,l^{-1}}$ of the active acyllactam group, which react with the monofunctional caprolactam–magnesium-bromide to initiate the polymerization reaction.

VISCOSITY MODEL

The following relation was used for determining the complex viscosity of the polymerizing system[3]:

$$|\eta^*| = |\eta_0^*|\exp(kX) \qquad (1)$$

where $|\eta^*|$ is the complex viscosity of nylon 6 anionically polymerizing in its monomer, $|\eta_0^*|$ is the complex viscosity of caprolactam monomer, k is a constant, and X is fractional conversion. The complex viscosity of the monomer, $|\eta_0^*|$, follows an Arrhenius temperature dependence[3]

$$|\eta_0^*|(T) = 2.7 \times 10^{-7}\exp(3525/T)(\mathrm{Pa\,s}) \qquad (2)$$

RESULTS AND DISCUSSION

Rheology of nylon 6 anionically polymerizing in its monomer

All measurements were performed with the formulation specified above. Upon mixing and injection of the caprolactam monomer streams into the rheological instrument, polymerization was initiated and continued, while simultaneously monitoring the complex viscosity of the polymerizing system. The maximum measurable complex viscosity levels were achieved in about 100 s or less, depending on temperature.

At each temperature, the expected rapid rise of the complex viscosity with conversion, molecular weight build-up, and ultimate solidification was observed and

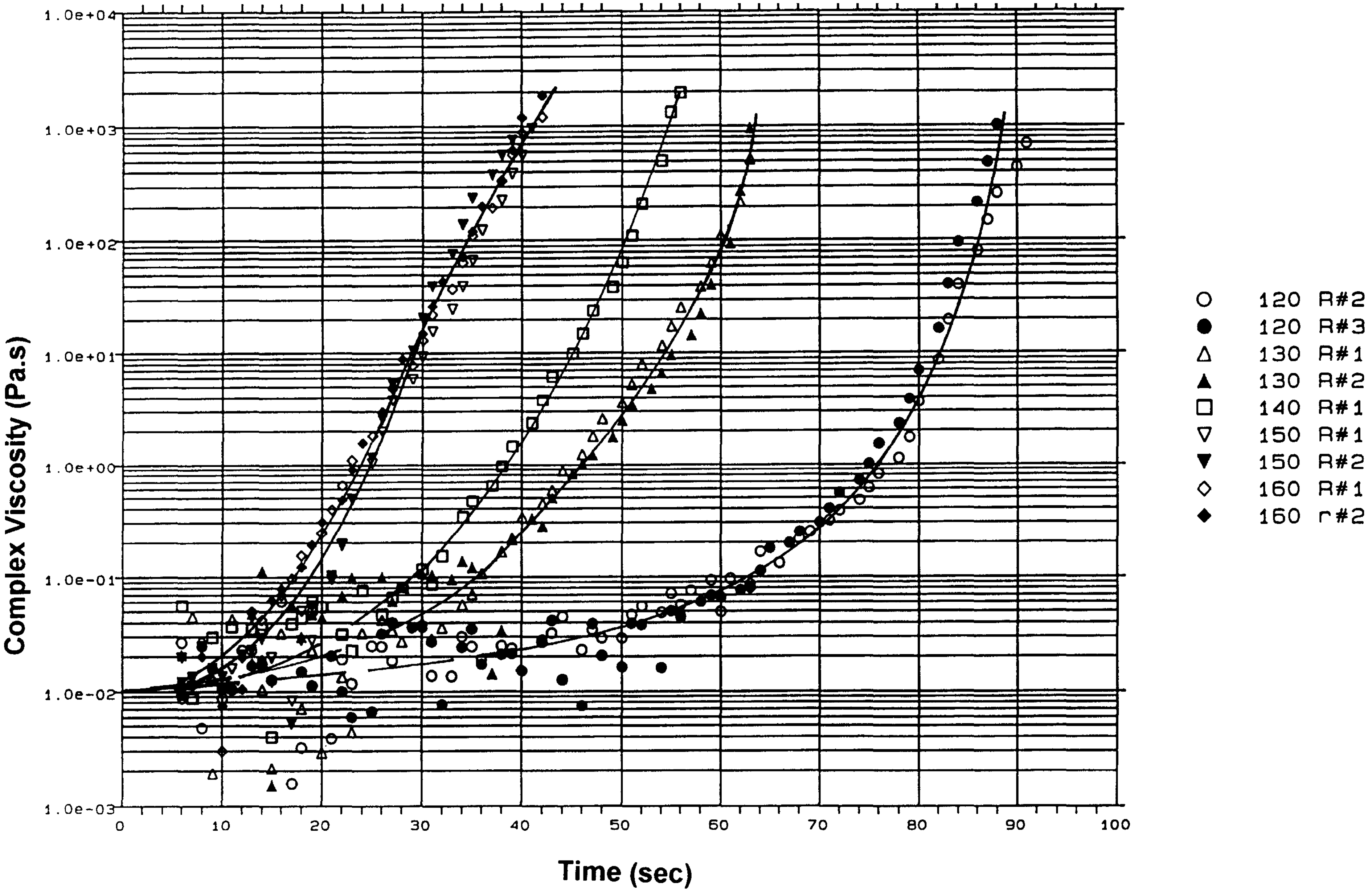

Figure 2 Isothermal complex viscosity rise during anionic polymerization of caprolactam using caprolactam–magnesium-bromide/isophthaloyl-bis-caprolactam as the catalyst/initiator system. Run numbers and polymerization temperatures are shown in the legend

the complex viscosity–time relationship was quantified. The time to achieve maximum permissible torque on the instrument ranged from about 90 s at 120°C to 40 s at 160°C. This corresponds to 10^3 Pa s (10^4 poise) for the geometry used and is on such a steep slope of the complex viscosity–time curve that it is very close to the time for near infinite complex viscosity, i.e. total solidification.

Figure 2 shows replicated complex viscosity–time curve for all five temperatures. Some difficulty in reproducibly filling the gap between the parallel plates was encountered, leading to the requirement of measurement replication and averaging of results. Moreover, the initial (very early time) viscosities were about 0.01 Pa s (ten times that of water) and are outside the sensitivity range of the instrument, leading to very large scatter at low times. These caveats notwithstanding, the data is relatively good, and provided a quantitative basis for modelling the matrix complex viscosity build-up during the reaction injection pultrusion process.

Figure 3 shows time to achieve a given complex viscosity as a function of polymerization temperature. (Numerical values are given in *Table 1*.) These curves are fitted with a quadratic equation (second order polynomial).

Correlation of rheology with kinetics of polymerization

Figure 4 shows complex relative viscosity ($|\eta^*|/|\eta_0^*|$) as a function of conversion at 130, 140, and 160°C. Conversion was calculated by the kinetic model described previously[2]. *Figure 4* shows that between 130 and 160°C (except 150°C) all curves are nearly identical below 50% conversion. For polymerizations at 130 and 140°C, a sharp increase in complex relative viscosity was observed beyond 50% conversion. Sibal *et al.*[3] suggest that the sharp increase in complex relative viscosity during anionic ring-opening polymerization of caprolactam is due to physical gelation that probably results from mechanical interlocking of the crystallites being formed during polymerization. The conversion at which the complex relative viscosity curve deviates from the linear, straight-line fit depends on the polymerization temperature, because both kinetics of polymerization and kinetics of crystallization are temperature dependent. For polymerizations near 145°C, where the crystallization rate is greatest[4], crystallization kinetics strongly competes with chemical kinetics. On the other hand, for polymerization at 160°C, crystallization rate is drastically reduced[4] and, therefore, the 160°C curve does not exhibit the gelation effect.

Even though a mechanistic explanation of the complex viscosity rise and gelation is not available at this time, the information in *Figure 4* is useful in understanding and modelling reaction injection moulding, reaction injection pultrusion, and other fibre-reinforced composite processes that are based on anionic ring-opening polymerization of caprolactam. Below 50% conversion all the curves are almost linear, suggesting a phenomenological equation of the form

$$|\eta^*|/|\eta_0^*| = \exp(19.6X) \text{ for } X < 0.5 \qquad (3)$$

where 19.6 is the constant that defines the complex relative viscosity rise during anionic ring-opening polymerization of caprolactam using caprolactam–magnesium-bromide/isophthaloyl-bis-caprolactam as the catalyst/initiator system. In *equation (3)* the temperature dependence of $|\eta^*|$ is that for $|\eta_0^*|$ defined in *equation (2)*.

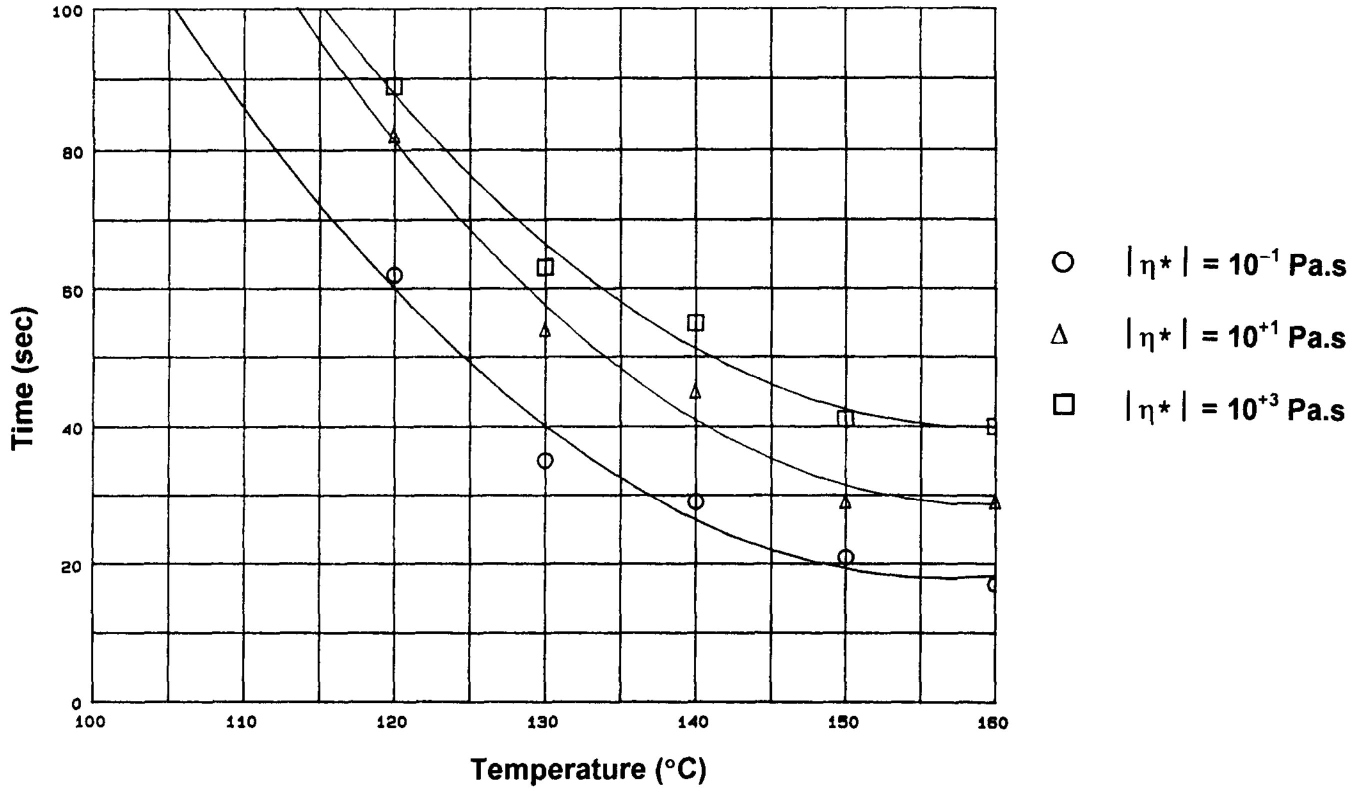

Figure 3 Time to reach complex viscosity of 0.1, 10, and 1000 Pa s as a function of temperature during anionic polymerization of caprolactam using caprolactam–magnesium-bromide/isophthaloyl-bis-caprolactam as the catalyst/initiator system. Complex viscosity is shown in the legend

For sodium/hexamethylene-1,6-bis-carbamidocaprolactam system, Sibal *et al.*[3] found the value of the constant k in equation (1) to be 17.5. Note that the values of the constant k in equation (1) which define the complex relative viscosity rise during anionic ring-opening polymerization of caprolactam are comparable for both caprolactam-magnesium-bromide/isophthaloyl-bis-caprolactam and sodium/hexamethylene-1,6-bis-carbamidocaprolactam as the catalyst/initiator systems even though the kinetic constants for anionic polymerization for these systems are extremely different (see Table 2 in ref. 2).

Figure 5 shows complex relative viscosity as a function of conversion at 120 and 150°C. The 150°C curve shows a dramatic rise due to the simultaneous crystallization during polymerization. Also, notice in *Figure 2* that the complex viscosity–time curves of 150 and 160°C polymerizations tend to converge. Both these effects—the non-linear rise in complex relative viscosity in *Figure 5* and the convergence of 150 and 160°C curves in *Figure 2*—occur because of simultaneous crystallization and polymerization at 150°C. This temperature is near the maximum crystallization rate temperature (~ 145°C) of nylon 6 homopolymer[4]. The presence of solid crystallites increases the complex viscosity of the polymerizing system because of a filler effect.

Table 1 Time to reach a steady complex viscosity as a function of temperature during anionic polymerization of nylon 6 with catalyst and initiator concentration of 133 mmol l^{-1} of caprolactam–magnesium-bromide and 90 mmol l^{-1} of acyllactam

Polymerization temperature (°C)	Time to reach a steady complex viscosity (s) 10^{-1} Pa s	 10^{1} Pa s	 10^{3} Pa s
120	62	82	89
130	35	54	63
140	29	45	55
150	21	29	41
160	17	29	40

In *Figure 5*, the 120°C curve deviates from the straight line at a conversion of about 10%. This effect is due to 'sluggish' polymerization like that observed in the kinetics study (see Figure 5a in ref. 2). The predicted conversion (x-axis values in *Figure 5*) is based on Malkin's autocatalytic, phenomenological model (see ref. 2) that does not account for either crystallization or diffusion kinetics. However, in *Figure 5*, the polymerization at 120°C becomes diffusion controlled after about 10% conversion. Therefore, the predicted values of conversion by Malkin's autocatalytic rate equation are overestimated values of the true conversion resulting from diffusion controlled kinetics. This error results in the non-linearity of the 120°C curve.

As a final note, we question why the complex relative viscosity vs conversion curve for the 140°C polymerization did not deviate (up to 50% conversion) from the straight-line fit even though Magill's data on crystallization rate of hydrolytic nylon 6 (i.e. nylon 6 made by the conventional, hydrolytic process) vs temperature shows a maximum in the crystallization rate at about

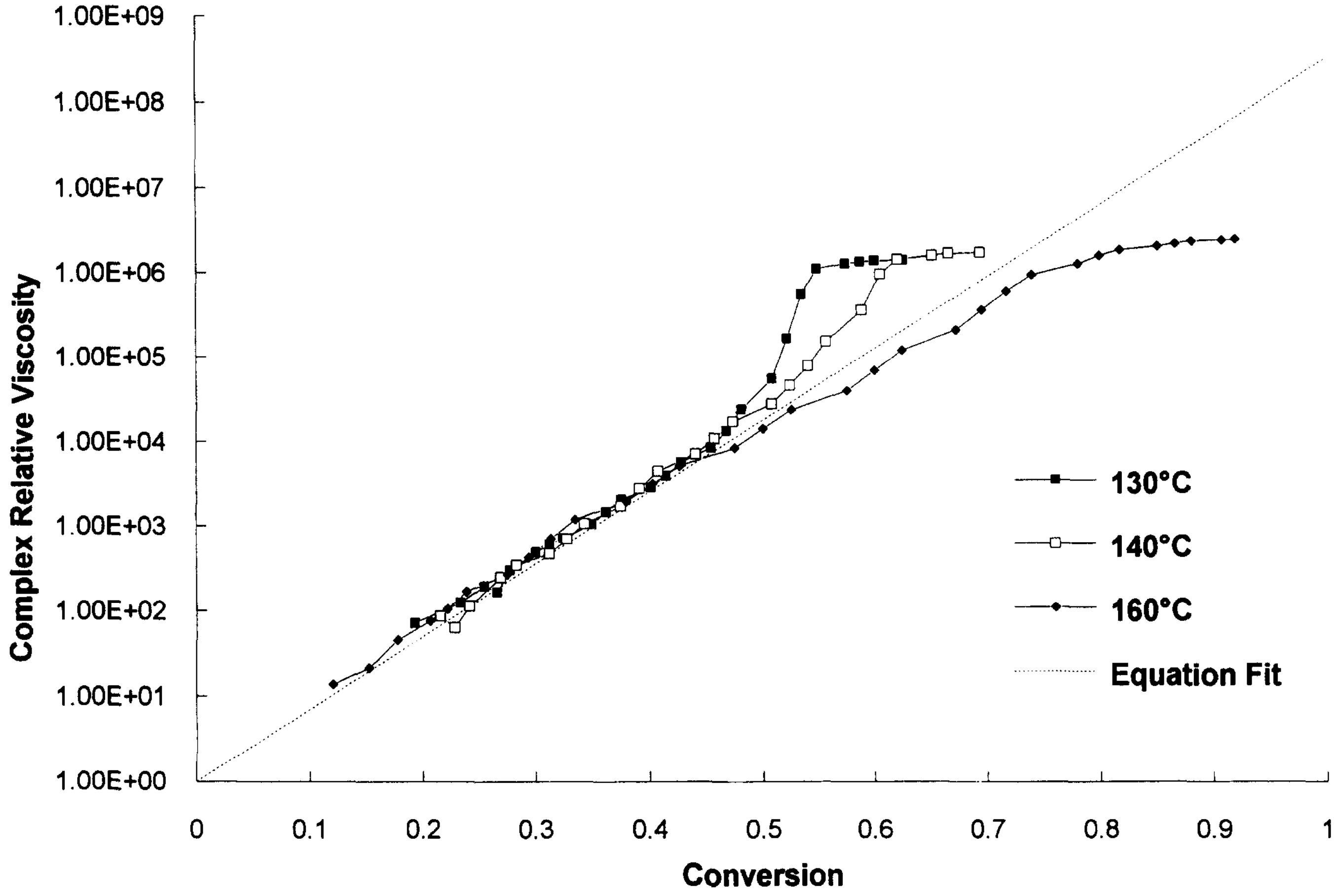

Figure 4 Complex relative viscosity ($|\eta^*|/|\eta_0^*|$) vs calculated conversion for polymerization at 130, 140, and 160°C. Phenomenological equation to fit the data prior to gelation is also shown

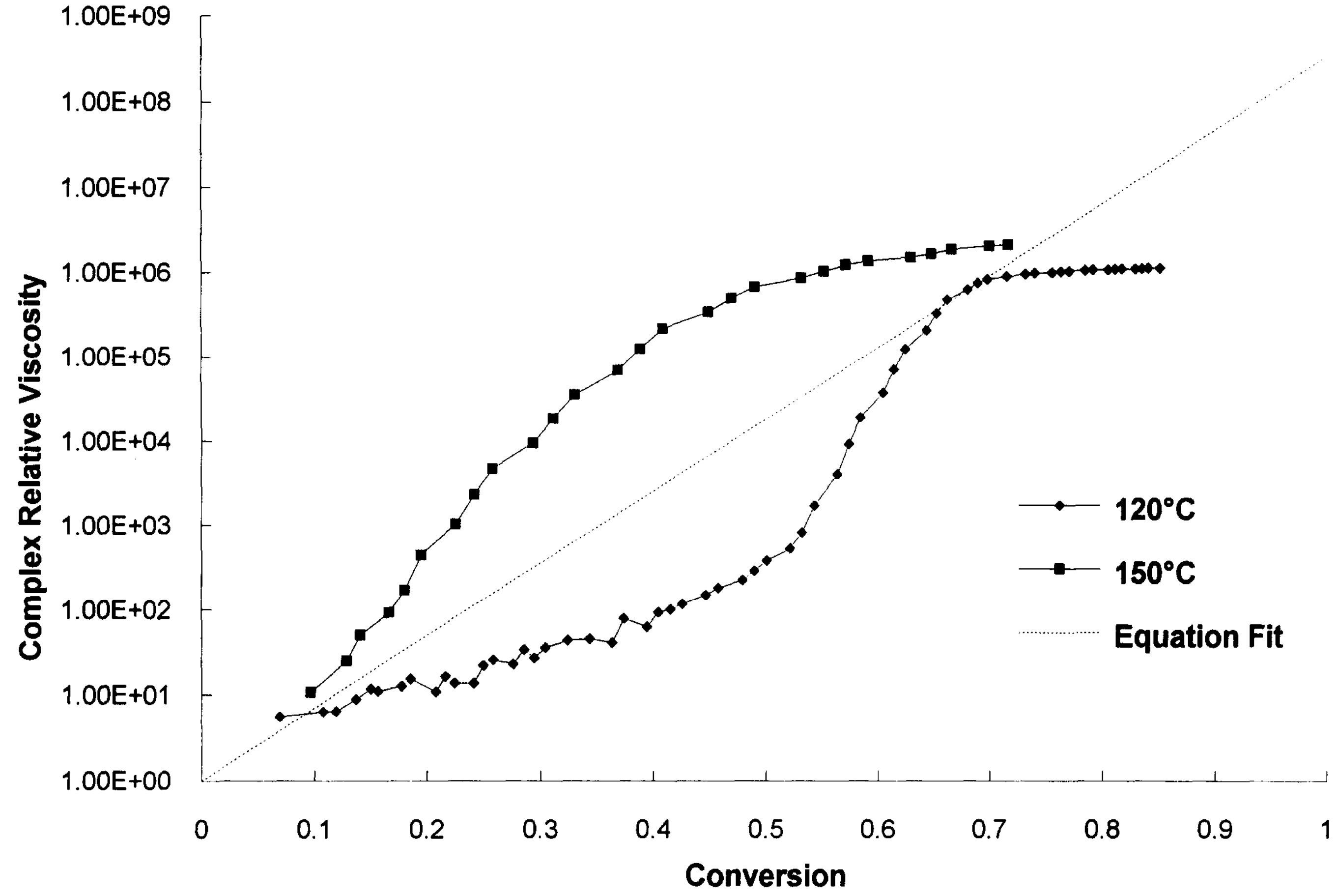

Figure 5 Complex relative viscosity ($|\eta^*|/|\eta_0^*|$) vs calculated conversion for polymerization at 120 and 150°C. Linear, straight-line fit to the phenomenological equation $|\eta^*|/|\eta_0^*| = \exp(19.6X)$ is also shown

140–145°C. One possibility is that nylon 6 formed by anionic polymerization below the melting point of nylon 6 is a mixture of two crystalline structures: α and γ (see ref. 1). The melting points of α and γ structures are about 256 and 228°C, respectively[5]. For anionically formed nylon 6 that is a mixture of α and γ structures, the temperature for maximum crystallization may be higher than the temperature for maximum crystallization of hydrolytic nylon 6 (γ structure). Since Magill's data were obtained on hydrolytic nylon 6, these data may not be directly applicable to the crystallization of nylon 6 polymerizing in molten caprolactam during anionic ring-opening polymerization of caprolactam.

CONCLUSION

Reaction times for caprolactam monomer, containing 133 $\mathrm{mmol\,l^{-1}}$ of caprolactam–magnesium-bromide and 90 $\mathrm{mmol\,l^{-1}}$ of acyllactam respectively, are extremely short; i.e. times ranging from 90 s at 120°C to less than 45 s at 160°C were required to polymerize to a complex viscosity level of 10^3 Pa s.

The rheo-kinetics of the polymerizing system demonstrates that below 50% conversion, the complex relative viscosity vs conversion of the nylon 6 homopolymerization can be defined by the phenomenological equation $|\eta^*|/|\eta_0^*| = \exp(19.6X)$, where $|\eta^*|$ is the complex viscosity of nylon 6 anionically polymerizing in its monomer, $|\eta_0^*|$ is the viscosity of caprolactam monomer, and X is fractional conversion.

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