Separation of polymerization and crystallization processes for nylon-6

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The relationship between onset of polymerization and crystallization for nylon-6 formed from caprolactam has been delineated via differential scanning calorimetry. The effect of initiator and activator concentration on the polymerization and crystallization process was examined. Adipoyl-bis-caprolactam was used for the activator so as to produce a slow polymerization. Polymerization followed by crystallization was observed when polymerization temperature, determined from heating the reactive components, was less than the crystallization temperature, determined by cooling the nylon from the melt. Crystallization was not observed for polymerizations at temperatures higher than the corresponding melt crystallization temperature.

(Keywords: crystallization; caprolactam; calorimetry; nylon-6)

INTRODUCTION

Anionic polymerization of caprolactam to form nylon-6 is well known. Usually, the reaction of caprolactam proceeds with caprolactamate anion (i.e. lithium-, sodium- or potassium-caprolactamate) as catalyst and acylated caprolactam as activator. Polymerization and crystallization of caprolactam often occur nearly simultaneously, so a separate determination of their exothermic processes is difficult. However, attempts are made to separate polymerization and crystallization processes and to evaluate their individual enthalpies and process kinetics by using trial-and-error curve-fitting methods on differential scanning calorimetry (d.s.c.) data[1].

Polymerization and crystallization of nylon-6 are studied under adiabatic, non-isothermal and isothermal conditions. Under adiabatic conditions, rate of reaction is shown to be affected by initial monomer temperature and concentrations of activator and catalyst[2]. On increasing temperature, an increase in reaction rate is observed; the adiabatic reaction where toluene diisocyanate instantly reacts with caprolactam to form the activator and is then attacked by sodium caprolactamate to initiate polymerization is complete within 20 s at 170°C[2]. Arrhenius curves developed from reaction rate and initial monomer temperature data do not overlap as expected, but rather shift toward lower rates as temperature is increased. A data fit is achieved and an activation energy of 20 kcal mol^{-1} is deduced, when the Arrhenius equation is modified to account for an autocatalytic factor[2,3]. This autocatalytic nature of the reaction is also confirmed under isothermal conditions[4].

According to the kinetic expressions developed by Wittmer and Gerrens, an increase in polymerization rate should occur as either activator or catalyst concentration is increased[2,5]. This is confirmed for increasing catalyst concentrations. However, a drop in rate is observed for increasing activator concentrations when the activator concentration exceeded that of the catalyst[2]. It is reported that under conditions of excess activator, the anion is consumed by side reactions. Thus, it is this lower catalyst concentration that results in the lower rate of polymerization[2,6].

Total crystallization enthalpy is affected by the activator since crystallization can occur only as polymer becomes available. The extent of crystallization depends on spatial structure of the macromolecules of the same type[4]. It is reported for fast adiabatic polymerization (less than 100 s) that crystallization rate is a maximum at 150°C[2]. It is suggested that crystallization is retarded at higher temperatures as well as at lower temperatures where crystallization is assumed to occur before polymerization is complete and as such tends to freeze-in lower molecular-weight species[7].

Semicrystalline nylon-6 is usually composed of three polymorphic forms: α, γ and pseudohexagonal γ^*[8,9]. Heat of fusion for the 100% crystalline α-polymorph extrapolated from crystalline densities is reported as 250 J g^{-1} (ref. 10). However, Illers reported values for the 100% crystalline polymorphs of 241 J g^{-1} for the α-form, 239 J g^{-1} for the γ-polymorph and 58 J g^{-1} for the pseudohexagonal γ^*-modification[8]. Generally, the percentage crystallinity for nylon-6 is based on a heat of fusion of 240 J g^{-1} for the 100% crystalline polymer[1,8].

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In this study, nylon-6 was non-isothermally polymerized from caprolactam with sodium caprolactamate as catalyst and adipoyl-bis-caprolactam (ABC) as activator. This composition resulted in a slow reaction, which might be due to the sterically hindered configuration of the activator. Thus, separation of the polymerization and crystallization processes was achieved. This paper delineates separation of polymerization and crystallization processes and the effects of heating rate, catalyst and activator concentration on kinetics of both processes.

EXPERIMENTAL

Materials utilized in this study were caprolactam (99% pure, Aldrich lot No. 03527CT), sodium hydride (NaH) (dry, 97% pure, Aldrich lot No. 06708TT) and adipoyl-bis-caprolactam (ABC), which was synthesized as follows. Dry tetrahydrofuran (800 ml), adipoyl chloride (100 g, 0.55 mol) and dry caprolactam (136 g, 1.2 mol) were placed in an oven-dried, argon-purged, 2000 ml Morton flask fitted with a mechanical stirrer, low-temperature thermometer and an addition funnel. A solution of dry triethylamine (120 g, 1.2 mol) in tetrahydrofuran (200 ml) was added over a period of three hours while the reaction temperature was maintained between 0 and 5°C. The solution was then allowed to warm to room temperature. Filtration yielded a clear solution which was evaporated to dryness. The white solid was recrystallized twice from ethyl alcohol/diethyl-ether. A yield of 75 g ABC with a melting point of 71–71.5°C was obtained.

Preparation of the d.s.c. samples was performed in a dry-nitrogen glovebox. Samples were made by first individually preparing initiator and activator. Initiator, Na–Cap, was formed by dissolving the desired concentration of NaH (0.14–1.08 mol%) in 25 g of caprolactam at 75 to 80°C. Hydrogen evolved as the mixture was stirred. Similarly, appropriate concentrations (0.14–1.08 mol%) of ABC were dissolved in 25 g of caprolactam at 75–80°C. Concentrations of both Na–Cap and ABC were chosen so as to achieve the desired Na–Cap:ABC ratios of 1:1, 2:1, 3:1 and 5:1 at an ABC concentration of 0.27 mol% and at a ratio of 2:1 with ABC concentrations of 0.14, 0.27, 0.41 and 0.54 mol%. Next, the two components were mixed together and then quickly cooled to ambient conditions by pouring into a glass dish located on a metal quench block. Large-volume stainless-steel d.s.c. pans were filled with 25–40 mg of the reaction components then O-ring sealed by crimping.

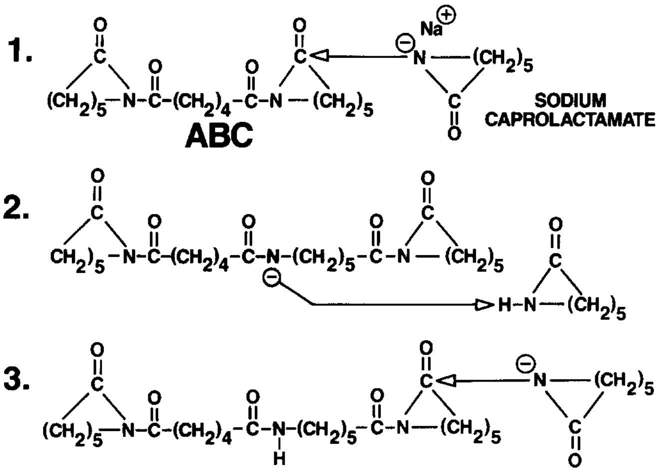

Figure 1 The scheme for polymerization of caprolactam monomer, sodium caprolactamate and adipoyl-bis-caprolactamate to form nylon-6

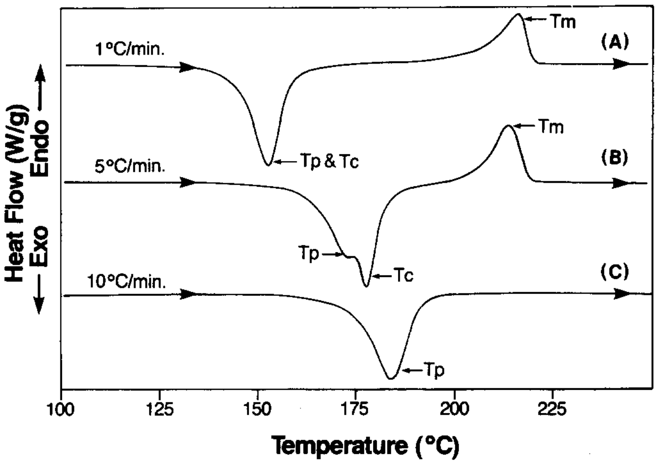

Figure 2 Thermograms of the reactive components as they were heated at the rates indicated

The thermal profile utilized for polymerization involved heating the reactive components at 1.25, 3, 5, 10 or 25°C min^{-1} from 30 to 250°C, holding for 5 min then cooling from 250 to 30°C at the same rate previously employed for heating. Polymerized and crystallized sample was then reheated as before. Each Na–Cap:ABC composition was examined at all the listed heating rates. Temperature and enthalpy were calibrated with indium and tin standards.

RESULTS AND DISCUSSION

Polymerization scheme

The reaction scheme for anionic polymerization of caprolactam with sodium caprolactamate (Na–Cap) catalyst and adipoyl-bis-caprolactam (ABC) activator to form nylon-6 is shown in *Figure 1*. Initiation occurred by nucleophilic attack of $^+$Na–Cap on the carbonyl group of the ABC, resulting in ring opening. This was followed by monomer insertion on the growing chain and regeneration of the amide anion. Polymerization proceeded as the polymeric anion abstracted a proton from caprolactam monomer to continue the process.

Separation of polymerization and crystallization processes

Onset of the polymerization and crystallization and their associated exothermic enthalpies were observed as the reactive components were heated at a constant rate via differential scanning calorimetry (d.s.c.). Effect of heating rate on polymerization and subsequent crystallization processes can be characterized with the three thermograms shown in *Figure 2*, where T_p denotes temperature of polymerization and T_c temperature of crystallization; the reactive components were heated at (A) 1°C min^{-1}, (B) 5°C min^{-1} and (C) 10°C min^{-1}. Each thermogram was normalized to the caprolactam melting endotherm (not shown) to eliminate rate effects on the size of the first-order transitions.

Melting of caprolactam at about 72°C was the first transitional event for each composition. In *Figure 2*, curve A, this was followed by the nearly simultaneous polymerization and crystallization of caprolactam and

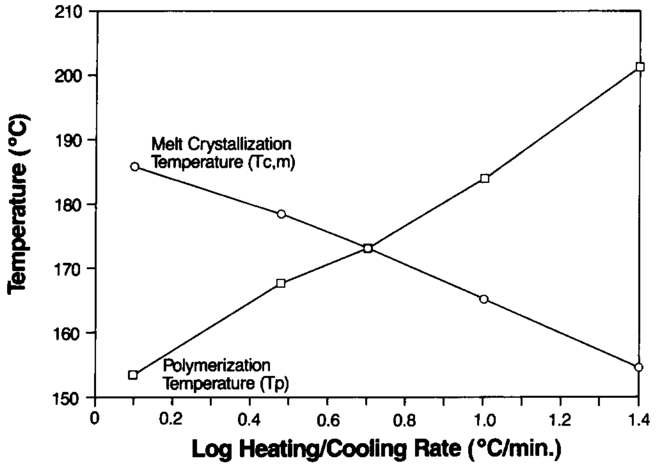

Figure 3 Plot of both polymerization temperature obtained during heating of the reactive components and melt crystallization temperature obtained subsequently during cooling of the newly formed nylon-6 as a function of heating/cooling rate

then at about 217°C by melting of crystalline nylon-6. In *Figure 2*, curve B, the exothermic polymerization and crystallization processes can be identified as separate events. At higher temperatures, melting of crystallized nylon-6 was observed as previously shown for the slower heating rate. At the fastest heating rate, *Figure 2*, curve C, melting of caprolactam was followed by its polymerization to form nylon-6. The absence of the nylon-6 melting endotherm at high temperatures indicates that the exotherm solely comprised heat from the reaction. So process kinetics influenced not only formation of the nylon, but also its subsequent crystallizability.

Following polymerization and crystallization processes, nylon-6 can be melted and then subsequently recrystallized by cooling. Upon cooling from the melt a single, sharp crystallization exotherm was observed regardless of heating history. The peak temperature of this melt crystallization exotherm was cooling-rate dependent.

The kinetic effects of polymerization and crystallization processes observed by heating the reactive components can be understood by considering the relationship between polymerization temperature obtained upon heating and the temperature at which the nylon-6 crystallized upon cooling from the melt. A plot of both polymerization temperature obtained during heating of the reactive components and melt crystallization temperature obtained subsequently during cooling of the newly formed nylon-6 is shown as a function of rate (heating or cooling) in *Figure 3*. All temperatures were taken at the peaks of their respective exotherms.

At the slowest heating rate (1°C min^{-1}), the peak temperature of the polymerization exotherm was about 153°C, while cooling at the same slow rate resulted in nylon-6 crystallization from the melt at about 186°C. Thus the polymerization temperature was more than 30°C less than its corresponding melt crystallization temperature. So, as the reactive components were heated and nylon-6 formed, this large degree of supercooling provided the driving force for its immediate crystallization and consequently only a single exotherm was observed (*Figure 2*, curve A).

At faster heating and cooling rates, polymerization temperature increased and the corresponding melt crystallization temperature declined. At 5°C min^{-1}, the polymerization temperature approached the temperature at which crystallization would occur if nylon were melt crystallized. Thus at this rate, once nylon-6 was formed (via heating of the reactive components), a reduction in the driving force for its subsequent crystallization would be expected. It is this reduction in driving force that can account for separation of the polymerization exotherm from the crystallization exotherm (*Figure 2*, curve B).

As heating and cooling rates were further increased, polymerization temperature became greater than the associated melt crystallization temperature. Thus, once nylon-6 was formed, it was above the temperature where crystallization events could occur. Crystallization could only be achieved through subsequent cooling from the melt.

Na–Cap concentration effects

Sample nomenclature has been devised so that the concentrations of Na-Cap and ABC can be easily discerned. There is a factor of two difference between the molar percentage of Na–Cap and ABC due to the bifunctionality of the ABC. For example, a sample composed of a 2:1 ratio of Na–Cap:ABC consists of 1.08 mol% Na–Cap and 0.27 mol% ABC. In the naming scheme, each sample is identified with a three-digit number. The first digit represents the ratio of Na–Cap to one part of ABC. The second two numbers indicate the molar percentage of ABC. Application of this nomenclature for sample designation is illustrated in *Table 1*.

Effects of Na–Cap catalyst concentration on polymerization temperature at each heating rate are shown in *Figure 4* for the reactive compositions of 127, 227, 327

Table 1 Sample identification, Na–Cap concentration, ABC concentration and the ratio of Na–Cap to ABC for each reactive composition

Sample identifier	[Na–Cap] (mol%)	[ABC] (mol%)	Na–Cap:ABC
127	0.54	0.27	1:1
227	1.08	0.27	2:1
327	1.62	0.27	3:1
527	2.70	0.27	5:1
214	0.56	0.14	2:1
241	1.64	0.41	2:1
254	2.16	0.54	2:1

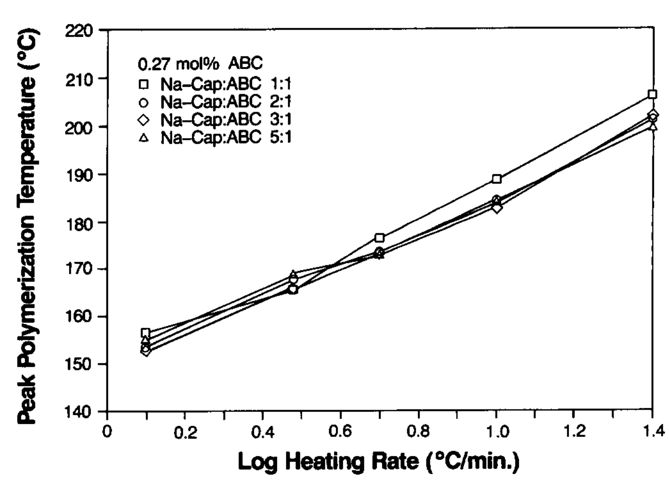

Figure 4 Effects of Na–Cap concentration on polymerization temperature at each heating rate for different reactive compositions

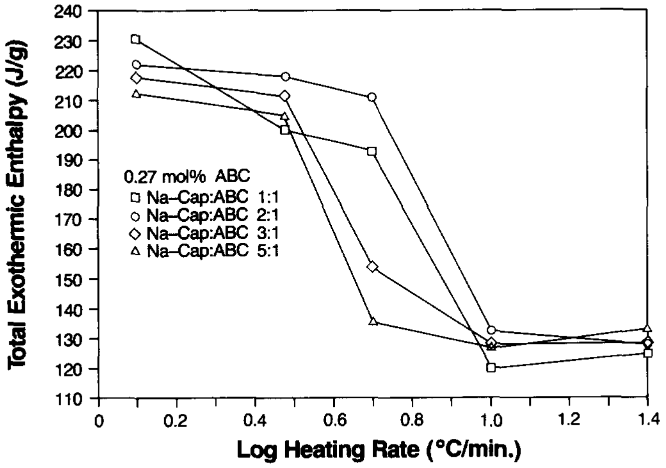

Figure 5 Effects of Na–Cap concentration on total exothermic enthalpy as a function of heating rate

and 527 (see *Table 1*). A reduction in polymerization temperature occurred as the ratio of Na–Cap to ABC was increased from 1:1 to 2:1. However, once the ratio of Na–Cap to ABC was 2:1 or more, no effect of Na–Cap concentration on polymerization temperature was observed. The expected increase in polymerization temperature with heating rate was noted.

In *Figure 5*, effects of Na–Cap concentration on total exothermic enthalpy are shown as a function of heating rate. The total exothermic heat generated during the reactions performed at slow heating rates consisted of enthalpic contributions from both polymerization and crystallization processes. However, at faster heating rates, total enthalpy was equivalent to the heat of polymerization. Examination of the heat of polymerization displayed at the fastest rates (10 and 25°C $\min^{-1}$) reveals that the 127 compositions have not completely polymerized. Average heat of polymerization of the 227, 327 and 527 (see *Table 1*) compositions was determined to be $129.1 \pm 2.9\ \mathrm{J\,g^{-1}}$. This is lower than literature values for heat of polymerization of caprolactam, which ranged from 140.8 to $144\ \mathrm{J\,g^{-1}}$. This suggests that even at the highest levels of Na–Cap, the reaction may not be complete due to the highly hindered amide anion and competing side reactions.

The effects of Na–Cap on the crystallization process can be evaluated from exothermic enthalpy determined at slower heating rates, as also shown in *Figure 5*. Enthalpies greater than about $129\ \mathrm{J\,g^{-1}}$ can be associated with heat of crystallization. Increase in crystallinity as the heating rate was lowered can be primarily accounted for by considering the contribution to the enthalpy from annealing of the crystalline nylon during the slower rates.

Increasing concentrations of Na–Cap acted to inhibit the crystallization process and so reduce the overall degree of crystallinity for the 227, 327 and 527 (see *Table 1*) compositions. Iobst has shown that the rate of polymerization increases with increasing catalyst concentration and suggests that crystallization can be retarded if it occurs before the polymerization is complete[2]. Since the level of crystallinity also depends on the completeness of the reaction, the seemingly anomalous enthalpy values for the 127 compositions may be attributed to their incomplete polymerization or side reactions.

ABC concentration effects

Polymerization temperatures at each heating rate examined are shown in *Figure 6* for ABC concentrations of 0.14, 0.27, 0.41 and 0.54 mol% in a 2:1 ratio of Na–Cap:ABC. A reduction in polymerization temperature, except at the lowest heating rates, was observed with increasing concentration of ABC from 0.14 to 0.41 mol%. However, further increase in the ABC concentration resulted in seemingly erratic polymerization temperatures. This behaviour may be attributed to the anion participating in side reactions due to high concentrations (large quantities) of both catalyst and activator.

The total exothermic heat is shown in *Figure 7* as a function of heating rate for concentrations of 0.14, 0.27, 0.41 and 0.54 mol% ABC at a 2:1 ratio of Na–Cap:ABC. As previously shown for variation in Na–Cap concentration, total enthalpy at the slow heating rates was composed of contributions from heats of polymerization and crystallization, while at faster rates the heat of polymerization was the sole contributor. Low values of heat of polymerization for the 0.14 mol% ABC compositions indicate that the reaction was incomplete. An average enthalpy of $129.0 \pm 3.8\ \mathrm{J\,g^{-1}}$ was determined for the remaining compositions. This is consistent with

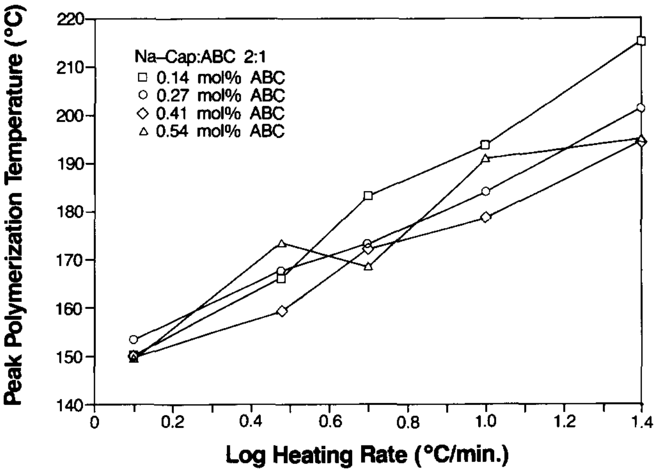

Figure 6 Polymerization temperatures as a function of heating rate for various ABC concentrations in a 2:1 ratio of Na–Cap:ABC

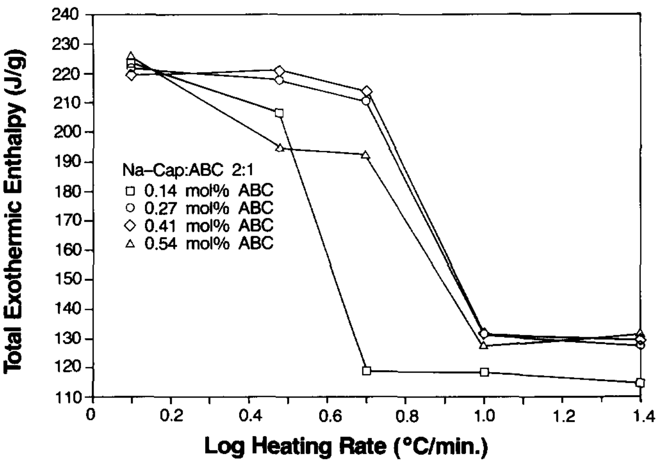

Figure 7 Total exothermic heat as a function of heating rate for various ABC concentrations in a 2:1 ratio of Na–Cap:ABC

the heat of polymerization obtained for compositions containing higher ratios of Na–Cap.

Dependence of degree of crystallinity on ABC concentration can be assessed from enthalpy values obtained at slow heating rates, which are also shown in *Figure 7*. Incomplete polymerization of 0.14 mol% ABC compositions resulted in lower levels of crystallinity than observed for the more highly polymerized 0.27 mol% compositions. Crystallinity levels were unaffected by ABC concentrations in the range 0.27–0.41 mol% ABC. However, compositions of 0.54 mol% ABC displayed a drop in degree of crystallinity.

CONCLUSIONS

The relationship between the onset of polymerization and crystallization of nylon-6 formed from caprolactam has been determined. The nature of the exothermic peak displayed was dependent on the interval between polymerization temperature and melt crystallization temperature. A single exotherm composed of the heats of polymerization and crystallization was produced when the polymerization temperature determined from heating the reactive components at a constant rate was significantly less than the crystallization temperature evaluated by cooling nylon from the melt. The driving force for immediate crystallization following the polymerization was attributed to the large degree of supercooling. As the degree of supercooling was reduced and the polymerization temperature approached the melt crystallization temperature, polymerization and crystallization processes were observed separately. As the heating rate increased further, polymerization occurred at a higher temperature than its associated melt crystallization, which consequently led to observance of only the polymerization process.

Varying Na–Cap and ABC concentrations on the polymerization and crystallization process revealed that complete polymerization occurred for Na–Cap:ABC ratios of 2:1 or greater and for ABC concentrations of 0.27 mol% or more. However, high levels of either Na–Cap or ABC resulted in a decline in crystalline content.

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