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Polyamides from lactams via anionic ring-opening polymerization: 1. Chemistry and some recent findings*

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This paper summarizes a study of the anionic polymerization of caprolactam employing a bisimide (isophthaloyl-bis-caprolactam) as the initiator and caprolactam–magnesium bromide as the catalyst. Polymerization temperature had a direct effect on monomer conversion, polymer molecular weight, and level of crystallinity. At initial temperatures of 140°C and higher, equilibrium conversions (~94%) were reached, whereas at temperatures <140°C, the monomer conversions were considerably lower. A similar trend was observed for molecular weights. Percent crystallinity in the nylon was higher when the polymerization temperature is about 150°C. At higher temperatures, the crystallinity is less. In addition to actual polymerization temperature, the heat history had a profound influence on the level of crystallinity in the polymer. Expectedly, the rate of polymerization increased with polymerization temperature and initiator concentration. In experiments where the difunctional bisimide (isophthaloyl-bis-caprolactam), which has two acyllactam groups per molecule, was replaced on a molar basis by the monofunctional *N*-acetylcaprolactam, which has one acyllactam group per molecule, the polymerization rate was slower by about 50% because the concentration of the acyllactam group was reduced by half. The initiator concentration had a direct influence on the polymer molecular weight. Up to a concentration of about 3.5 mmol of bisimide initiator/mol of caprolactam, the molecular weight decreased with increasing concentration, and this was consistent with the known mechanism. At higher levels, however, the molecular weight increased with increasing bisimide concentrations, contrary to our expectations. A mechanism that explains this anomaly is proposed. With the monofunctional initiator, the molecular weight decreased with increasing concentration. Incorporation of other monomers in poly(caprolactam) have produced several copolymers with interest properties. Incorporation of about 30 wt% laurolactam resulted in a copolymer that had a crystalline melting point that was only slightly lower than that of nylon 6, but had considerably lowered moisture absorption. The moisture absorption of the copolymer was comparable to that of nylon 12.

(Keywords: anionic polymerization; crystallinity; caprolactam)

INTRODUCTION

This paper is the first of the three-part series on polyamides from lactams via anionic ring-opening polymerization[1,2]. Anionic ring opening polymerization of lactams to generate polyamides has been studied quite extensively by Sebenda[3-6], Wichterle and coworkers[7,8], and Sekiguchi[9,10] among others in academia, and by Gabbert and Hedrick[11] in industry. Caprolactam is by far the most studied lactam, and the nylon 6 prepared by this route compares favourably in properties with that prepared by conventional hydrolytic polymerization.

Most of the work reported in the literature employs sodium lactamate salts as catalysts and isocyanate/lactam adducts as initiators. Gabbert and Hedrick[11] preferred to work with acyllactam as the initiator and Grignard salts of caprolactam as the catalyst in view of the ease of handling and fewer side reactions compared to the sodium lactamate and isocyanate system. Anionic ring opening polymerization is primarily directed at producing reaction injection moulded parts. Fast reaction kinetics, clean polymerization reaction without any by-products and a crystalline end-product make this process a compelling choice for such application.

This paper summarizes the chemistry and some recent findings in the study of caprolactam polymerization employing isophthaloyl-bis-caprolactam as the initiator and caprolactam–magnesium-bromide as the catalyst. In particular, the effect of polymerization temperature on the crystallization behaviour of the polyamide generated and the role of a higher lactam such as

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laurolactam on the moisture absorption characteristics of the copolymers are discussed. Phenomenological polymerization kinetics and rheology are discussed in companion papers[1,2].

EXPERIMENTAL

Monomers

Caprolactam used for this study was either supplied by DSM or BASF. Several grades of caprolactam are available commercially, but anionic polymerization (AP) grade was used exclusively in this study. This choice was influenced by its low moisture level (<100 ppm). Laurolactam (azacyclotridecan-2-one), obtained from Aldrich Chemicals, was used after drying.

Grignard catalysts

A 1.0 M concentration of caprolactam–magnesium bromide in caprolactam, supplied by Grant Chemical, was used. It was stored in sealed polyethylene lined aluminium bags.

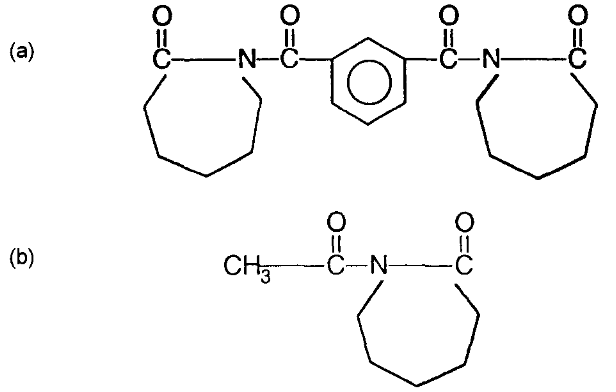

Figure 1 Structure of the initiator used in this study: (a) isophthaloyl-bis-caprolactam and (b) *N*-acetylcaprolactam

Initiators

The initiators used in this study were isophthaloyl-bis-caprolatam and *N*-acetylcaprolactam. The structure of isophthaloyl-bis-caprolatam and *N*-acetylcaprolactam are shown in *Figures 1a* and *1b*. In the structure of isophthaloyl-bis-caprolatam, the 5-member ring joining C and N represents $(CH_2)_5$. The sample of isophthaloyl-bis-caprolatam used in this study was synthesized in Monsanto, and it is about 99% pure (*Figure 2*, nuclear magnetic resonance (n.m.r.) spectrum). Isophthaloyl-bis-caprolatam's melt onset is 139.3°C (*Figure 3*, differential scanning calorimetry (d.s.c.) trace). *N*-Acetylcaprolactam was purchased from Aldrich Chemical Co., and was used as received, without any further purification.

Miscellaneous chemicals

Reagent grade methanol received from Fisher was used as received, without any further purification.

Drying procedures

Since anionic polymerization of caprolactam is very sensitive to moisture, all the materials were dried thoroughly before use. The catalyst, as pointed out earlier, was kept dry in a sealed, polyethylene lined, aluminum foil pouch. Caprolactam monomer was dried by distilling off about 5% by weight of caprolactam under vacuum at 140°C. The distillation removes moisture from caprolactam and leaves behind dry caprolactam. The monofunctional initiator was dried in the same manner as caprolactam. The difunctional initiator was dried overnight in a vacuum oven at 85°C under vacuum.

Storage

All materials were stored in sealed air tight packaging in a dry room with a relative humidity below 20%. Alternately, a dry box or vacuum desiccator was used.

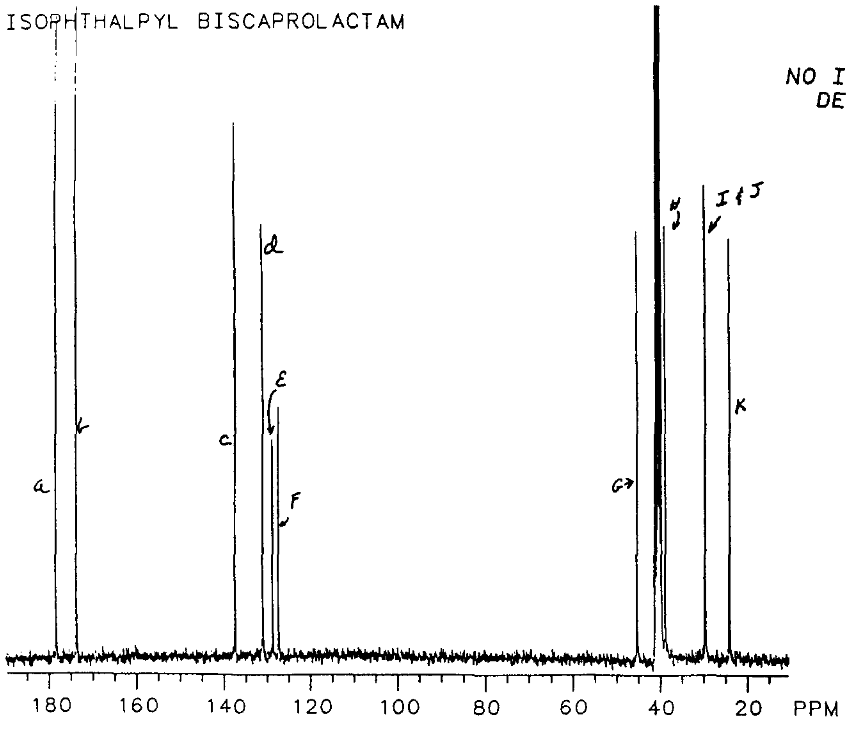

Figure 2 N.m.r. spectrum of isophthaloyl-bis-caprolactam

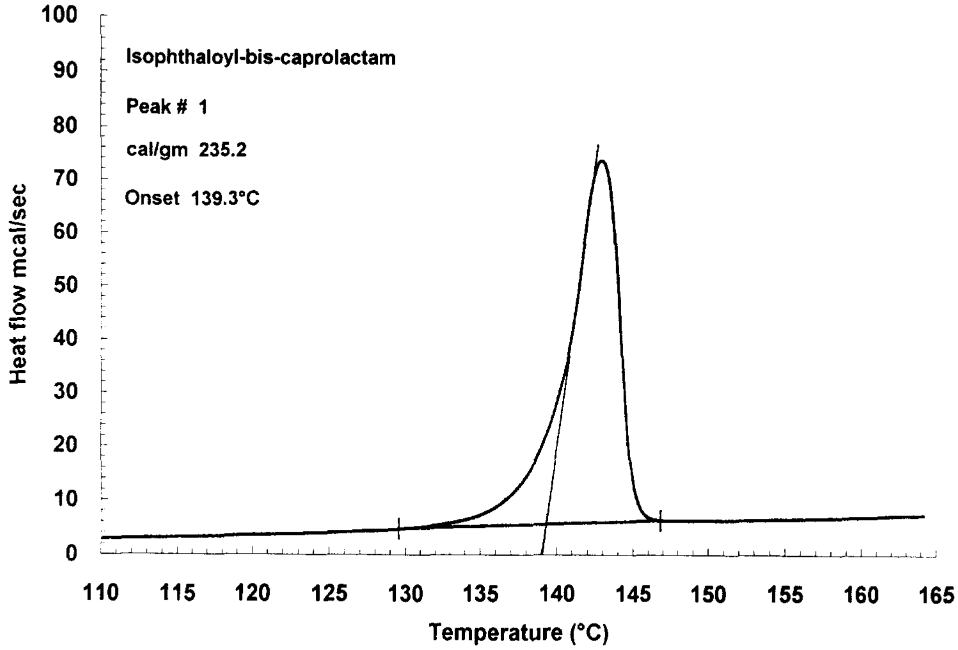

Figure 3 D.s.c. trace of isophthaloyl-bis-caprolactam

Polymerization press

Polymerization was conducted in a heated vertical press whose temperature was monitored by a thermocouple which interfaced with a temperature controller to maintain a set temperature of the polymerization press. Between the press were two metal plates, each having a 1/8 inch thick Teflon sheet bonded to one side. Between the Teflon surfaces of the two plates was placed a silicone rubber gasket, which functioned as the mould. The plates, with the mould sandwiched between them, were clamped between the heated press platens. When the mould attained the set temperature, the mixed reactants were quickly poured into the mould through a funnel and allowed to polymerize. The polymerization temperature and exotherm were monitored continuously.

Data acquisition

During polymerization, the time–temperature data were collected and stored on an IBM PC using software packages from Labtech and Strawberry Tree Inc. The temperature was monitored inside the polymerizing monomer via a 36 gauge J or K thermocouple.

Monomer conversion

Monomer conversion was measured by first grinding up the dry polymer in a Thomas Mill at room temperature and then carrying out a Soxhlet extraction of an accurately weighed (about 2–5 g) sample with hot methanol for 16–24 h. The thimble containing the extracted sample was removed when the extraction was complete, allowed to dry for 1 h in a hood, and then further dried in a vacuum oven at 90°C under full vacuum, overnight. The sample was removed from the oven and placed in a desiccator to cool. Once the sample had cooled to room temperature it was weighed and the percent conversion calculated.

$$\text{Percent monomer conversion} = \frac{\text{Polymer weight after extraction}}{\text{Polymer weight before extraction}} \times 100$$

Molecular weight

Molecular weights and molecular weight distributions were determined by size exclusion chromatography coupled with low angle laser light scattering (s.e.c./LALLS), employing hexafluoro-2-propanol (HFIP) as the solvent. The test conditions of s.e.c./LALLS were: column temperature was 46°C; column packing was PL-GEL linear; packing size was 10 μm; supplier of the packing was Polymer Laboratory; the LALLS detector temperature was 30°C.

A note on the units of concentration

In this paper, as well as in the companion papers, the basis of concentration is either per mol or per litre *of caprolactam*. Therefore, whether the term 'of caprolactam' is specifically mentioned or not after the concentration unit, it implies that the concentration is either per mol or per litre of caprolactam. In the kinetics and rheological studies[1,2], the units of concentration are $\mathrm{mol\,l^{-1}}$ or $\mathrm{mmol\,l^{-1}}$ of caprolactam because kinetic constants are based on unit volume. In the polymerization study (this paper), the units of concentration are $\mathrm{mol\,mol^{-1}}$ or $\mathrm{mmol\,mol^{-1}}$ of caprolactam.

RESULTS AND DISCUSSION

Chemistry of anionic ring-opening polymerization of caprolactam

Anionic ring-opening polymerization of caprolactam (as in other lactams) follows an activated monomer mechanism as against a conventional activated chain end mechanism. That is, the chain growth reaction proceeds by the interaction of an activated monomer (lactam anion) with the growing chain end (*N*-acylated chain end in this case). The anionic attack, in fact, constitutes the rate determining step in the propagation. The other characteristic of this mechanism is that activated monomer is regenerated after every unit growth reaction. A typical reaction path for the polymerization of caprolactam is shown in *Figure 4*.

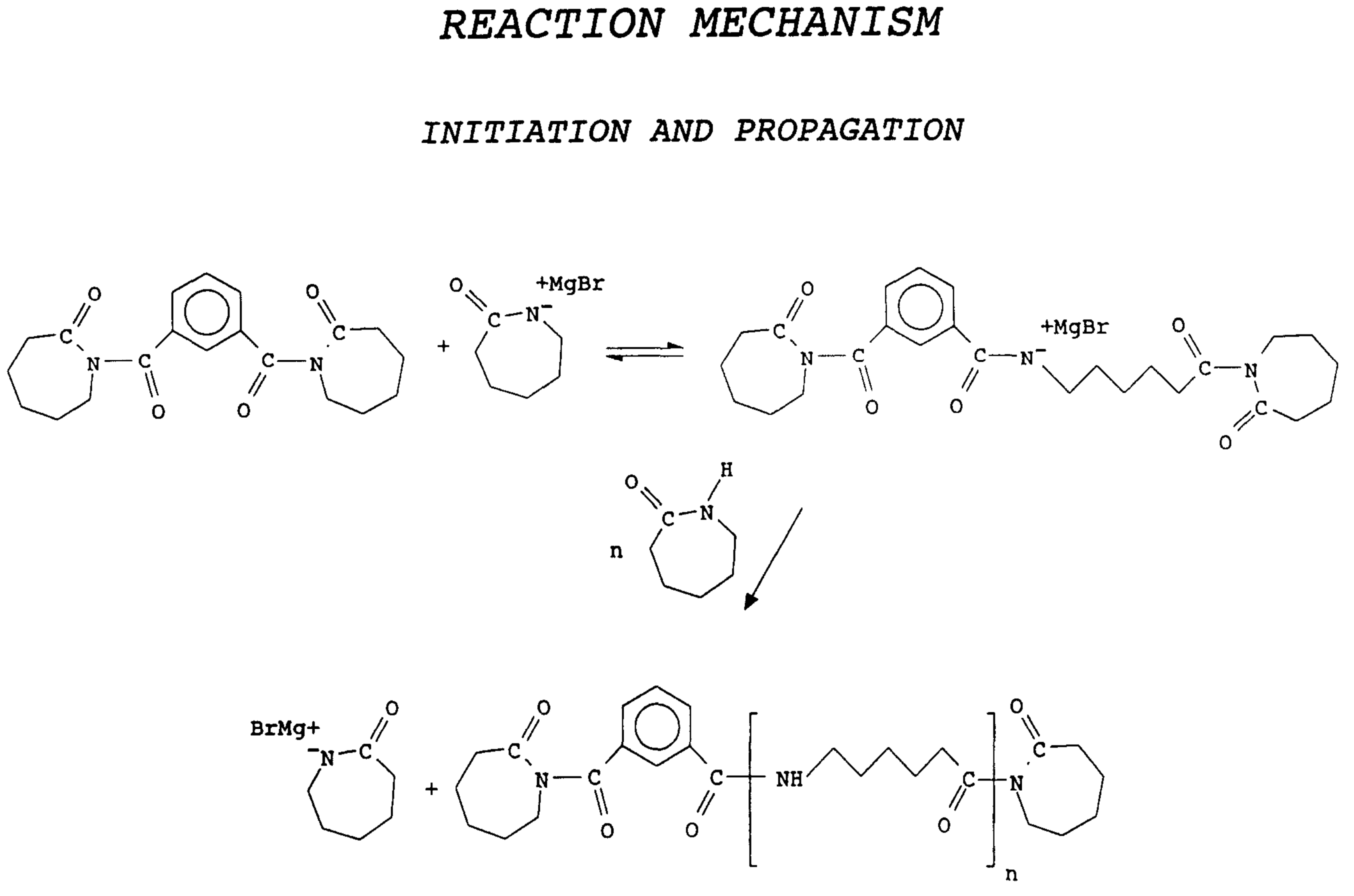

Figure 4 Mechanism of anionic polymerization of caprolactam

Nucleophilic attack of the amide anion can either be on the exocyclic or endocyclic carbonyl. The former only regenerates the lactamate anion, whereas the latter results in polymerization. Although the locus of nucleophilic attack has no major implications in a homopolymerization such as is discussed here, the same can exert considerable control over copolymerization mechanism, and consequently on the copolymer structure, as will be discussed later in this paper.

From the scheme in *Figure 4*, it is also apparent that the propagation of anionic polymerization requires two active species: the lactam anion and the *N*-acyllactam end group. Since the monomer is only consumed via its anion, it is imperative that a certain level of basicity is maintained in the polymerization mixture. The basicity is generally achieved by replacing the proton of the monomer by a less acidic cation such as MgBr$^+$. A large number of catalysts have been reported in the literature, such as alkali metals[11-14], alkali metal hydroxides[12,15-17], alcoholates[18], carbonates[19,20], Grignard reagents[21], alkylaluminiums[22], alkalialuminium hydrides[23] and their partial or total alkoxides[24-26] or their lactam salts[27], quaternary ammonium salts of lactams[28] or of other compounds[29-33], and guanidinium salts of lactams[34].

The anionic catalysts listed above react with lactam monomer to first form the salt which in turn will dissociate to the active species, namely, the lactam anion. Accordingly, a strongly dissociating catalyst in low concentrations is always preferable to weakly dissociating catalysts in higher concentrations. The catalytic activity of the various alkali metal and quaternary salts of a lactam generally follow the extent of their ionic dissociation, which in turn depends on the cation. Activity of a salt decreases with increasing size of the cation due to restricted mobility and decreased ionization potential.

Among the various catalyst systems described above, the alkali metal (sodium) lactamate is perhaps the most widely reported in the literature. The Grignard system (caprolactam–magnesium bromide), despite its many advantages such as ease in handling and a less acidic MgBr$^+$ cation, has received much less attention. Other catalyst systems may have equal or better reactivity than the Grignard systems, but they have not been examined at Monsanto to the same extent as the Grignard. Two of the catalyst systems that have received continued investigation outside Monsanto[35] are complexes derived from caprolactam–magnesium bromide and aluminium alkyls, and the quaternary salts of lactams often referred to as the onium salts. Results to date are quite inconclusive to claim that these systems have a definite advantage over the Grignard.

As initiators, the *N*-acyllactams have proved to be by far the most efficient among those investigated. Such end groups in a growing chain, containing an imide linkage, possess strong acylating power, especially when it involves an already strong nucleophile in a lactam anion. *N*-acyllactams are generally prepared by the reaction of a lactam with either an anhydride, acid chloride, or an isocyanate. By and large, most of the work reported in the literature is based on monofunctional initiators, although in principle multi-functional initiators can be employed. Initiators with functionality higher than two can be expected to produce branched polymers.

Table 1 Effect of initiator type and concentration on polymerization time, monomer conversion, and polymer molecular weight

Initiator[a]	Polymerization time (min)	Conversion (%)	Measured M_w^b, mol wt (kg mol^{-1})	Calculated M_n^b, mol wt (kg mol^{-1})
N-Acetylcaprolactam				
2.0	9.0	84.0	92.6	56.6
3.5	5.0	90.0	66.9	32.3
5.0	3.0	93.0	50.3	22.6
Isophthaloyl-bis-caprolactam				
2.0	5.0	84.0	82.0	56.6
3.5	2.5	90.0	106.0	32.3
5.0	1.5	93.0	124.0	22.6

[a] mmol mol^{-1} of caprolactam

[b] M_w = weight average molecular weight. Measured values of M_n, number average molecular weight, are not listed because of low end molecular weight limiting factor when using s.e.c./LALLS

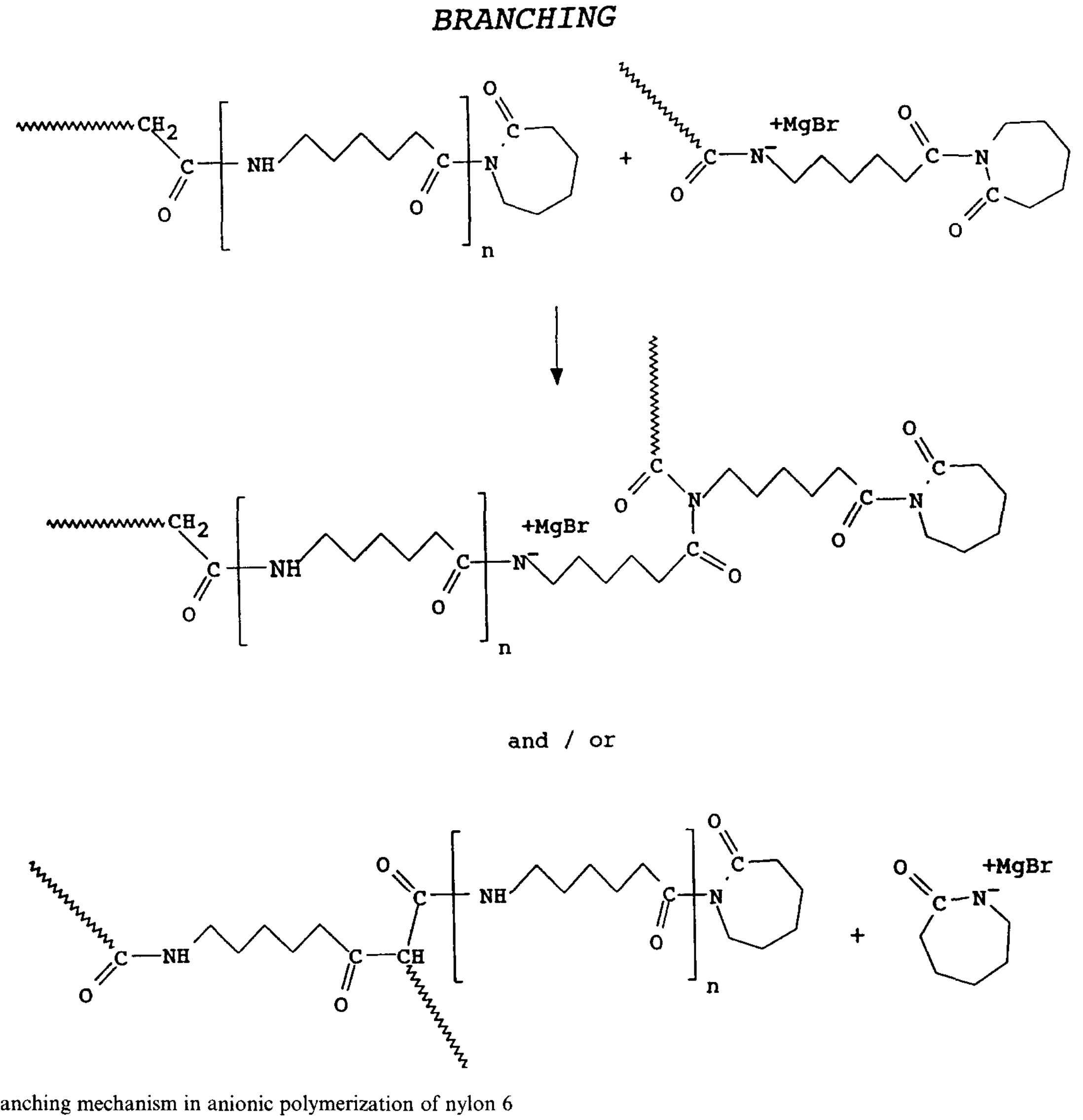

Figure 5 Branching mechanism in anionic polymerization of nylon 6

Effect of initiator type and level on polymerization time, monomer conversion, and polymer molecular weight

Table 1 summarizes the effect of initiator concentration on the polymerization time, monomer conversion, and molecular weight for adiabatic polymerization at 160°C. Both mono- and difunctional initiators, *N*-acetylcaprolactam and isophthaloyl-bis-caprolatam, were examined in this study. The concentration of the catalyst caprolactam-magnesium bromide was 4 mmol mol^{-1} in excess of the concentration of the acyllactam end group concentration.

As expected, the polymerization time for 'complete' conversion with the monofunctional initiator was nearly twice that with the difunctional initiator. While the functionality of the initiator did not seem to make a noticeable difference to the monomer conversion, the initiator level did. At 2.0 mmol mol^{-1} of caprolactam, the monomer conversion with initiator of either functionality

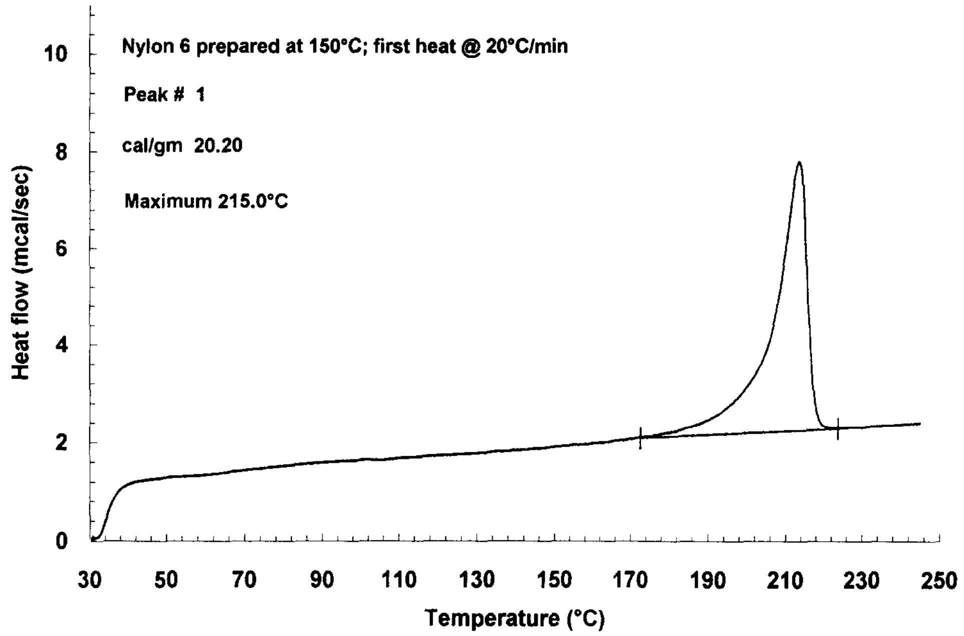

Figure 6 D.s.c. trace – during first heat – of nylon 6 anionically polymerized at 150°C

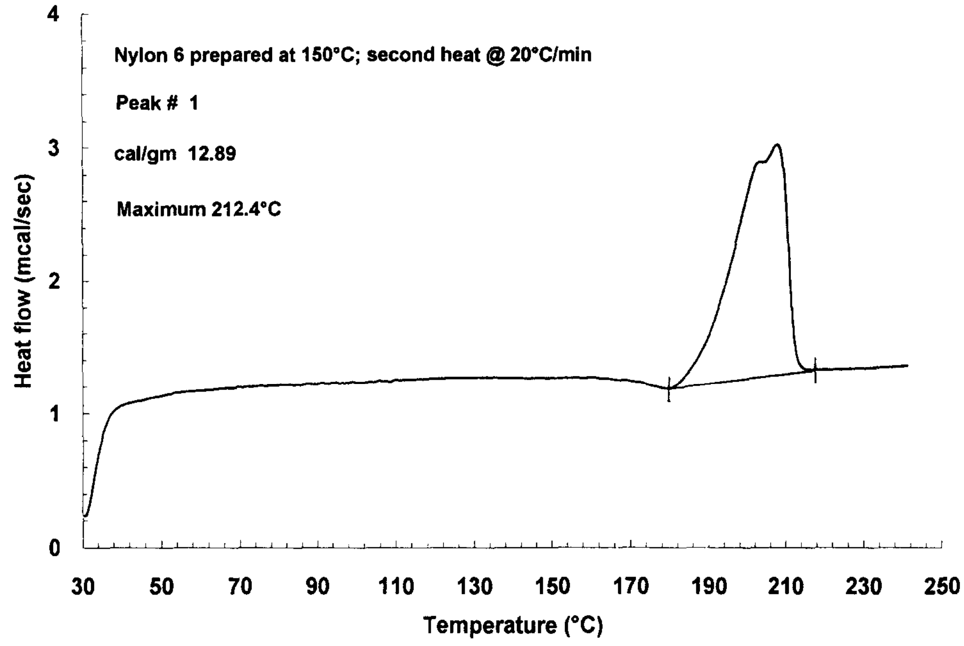

Figure 7 D.s.c. trace – during second heat – of nylon 6 anionically polymerized at 150°C

was low. The low conversion is believed to be due to very slow kinetics. In addition, it is conceivable that the polymer chains, as they get formed, could precipitate, crystallize, and 'bury' the active sites for chain growth. Consequently, the access to monomer units to regenerate the catalyst species is restricted. Similar observations were also made by Mottus *et al.*[36], who found that the polymer formed by initiated polymerization of caprolactam using *N*-acetylcaprolactam and sodium as the initiator and catalyst, respectively, precipitated from the monomer for polymerization temperatures up to 150°C. What is intriguing, however, is the increase in weight average molecular weight (M_w) with increasing initiator concentration in the case of the difunctional initiator. Anionic polymerization mechanism dictates that with increased initiator level, molecular weight should drop. Results with the monofunctional initiator are consistent with this rule and the deviation in the case of the difunctional initiator is likely a result of branching (*Figure 5*). Similar results have been reported by Mottus *et al.* and attributed to branching reactions which can lead to some very high molecular weight species. At high conversions, coupling and (or) condensation (Claisen type) reactions take place resulting in branching and high M_w. It is believed that at high levels of initiator, due to fast polymerization kinetics, the monomer concentration depletes rather rapidly and the active amide anions are likely to attack neighbouring polymer chains to cause branching when they cannot find monomer units to regenerate catalyst species.

Crystallinity

Most aliphatic nylons are semi-crystalline. The level of crystallinity in these polymers is largely determined by

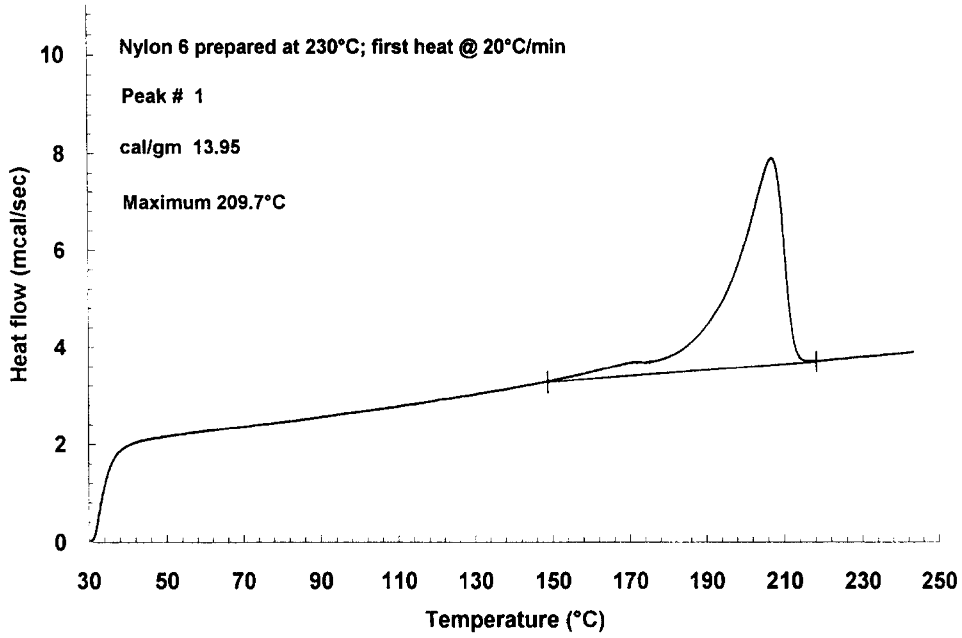

Figure 8 D.s.c. trace – during first heat – of nylon 6 anionically polymerized at 230°C

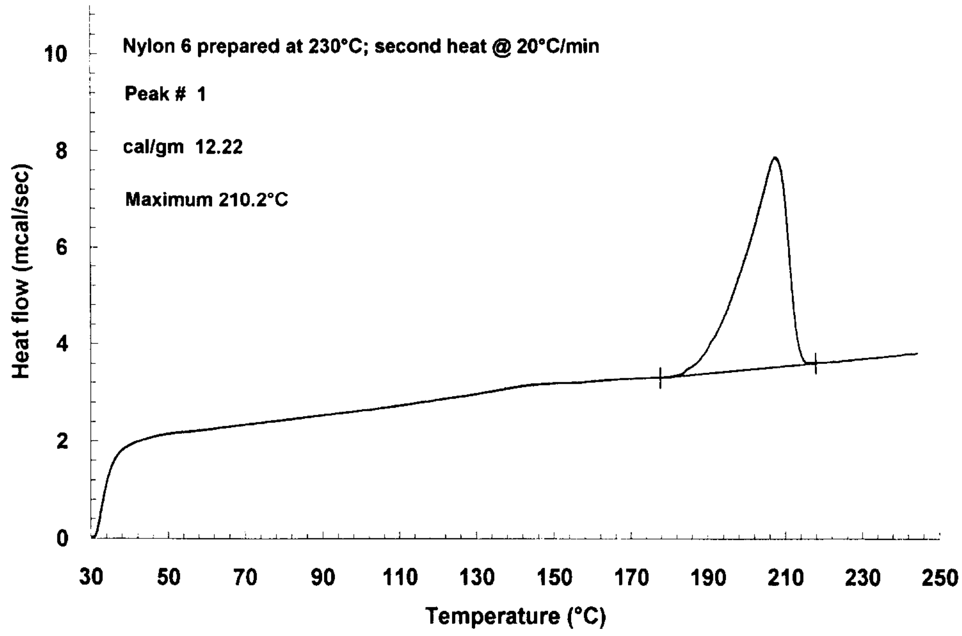

Figure 9 D.s.c. trace – during second heat – of nylon 6 anionically polymerized at 230°C

the heat history during solidification from melt. The crystalline content of these polymers, by and large, define the properties such as tensile elongation, tensile strength, and modulus. Expectedly, higher crystallinity leads to higher modulus and tensile strength and lower elongation. Typically, nylon 6 obtained through hydrolytic polymerization exhibits a glass transition temperature (T_g) of 50°C, a melting point of 210°C, a crystallinity of about 30–40%, a tensile modulus of about 3 GPa, a tensile strength of about 75 MPa, and an elongation to break of about 50–100%. However, with our anionically polymerized nylon 6 this was not always the case. The properties changed drastically as a function of polymerization temperature. Nylon 6 polymerized at 150°C exhibited a much lower elongation to break and a higher tensile strength and tensile modulus. When polymerized at 230°C, these mechanical properties were closer to those of the hydrolytic nylon 6 which is polymerized at 250–260°C. It was for this reason that crystallinity as a function of temperature was examined. Two polymerization temperatures, 150°C and 230°C, were examined for their effect on crystallinity. The lower temperature was below the melt temperature of nylon 6 and the latter, 230°C, above the melt temperature of about 210°C. Good polymerization rates, normal conversions and molecular weights were obtained at both these polymerization temperatures. Note, in context with this study, the phrase 'polymerized at 150°C' implies that the catalyst and initiator solutions and the polymerization press were preheated to 150°C prior to polymerization. After polymerization, the nylons were analysed by d.s.c. for crystallinity.

The d.s.c. traces for the two nylons are shown in *Figures 6*–*9*. In *Figure 6*, the first heat trace of the 150°C polymer exhibits crystallinity of 44.3% (considering the

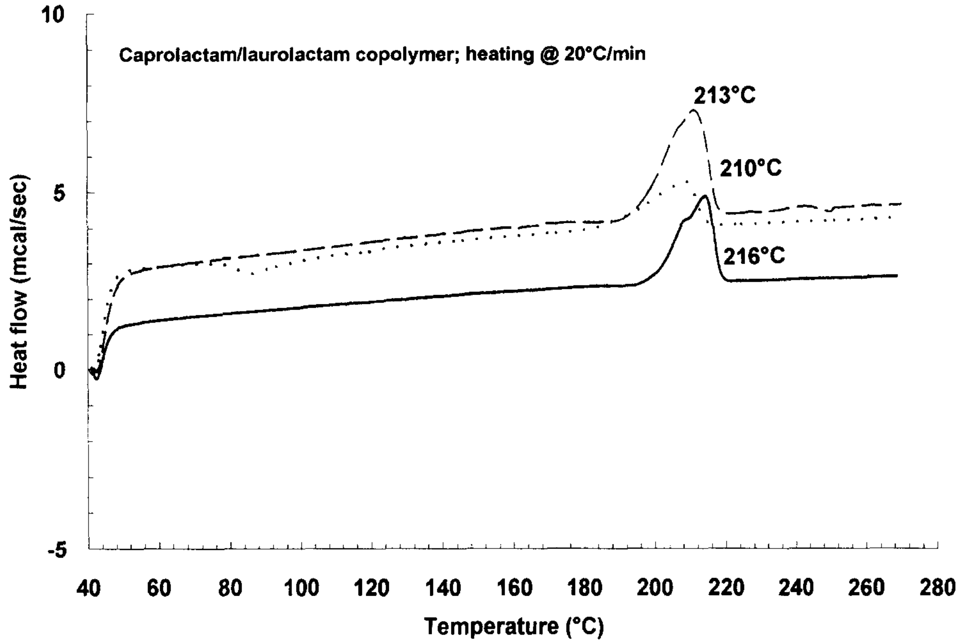

Figure 10 D.s.c. trace – during heating cycle – of caprolactam and laurolactam copolymers. Curves are for copolymers with 10% laurolactam (solid line), 30% laurolactam (dashed line), and 50% laurolactam (dotted line)

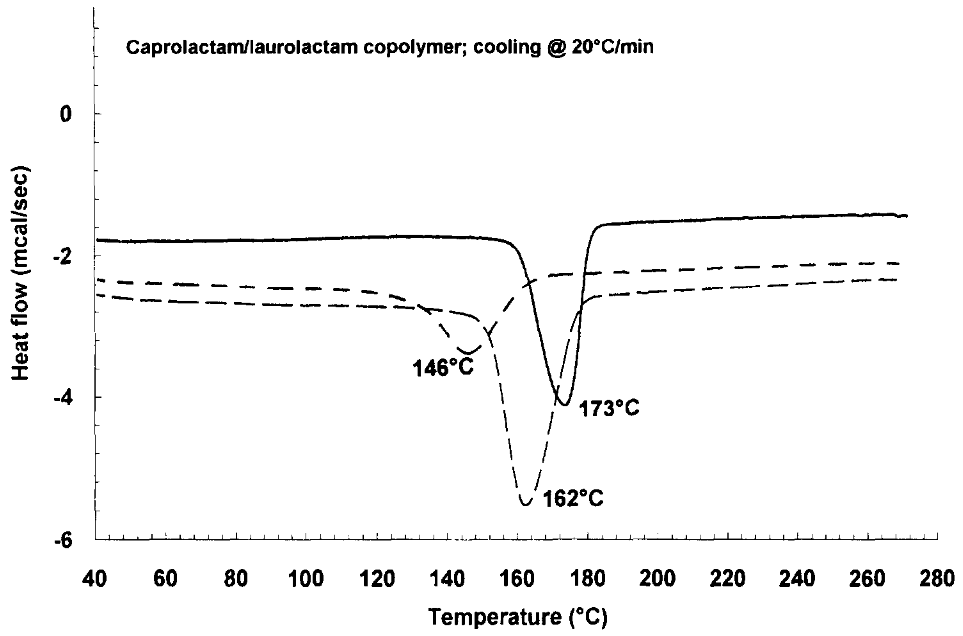

Figure 11 D.s.c. trace – during cooling cycle – of caprolactam and laurolactam copolymers. Curves are for copolymers with 10% laurolactam (solid line), 30% laurolactam (dashed line with long dashes), and 50% laurolactam (dashed line with small dashes)

heat of fusion of the crystalline region[37] to be 45.6 cal g^{-1}), which is higher than that of hydrolytic nylon 6. The second heat trace (*Figure 7*) of the same sample exhibits 28.3% crystallinity. The first and second heat traces for the 230°C polymer (*Figures 8* and *9*) were almost identical to one another, with 30.6% and 26.8% crystallinity, similar to a conventional, hydrolytic nylon 6. During polymerization at 150°C, the heat history is highly conducive to both crystallization and annealing, since the polymer is held at a temperature below the melt temperature of the crystallites and above the T_g of the amorphous phase of the formed nylon. This is believed to result in a high level of crystallinity in the polymer and therefore in high modulus and low elongation. During the second heat cycle, the polymer melt is subjected to a different heat history (cooling rate) and this results in a lower level of crystallinity. When the polymerization is carried out at 230°C, i.e. above the melt temperature of the crystallites, the extent of crystallization is determined by the rate at which the polymer cools and such a heat history does not permit any annealing. As a result, the anionic nylon made at 230°C exhibits a lower level of crystallinity and behaves more like the conventional nylon 6.

Another point worth mentioning is the presence of two peaks in the second heat trace of nylon polymerized at 150°C (*Figure 7*). On second heat, the new peak is observed at the normal melting point and lower than the original peak. One possibility is that nylon 6 formed by polymerization at 150°C (i.e. below the melting point of nylon 6) is a mixture of two crystalline

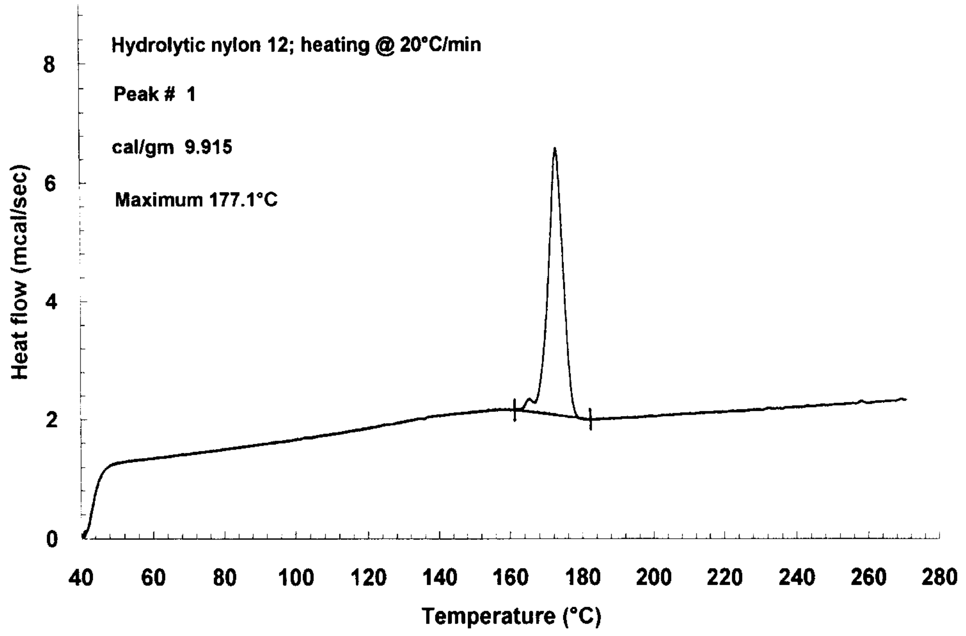

Figure 12 D.s.c. trace – during heating cycle – of commercial hydrolytic nylon 12

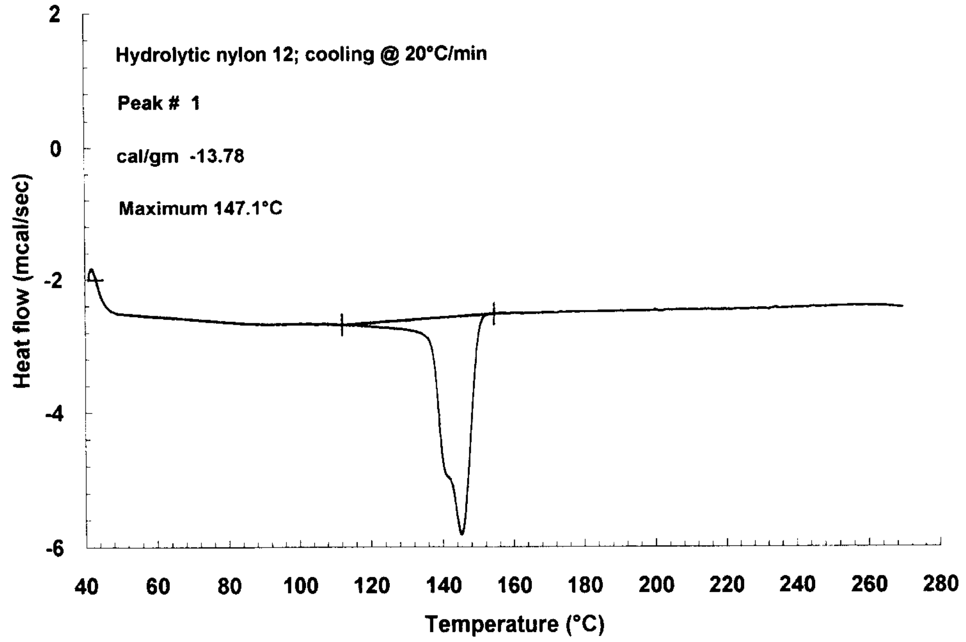

Figure 13 D.s.c. trace – during cooling cycle – of commercial hydrolytic nylon 12

structures: α and γ. The melting points of α and γ structures are about 256 and 228°C, respectively[38]. Puffr *et al.*[38] have stated that as many as five melting endotherms may occur in samples of nylon 6 with the mixed α and γ structure: the peaks of original and recrystallized γ structures; the peaks of original and recrystallized α structures (higher by several degrees); and also a small peak approximately 10°C above crystallization temperature (T_c), assigned to the most defective crystals formed by secondary crystallization. In *Figure 7*, the two peaks seen on the d.s.c. thermogram possibly arise from the original α and γ structures formed during polymerization because the sample was not exposed to thermal history for recrystallization.

Anionic copolymerization of caprolactam–laurolactam

It is well recognized that nylon 12, i.e. poly(laurolactam), has a low moisture uptake, excellent ductility, good electrical properties, and significant chemical resistance. However, due to the long methylene sequences between the amide linkages, it also has a lower melting point (172°C) compared to nylon 6 (210°C) or nylon 6,6 (268°C). Nylon 6 has an equilibrium moisture content of about 6%, which leads to undesirable dimensional changes and loss in modulus with changes in humidity. The purpose of copolymerizing laurolactam with caprolactam was to determine if laurolactam, preferably at low levels, would lower the moisture absorption without unduly lowering the melting point or the level of crystallinity.

Copolymerizations with feed compositions containing 0, 10, 30, and 50 wt% laurolactam were carried out using isophthaloyl-bis-caprolatam as the initiator (at 5.0 mmol mol^{-1} of monomer mixture) and caprolactam–

Table 2 Equilibrium moisture content of nylon 6, nylon 12, and copolymers of caprolactam and laurolactam

Copolymer composition CL/LL[a]	Equilibrium moisture content (%)
100/0	6.4
90/10	6.0
70/30	2.4
50/50	2.1
0/100	1.7

[a] CL = caprolactam, LL = laurolactam, composition by weight

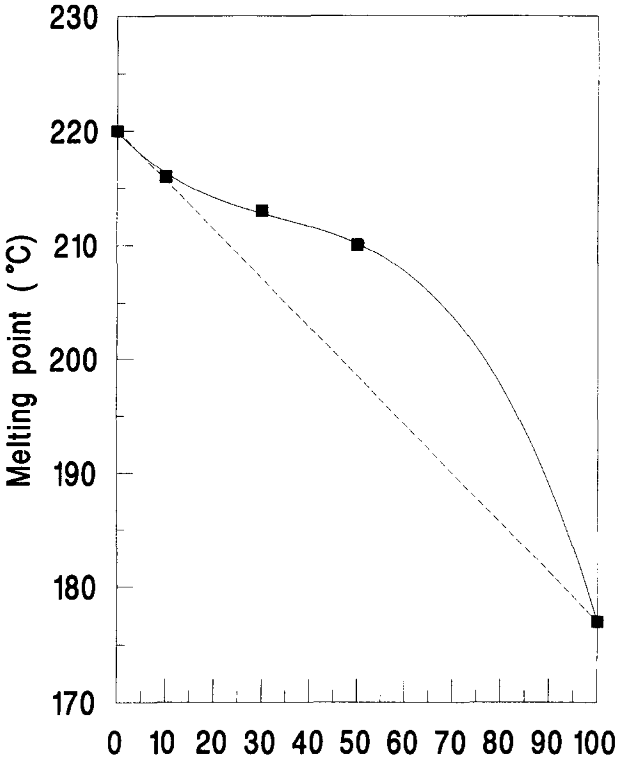

Figure 14 Melting points of caprolactam and laurolactam copolymers. Curves are for experimental data (solid line) and linear fit (dashed line)

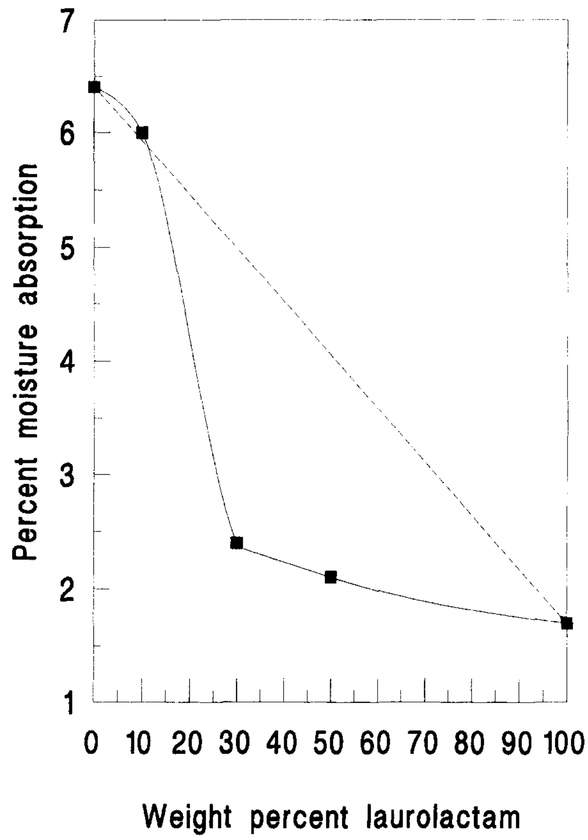

Figure 15 Moisture absorption in caprolactam and laurolactam copolymers. Curves are for experimental data (solid line) and linear fit (dashed line)

magnesium bromide as the catalyst (at 12.0 mmol mol^{-1} of monomer mixture). The polymerization temperature was 160°C instead of 150°C, as in the homopolymerization of caprolactam described earlier, to facilitate polymerization. Copolymerizations were carried out for about 3 min and monomer conversions in the 88–92% range were achieved. As the laurolactam level in the feed was increased, the polymerization exotherm decreased. This is consistent with the very low heats of polymerization of laurolactam, 2.9 kJ mol^{-1} vs 13.8 kJ mol^{-1} for caprolactam reported in the literature[10]. The copolymer crystallinity reduced with increasing laurolactam levels. The copolymer crystallinity was measured by d.s.c. on three samples (10%, 30%, 50% laurolactam). The d.s.c. traces are shown in *Figures 10* and *11*.

D.s.c. traces of nylon 12 are shown in *Figures 12* and *13*. It is apparent from the traces that the melting endotherm for the copolymers decrease in intensity with increasing levels of laurolactam. At about 50 wt% laurolactam in the feed, the copolymer exhibits very low levels of crystallinity. However, the crystalline melting point for the copolymers that exhibited measurable levels of crystallinity was only slightly reduced from that of nylon 6.

Table 2 summarizes the moisture absorption characteristics of nylon 6, nylon 12, and some copolymers. The equilibrium moisture level in the copolymer decreases with increasing laurolactam levels. It is apparent from *Table 2* and *Figures 14* and *15* that at about 30 wt%, i.e. 20 mol%, laurolactam in the copolymer, the melting point is lowered by only 7°compared to nylon 6. On the other hand, the equilibrium moisture content is lowered to about 2.4% – closer to that of nylon 12 which has an equilibrium moisture content of 1.7%. The d.s.c. thermograms also indicate that up to about 20 mol% incorporation of laurolactam, the copolymer crystallizes well. At higher levels (>40 mol%), however, we observe adverse effects on crystallization.

A copolymer containing 20 mol% laurolactam crystallizes well since the nylon 6 sequences are high enough in number and length as not to jeopardize the hydrogen bonding. What is, however, surprising is the remarkably lower moisture absorption of the copolymer with incorporation of only 20 mol% of laurolactam. This unusual result warrants an explanation.

The rate of monomer incorporation in copolymer, and therefore the copolymer structure is mainly determined by the rate of reaction between the lactam anion and the acyllactam. In the case of caprolactam–laurolactam copolymerization, the two monomers give rise to eight effective reactions depending upon whether the nucleophilic attack is on the endo- or exo-cyclic carbonyl, as shown in the scheme in *Figure 16*. Relative acidities of the lactams determine the basicities of the counter anions and, therefore, their nucleophilicity. Thus the more

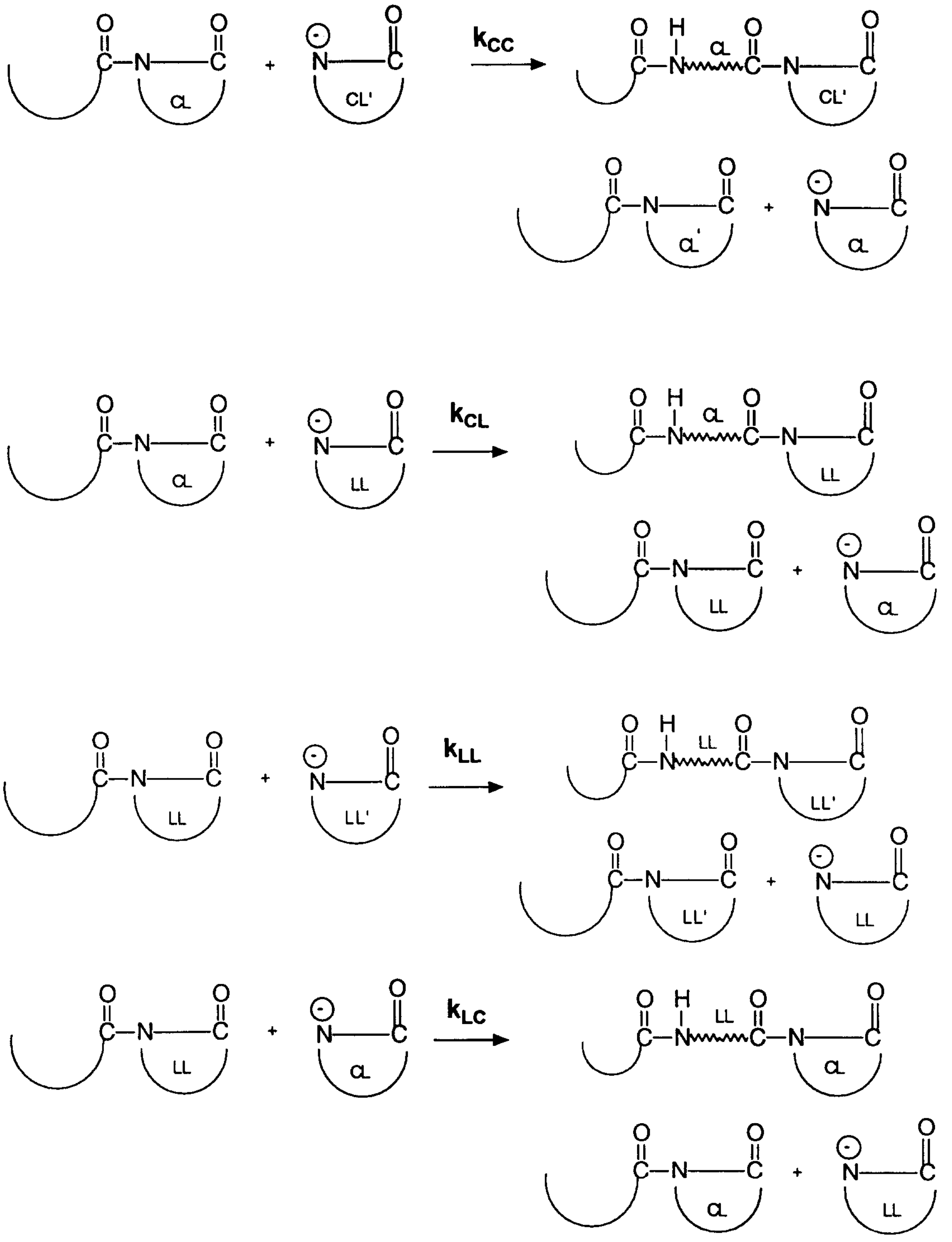

Figure 16 Mechanism of the possible reactions during the copolymerization of caprolactam and laurolactam

acidic the lactam, the higher will be its anion's nucleophilicity and reactivity in copolymerization. If such reactivities are markedly different, one would expect a certain degree of blockiness in a copolymer. Alternatively, if the reactivities are close to each other, the copolymer would tend to be more random. Furthermore, the dielectric constant of the polymerization medium, as determined by the polarity of monomers, will control the copolymerization kinetics.

Data in the literature[39–41] indicates that the basicities of the lactamate anions from caprolactam and laurolactam are not too dissimilar, despite the fact that one has seven more methylene linkages than the other. The dipole moments and the hydrogen bonding energies for the two monomers are also relatively close. Based on these considerations, it is expected that these copolymers would be more random than blocky. Frunze and coworkers[42,43] prepared a series of caprolactam–laurolactam copolymers employing acetyl caprolactam as the initiator and sodium caprolactamate as the catalyst. Although their catalyst is different from ours, their results are, indeed, interesting and relevant. They characterized their copolymers by infra-red (i.r.) and n.m.r. spectroscopy. From the copolymer compositions at low conversions, they determined the reactivity ratios: $r_{\mathrm{cap}} = 2.26$ and $r_{\mathrm{lauro}} = 0.27$, where $r_{\mathrm{cap}} = k_{\mathrm{CC}}/k_{\mathrm{CL}}$, $r_{\mathrm{lauro}} = k_{\mathrm{LL}}/k_{\mathrm{LC}}$, and ks are the rate constants shown in *Figure 16*. It is important to note, however, that the copolymer equations proposed by Frunze and coworkers may not be applicable for equilibrium polymerizations that were carried out in our study because the copolymer equations are applicable at low conversions, not equilibrium polymerizations. Based on their results, Frunze and coworkers concluded that the copolymers tended to be more random than alternating or blocky ($0 < r_{\text{cap}} \times r_{\text{lauro}} = 0.61 < 1.0$). (The blockiness could be due to the fact that it is easier to reform a 7-member ring than a 13-member ring.) In the composition range of interest to us (20 mol% laurolactam), the random copolymer has caprolactam units with pentadic and higher sequences, whereas, the laurolactam units are essentially randomly distributed in the copolymer. The long caprolactam sequences can crystallize and force the laurolactam containing random sequences into the amorphous phase. The above explanation is consistent with our observed results. The copolymer has a melting point close to that of nylon 6, and the moisture absorption, which is a characteristic property of the amorphous phase, is reduced because of the enrichment of the amorphous phase by the laurolactam units. Poly(laurolactam) absorbs less moisture than poly(caprolactam) because on a molar basis poly(laurolactam) contains half as many amide groups, which are prone to water absorption, as poly(caprolactam).

CONCLUSION

Anionic ring opening polymerization caprolactam at temperatures below 130°C result in low conversion of caprolactam into nylon 6. Also, polymerization at temperatures below 130°C forms low molecular weight nylon 6. Polymerization conducted at or above 130°C produce conversion of about 94%. Polymerization at temperatures above the melt temperature (220°C) produces nylon 6 with lower crystallinity than that made at 150°C.

Increasing the initiator or catalyst concentration within the limits studied causes an increase in the polymerization rate. At 2.0 mmol mol^{-1} of caprolactam or lower, the polymerization is extremely slow and results in low monomer conversions. Increasing the monofunctional initiator concentration lowers the molecular weight. A difunctional initiator behaves similarly, but at concentrations above 3.5 mmol mol^{-1} of caprolactam an increase in molecular weight is observed.

Copolymerization of caprolactam with about 30 wt% laurolactam results in a copolymer that has a melting point close to that of nylon 6 and has a lower moisture absorption approaching that of nylon 12.

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