# Characterization of Polyamide 6 Made by Reactive Extrusion. I. Synthesis and Characterization of Properties

P. R. HORNSBY,* J. F. TUNG, and K. TARVERDI

Department of Materials Technology, Brunel University, United Kingdom

## SYNOPSIS

The anionic polymerisation of $\epsilon$-caprolactam in a corotating, intermeshing twin-screw extruder is discussed in terms of the materials formulation, extruder screw profile, and processing parameters such as temperature and screw speed. Using a variety of analytical characterization techniques, it is demonstrated that molecular mass, residual monomer content, and mechanical properties of the polyamide 6 are very sensitive to the reactive processing conditions employed. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Polyamide 6 (PA6) can be prepared by activated anionic polymerization of $\epsilon$-caprolactam in the presence of alkaline catalysts, such as alkali carbonates, hydrides, or organometallic compounds.[1] Continuous anionic polymerization of $\epsilon$-caprolactam may be undertaken in a twin-screw extruder through appropriate control of the process parameters, in particular, the screw geometry and other necessary functional characteristics of the machinery such as the nature of feeding, melting, mixing, reaction, and devolatilization zones.[2] Procedures have been reported for combined polymerization of $\epsilon$-caprolactam in a twin-screw extruder together with die forming of the resulting PA6 into a semifinished product with claimed economic and technical benefits.[3] However, very limited attention has been given to the effect of polymerization processing conditions on the molecular mass and residual monomer content, both of which are likely to influence its physical properties.

This article addresses these issues through detailed analysis of PA6, made using different processing conditions on a corotating, intermeshing twin-screw extruder. A subsequent article will consider structural characteristics induced.

## EXPERIMENTAL

### Materials and Preparation of PA6

High polymer was prepared by anionic polymerization of $\epsilon$-caprolactam using 3% by weight of sodium caprolactamate catalyst and 2% by weight of bisacyllactam hexamethylene diamine activator, designated V5. All materials were supplied by DSM Chemicals. Preliminary work using various catalyst/activator ratios demonstrated that this system permitted acceptable reaction rates and high degrees of monomer conversion.

Polymerization was undertaken in a 40-mm screw diameter, corotating, intermeshing twin-screw extruder (BTS 40, Betol Machinery Ltd., UK). This was assembled in a 21/1 L/D ratio with screws configured to permit specified functions of feedstock conveying, melting, mixing, devolatilization, and melt delivery to the die (Fig. 1). A reaction zone was also defined using segmented disc and trilobal kneading elements to provide a melt seal at the entrance and exit portions of this zone, in addition to contributing to compositional homogeneity. Screw sections in this design were trapezoidal, which result in positive material conveyance together with effective cross and interchannel mixing.[4,5]

During the early stages of the work, several different screw assemblies were evaluated and the configuration shown in Figure 2 found to give optimum operating performance. In the devolatilization zone, a reduced pressure of 50 mmHg was applied to fa-
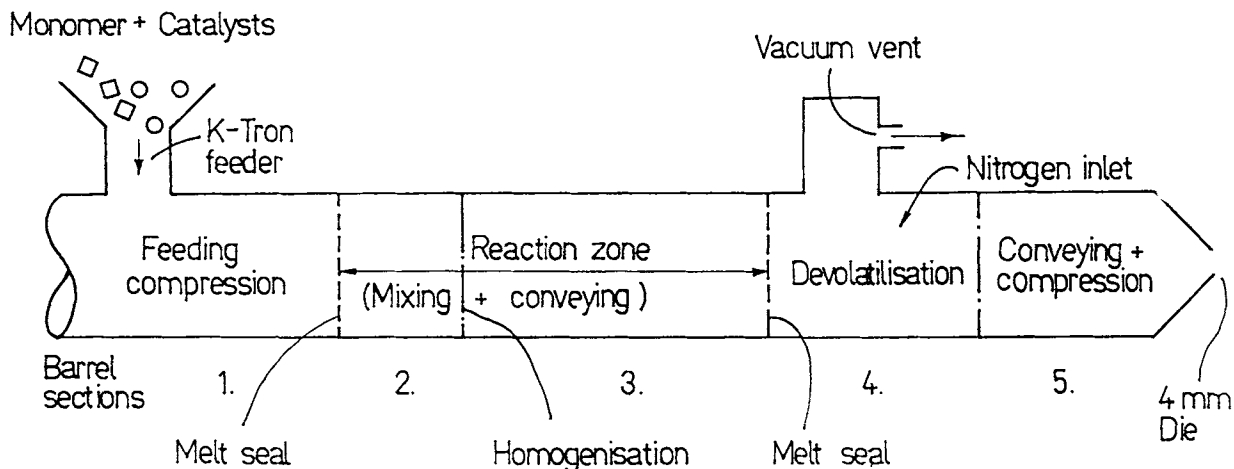
**Figure 1**    Schematic representation of twin-screw extruder functional zones.

cilitate volatile extraction and the removal of un-reacted monomer.

A preblend of the monomer/catalyst/activator feedstock was delivered at a constant rate to the extruder using a K-Tron twin-screw volumetric feeder. After the polymerization stage, the PA6 was die-formed into a 4-mm diameter rod and quenched in water at 23°C. In some experiments, samples for later structural analysis were prepared by allowing extrudate to cool slowly in air to room temperature.

Temperature profiles along the length of the extruder barrel were set according to the functional requirements of the particular zones. Hence, to effect melting of the caprolactam monomer and subsequent polymerization to PA6, the thermal conditions must accommodate the changing rheology of the material. Based on results obtained from model experiments undertaken to determine the effects on viscosity of temperature and reaction time[6] together with observation of the condition of the extrudate, the barrel temperature profile shown in Figure 2 was selected and used for all reactive extrusion proce-

dures, at extruder screw speeds ranging from 50 to 150 rpm. Approximate material throughput rates of $4 \text{ kg h}^{-1}$ were obtained at a screw speed of 150 rpm.

## Determination of Molecular Weight

The limiting viscosity number (intrinsic viscosity) of PA6 in 90% formic acid solution was determined according to the procedure recommended in ISO 307 : 1984. With this technique, however, meaningful results were only obtained using polymer solution concentrations of less than $0.001 \text{ g mL}^{-1}$. Concentrations above this value, although within the guidelines of the standard, were found to give an unexpected trend of decreasing viscosity with increasing solution concentration.[7] Selected samples were also analyzed by gel permeation chromatography (GPC) using 1,2 cresol solvent at 120°C.

## Residual Monomer Content

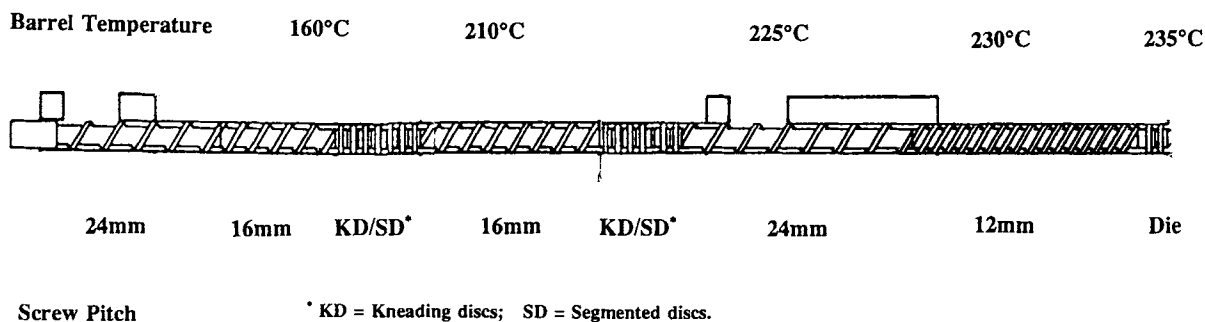Other than using a negative pressure in the devolatilization zone, no attempt was made to minimize



**Figure 2**    Extruder screw profile (only one screw shown) and barrel temperatures.

residual monomer level, for example by using multistage venting or through the addition of a volatile carrier liquid, as has been reported by other workers.[8]

Monomer remaining in the extrudate was measured by gas chromatography based on determinations of monomer concentration in distilled water. First, a calibration curve of eluant peak area as a function of monomer content was constructed from known aqueous caprolactam solutions containing 1–12% by weight of monomer. Caprolactam was first removed from the PA6 extrudate by boiling in distilled water for 24 h using Soxhlet extraction apparatus. The resulting solution was then analyzed in the gas chromatograph and the elution data compared against the calibration curve to determine monomer concentration.[7]

## Measurement of Mechanical Properties

Mechanical property data was obtained at 23°C using pelletized PA6 extrudate made under various extrusion conditions. Residual monomer was extracted from these samples by immersion in boiling water for 24 h followed by drying in vacuo for 48 h at 90°C prior to injection molding of test specimens suitable for evaluation of tensile, flexural, and notched Izod impact properties as stated in ISO 1874-2.

Tensile test results were obtained following ASTM D638 at a strain rate of 50 mm min$^{-1}$, and specimen elongation measured using an infrared noncontacting extensometer. Flexural modulus was determined according to ASTM D790 Method 1 and Izod impact strength using ASTM D256 with a Type A notch.

## RESULTS AND DISCUSSION

It is well known that the polymerization of $\epsilon$-caprolactam in the presence of alkaline catalysts such as sodium caprolactamate can yield high molecular weight polymer in a few minutes, whereas preparation by hydrolytic polymerization may require a reaction period of several hours.[9]

After a short induction time, the anionic polymerization proceeds rapidly at a reaction temperature of about 200°C and is therefore ideally suited to continuous processing in an extruder, where the residence times may be of the order of minutes, and thermal homogeneity of the reactants can be closely controlled.

The reaction mechanism is well understood[10] commencing with the ionic catalyst (sodium caprolactamate) associating with the caprolactam as indicated in reaction I of Figure 3. The sodium salt formed, in turn, reacts with any free caprolactam to generate acyllactam product (reaction II). This growth center will further react very rapidly with caprolactam to yield high molecular weight PA6.

In the absence of impurities such as air or oxygen, there is no termination reaction. Polymerization stops when the monomer level is reduced to an equilibrium amount, which is a function of temperature. However, impurities do influence the final conversion thereby affecting the concentration of residual monomer in the final polymer.[11,12]

In order to facilitate the formation of acyllactam growth centers and reduce the necessary temperature to effect polymerization, an acyllactam-based activator such as bis-acyllactam hexamethylene diamine is also required.[10]

The relative amounts of caprolactam, catalyst, and activator also have a critical bearing on the reaction kinetics and degree of polymerization.[13] In this study, relative weight percentages of 95 : 3 : 2 of these components was found to yield high molecular product using the reported operating conditions. However, under similar process conditions, preliminary trials using relative compositions of 95 : 4 : 1% and 95 : 2.5 : 2.5%, for example, were less successful because only soft extrudate was produced, indicative of a low degree of conversion from monomer to high polymer.

Other factors considered important for the preparation of high molecular weight product include the need to minimize the presence of moisture that could deactivate sodium caprolactamate catalyst. There is also a requirement for effective material blending, particularly within the extruder reaction zone, to ensure thermal and compositional uniformity, together with use of an optimized temperature profile. In the context of the present study, feedstock preblend temperature was raised as rapidly as possible to 160°C, while maintaining regular flow into the extruder feed port, in order to maximize monomer conversion to polymer. Higher temperatures (> 210°C) were required to enhance volatile diffusion rates in the melt devolatilization zone and to permit conveyance and discharge of the viscous PA6 melt. Average material residence time in the extruder was observed to be between 90 and 82 s at the two extremes of extruder screw speeds used, 50 and 150 rpm.

Molecular mass of PA6 produced by reactive extrusion is listed as a function of extruder screw speed
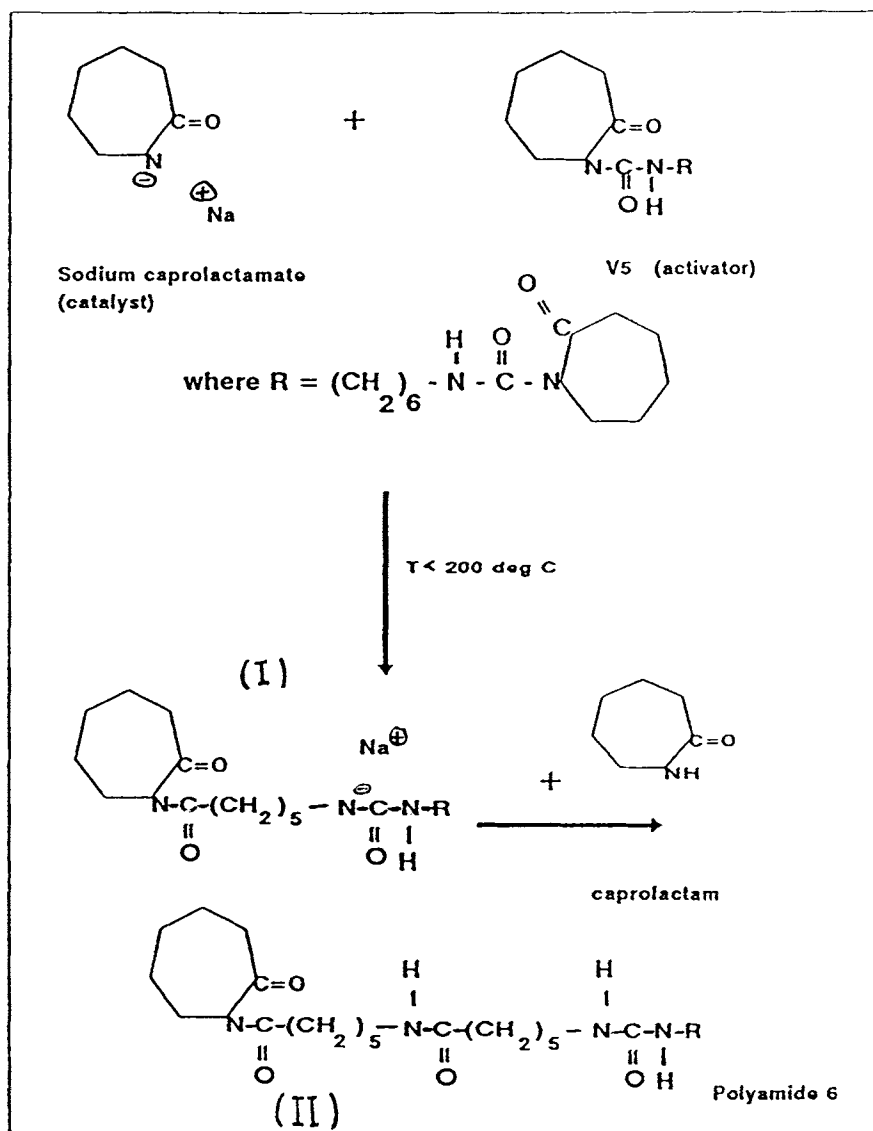
**Figure 3** Reaction mechanism for activated anionic polymerization of ε-caprolactam.

in Tables I and II. Data are expressed in terms of weight ($\bar{M}_w$) and number average ($\bar{M}_n$) molecular mass determined by GPC, together with the derived polydispersity index $\bar{M}_w/\bar{M}_n$, and values for limiting viscosity number, with corresponding molecular mass derived from intrinsic viscometry measurements. Results obtained from these two techniques show good agreement. Also included are data for CAPRON 8202C (Allied Chemical Corp.), a commercial injection grade of PA6 made by hydrolytic polymerization.

It is significant that, whereas commercial grades of PA6 for injection molding made by hydrolytic polymerization are supplied with molecular masses between 20–30 kg mol$^{-1}$, PA6 synthesized by anionic

polymerization in the twin-screw extruder has much greater values. However, molecular mass is greatly influenced by extrusion conditions, being smallest at the lowest and highest screw speeds employed. These observations may be largely accounted for by the influence of shear rate and/or material residence time on PA6 degradation. Hence, at the highest screw speeds (120 and 150 rpm) extensive shear degradation is likely to occur, which would most strongly influence the higher molecular mass chains (and hence $\bar{M}_w$), leading to a narrowing of the molecular mass distribution and fall in polydispersity index. At lower screw speeds, the longer material residence times may also result in greater thermal degradation, perhaps exentuated by the presence of

**Table I  Limiting Viscosity Number and Viscosity Average Molecular Weight of PA6 Variants**

| Screw Speed[a] (rpm) | GPC | | Viscometry | |
|---|---|---|---|---|
| | Limiting Viscosity Number (mL g$^{-1}$) | $\bar{M}_v$ (kg mol$^{-1}$) | Limiting Viscosity Number (mL g$^{-1}$) | $\bar{M}_v$ (kg mol$^{-1}$) |
| 50 | 221 | 53.7 | 215 | 49.6 |
| 70 | 412 | 110.3 | 443 | 122.3 |
| 90 | 562 | 140.5 | 540 | 156.7 |
| 120 | 201 | 55.8 | 232 | 54.5 |
| 150 | 235 | 60.5 | 241 | 57.2 |
| Capron 8202C[b] | 100 | 25.1 | 110 | 21.4 |

Values determined by solution viscometry and GPC.

[a] Conditions used during reactive extrusion process.

[b] Commercial grade PA6 made by hydrolytic polymerization process.

oxygen. It is also possible that under these conditions, mixing of the reactants is less effective due to the lower shear rates encountered, again leading to products with lower molecular mass.

The trends seen with the molecular mass results correlate well with observed levels of residual monomer found in the PA6 extrudate. A calibration curve was first obtained from a series of aqueous caprolactam solutions of known concentrations, and relates output peak areas from the gas chromatogram with monomer content. Using this approach residual caprolactam extracted from PA6 samples was determined (Fig. 4). Substantially lower residual monomer levels were detected in the sample with highest molecular mass (90 rpm). The commercial grade PA6 prepared by the hydrolytic polymerization process followed by water extraction and drying has a monomer content of < 1%.

Comparing the mechanical properties of these materials, it is evident that highest tensile strength

**Table II  Molecular Weight and Molecular Weight Distribution of PA6 Variants**

| Screw Speed[a] (rpm) | $\bar{M}_w$ (kg mol$^{-1}$) | $\bar{M}_n$ (kg mol$^{-1}$) | $\bar{M}_w/\bar{M}_n$ |
|---|---|---|---|
| 50 | 53.7 | 16.7 | 3.2 |
| 70 | 110.3 | 18.5 | 5.9 |
| 90 | 140.5 | 19.0 | 7.4 |
| 120 | 55.8 | 16.6 | 3.4 |
| 150 | 60.5 | 17.4 | 3.5 |
| Capron 8202C[b] | 25.1 | 14.0 | 1.8 |

Values determined by solution viscometry and GPC.

[a] Conditions used during reactive extrusion process.

[b] Commercial grade PA6 made by hydrolytic polymerization process.

and flexural modulus occur in polymer with the highest molecular mass (Table III), although these measured values were 15–20% lower than the commercial material made by hydrolytic polymerization with much lower molecular weight. Interestingly, the reverse trend is seen with both the elongation at break and Izod impact properties, PA6 made by reactive extrusion yielding markedly higher values than the commercial variant.

Considering an explanation for these effects, the influence of residual monomer on the properties of these materials can be discounted because with the anionically polymerized forms, this was extracted prior to testing. Some differences in equilibrium moisture content were detected between these materials after 7 days at 50% relative humidity (23°C), however these were not significant.

It therefore seems probable that differences in mechanical behavior reported in this study arise from variations in molecular weight and/or crystalline morphology. The last mentioned aspect will be discussed more fully in a subsequent article. It is sufficient to report here that about 7% less crystallinity was detected in the PA6 materials made by extrusion compared to the commercial product, which additionally is known to be nucleated leading to a predominantly $\alpha$ crystalline morphology.[13] This would be expected to yield stronger and stiffer polymer.[14]

## CONCLUSIONS

PA6 materials prepared by reactive polymerisation of $\epsilon$-caprolactam, using various extruder screw speeds, yield different $M_W$, $M_{WD}$, and residual monomer contents. The molecular weights obtained
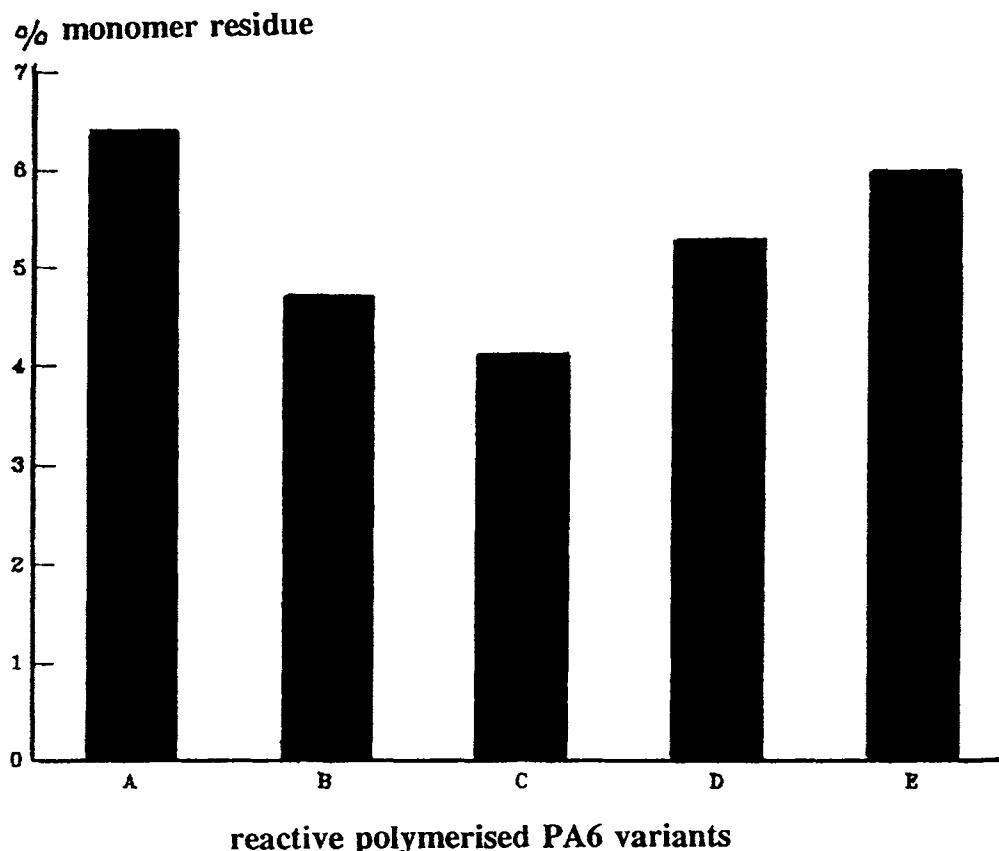
**Figure 4**  Residual monomer content of PA6 made by anionic polymerization of ε-caprolactam. A–E represent PA6 made at extruder screw speeds of 50, 70, 90, 120, and 150 rpm, respectively.

are generally much higher than commercial PA6 materials formed by hydrolytic polymerization. Anionically polymerized PA6 materials also exhibited superior impact and elongation properties but have lower tensile strength and flexural modulus properties. It is probable that this difference in mechanical behavior arises from a variation in molecular weight and/or crystallinity associated with the different synthesis processes.

Plasticization effects arising from the presence of residual monomer have been minimized because PA6 materials made by anionic polymerization were

**Table III  Mechanical Properties of PA6 Variants**

| Sample[a] | Young's Modulus $E$ (GPa) | Stress at Yield $\sigma_y$ (MPa) | Elongation at Break (%) | Impact Strength (J m$^{-1}$) | Flexural Modulus (GPa) |
|---|---|---|---|---|---|
| 50 rpm | 2.41 | 56.2 | 90.1 | 82.4 | 2.53 |
| 70 rpm | 2.72 | 68.1 | 77.3 | 77.1 | 2.81 |
| 90 rpm | 2.74 | 69.0 | 75.8 | 69.4 | 2.87 |
| 120 rpm | 2.46 | 60.2 | 80.0 | 80.6 | 2.49 |
| 150 rpm | 2.68 | 66.4 | 88.7 | 93.8 | 2.72 |
| CAPRON[b] | 2.84 | 76.4 | 12.2 | 60.1 | 3.12 |

*Note.* All samples tested in "dry as-molded" condition @ 23°C.
[a] PA6 prepared at different extruder screw speeds.
[b] Commercial PA6 made by hydrolytic polymerization.

subjected to an aqueous extraction procedure before determination of properties. Mechanical tests were undertaken on injection-molded test specimens in their "dry," as-molded state, hence all materials received the same thermal and storage history. The influence of residual monomer on PA6 plasticization is considered further in a subsequent article.

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