

# **Influence of Processing Conditions on some Properties of Anionically Synthesized Polycaprolactam in Presence of Lithium Chloride**

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## **Synopsis**

Nylon 6–LiCl systems of various concentrations were prepared by anionic polymerization of caprolactam in the presence of salt. A depression of both crystallization rate and melting temperature was evidenced through x-ray, density, and DSC analyses. Such a preliminary characterization allowed for choosing the proper conditions in order to obtain amorphous fibers from a spinning operation which was performed at a temperature lower than the pure polymer melting point. These results are of technological relevance, especially in view of obtaining, as in similar cases, large amorphous orientations through a spinning–drawing process and high-modulus fibers after subsequent crystallization. Also, the possibility of restoring some crystallinity in the material has been proven.

## **INTRODUCTION**

In recent works<sup>1,2</sup> the anionic polymerization of caprolactam in the presence of lithium chloride has been successfully attempted. This has been considered an interesting method for bypassing the mixing step in a high-modulus fibers production process from the polycaprolactam/inorganic salts systems already presented.<sup>3,4</sup>

A preliminary characterization through rheological measurements<sup>5</sup> suggested the existence, in this case, of strong interactions between Li<sup>+</sup> ions and the carbonyl groups of the polymer which were considered responsible for the drastic physicochemical changes in the mixed systems.<sup>6–8</sup>

Therefore, it has been considered important to test the new polymeric systems with regard to the processing characteristics most relevant, in view of a spinning–drawing process, similar to the one previously described.<sup>3,4</sup>

## **EXPERIMENTAL**

Nylon 6–LiCl mixtures were obtained by anionic polymerization of caprolactam in bulk, directly in the presence of salt, as described in the literature.<sup>1,2</sup> Systems of various concentrations were prepared: in particular the salt contents, as determined by argentometric titration on the water-extracted products were 1.8, 3.2, and 3.7% w/w. The pure polymer was also considered for the sake of comparison.

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Two types of samples were used in characterization tests. Some of them, indicated as A, were obtained by compression molding of the mixtures which, after being at 260°C for about 10 min, were cooled at a rate of about 1°C/sec. The others, indicated as B, were prepared by further processing of the previous ones. In particular, these were heated again to 260°C, held at this temperature for about 10 min, and then cooled at a rate of about 50°C/sec. Such a cooling rate was obtained by quenching the sample, allocated in a suitable metal frame, in an acetone/dry-ice bath. In both cases, the samples were maintained at 260°C in order to destroy any crystallite.

Because the physicochemical properties of the nylon 6–LiCl mixtures are remarkably influenced by moisture,<sup>9</sup> the samples were held in a vacuum in the presence of silica gel for at least three days before all tests.

Wide-angle x-ray patterns were obtained with a Philips instrument using Cu K<sub>α</sub> radiation (40 kV, 25 mA) filtered through a thin Ni film. The tests were performed in a moisture-free atmosphere.

A Perkin–Elmer DSC 1B instrument was used for differential scanning calorimetric tests. The heating rate was 8°C/min.

A Leitz polarizing hot-stage microscope (HSM) was used for confirming determinations of melting temperatures. The heating rate was again ~8°C/min.

Density measurements were performed in a density gradient column prepared with solutions of *n*-heptane and carbontetrachloride and operating at 22°C.

A piston-type extruder equipped with a 2.096-mm die (*L/D* ≈ 4) and operating under constant load was used for melt-spinning experiments. Runs were performed at 260 and 210°C. In the latter case, as for the molding operation, the polymer heated to 260°C was held at this temperature for about 10 min, then was cooled to 210°C, and spun. The flow rate was in both cases ~5 × 10<sup>-3</sup> g/sec and the maximum take-up velocity was 10<sup>2</sup> cm/sec.

Elastic moduli were measured at room temperature using an Instron universal testing machine (1115) at the elongation rate of 0.25 min<sup>-1</sup>.

## RESULTS AND DISCUSSION

Diffraction patterns of samples A are shown in Figure 1. The α-crystalline form<sup>10</sup> is predominant in the case of a pure polymer; the lithium chloride, on the contrary, favors the appearance of the γ form.<sup>3</sup> Furthermore, a decrease of crystallinity is evident as the salt content increases, and, at the largest salt concentration, the sample appears essentially amorphous. Such a result has been confirmed with the DSC measurements.

Melting temperatures have also been obtained from the thermograms and are reported in Figure 2 versus the salt concentration. A good agreement is observed with the HSM results reported in the same figure. All the data show a melting point depression which increases with salt concentration and soon becomes quite remarkable.

The effect of the cooling rate in sample preparation can be seen from the results of density measurements performed on both sample types A and B and reported in Table I. It is very pronounced at 1.8% salt concentration, becomes much smaller at 3.2%, and disappears at 3.7%. The latter result was of course expected in view of the previously reported x-ray patterns from which an amorphous

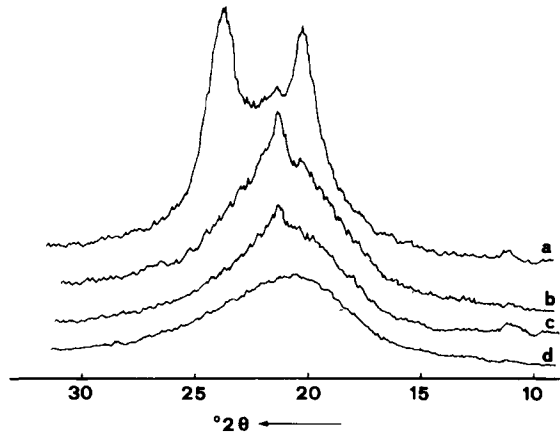


Fig. 1. Diffractograms of nylon 6-LiCl systems, samples A: (a) pure nylon 6; (b) nylon 6-1.8% LiCl; (c) nylon 6-3.2% LiCl; (d) nylon 6-3.7% LiCl.

structure was evident at this concentration. The density decrease for sample B at other concentrations is associated with a decrease of crystallinity which has been confirmed by x-ray and DSC analyses.

Obtaining a high-amorphous orientation during a spinning-drawing operation and a subsequent crystallization of the oriented material has been shown to be an efficient process for obtaining high-modulus fibers. Such a process, already favorably exploited with nylon-lithium halide mixtures obtained by homogenizing the salt with a commercial polymer,<sup>3,4</sup> may obviously be applied only to

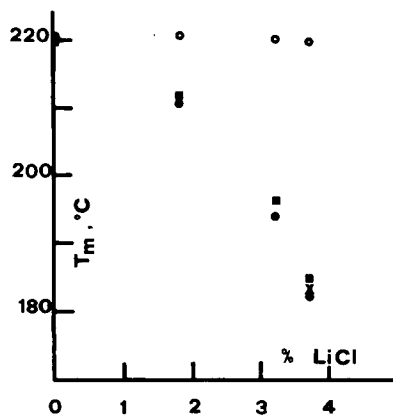


Fig. 2. Melting temperatures of nylon 6-LiCl systems vs. salt content (samples A): (■, ●) untreated samples; (○) water-treated samples; (x) heat-treated samples. (■) DSC; (●, ○, x) HSM.

TABLE I  
Density, g/cm<sup>3</sup>, of Nylon 6-LiCl as a Function of Salt Content and Processing Conditions

Sample	LiCl, % w/w		
	1.8	3.2	3.7
A	1.132	1.119	1.125
B	1.108	1.115	1.124

a material that does not crystallize along the spinning line. Moreover, large orientations may be more easily induced, during the spinning, in highly viscous materials. The increase of melt viscosity with the salt content of the mixtures considered in this work was already observed.<sup>5</sup> The cooling rate along a spinning line is possibly in between those adopted for the processing of samples A and B, and, as already observed, the only mixture which did not crystallize using process A is that 3.7% w/w LiCl concentration. Thus, such a concentration was chosen for some exploratory spinning as described in the Experimental section.

It is worth mentioning that one of the spinning runs was performed at 210°C, a temperature which is lower than the melting point of the pure polymer. Of course, such a low processing temperature is very appealing from a technological point of view, as well as in relation to possible material degradation.

The moduli of the as-spun fibers are reported in Figure 3 vs.  $V_f/V_o$ , the ratio between the takeup velocity and that at the die exit. Slightly larger values correspond to the fibers spun at the lower temperature in line with the previous discussion on the influence of viscosity on the orientation during spinning. The most relevant result is, however, the attainment of moduli for amorphous fibers of at least the same order as those of the pure nylon which conversely crystallizes along the spinline.<sup>11</sup>

Confirmation of the amorphous state of these fibers has been drawn from density measurements. For instance, fibers spun with a  $V_f/V_o \approx 100$  have a density of 1.127, corresponding to a crystallinity degree of about 3%, evaluated with a value of 1.21 for the crystalline phase density.<sup>7</sup> The small amount of crystallites which are present, however, are only slightly oriented (see Fig. 4), and we may thus infer from the moduli that some non-negligible orientation has also been induced in the amorphous phase.

The last step of the present investigation is concerned with the possibility of restoring some crystallinity to the material in view of the increasing modulus in highly oriented amorphous filaments.<sup>3,4</sup>

In Figure 5 diffractograms are reported for samples subjected to different treatments: in one case a four-day annealing at 140°C and, in the other case, a 90-min water treatment at room temperature. Both diffractograms indicate an appreciable crystallinity content.

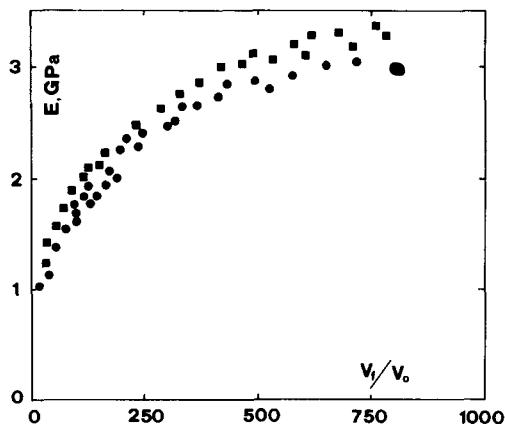


Fig. 3. Elastic modulus of nylon 6–3.7% LiCl fibers vs. the spinning ratio,  $V_f/V_o$ . (■)  $T = 210^\circ\text{C}$ ; (●)  $T = 260^\circ\text{C}$ .

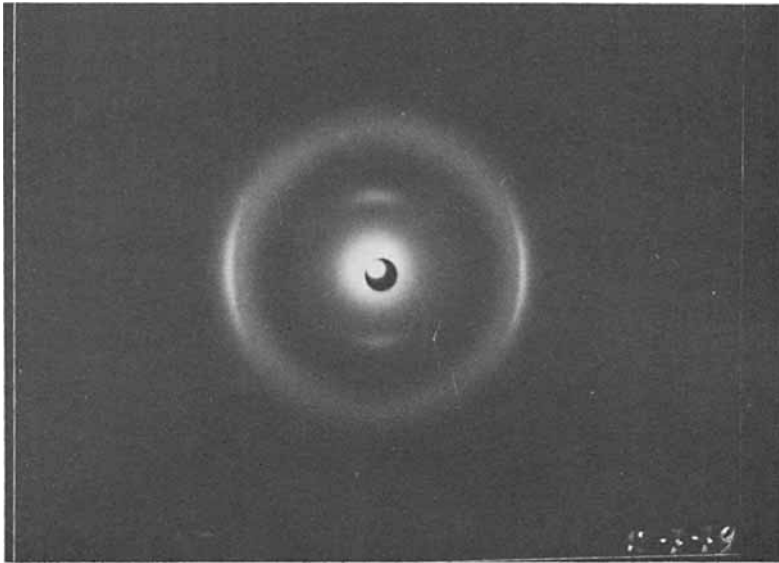


Fig. 4. Wide angle x-ray pattern for a nylon 6-3.7% LiCl fiber spun at 260°C with  $V_f/V_o \approx 400$ .

It is also worth mentioning that the water treatment washes out the salt, and therefore a restoring of the melting temperature of the pure polymer is produced. However, there was no appreciable differences in the melting behavior corresponding to the heat treatment. The experimental  $T_m$  results are included in Figure 2.

## CONCLUSIONS

Amorphous fibers have been obtained by spinning a system prepared by anionic polymerization of caprolactam in the presence of lithium chloride. This is of interest in view of being able to obtain, as in similar cases, large amorphous orientations through a spinning-drawing process and high-modulus fibers after subsequent crystallization. Also, the possibility of restoring some crystallinity in the material has in fact been proven. Furthermore, a remarkable melting

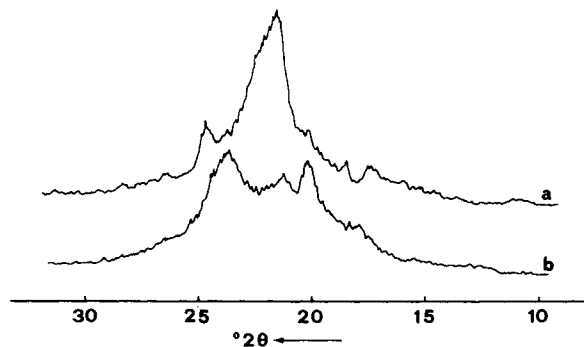


Fig. 5. Diffractograms of nylon 6-3.7% LiCl. (a) After a 90-min water treatment at room temperature. (b) After a four-day annealing at 140°C.

temperature depression caused by the salt has been observed. This allowed for a processing temperature even lower than the melting point of the pure polymer to be used.

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