Optimization of Spinning, Drawing, and Annealing Conditions in the Production of Highly Oriented Fibers from the Polycaprolactam/3.7% LiCl System

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Synopsis

A polycaprolactam/3.7% w/w LiCl system, obtained by anionic polymerization of caprolactam directly in the presence of salt, has been employed for the production of highly oriented fibers. More particularly, an optimization of spinning, drawing, and annealing conditions has been performed, finally obtaining fibers which show very satisfactory mechanical results. Namely, average moduli values up to 12 GPa and strength values up to 1 GPa, when fracture is far from clamps, have been observed.

INTRODUCTION

Following previous indications[1-7] in recent works, physicochemical[8,9] and rheological[10] characterizations have been performed on samples of anionically synthesized polycaprolactam in presence of lithium chloride.[11,12] These preliminary experiments led to the choice of LiCl concentration more appropriate to induce orientation in the polymer, and a few spinning tests were performed, obtaining well-oriented mostly amorphous fibers.[8] The aim of this work has been establishing optimum conditions in the spinning, drawing, and annealing parameters in order to obtain highly oriented crystalline fibers.

EXPERIMENTAL

Material and Fibers Production

A polycaprolactam/3.7% w/w LiCl system was obtained by anionic polymerization of caprolactam in bulk, directly in presence of the salt, as described in Refs. 11 and 12.

A piston type of extruder, equipped with a 2.096 mm die ($L/D \simeq 4$) and operating under constant load, was used for the spinning experiments. Tests were performed at 210°C and 260°C always with the filaments extruded in air at room temperature.[8] In the case of the spinning at 210°C, the polymer was first heated at 260°C, held at that temperature for about 10 min in order to destroy any possible residual crystallinity, and, after cooling at the chosen temperature, finally spun.

The flow rate was in both cases about 5×10^{-3} g/s and the take-up velocity was up to 10^2 cm/s.

The as-spun fibers were drawn, with aid of an Instron machine, Model 1115, equipped with a thermostated chamber, in the temperature range 90–135°C,

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at velocity between 0.5 and 50 cm/min. The initial length was in all cases about 4 cm.

Annealing was carried out in the temperature range 130–160°C for times of the order of 300 h in a vacuum oven, with the filaments held at constant length.

Mechanical Properties

Stress–strain curves were obtained again with an Instron machine at room temperature at an elongation rate of 0.25 min^{-1}. All the data reported in the following are average values of 10 individual measurements, performed on samples held under vacuum in presence of silica gel for at least 3 days because of the strong influence of moisture on all physicochemical properties of this type of systems.[13]

Structural Determinations

Density measurements were performed using a density gradient column filled with solutions of *n*-heptane and carbon tetrachloride and operating at 22°C.

A Leitz polarizing microscope equipped with a Berek compensator was used to determine the optical retardation for spun and drawn fibers. Similar determinations were impossible for the annealed samples, due to some oxidative degradation.

Wide angle X-ray patterns were obtained with a Philips instrument using an Astbury flat camera and CuK_α radiation (40 KV, 25 mA) filtered through a thin Ni film. The tests were performed in a moisture-free atmosphere.

RESULTS AND DISCUSSION

The moduli of the as-spun fibers were reported in Ref. 8 as a function of the spinning ratio for both temperatures. Slightly larger values were observed in the fibers spun at lower temperature and correspondingly larger values were obtained also for the birefringence (Fig. 1), confirming the attainment of larger orientations as a consequence of the larger viscosity.

A further consideration can be made comparing the above-mentioned results with those corresponding to the pure polymer.[5,14] The elastic moduli are in fact of the same order, although the salted samples are essentially amorphous and the pure polymer semicrystalline. More particularly, the densities of the salted fibers obtained at 210°C and 260°C are about 1.125 and 1.127 g/cm^3, respectively, corresponding to crystallinity degree of ~1.5–3.5%,[8,9] while the nylon fibers show crystallinity around the 30%.[15] The peculiarity of the increase of density with extrusion temperature, in presence of the salt must also be observed: The pure nylon does, in fact, not show such a behavior, which has been, however, previously reported in other cases.[16]

Although the above differences were not very large, the fibers obtained at the two different temperatures showed a strikingly different behavior in the drawing. And, in fact, fibers spun at 210°C could be drawn only up to a 150% while those spun at 260°C could be drawn up to 500%, as discussed in the following. High draw ratios could, however, be imposed to fibers spun at 210°C after a short

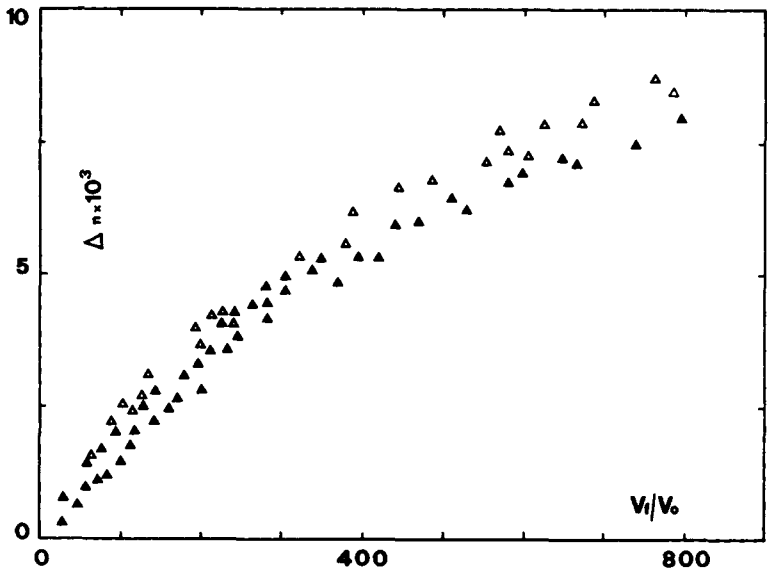

Fig. 1. Birefringence of function of the spinning draw ratio, for two temperatures. (△) T = 210°C; (▲) T = 260°C.

annealing (15 min at 120°C), which also induced a change in density (from 1.125 to 1.127 g/cm^3).

For sake of simplicity, the optimization in the drawing conditions was performed for the fibers spun at 260°C and more particularly on fibers obtained with a spinning draw ratio of about 200. First some fibers were drawn at a fixed draw ratio (namely 4) and at several different temperatures and three velocities. The results in terms of moduli vs. temperature are reported in Figure 2, with the velocity being the parameter. All curves present a maximum at a temperature which slightly increases with the velocity; also, the value of the maximum depends on the velocity and, of course, is larger, the larger the velocity. For the so-obtained "optimum" temperatures, elastic moduli are reported in Figure 3 as a function of the draw ratio again at the three different velocities. The best value (~8 GPa) is observed at the two higher velocities for slightly different draw ratio

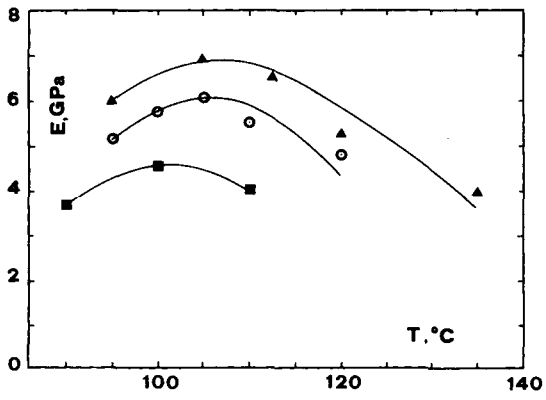

Fig. 2. Moduli vs. drawing temperature, for fibers with a draw ratio 4 and different velocities. (▲) V = 50 cm/min; (⊙) V = 5 cm/min; (■) V = 0.5 cm/min.

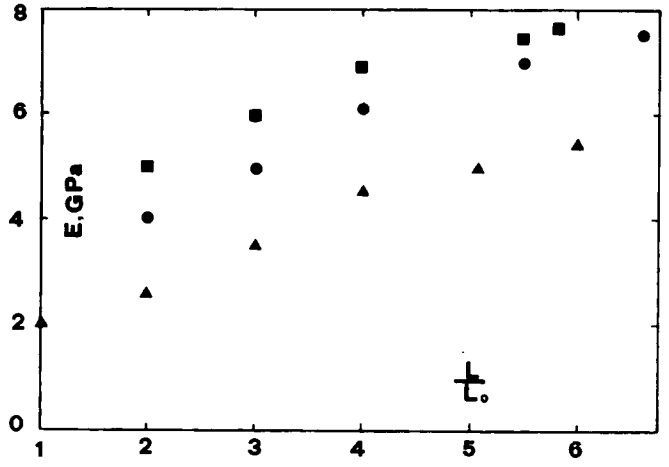

Fig. 3. Moduli vs. draw ratio. (■) V = 50 cm/min, T = 107°C; (⊙) V = 5 cm/min, T = 105°C; (▲) V = 0.5 cm/min, T = 102°C.

values and is much higher than that corresponding to the pure nylon[5,14] and also larger than that previously reported for samples obtained by mixing the salt and commercial nylon.[5]

The birefringence data, reported in Figure 4, confirm the increase of orientation, which is essentially in the amorphous portion of the polymer. The X-rays do not show, in fact, a large crystallinity (see Fig. 5), and, more quantitatively from density results, a maximum crystallinity degree of about 13% has been evaluated. Birefringence has been thus used, as a measure of the orientation, to correlate the mechanical properties: in particular, in Figure 6 moduli are reported vs. Δn, while Figures 7 and 8 show the strength and the elongation at break as a function of the birefringence respectively. The moduli show the usual trend, i.e., a monotonic increase with birefringence. The σ_r and ϵ_r curves show a discontinuity for $\Delta n \sim 25.10^{-3}$: This is especially evident for the elongation

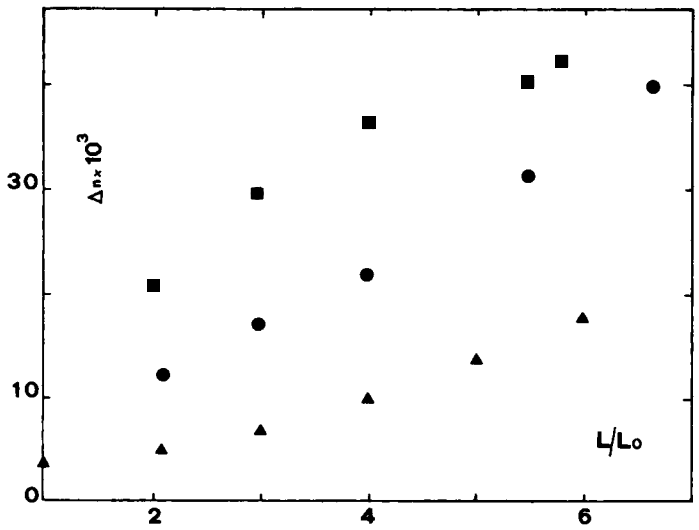

Fig. 4. Birefringence vs. draw ratio. Symbols are as in Figure 3.

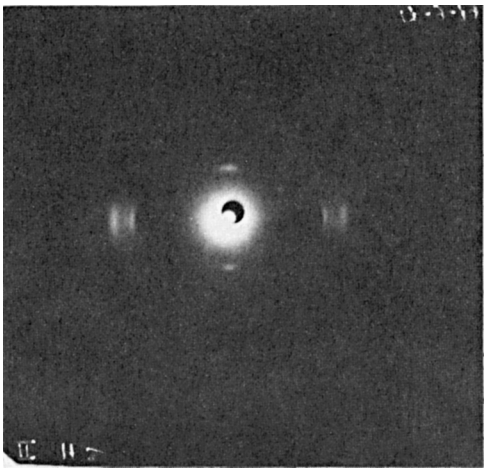

Fig. 5. X-ray patterns for a fiber draw at 107°C and with V = 50 cm/min up to a draw ratio 5.5.

at break which first increases steeply and then decreases also quite rapidly. A similar behavior has been already reported for a typical amorphous polymer, like polystyrene.[17] Furthermore, observing the absolute values of σ_r we notice that such values are similar to maximum values obtained for pure nylon,[14] i.e., for fibers much more crystalline. The ϵ_r's are also in the range of those corresponding to the above fibers.[14]

The last step of the experiments has been establishing the best annealing conditions for the above fibers. Again, as in the optimization of the drawing conditions, tests have been performed on fibers drawn at a fixed draw ratio, namely 5.5, and with a fixed velocity (50 cm/min), and, following previous results obtained on unoriented samples,[9] the explored temperature range has been limited to 130–160°C and annealing time has been 300 h. The results are reported in Figure 9 in terms of crystallinity degree x_c vs. temperature. As expected, an increase of x_c is observed with respect to the isotropic samples; the

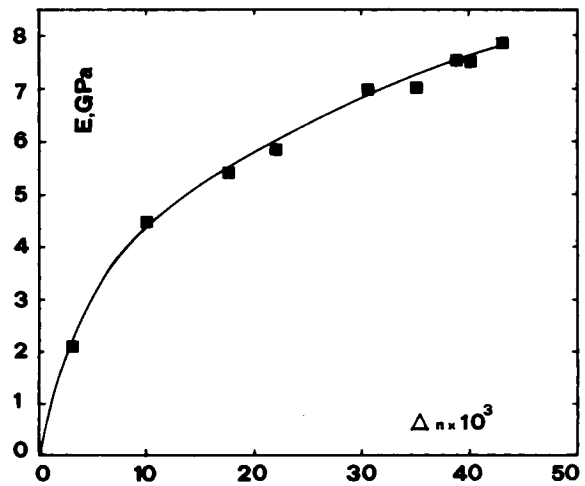

Fig. 6. Moduli vs. birefringence for drawn fibers.

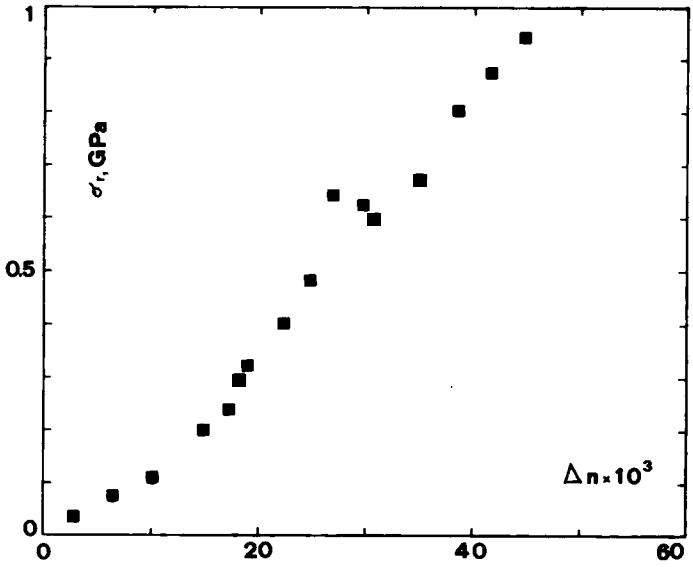

Fig. 7. Strength vs. birefringence for drawn fibers.

best temperature is, however, only a few degrees larger than that obtained with isotropic samples.

Fibers drawn at the maximum draw ratio have been crystallized at 145°C, and the corresponding mechanical results are very satisfactory. More particularly, an increase of modulus of the order of 40% has been observed which corresponds to average moduli values of ~12 GPa. For the ultimate properties a fragile behavior has been clearly evidenced and, due to the limited number of tests, we shall not give a figure for the elongation at break, which is, however, in the range of a few percentage points. It is also difficult to give a figure for the strength, which ranges, when fracture is away from the clamps, around 1 GPa.

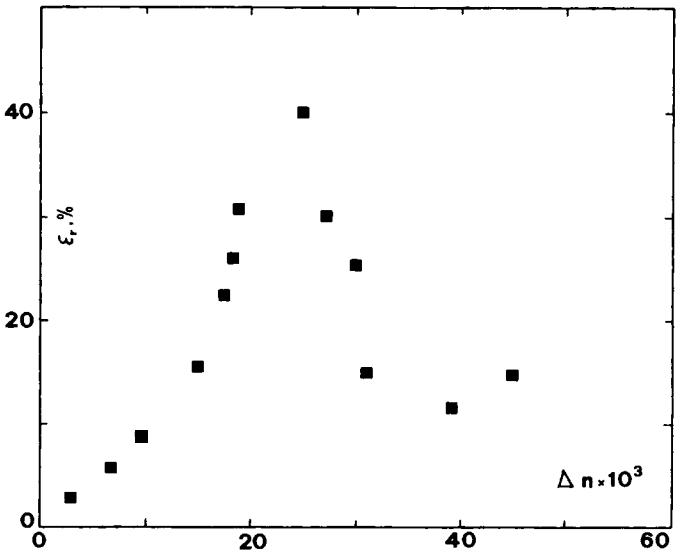

Fig. 8. Elongation at break vs. birefringence for drawn fibers.

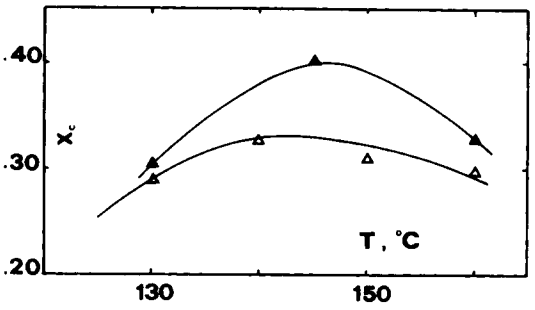

Fig. 9. Crystallinity degree vs. annealing temperature for isotropic (△) and anisotropic samples (▲).

CONCLUDING REMARKS

When optimum spinning–drawing conditions are chosen, the system polycaprolactam/3.7% LiCl yields fibers with interesting mechanical properties, although in an essentially amorphous state: namely, the elastic modulus is even higher than that obtained with nylon 6, and the strength and the elongation at break are of the same order of those from the pure polymer.

When annealing operations are performed on the above highly oriented samples, fragile, crystalline fibers are obtained which, however, are further improved as far as modulus and strength are concerned. And, in fact, average moduli values up to 12 GPa and strength values up to 1 GPa, when fracture is away from the clamps, have been obtained.

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