

Changes in the Morphology of Cast Nylon 6 Through Copolymerization

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Synopsis

Correlations were made between several physical and mechanical properties and crystal morphology for copolyamides composed of caprolactam and either capryllactam or lauro-lactam as a minor comonomer. Incorporating a comonomer into the nylon 6 chain decreases the crystallinity and crystal size and, in addition, depresses the melting point of the polymer much more than predicted by the classical Flory theory on random copolymers. This fact, along with the change in the x-ray diffraction patterns, indicates that small amounts (up to 10 mole-%) of comonomer can enter the polymer crystals without any basic change in the α -form crystal structure. The variation of copolyamide densities with comonomer content also supports this theory. The initial moduli of the copolyamides, when tested above their glass transition temperatures, obey a linear relationship with the reciprocal of the amorphous content of the polymers. The impact strength increases dramatically with decreases in crystallinity and crystal size. Some of these materials have extremely large ultimate elongations and have glass transition temperatures below room temperature.

INTRODUCTION

The incorporation of a comonomer into a semicrystalline polymer leads to modification of its properties. Although the anionic copolymerization of lactams has been described in patents^{1,2} and other reports,³ details on the properties of the resultant copolymers, especially the relationship between morphology and mechanical properties, remain unreported. Therefore, using cast nylon 6 (polycaprolactam anionically polymerized below its melting point),⁴ we have investigated the effect of comonomer on the crystal morphology, that is, crystallinity and crystal size and shape. This morphology was correlated to the physical and mechanical properties of the copolyamides. Since conventionally processed nylon usually has physical anisotropy caused by orientation during processing, it is difficult to separate the effect of orientation from that of the crystal morphology. Unlike conventionally processed nylon, cast nylon and its copolymers should have no orientation because they are prepared directly from the monomer or monomers without external stresses. They are therefore more suitable for investigating the effect of crystallinity on mechanical properties.

Differential scanning calorimetry (DSC) was used to study the crystalline morphology. The results were then correlated with density and x-ray diffraction patterns. Finally, some of the mechanical properties of the copolyamides were interpreted in terms of crystallinity.

TABLE I
Glass Transition Temperatures (T_g) and Intrinsic Viscosities ($[\eta]$)
of Copolyamides and Polycaprolactam

Capryllactam, mole-%	T_g , °C	$[\eta]^a$	Lauro- lactam, mole-%	T_g , °C	$[\eta]^a$
0.0	48	1.80	0.0	48	1.80
3.3	—	1.72	3.3	48	1.82
6.7	42	1.53	5.0	45	1.81
10.0	34	1.48	10.0	—	1.79
20.0	26	1.80	20.0	15	1.67
30.0	18	insoluble in this solvent	30.0	12	1.72

^a Trifluoroethanol Solution at 35°C.

EXPERIMENTAL

Polymer Preparation

Commercially available monomers, caprolactam (mp 70°C), capryllactam (mp 78–79°C), and lauro lactam (mp 150.0–151.5°C), were used without further purification. Anionic copolymerization was initiated with a cocatalyzed sodium hydride system. The initial temperatures of anionic copolymerization were varied from 145° to 170°C depending on the ratio of the monomers. Because of the exothermic nature of this anionic reaction, the temperature of the polymerizing mass exceeded the initial temperature by 13–20°C. The initial temperature and the temperature of the oven in which the mold was kept during polymerization were so adjusted that the monomers stayed in a liquid state, and yet the maximum temperature attained was at least 10°C below the melting point of each copolymer.

The copolymerization of caprolactam with capryllactam proceeded much faster than that of caprolactam with lauro lactam or that of caprolactam alone. After polymerization in a flat mold for 20 min in an oven, the mold was removed from the oven and allowed to cool for 2 hr at room temperature before the slab of nylon or nylon copolymer was removed from the mold. The slab was then placed in a desiccator.

Extraction of the nylon 6 shavings for 24 hr in boiling water revealed that the hot water-soluble fraction comprised 4.3% of the weight and consisted primarily of monomer and oligomer. Extraction of the nylon copolymers with a boiling water/methanol (50/50) solution for 24 hr revealed that the soluble fraction comprised 4.4% to 6.1% of the total weight. The molecular weights of the nylon and its copolymers were estimated from the intrinsic viscosities which are shown in Table I.

Differential Scanning Calorimetry (DSC)

A du Pont 900 DTA with a high-pressure DSC cell was used to obtain DSC curves at 14.7 psi in dry nitrogen. Equation (1) relates the recorded ΔT to the heat capacity difference between the sample and the reference (the first term),

the thermal change taking place in the sample (the second term), and the thermal lag inherent in the instrument^{5,6};

$$\Delta T = T_{rp} - T_{sp} = R_c(C_s - C_r) \frac{dT_r}{dt} + R_c \frac{dQ}{dt} - C_s(R_c + R_s) \frac{d(\Delta T)}{dt} \quad (1)$$

where T_{rp} , T_{sp} = reference and sample platform temperatures, respectively; C_s , C_r = sample and reference heat capacities, respectively; dT_r/dt = heating rate; R_c = thermal resistance of the constantan disc; R_s = thermal resistance between sample pan and sample platform; and dQ/dt = the instantaneous heat of fusion.

Assuming that the third term in the equation has no effect on the DSC curve, the proportionality constant (R_c) was determined as a function of temperature through the first term. Aluminum oxide from the National Bureau of Standards was used. In addition, R_c was determined using the second term of the equation at the following temperatures: 122.4°C, melting point of benzoic acid; 156.7°C, melting point of indium; 232.0°C, melting point of tin.

The R_c value obtained from the heat of fusion is in good agreement with the R_c value obtained by measuring the specific heat of aluminum oxide at a programmed heating rate of 10.0°C/min.

By using the calibration curve ($1/R_c$ vs. T), we can now calculate dQ/dt , the instantaneous heat of fusion, as a function of temperature. The heat of fusion can then be obtained from eq. (2):

$$\Delta H = \int_{T_i}^{T_f} \frac{dQ}{dt} dT \quad (2)$$

where ΔH is the heat of fusion, and T_i and T_f are the initial and final temperatures of melting. The programmed heating rate was 10.0°C/min in this study.

Although several authors⁷⁻⁹ have reported the heat of fusion (ΔH_f) of 100% polycaprolactam crystals in the range of 34.0 to 45.6 cal/g, the value reported by Inoue,⁸ 45.6 cal/g, was used to calculate the calorimetric crystallinity. The crystallinity at temperature T , $\alpha(T)$, was calculated using eq. (3):

$$\alpha(T) = \frac{1}{\Delta H_f} \left[\Delta H - \int_{T_i}^T \frac{dQ}{dt} dT \right] \quad (3)$$

where ΔH_f is 45.6 cal/g.

To determine the melting point and the glass transition temperature of the copolyamides, differential thermal analysis (DTA) of these copolyamides were run on 2.5 ± 0.2 mg of the sample at a programmed heating rate of 5°C/min.

Density Measurement

A density gradient column made from *o*-dichlorobenzene and cyclohexanone was used to determine the densities of the polymer samples at $23 \pm 0.05^\circ\text{C}$.

X-Ray Diffraction Measurement

A Norelco x-ray diffractometer was used to obtain x-ray diffraction patterns of the polymer samples in the range of 2θ equal to 8–40 degrees at room temperature. The beam was nickel filtered Cu-K α radiation.

Measurement of Mechanical Properties

Tensile specimens (Type I, ASTM D638) machined from the as-polymerized slabs of polyamide and copolyamides were tested at a strain rate of 0.2 in./min using an Instron testing machine. Initial moduli of the samples were determined from the linear portion of the stress-strain curves at 0.1–0.3% strain. The ultimate elongation and the nominal maximum stress were also determined. Izod impact strengths were determined on unnotched $\frac{1}{2} \times \frac{1}{2} \times 2\frac{1}{2}$ in. specimens using a Tinus Olsen impact tester.

RESULTS AND DISCUSSION

Melting Behavior and Heat of Fusion

Figure 1 shows the melting thermograms of three nylon homopolymers, polycaprolactam, polycapryllactam, and polylauro lactam. Their respective heats of fusion (ΔH) are 21.8, 17.9, and 13.4 cal/g. The ΔH values of polycaprolactam

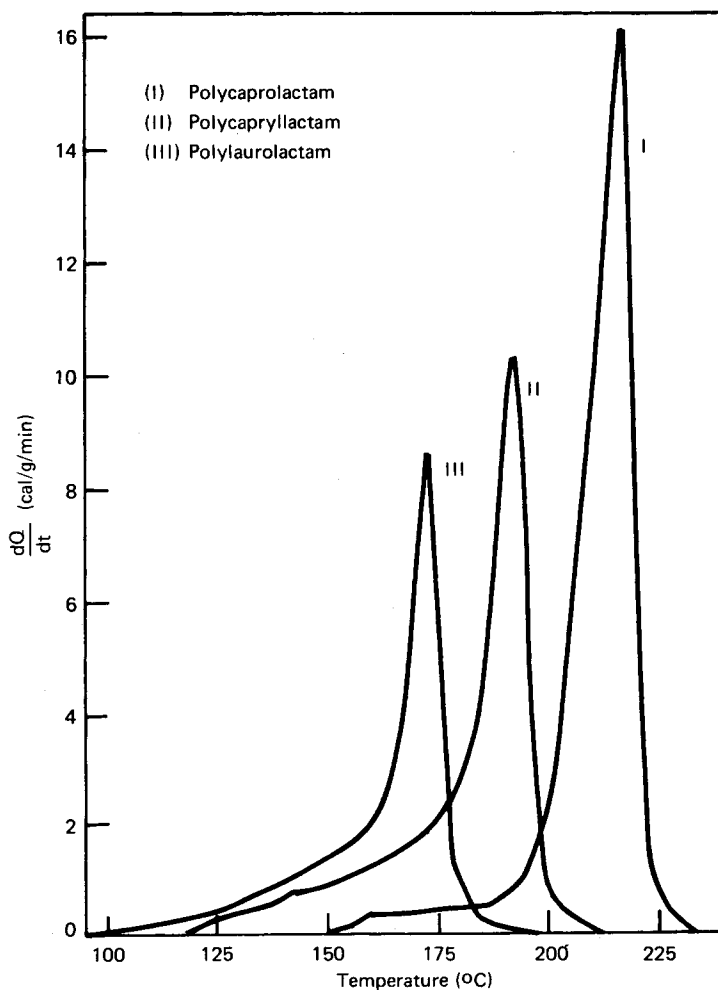


Fig. 1. Melting thermograms for polycaprolactam, polycapryllactam, and polylauro lactam.

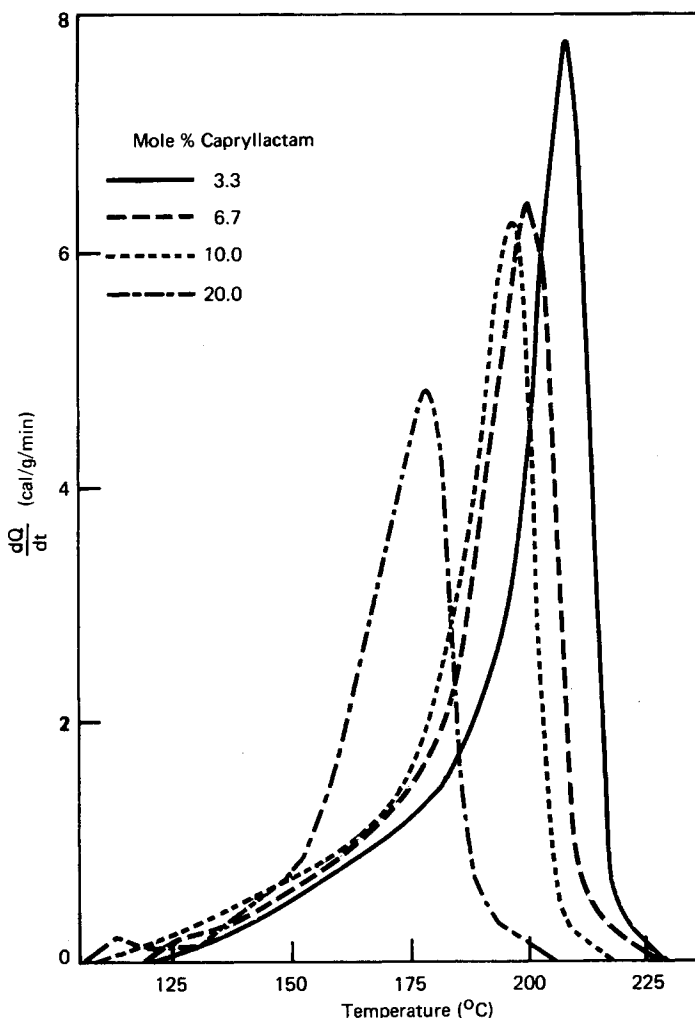


Fig. 2. Melting thermograms of four caprolactam-capryllactam copolymers.

(nylon 6) and polycapryllactam (nylon 8) indicate the relatively high crystallinity of these two nylons. The melting thermograms of copolyamides based on caprolactam and capryllactam are shown in Figure 2, and those of copolyamides based on caprolactam and laurilactam are shown in Figure 3. Unlike the other copolyamides, copolyamides made with 30 mole-% of the comonomer exhibit a broad exothermic peak in the neighborhood of 80°C, presumably caused by further crystallization during heating. Such a peak is shown on the DSC curve in Figure 4. Although, in this case, it is difficult to draw a baseline for the purpose of calculating a quantitative melting thermogram such as the ones in Figures 1-3, the heat of fusion is estimated to be 6-7 cal/g for the copolymers made of 30 mole-% of the minor monomer. In Figures 5 and 6, the crystallinity of nylon 6 and several of its copolymers is plotted as a function of temperature. In calculating the crystallinity for the copolymers, it was assumed that the incorporation of up to 20 mole-% of the comonomer does not appreciably change the ΔH_f of the polymer crystals. The presence of comonomer units in the

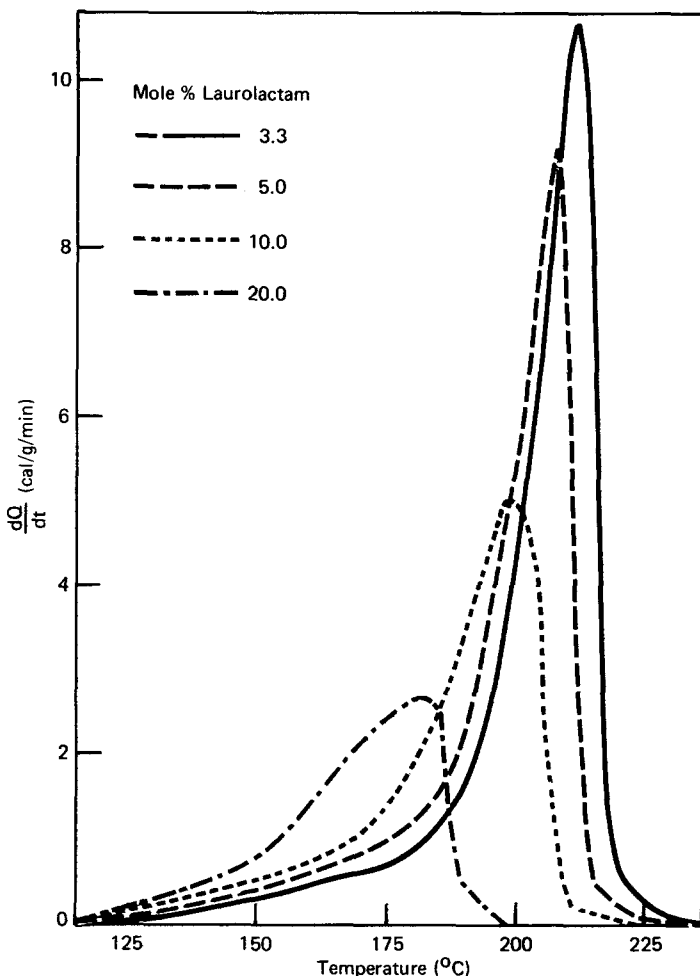


Fig. 3. Melting thermograms for four caprolactam-lauro lactam copolymers.

polymer chain depresses the melting point (Fig. 7) and broadens the melting range (Figs. 2 and 3) indicating both a decrease in the crystal size and a wider crystal size distribution.¹⁰ Although both the depression of the melting point and the diffuseness in the fusion curve are expected from the classical theory on a random copolymer,¹¹ the melting point depression of these particular copolyamides is much larger than calculated from eq. (4):

$$\frac{1}{T_m} - \frac{1}{T_{m0}} = - \frac{R}{\Delta H_f} \ln X_A \quad (4)$$

where ΔH_f is the heat of fusion of the crystals of polymer A, T_{m0} is the melting point of polymer A, T_m is the melting point of the copolymer, and X_A is the mole fraction of monomer A (Fig. 7). Of course, eq. (4) was derived from a random copolymer whose minor comonomer does not enter the polymer crystals and also under the assumption of an equilibrium state during the crystallization of the copolymer. There are, however, a few studies^{12,13} that assume a nonequilibrium state during copolymer crystallization. Helfand and Lauritzen,¹³ for example,

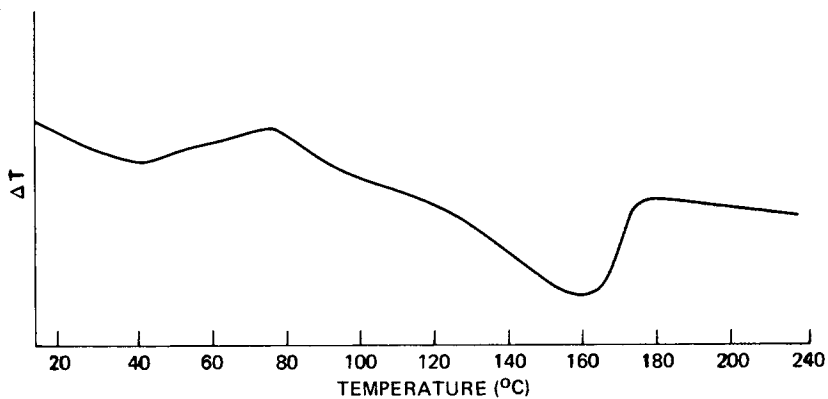


Fig. 4. DSC curve for a 30 mole-% lauro lactam copolyamide.

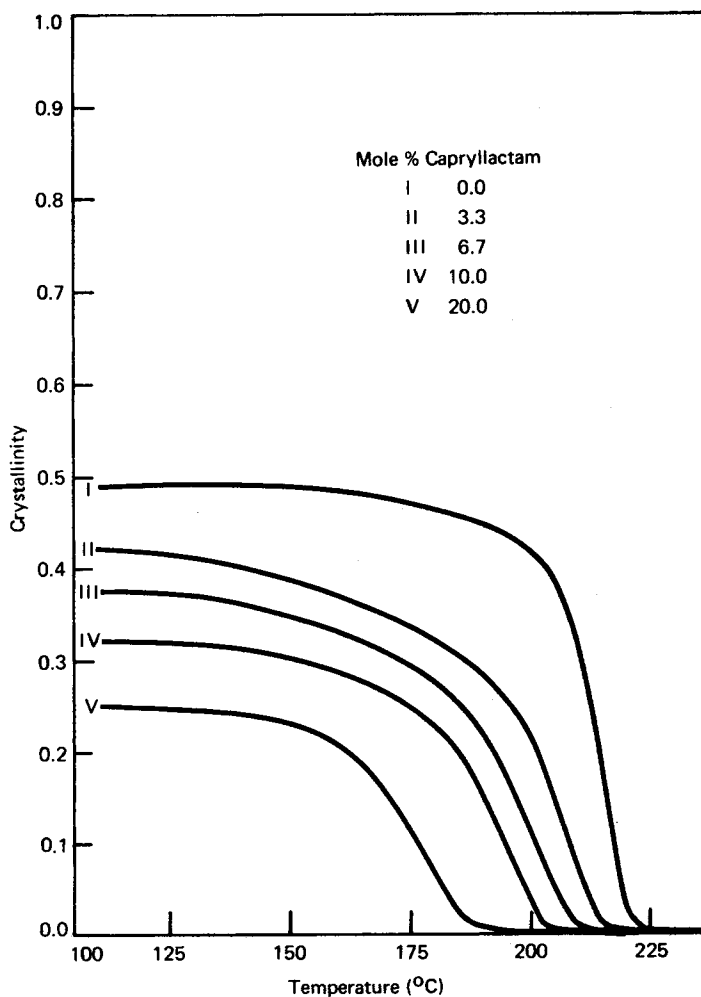


Fig. 5. Crystallinity vs. temperature curves for caprolactam-capryllactam copolymers and polycaprolactam.

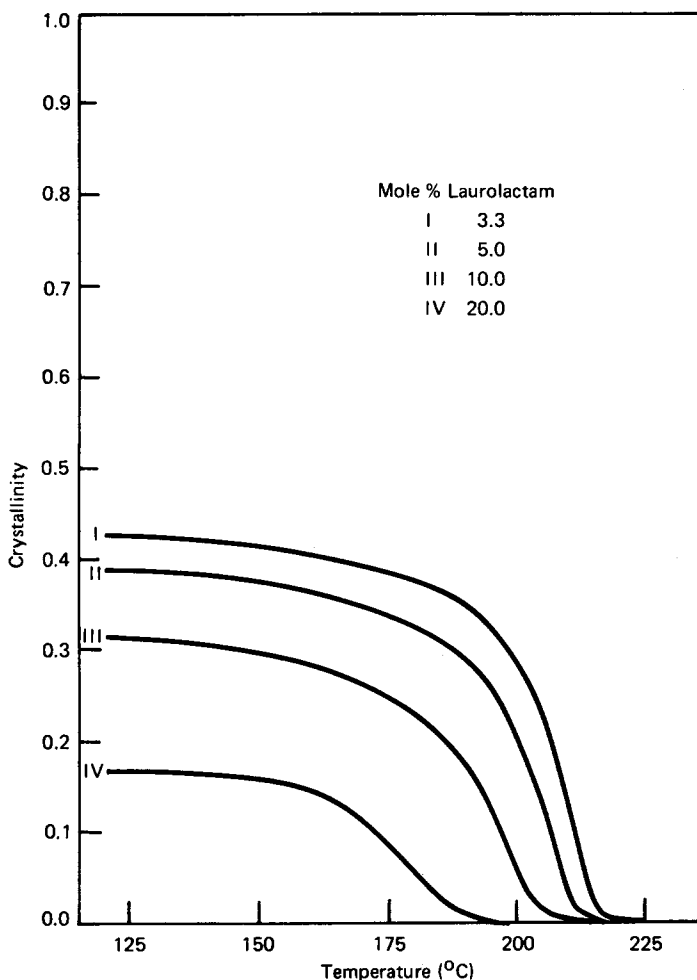


Fig. 6. Crystallinity vs. temperature curves for caprolactam-laurolactam copolymers.

proposed a kinetic control theory copolymer crystallization which predicts a significantly greater concentration of comonomer B in the polymer crystals, if B is crystallizable, than would be predicted by the equilibrium theory, and therefore a lower melting point for the copolymer. The high rate of crystallization of these copolyamides does not assure an equilibrium distribution of copolymer units. Obviously, a nonequilibrium state prevails during this type of crystallization, which is accompanied by a simultaneous polymerization. In addition, similarities in the crystalline structure of the various lactam homopolymers^{14,15} make it possible for the minor comonomer to enter the polymer crystals. These are the possible factors that depress the melting point of copolyamides to values lower than those predicted by eq. (4).

X-Ray Diffraction Patterns

Figures 8 and 9 show how the presence of a comonomer in the polymer chain affects the crystalline structure of nylon 6. The basic monoclinic structure of α -form nylon 6 is maintained in the copolyamides up to a minor comonomer

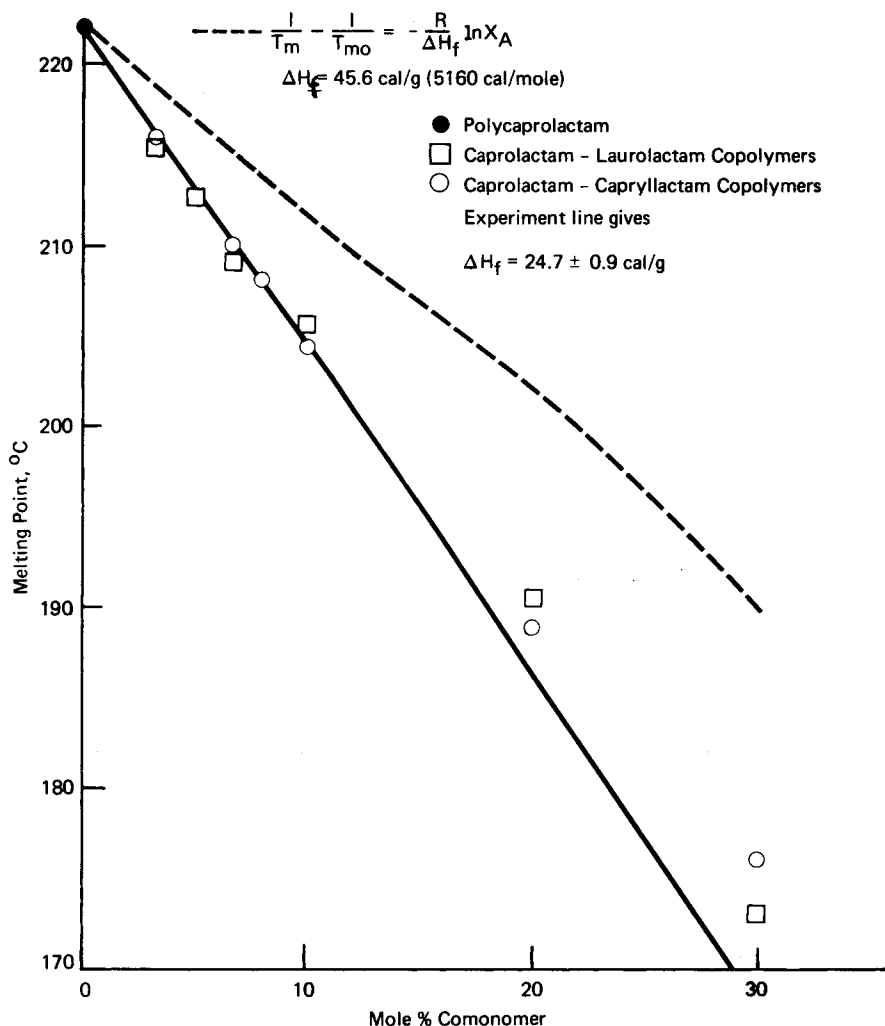


Fig. 7. Melting points of copolyamides compared to theoretically predicted values from

$$\frac{1}{T_m} - \frac{1}{T_{m0}} = -\frac{R}{\Delta H_1} \ln X_A$$

concentration of 10 mole-%. The presence of the comonomer, however, does change the ratio, $I_{(200)}/I_{(020+202)}$, where $I_{(200)}$ is the intensity at 2θ equal to 24.0° and $I_{(020+202)}$ is the intensity at 2θ equal to 20.4° (Fig. 10). For α -form nylon 6, $I_{(200)}/I_{(020+202)}$ has been calculated¹³ to be 1.61. Deviations from this value are caused by the rotation of the polymer chain, that is, by a change in the β -angle of the unit cell.¹⁶ There are similarities in the unit cell dimensions of at least two of the α -form nylons referred to in this paper. Alpha-form nylon 6 and nylon 8 have the following unit cell dimensions^{14,15} (there is no report of an α -form nylon 12):

	a , Å	b , Å	c , Å	β , degrees
nylon 6	9.56	17.24	8.0	67
nylon 8	9.80	22.40	8.3	65

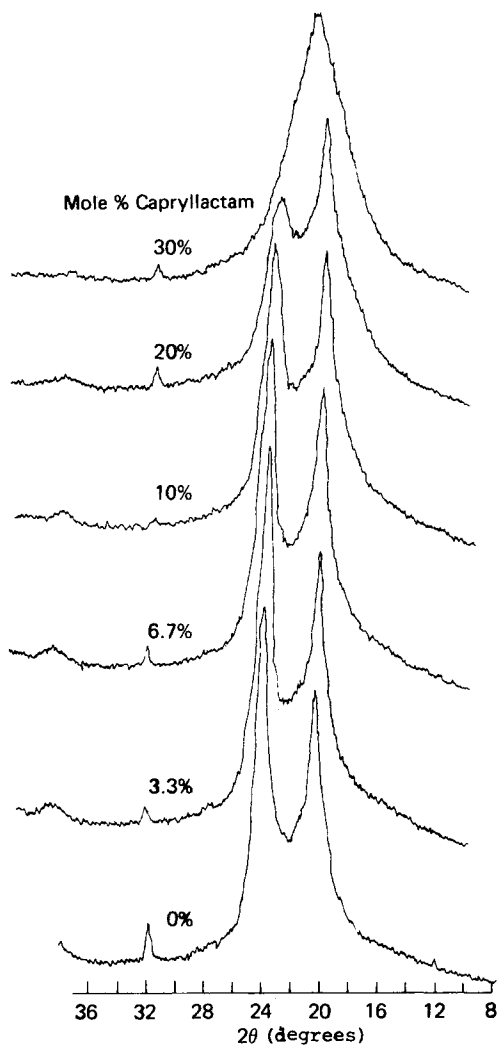


Fig. 8. X-Ray diffraction patterns for caprolactam-capryllactam copolymers and polycaprolactam

Because of the similarity in unit cell structure, the inclusion of a small number of comonomer units in the nylon 6 crystals could take place with only a slight rotation of the polymer chain but without any appreciable effect on d -spacing. Thus, the basic monoclinic structure of the original nylon 6 is preserved. The inclusion of larger amounts of the comonomer causes a change in the d -spacing of the (020 + 202) planes from 3.705 Å in nylon 6 to 3.767 Å in the 20 mole-% copolymer. The ratio $I_{200}/I_{(020+202)}$ also decreases with increases in the amount of comonomer (Fig. 10). When the monomer content exceeds 20 mole-%, a different x-pattern is observed, indicating a rearrangement of the antiparallel fully extended chains of the α -form.

Thus, the monoclinic structure has to be modified to accommodate comonomer in the polymer crystals. This process of crystalline transition caused by increasing comonomer content is accompanied by a drastic increase in crystal defects and

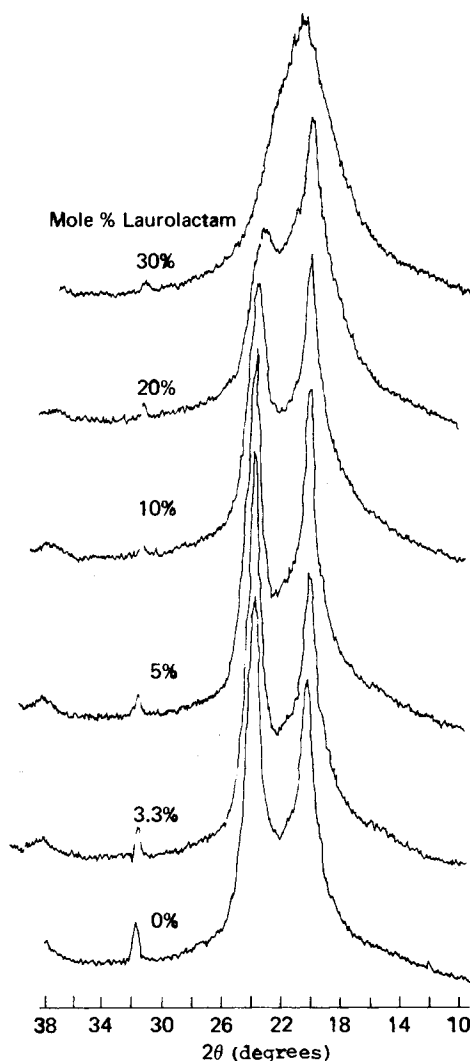


Fig. 9. X-Ray diffraction patterns for caprolactam-lauro lactam copolymers and polycaprolactam.

a decrease in both crystal size and crystallinity. The crystalline structure of the 30 mole-% copolyamides in Figures 8 and 9 is essentially that of γ -form nylon 6. In fact, as in γ -form nylon 6,¹⁷⁻²⁰ a $\gamma \rightarrow \alpha$ transition of these copolyamides can occur to some extent during heat treatment under high pressure (Fig. 11).

Density

The density of nylon 6 prepared by this monomer casting technique is 1.1541 at 23°C. From this density value, the crystallinity of the polymer was calculated by the equation

$$C(\text{crystallinity}) = \frac{V_s - V_a}{V_c - V_a} \quad (5)$$

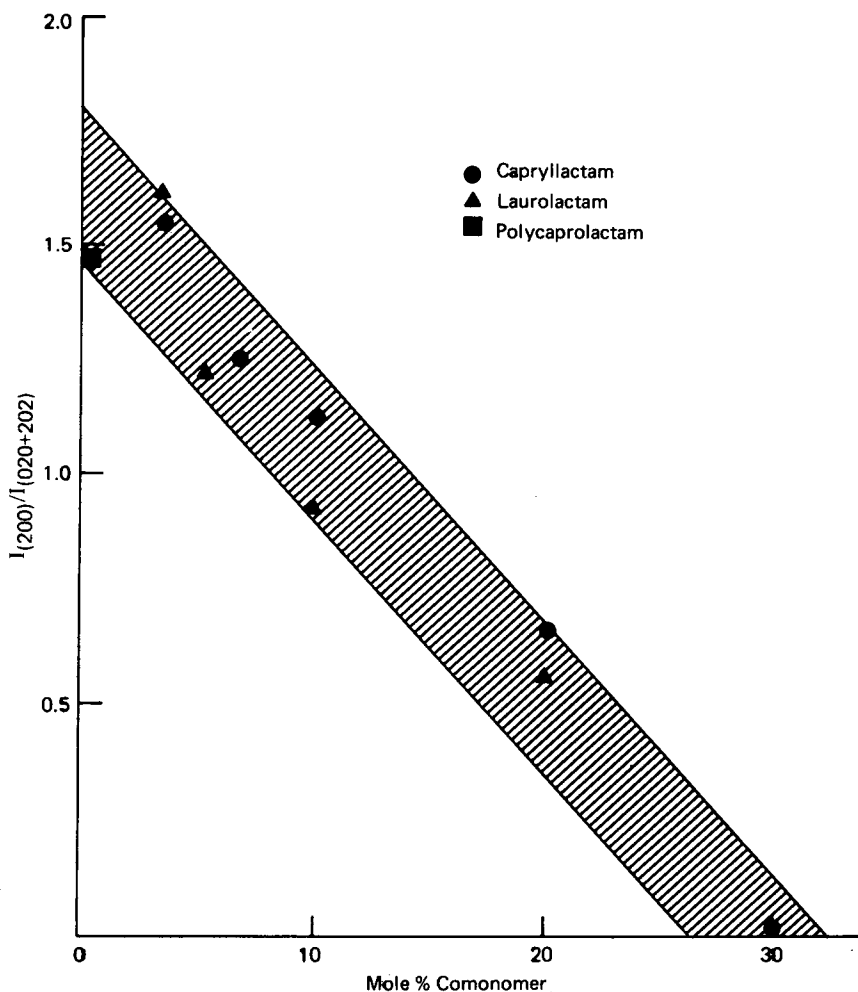


Fig. 10. Ratios of x-ray peak intensities vs. copolyamide composition.

where V_s is the specific volume of the sample; V_a is the specific volume of amorphous nylon 6; and V_c is the specific volume of 100% crystalline nylon 6 (α -form). The specific volumes of amorphous and 100% crystalline α -form nylon 6 are 0.9225¹⁶ and 0.816,¹⁴ respectively. The crystallinity thus obtained is 51%, which is in good agreement with the crystallinity obtained from the heat of fusion, 48%.

The density of the copolyamides progressively decreases with an increase in the comonomer content of the polymer. Although it is impossible to calculate the crystallinity of copolyamides from their densities, their heats of fusion vary linearly with specific volume at least up to a minor comonomer content of 10 mole-% (Figs. 12 and 13). Copolyamides containing 20 mole-% comonomer and especially those containing 30 mole-% deviated from this linear relationship, assuming the heats of fusion for the 30 mole-% copolymer to be 6-7 cal/g as discussed previously. It is interesting to note that this linear relationship is valid up to a comonomer concentration of 10 mole-%, the same concentration

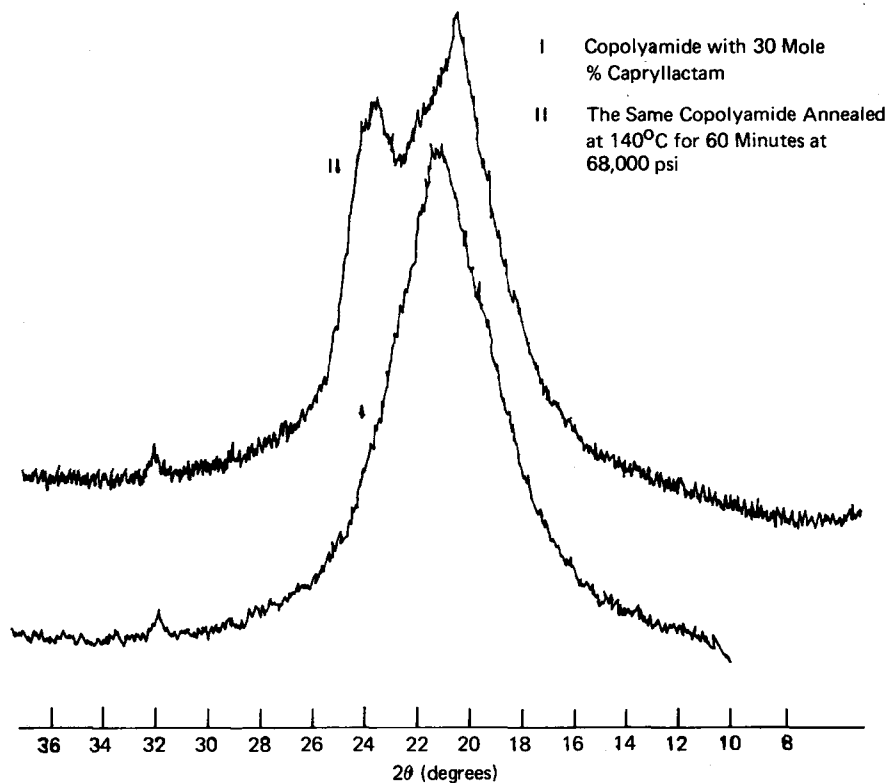


Fig. 11. Crystal transition during heat treatment of a caprolactam-capryllactam copolymer.

above which the x-ray diffraction patterns indicate the initiation of a crystalline transition.

Effect of Crystallinity on Mechanical Properties

The mechanical properties of copolyamides vary with comonomer content. One of the basic parameters controlling these properties in semicrystalline polymers is the crystallinity. Since the copolyamides used in this study were prepared directly from monomers in the absence of external stress, they should have no orientation, and therefore it is possible to isolate the effect of crystallinity on their mechanical properties. In addition, the crystallinity of these copolyamides varies over a rather wide range, from 17% to 48%, a range encompassing rigid materials at one end and materials displaying elastomeric characteristics at the other. In spite of a wide variation of crystallinity among the copolymers, the copolymer molecular weights estimated from their intrinsic viscosities (Table I) are fairly constant and high enough that the mechanical properties of the copolymers are not affected by the molecular weight.

Many studies, both theoretical and experimental, have been published on the relationship between modulus and crystallinity. Most of the theoretical studies²¹⁻²³ are based on a more or less similar model which treats the crystallites as crosslinks or rigid fillers in an elastomeric medium. The theories based on this model rarely succeeded in predicting the modulus. The shortcoming is

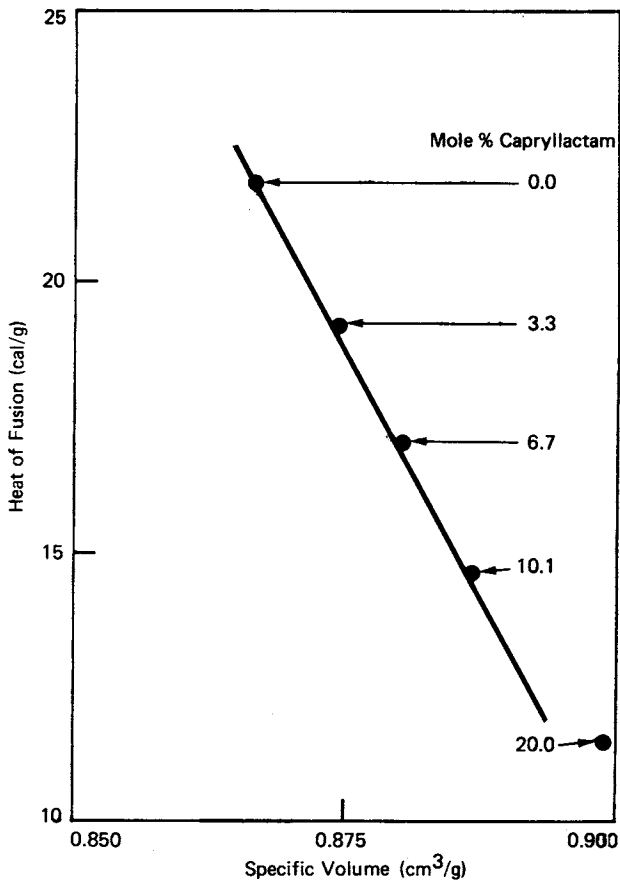


Fig. 12. Relationship between specific volume and heat of fusion for caprolactam-capryllactam copolymers.

caused by the differences between the amorphous phase of a semicrystalline polymer and that of an elastomeric system. A recent theory by Krigbaum et al.,²⁴ which assumed a highly strained state in the amorphous chains even in the absence of macroscopic external stresses, states that the modulus of semicrystalline polymers is related to $(1 - C)^{-1}$ at temperatures above the glass transition temperature (T_g), where C is crystallinity. In Figure 14, the initial modulus is plotted as a function of $(1 - C)^{-1}$ using the crystallinities of a series of copolyamides. The initial moduli were measured at 90°C, a temperature which is well above the T_g of the copolyamides and polycaprolactam, yet well below their melting points. A fairly linear dependence of the initial modulus on $(1 - C)^{-1}$ prevails in the crystallinity range of 25% to 50% (Fig. 14), while the same relationship at room temperature does not exhibit good linearity.

The values of tensile strength and ultimate elongation shown in Tables II and III scattered much more than those of the initial moduli and are difficult to correlate to crystallinity. One of the reasons for this is assumed to be the water absorption by the amorphous part of copolyamides which took place during the preparation and testing of the tensile specimens. In the crystallinity range of 37% to 48%, the change in crystallinity has little effect on either tensile strength or ultimate elongation. Especially noticeable are, however, the extremely large

TABLE II
Tensile Properties of Capryllactam-Caprolactam
Copolyamides at Room Temperature

Capryllactam, mole-%	Crystal- linity	Tensile strength, psi	Ultimate elongation, %
0.0	0.48	10,800	2.4
3.3	0.42	9,400	2.3
6.7	0.375	9,400	3.6
10.0	0.32	9,000	10.0
20.0	0.25	6,800	174.0
30.0	...	8,400	310.0

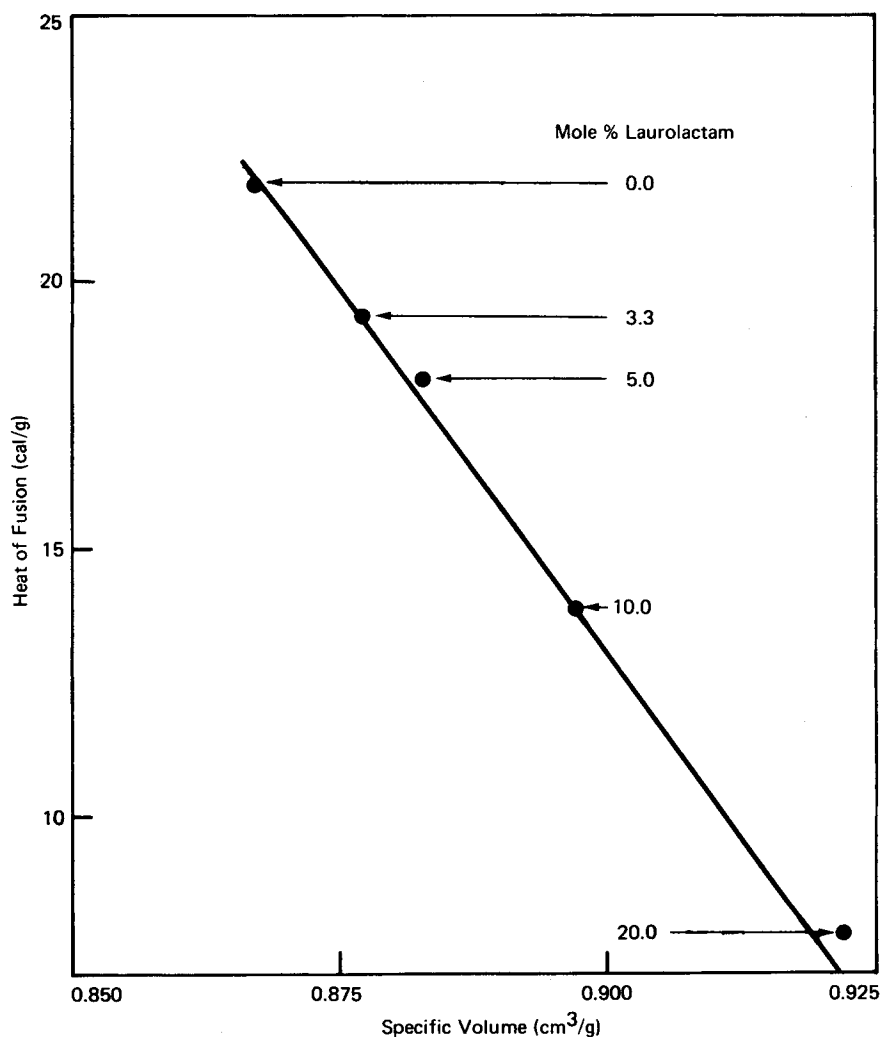


Fig. 13. Relationship between specific volume and heat of fusion for caprolactam-lauro lactam copolymers.

TABLE III
Tensile Properties of Laurolactam-Caprolactam
Copolyamides at Room Temperature

Laurolactam, mole-%	Crystal- linity	Tensile strength, psi	Ultimate elongation %
0.0	0.48	10,800	2.4
3.3	0.425	10,200	2.5
5.0	0.38	9,500	2.3
10.0	0.32	7,600	63.0
20.0	0.17	6,600	130.0
30.0	...	7,400	370.0

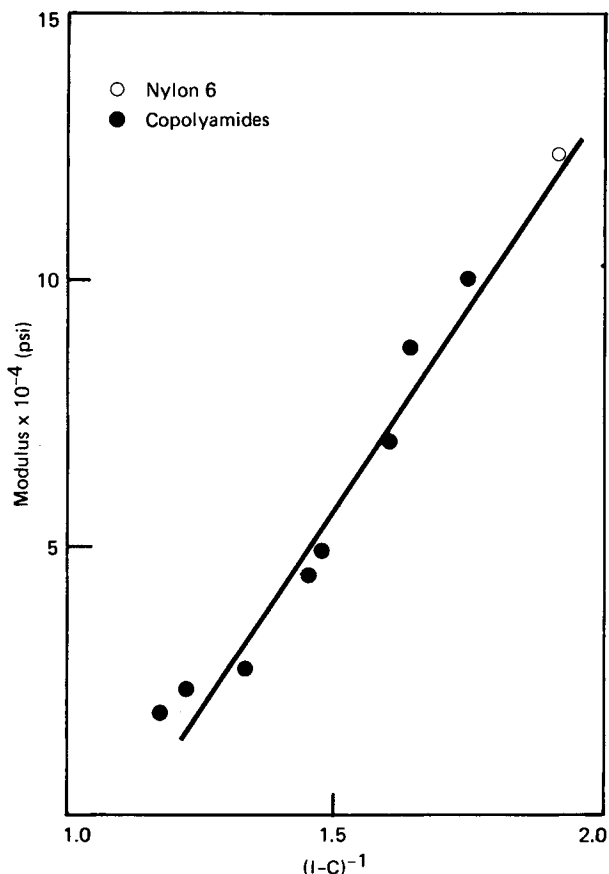


Fig. 14. Dependence of initial tensile modulus (90°C) on $(1 - C)^{-1}$ (C = crystallinity).

ultimate elongations of the copolymers containing 20 mole-% or more comonomer, i.e., those with crystallinities of less than 25%. In effect, some of these copolymers which have T_g values below 20°C (Table I) are elastomer-like materials at room temperature.

The impact strengths of the copolyamides also increase with decreases in crystallinity as reported in the cases of nylon 610 and nylon 66.²⁵ The broad

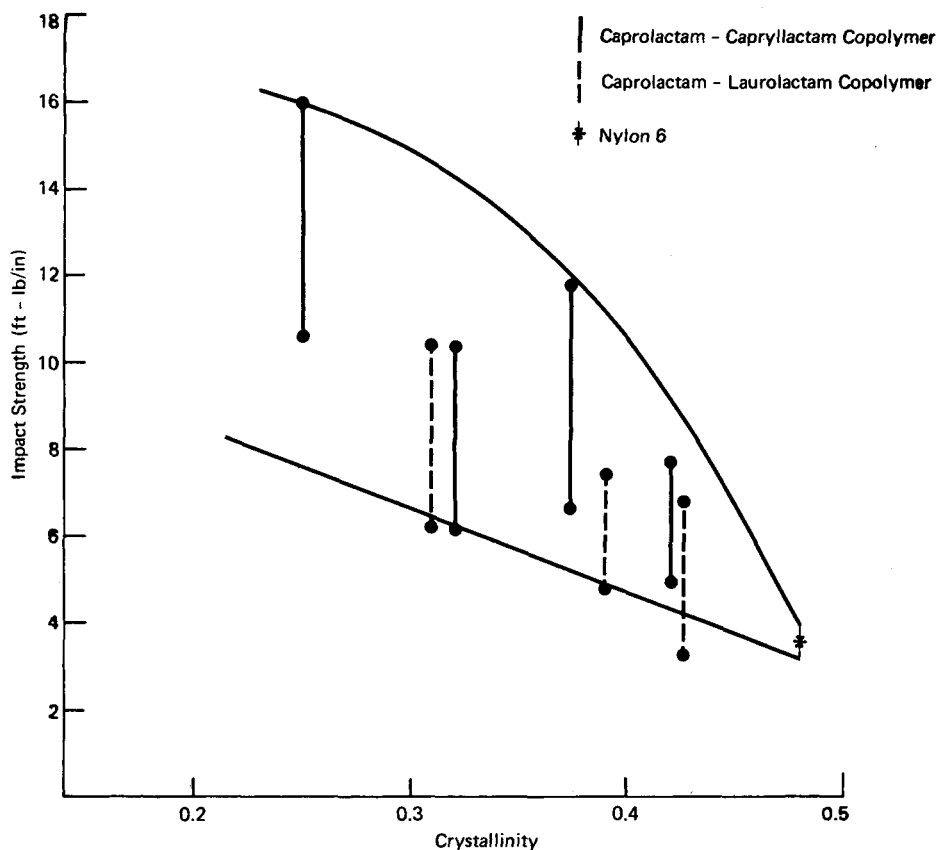


Fig. 15. The effect of crystallinity on unnotched impact strength.

spread of the results, which is not uncommon with this type of impact test, does not permit the determination of meaningful differences in impact strength between the two copolyamide series (Fig. 15). The copolyamides with crystallinities less than 30% have very large impact strengths. In fact, the 20 mole-% lauro lactam copolymer (17% crystallinity) has an impact strength in excess of 30 ft-lb/in. at room temperature, but this temperature is above T_g of the copolymer (Table I). When the same impact test was run at considerably below the T_g , namely, at 0°C, the average value of its impact strength was 8 ft-lb/in. In general, the copolymerization of caprolactam with a comonomer lactam results in a significant improvement in impact strength.

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