The Effect of Composition on the Properties of Nylon 612 Copolymers

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Synopsis

The series of nylon 612 copolymers was synthesized from caprolactam (C) and laurolactam (L) at 145°C. The 50/50 C/L molar ratio copolymer was found to have the minimum melting temperature (T_m) for the series. The glass transition temperatures $(T_g$'s) of the copolymers were affected by the crystallinity of the copolymers. The T_g was at a minimum for the 50/50 copolymer for crystalline samples. However, for amorphous samples there was a decrease in T_g with increasing L content. Percent crystallinity was determined by differential scanning calorimetry and X-ray techniques. It was found that the degree of crystallinity was at a minimum for copolymers of 70/30 to 40/60 C/L ratios. Coefficients of linear thermal expansion (CLTE) were obtained for the copolymers at 10°C intervals from 20 to 70°C for dry and from 20 to 50°C for samples conditioned at 50% relative humidity and 50°C. The dry samples gave lower initial values, but had a greater temperature dependence than the conditioned samples. As expected, the CLTE was found to be lowest for samples exhibiting the highest crystallinity. The tensile strengths and moduli decreased rapidly with increasing L up to the 70/30 C/L ratio after which they remained relatively constant. Elongations reached maximums between 70/30 and 40/60 C/L ratios. An inverse relationship was found between crystallinity and impact strength.
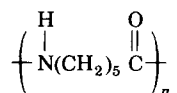
INTRODUCTION

During the last decade, the reaction injection molding (RIM) process has been used for the manufacture of plastic parts due to its fast cycle time, ability to form larger parts, and relatively low power requirements.[1] While initially restricted to lower operating temperatures, improvements in technology have gradually evolved equipment that operates at higher temperatures. At that time RIM technology adaptable to nylon 6 became a reality.[2]

Nylon 6, as with any plastic, has both desirable and undesirable characteristics associated with its properties. Nylon 6 is a semicrystalline plastic in which up to 50% of the polymer can be in the crystalline state. The plastic has, therefore, both crystalline and amorphous areas. The polymer crystals contribute to nylon 6's high melting temperature $(T_m \sim 225°C)$, high modulus, and high tensile strength. The polar amide groups of nylon 6, which are responsible for the crystallinity and the desirable properties mentioned above, are also found in the amorphous areas. The abundance of polar groups, which promote crystallinity, also increase the glass transition temperature (T_g) $(60°C$ dry, $\sim 25°C$ at equilibrium). Nylon 6 is brittle when dry and will only develop fair impact strength on standing. Water, a polar solvent, is readily absorbed into the amorphous areas of nylon 6. This plasticization does lower the T_g of the polymer,[3] but it also changes the dimensions of a part. Thus, as one cycles

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from dry to moist environments, changes in size, causing poor fits, cracking and failure of coatings, and warpage of large parts are found.

Increased impact strength and increased dimensional stability would be very desirable modifications to nylon 6. One approach to modifying the properties of nylon 6 would be to synthesize nylon 6 copolymers. Nylon 6 is made commercially from the anionic polymerization of caprolactam to yield the structure shown below.

$$\left(\begin{array}{cc} \overset{\displaystyle H}{\underset{\displaystyle |}{}} & \overset{\displaystyle O}{\underset{\displaystyle \parallel}{}} \\ N(CH_2)_5 & C \end{array} \right)_n$$

To be compatible in a RIM process, the comonomer would then have to polymerize via an anionic reaction as well. Fortunately, the lactams (cyclic amides) form a family of anionically polymerizable molecules, including γ-pyrrolidinone (C_4), caprolactam (C_6), capryllactam (C_8), and laurolactam (C_{12}). All of the above monomers have been successfully copolymerized with caprolactam.[4-6] In all cases, the T_g's of the copolymers were lower because of the disruption of the hydrogen bonding of the chains. Unfortunately, the T_m's of the respective copolymers were lowered as well.

There are several prior studies on the preparation and characterization of the nylon 612 copolymer series in the literature. The work by Schirawski[6] studied the kinetics of the caprolactam and laurolactam copolymerization to form nylon 612 copolymers. Papers by Frunze et al.[7] and Godovskii et al.[8] were concerned with crystallinity as determined by X-ray and optical microscopy techniques and by thermal methods, respectively, of cast nylon 612 copolymers of various copolymer ratios. More extensive studies of the thermal and mechanical properties of the cast nylon 612 copolymer series were reported by Simunkova et al.[9] and later by Kehayoglou[10] and Goodman.[11] However, these authors used extraction procedures to remove unreacted monomers from the copolymers prior to thermal and mechanical testing, and the mechanical testing by Goodman and Kehayoglou was performed on compression molded samples.[11] These samples then were not "as molded" as would be found for parts made by a RIM process. Kubota and Nowell[5] used "as-molded" samples for their work, but only examined copolymers containing less than 30 mol% laurolactam.

The purpose of the present investigation was to expand the study of the "as-molded" nylon 612 copolymers to include copolymers containing high levels of laurolactam. Furthermore, reliable values for the physical properties of "as-molded" materials were desired. The T_g, T_m, impact strength, and water absorption as well as the coefficient of linear thermal expansion (CLTE) and percent crystallinity for nylon 612 copolymers were obtained.

EXPERIMENTAL

Casting of Plaques

In general, approximately 200 g of monomer was reacted with 2 mol% sodium hydride (NaH) and 1 mol% cyclohexyl isocyanate (CI). The monomer ratios C/L were: 100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70,

and 20/80. The reactions involving the higher concentrations of laurolactam presented some problems due to the high reactivity coupled with the high temperature needed to melt the laurolactam. The 30/70 and 20/80 compositions were made using 1.5 and 0.75 mol% (NaH and CI), respectively. All attempts to cast plaques at the 10/90 ratio failed.

The initiator (NaH) and activator (CI) were added to the equally divided monomers in 250- and 500-mL glass jars, respectively, and kept in an argon atmosphere. The jars were then immersed in a 145°C oil bath until 140°C was reached. Using this technique, the NaH reacted with the melting lactam monomers at a reasonable rate, and the resulting reactant solution did not show the extensive oxidation that can characterize such reactions.

Upon reaching 140°C, the solutions were rapidly combined, stirred, and poured into plaque molds (22 × 20 × 0.3 cm) preheated to 145°C and placed in an oven set at 145°C for 15–20 min. After removal from the oven, the mold was allowed to cool to room temperature before removal of the plaque from the mold. All plaques were immediately placed in desiccator bags to insure dryness. All analyses were performed on the as-molded samples except where noted.

Thermal Analysis

A DuPont 990 thermal analyzer with a differential scanning calorimeter (DSC) cell was used to establish T_g, T_m, and percent crystallinity for all nylon samples. The polymer samples were frozen in liquid nitrogen (N_2) and shattered into small particle sizes for the analysis. Approximately 10 mg samples of polymer were placed in hermetically sealed pans. An empty hermetically sealed pan was used as a reference.

Determination of Glass Transition and Melting Temperatures. Samples were heated from $-50°C$ through their melt at a programmed rate of $10°C/min$. This yielded the T_g of the crystalline polymer (T_{gc}) and the crystalline T_m. Once above the melt temperature, the samples were rapidly cooled by dropping them into liquid N_2, but they were again warmed to $> 0°C$ to allow them to be reinserted into the DSC cell. The samples were again cooled and then heated from $-50°C$ through their previously established melt. This second cycle yielded the T_g of the amorphous polymer (T_{ga}), crystallization exotherm, and, in most cases, the crystalline T_m.

Determination of Crystallinity by DSC. Indium was used to calibrate the instrument as well as obtain a calibration coefficient (E). The weight of polymer samples prepared as described above was determined to within 0.01 mg. The experiment was conducted from 30°C below to 50°C above the previously established melting temperature at a rate of $10°C/min$. All experiments were done in time base mode.

X-Ray Analysis

X-ray analysis to determine percent crystallinity was performed on nylon 6, nylon 12, and nylon 612 copolymers using a Siemen Allis D-500 X-ray diffractometer. The samples were prepared for analysis by obtaining two adjacent samples (approximately 25 × 25 × 3 mm) of each polymer from a

cast plaque. Zero crystallinity standards were made by placing one of the samples of each polymer on aluminum foil and heating it in an inert atmosphere in a vacuum oven at approximately 30°C above the polymer's T_m. After 30 min at that temperature the samples were rapidly removed from the oven and dropped into liquid N_2. These samples were then kept in liquid N_2 until the time of analysis. Unfortunately, all samples except nylon 612 compositions 60/40, 50/50, and 40/60 showed residual crystallinity. However, the amorphous halos of all samples were very similar so the zero crystallinity sample of the 50/50 copolymer was used as a reference for all samples. Strip chart X-ray diffractograms were performed on each sample, and the integration and subsequent analysis were done manually.

Coefficient of Linear Thermal Expansion

CLTE measurements for all polymers were made using a 313 Unitherm automatic dilatometer on bars approximately $75 \times 25 \times 3$ mm measured accurately to 0.01 mm. Measurements were made over the temperature range of 20–70°C for dry samples or 20–50°C for samples equilibrated at 50°C and 50% relative humidity. The CLTE readings were printed at 10°C intervals with a temperature equilibration time of 30 min between measurements.

Mechanical Testing

Plaques of nylon 6 and nylon 612 were machined into test samples using a Tensile-Kut® router. Tensile test specimens were type I according to ASTM D 638-82. Data were obtained for tensile modulus, tensile strength, and elongation of each copolymer in the series. These tests were run on an Instron Model 1125 universal testing machine. Impact resistance on notched samples (63.5 × 12.7 × 3.17 mm) was measured using a Tinius Olsen with a cantilever beam. Test procedures and specimen size were according to ASTM D 256-81, method A.

Water Absorption Tests

Water absorption tests were performed on the nylons with the dimensional stability of the nylons being monitroed in some cases. The method used was the ASTM 570-81 long term immersion procedure. The specimens were conditioned at 110°C for 24 h and cooled in a desiccator. The dimensions of each specimen were measured and weighed analytically. They were then immersed in water. Consecutive weighings were taken at 24 h, 1 week, and then every 2 weeks thereafter until the weight increase in a 2-week period averaged less than 1.0% of the total weight increase. Upon reaching an equilibrium saturated weight (approximately 11 weeks), the samples were reconditioned at the same temperature and time used in the original conditioning. This reconditioning accounts for any water-soluble material that might have been extracted during immersion. The samples were cooled in a desiccator and immediately reweighed. The dimensions were remeasured. The percent water absorbed was calculated, the dimensional changes were recorded, and any observations were noted.

Nylon copolymer caprolactam/laurolactam	T_m (°C ± 3°C)	$1/T_m$ (×10⁻³ K⁻¹)	T_{gc}[a] (°C ± 2°C)	T_{ga}[b] (°C ± 2°C)
100/0	225	2.008	60	46
90/10	205	2.092	52	36
80/20	190	2.160	43	29
70/30	168	2.268	28	24
60/40	140	2.421	21	23
50/50	135	2.451	18	20
40/60	137	2.440	22	18
30/70	151	2.358	30	18
20/80	162	2.300	35	20
0/100	182	2.198	37	—

[a] Glass transition temperature for crystalline nylon.
[b] Glass transition temperature for amorphous nylon.

RESULTS AND DISCUSSION

Glass Transition and Melting Temperatures of Nylon 612 Copolymers

The thermal properties for nylon 6, nylon 12, and the nylon 612 copolymers of various composition ratios are shown in Table I. A plot of $1/T_m$ vs. the ln of the copolymer composition yields, as shown in Figure 1, two intersecting lines. This is in agreement with Flory's theoretical predictions[12] for crystalline polymers containing comonomers and is superimposable with Kehayoglou's[10] results for a similar nylon 612 copolymer system. When caprolactam was the monomer in excess, the copolymer had the melting characteristics of nylon 6 with varying degrees of comonomers, and when laurolactam was in excess, then the melting characteristics were those of nylon 12 with comonomers. An exception was the 50/50 copolymer which had a higher T_m than would have been predicted based on either homopolymer with 50% comonomers.

Both T_{gc}'s (glass transition temperatures of the crystalline nylon) and T_{ga}'s (glass transition temperatures of the amorphous nylon) were determined for all samples and are shown in Table I. The T_{ga}'s deviated significantly from the T_{gc}'s for copolymers containing the higher degrees of crystallinity (Table II). Whereas the T_{gc}'s for the copolymer yielded a minimum at the 50/50 ratio when plotted as a function of mole percent, the T_{ga}'s (Fig. 2) yielded a gradual decrease to the 30/70 ratio copolymer. This data is in agreement with the theoretical predictions for amorphous copolymers.[13] Thus, increasing crystallinity increases the apparent T_g of nylon copolymers. This tendency has been shown for other semicrystalline polymers.[14]

Figure 3 shows the second cycle DSC thermograms for the homopolymer and copolymers. The rapid drop in T_g (from T_{gc} to T_{ga}) for the copolymers containing predominantly nylon 6 (100/0 to 70/30) is quite obvious. It is also interesting to note that the recrystallization exotherm occurs at lower temperatures for the copolymers rich in nylon 6 and nylon 12 rather than for the
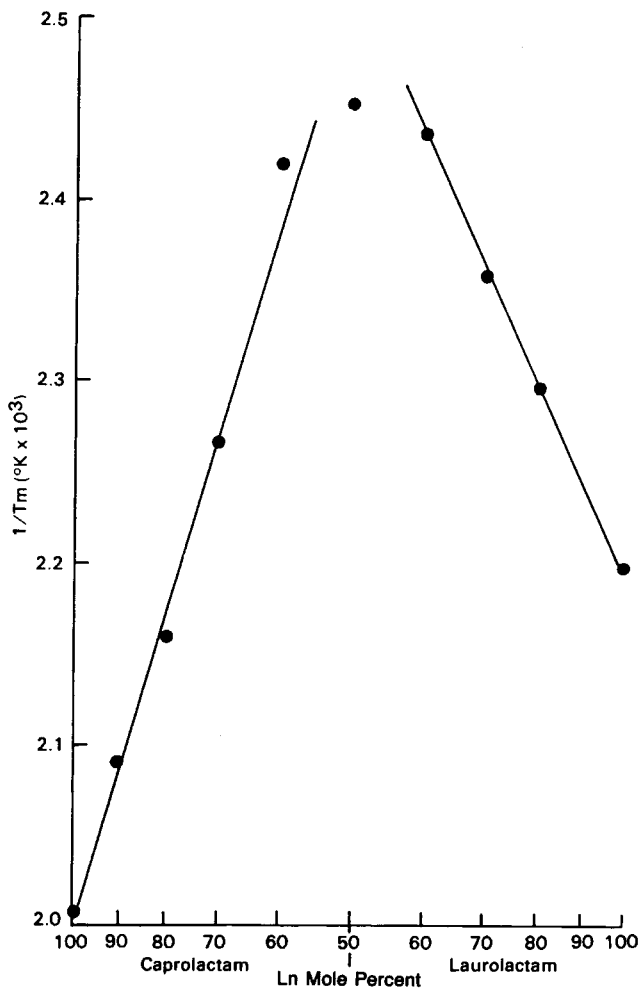
Fig. 1. The effect of composition on the melting temperature for the nylon 612 copolymer series.

intermediate values, aside from also being much larger. In fact, for the 30/70 and 20/80 copolymers, the recrystallization may be interfering with the determination of T_{ga}, and for nylon 12 we were unable to obtain a recrystallization exotherm or a T_g for the amorphous sample. Yet a crystalline melt was observed. Either the recrystallization rate was greater than the rate of cooling (quenching) from the melt, or more likely, the temperature at which recrystallization occurred was lower than 10°C. (Samples were allowed to warm to > 0°C before reinsertion into the DSC cell.) Both the amorphous T_g and the recrystallization exotherm for the nylon 6 sample are in close agreement with previously published values.[15]

DSC Determination of Crystallinity

The area of each DSC thermogram associated with the crystalline melt was measured with a planimeter. The calibration coefficient (E) was calculated

TABLE II
Percent Crystallinity as Determined by DSC and X-Ray

Nylon copolymer caprolactam/ laurolactam	Avg ΔH_f (mJ/mg)	Avg ΔH_f[a] 100% crystalline (mJ/mg)	Avg crystallinity by DSC (%)	Avg crystallinity by X-ray (%)
100/0	91.12	190.79	48	47
90/10	64.68	194.18	33	54
80/20	36.94	197.57	19	37
70/30[b]	—	—	—	12
60/40	23.24	204.34	11	12
50/50	22.95	207.74	11	15
40/60	25.54	211.13	12	10
30/70	35.37	214.52	16	16
20/80	42.03	217.90	19	19
0/100	64.99	224.68	29	31

[a] Based on ΔH_f 100% nylon 6, 190.79 mJ/mg[11] and nylon 12, 224.68 mJ/mg.[11]
[b] Unable to determine crystallinity by the DSC method.

using indium as the standard. The equation used for calculating the heat of fusion for each sample is

$$\Delta H_f = A[(60 \text{ s/min})(B)(E)(\Delta q)]/m$$

where ΔH_f = heat of fusion of sample (mJ/mg), m = mass of sample (mg), A = area of endotherm (cm^2), B = time base setting (min/cm), Δq = sensitivity range (mV/cm), and E = calibration coefficient (mW/mV).

By ratioing the heat of fusion to a standard heat of fusion for a theoretical 100% crystalline polymer, the percent crystallinity was determined. The values used for the 100% crystalline copolymers were calculated based on the contributions of the mole percent of each homopolymer in the respective copolymer:

$$\% \text{ crystallinity} = \frac{\Delta H_f \text{ (sample [calculated])} \times 100\%}{\Delta H_f \text{ (100\% crystallinity [calculated])}}$$

The average area of the melting endotherm, the average weight of each copolymer sample, the average ΔH_f calculated for each sample, the ΔH_f for 100% crystalline material for each polymer, and the percent crystallinity as determined for each polymer by DSC are presented in Table II. Figure 4 shows a plot of percent crystallinity vs. ln mol% composition. This plot yields a minimum at the 60/40 and 50/50 copolymer ratios. However, the plot is skewed toward higher caprolactam content. This implies a dependence on weight percent rather than mole percent, but percent crystallinity did not correlate well with ln weight percent. It is possible that the best means of expressing the data would be as a function of volume percent,[16] but a determination of volume percent of each comonomer at all copolymer ratios and percent crystallinity is beyond the scope of this work and, therefore, has not been done.
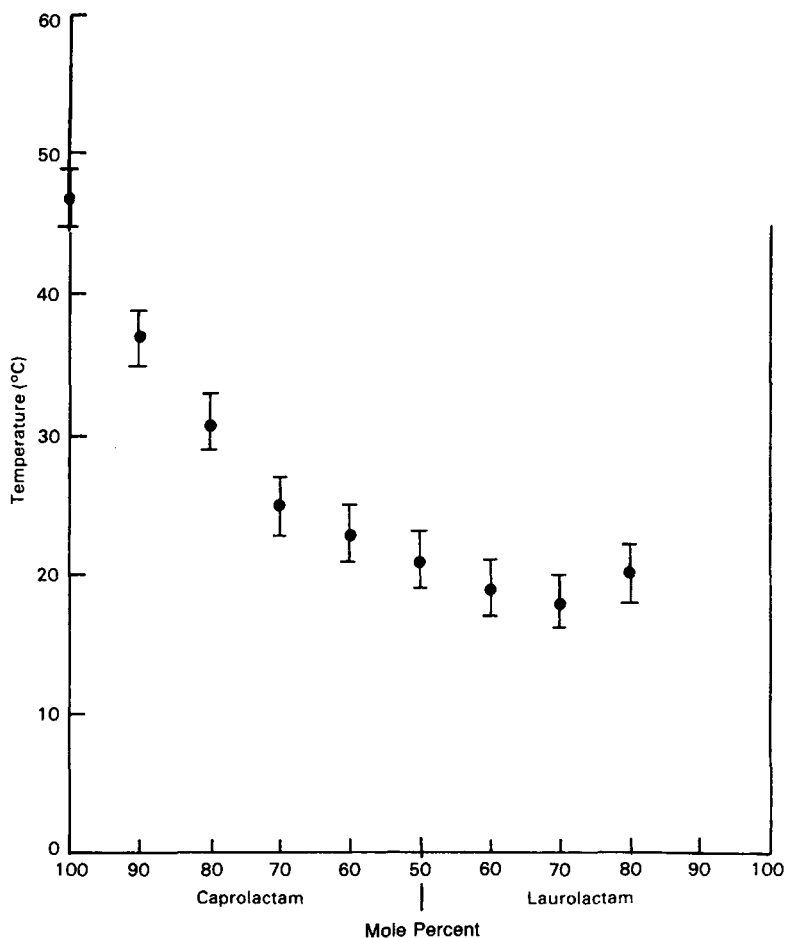
Fig. 2. The effect of composition on the $T_{g\alpha}$ of the nylon 612 copolymer series.

X-Ray Determination of Crystallinity

The procedure for the determination of crystallinity for the copolymers involved defining two specific points (theta values) on either side of the diffraction band, constructing a baseline between the two points, and employing a planimeter for the integration. Two methods of calculation were used depending upon whether the crystallinity of a sample could be removed by annealing. For the successfully annealed (removal of all crystallinity) samples 60/40, 50/50, 40/60, and 30/70, two theta values outside of the band region were chosen to determine a scaling factor. This was achieved by ratioing the crystalline data to the amorphous data at those two particular theta values and averaging these to yield a K value. This K value was then multiplied by the area of the amorphous band and subtracted from the area of the crystalline band. This value, divided by the area of the crystalline band, then yielded a percent crystallinity. For those samples in which the annealing could not be accomplished adequately, a visual estimate of the amorphous band was made and the same procedure as above was performed neglecting the scaling factor. The percent crystallinity determined by the X-ray method for all samples is shown in Table II.
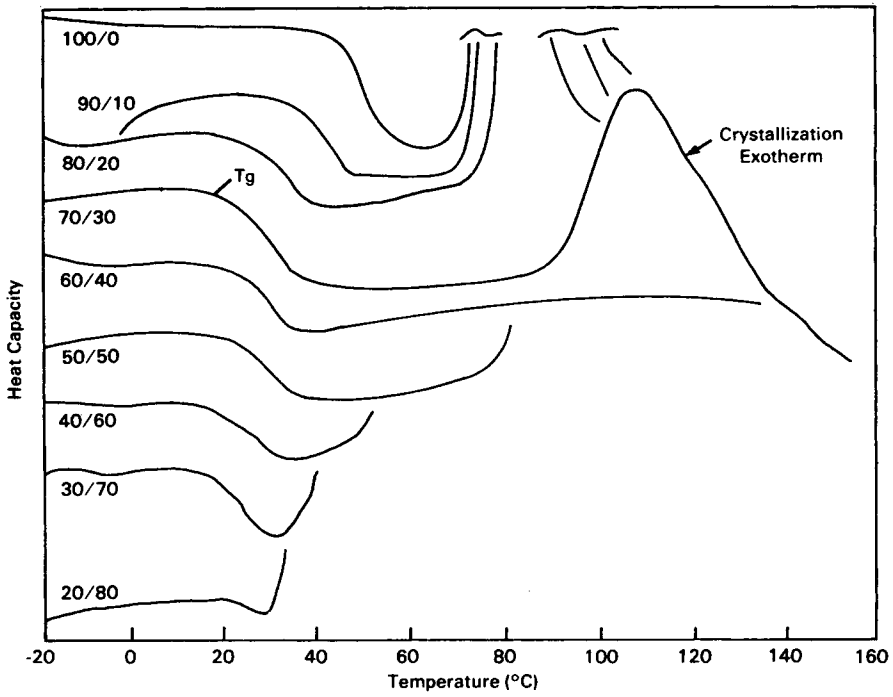
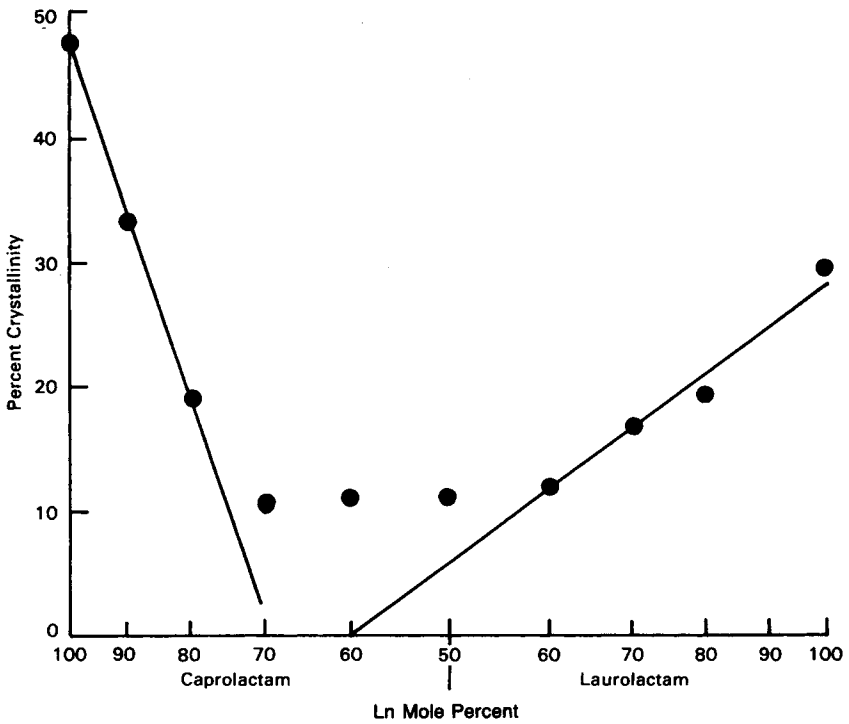Fig. 3.   DSC thermograms of the amorphous nylon 612 copolymer series.

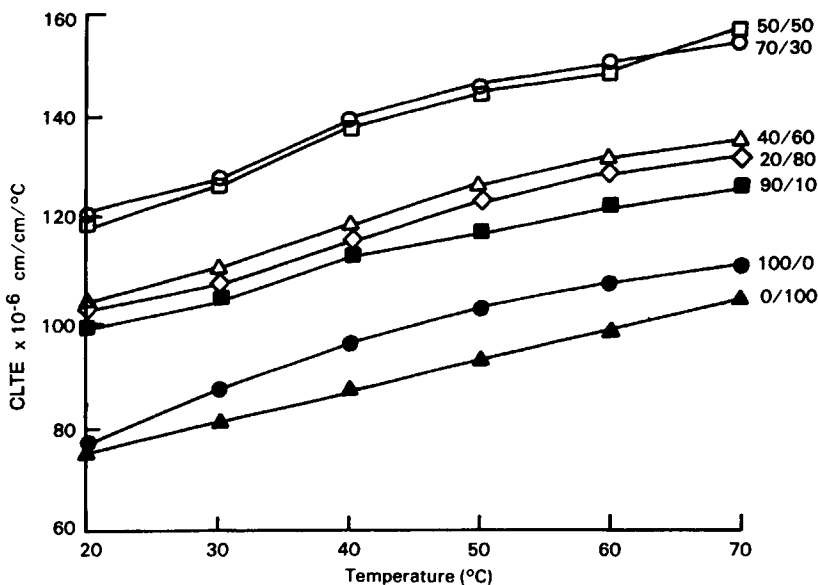Fig. 4.   The effect of composition on crystallinity for the nylon 612 copolymer series.

Fig. 5. Coefficient of thermal expansion measurements on dried samples of the nylon copolymer series.

There is excellent agreement between the X-ray and DSC estimates of crystallinity for all of the copolymers except the 90/10 and 80/20 ratios. The values that had the greatest differences were the samples where an accurate estimate of the contribution of the amorphous band was the most difficult to obtain. One is able to understand why zero crystallinity standards were so difficult to obtain by examining Figure 3. The DSC scans of all the copolymers except for the 60/40 copolymer showed large recrystallization exotherms at low temperatures, indicating the ability of the samples to recrystallize at rather low temperatures. The samples used for the X-ray determination were rather large and were therefore not instantaneously taken to $-196°C$ upon quenching in liquid N_2. Crystallinity would have an opportunity to develop. The 60/40 and 50/50 copolymers, on the other hand, had higher recrystallization temperatures and developed the least crystallinity upon quenching.

Coefficient of Linear Thermal Expansion

A plot of CLTE values for the dry nylon polymers is shown in Figure 5. The rate of expansion for all samples continued to increase over the temperature range of 20–70°C. The increase was greatest between 20 and 40°C or at approximately the T_{gc} of the polymer. The highly crystalline copolymers had lower CLTE values over the entire temperature range. The maximum expansion was observed for the samples of the copolymers of 70/30 to 50/50 mole ratios. Figure 6 shows the plots of CLTEs for samples conditioned at 50% relative humidity. The most interesting feature is that the initial values are higher than those for the dry samples, but the rate of increase in the CLTE is much less. The 60/40 copolymer showed the greatest values for CLTE at all temperatures. The plot of CLTE at 50°C vs. ln mole percent for dry and
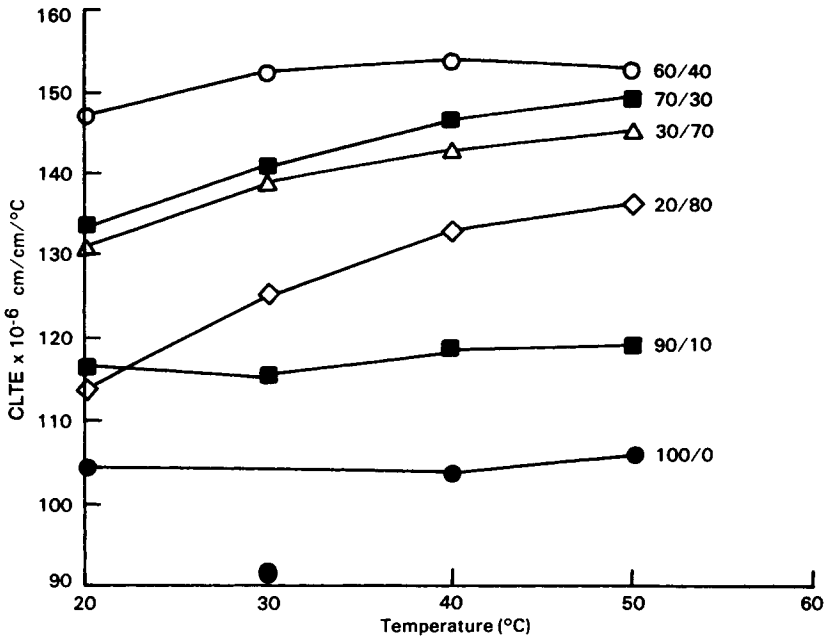
Fig. 6. Coefficient of thermal expansion measurements on conditioned samples of the nylon copolymer series.

conditioned samples shown in Figure 7 is very similar to the plot of percent crystallinity vs. ln mole percent shown previously in Figure 4. Again this data might better be explained by the effects of volume percent.

Water Absorption

Water absorption data was taken for selected polymer samples. Figure 8 shows the effect of copolymer ratios on the amount of water absorbed. On the graph, the literature values for nylon 6 and nylon 12 are given as reference points.[17] There was a decrease in water absorption over the range of synthesized copolymer compositions from nylon 6 to nylon 12 homopolymers. This was expected because with increasing laurolactam content in the copolymers there was a corresponding decrease in the number of water absorbing amide functions. With fewer amide functions less water was absorbed. However, all intermediate copolymer compositions absorbed more water than expected based on the literature values. A possible explanation for this data is based on the crystallinity of the copolymers. As shown in Figure 4, the intermediate nylon 612 compositions had low levels of crystallinity and, therefore, a large amorphous content. Since water can only be absorbed into the amorphous areas, and the intermediate nylon 612 compositions had a higher amorphous content than the homopolymers, then those compositions absorbed a larger amount of water than predicted.

Tensile and Impact Properties

Tensile strength, tensile modulus, percent elongation, and impact strength were obtained for nylon 6 and nylon 612 copolymers. These values are
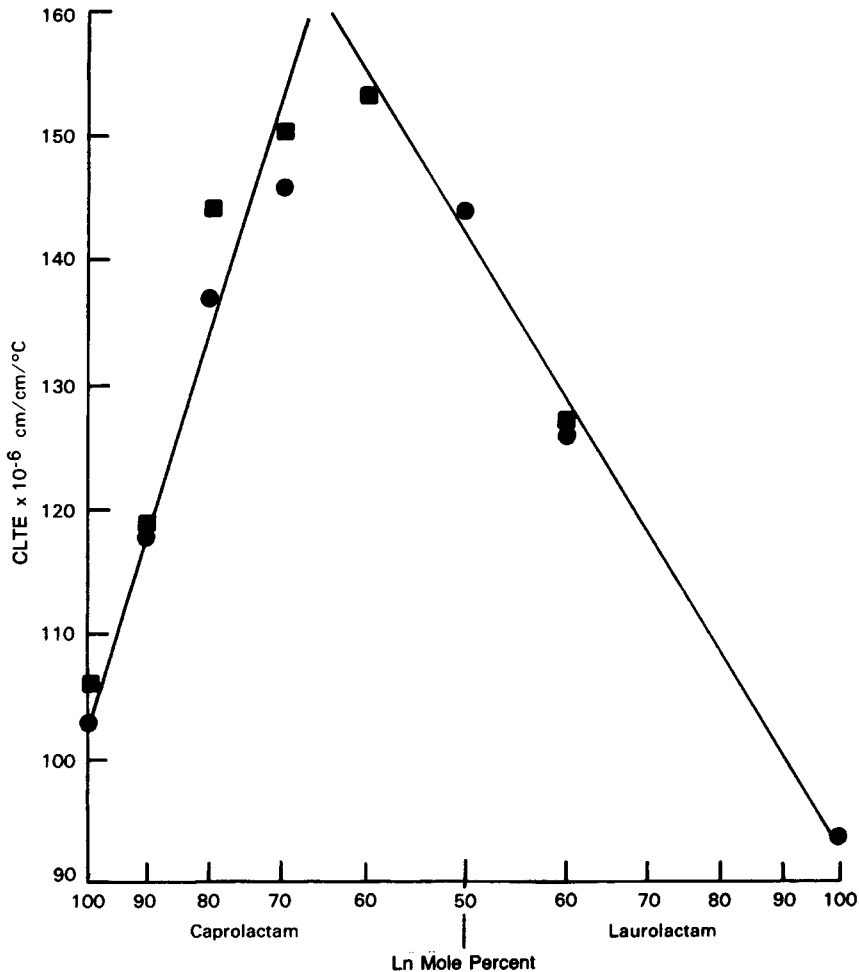
Fig. 7. The effect of composition on the coefficient of thermal expansion for dry (●) and conditioned [50% RH (■)] samples of the nylon 612 copolymer series.

presented in Table III. All values were obtained from "as-molded" polymer plaques.

The tensile strength of nylon 6 (89 MPa) was lowered to 66 MPa by the addition of 10 mol% laurolactam. Further addition of laurolactam reduced the tensile strength to 47 ± 9 MPa for all nylon 612 copolymers. The tensile strength values obtained for all these samples, which were cast, were well below the literature values for injection molded nylon 6 (125 MPa).[17]

The tensile modulus of the copolymers was at a minimum of 0.45 GPa for the 60/40 nylon 612 copolymer. Less laurolactam resulted in a rapid increase in tensile modulus to 3.2 GPa for nylon 6, while more laurolactam yielded a slower increase in modulus to 0.72 for the 30/70 nylon 612 copolymer. The percent elongation increased dramatically from 21% for nylon 6 to > 500% for the 70/30, 60/40, 50/50, and 40/60 nylon 612 copolymers. Further increases in laurolactam decreased the percent elongation of the 30/70 copolymer to 270%.
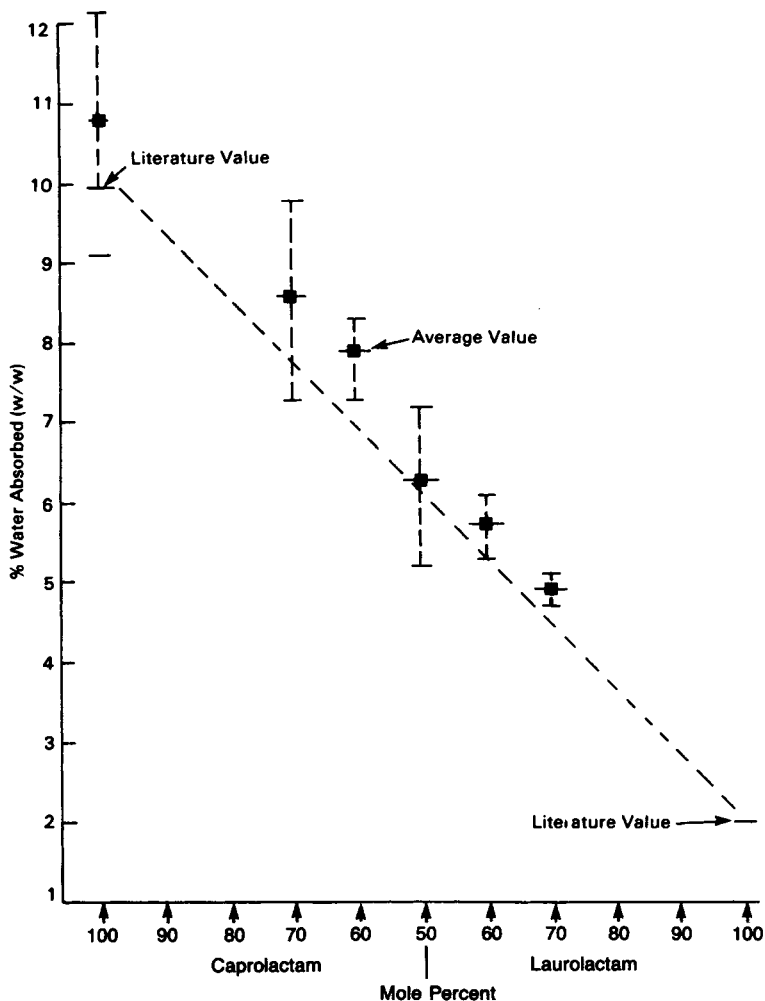
Fig. 8. Water absorption data for nylon 612 copolymers.

TABLE III
Tensile and Impact Properties

Nylon copolymer ratio	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation (%)	Impact strength (J/m)
100/0	89	3.2	21	20
90/10	66	2.7	60	55
80/20	38	1.8	160	110
70/30	51	0.63	580	700
60/40	53	0.45	530	No break
50/50	50	0.50	560	No break
40/60	43	0.55	500	No break
30/70	49	0.72	270	350
20/80	—	—	—	160
0/100	—	—	—	60

The changes in impact strength within the series were also large. The values ranged from 20 J/m for the nylon 6 sample to nonbreaking specimens for the 60/40, 50/50, and 40/60 nylon 612 samples. Again, further increases in laurolactam content caused decreases in impact strength with the 20/80 sample having an impact strength of 160 J/m.

Previously, it was stated that as the T_{gc} of the copolymer decreased, the ability of the sample to absorb impact should increase. That reasoning implied a correlation between T_{gc} and impact strength. Initially this was the case. The T_{gc} was 60°C and the impact strength was 20 J/m for the 100/0 nylon. The T_{gc} decreased 8°C and the impact strength doubled to 55 J/m for the 90/10 copolymer followed by a 9°C decrease in T_{gc} and again a doubling of the impact strength to 110 J/m for the 80/20 copolymer. However, the T_{gc} for the 70/30 copolymer decreased 15°C, while the impact strength jumped to 700 J/m. Further increases in laurolactam content, up to 30/70 copolymer, resulted in samples which did not break upon impact. The 30/70 copolymer had a T_{gc} of 30°C and an impact strength of 350 J/m, while the 20/80 copolymer had a T_{gc} of 35°C and an impact strength of 160 J/m. However, only a 2°C increase in T_{gc} for the 0/100 material resulted in a reduction in impact strength to 60 J/m. There was, therefore, not a good correlation between the T_{gc} and the impact strength of the copolymers.

There were some indications of the reasons for the large change in impact strength found in cast samples which were then compression molded. The 70/30 sample, when compression-molded, went from opaque to transparent and did not break upon impact. The 50/50 and 40/60 copolymers, on the other hand, became more opaque on compression molding, and their impact values were found to be 90 and 70 J/m, respectively. Furthermore, one 40/60 sample displayed some interesting characteristics after compression molding. Small areas within the plaque were opaque, while the majority of the plaque was transparent. Impact bars were cut from the opaque areas and an average impact value of 90 J/m was found. Yet the area immediately surrounding the opaque area yielded a no break sample.

Since these experiments were performed similarly, it was very difficult to explain the discrepancy. However, an explanation was found when the data was plotted as ln percent crystallinity vs. ln impact for cast samples as shown in Figure 9. Along this line a decrease from 20% crystallinity to 15% crystallinity caused an increase from 300 to 500 J/m in impact strength and a decrease from 15 to 10% crystallinity caused an increase from 500 to 1500 J/m in impact strength. Thus, small changes in crystallinity in this range can result in large changes in impact strength. This trend has already been shown for the Young's modulus of nylon 612 copolymers,[11] and increases in crystallinity have been shown to lower impact values for other polyamides.[18] In view of these factors, the behavior of the nylon 612 copolymer system can be understood.
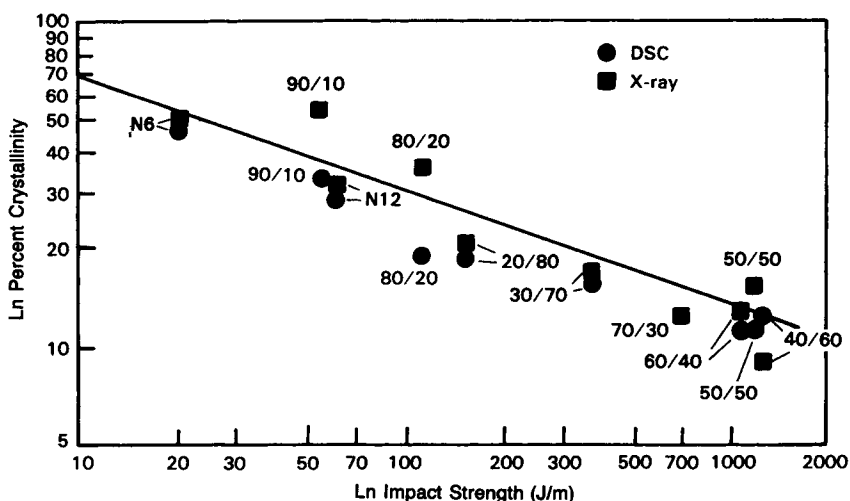
Fig. 9. Correlation of crystallinity with impact strength for the nylon 612 copolymer series: (●) DSC; (■) X-ray.

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