

## Thermal Behavior of Nylon 6 Copolyamides Containing Aromatic Rings

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### Synopsis

The thermal behavior of terpolymers of caprolactam (CL) and of hexamethylenediammonium isophthalate (IH) and terephthalate (TH) has been studied in a wide range of compositions by differential thermal analysis. It has been found that either amorphous or crystalline polymers having different crystallization rates can be obtained by changing the composition. The dependence of melting points and glass transition temperatures on the composition has been investigated. The dependence of  $T_g$  on the composition for the copolymers CL-IH, IH-TH, and CL-TH has been described by means of the Gordon-Taylor equation. It has been found that this equation fits the experimental data for the IH-TH system only if a parameter which takes into account interactions between the monomeric units is introduced. A ternary iso- $T_g$  map has been obtained through statistical analysis. The influence of the chain stiffness and bulkiness of the monomers on the glass transition temperature is discussed.

### INTRODUCTION

The copolymerization of  $\epsilon$ -caprolactam or of hexamethylenediammonium adipate with amino acids, diacid salts, and diamines containing aromatic or cycloalkane rings has been studied by some authors<sup>1-10</sup> in order to obtain isomorphous copolyamides,<sup>1-6</sup> to increase elasticity modulus, recovery properties, crease resistance, and moisture regain in respect to nylon 6 and 6,6 and to fulfill the advanced demands for tyre cords, carpet yarns, and silk-like fibers.<sup>7-10</sup>

The gradual introduction of the *p*-phenylene group brings about a noticeable increase in melting point; the polymers cannot be prepared and processed by conventional methods owing to thermal decomposition.

In the present work, the thermal properties of the terpolymers of  $\epsilon$ -caprolactam (CL), hexamethylenediammonium terephthalate (TH), and hexamethylenediammonium isophthalate (IH) have been studied. It has been thought that the presence of a comonomer containing a ring unsymmetrically substituted would decrease both crystallinity and melting point without decreasing the glass transition temperature. Moreover, it must be pointed out that very little is known on the composition dependence of  $T_g$  for ternary systems.

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## EXPERIMENTAL

### Materials

**Caprolactam.** Montecatini Edison S.p.A. commercial fiber-grade product.

**Hexamethylenediamine.** A Rhodiatocce commercial product was used; it was rectified before use.

**Terephthalic Acid.** Montecatini Edison S.p.A. commercial fiber-grade product.

**Isophthalic Acid.** Amoco commercial product, having 95% purity.

**Hexamethylenediammonium Terephthalate (TH salt).** The salt was prepared by dissolving equimolecular amounts of acid and amine in water at 100°C. The solubility in water of the salt was found to be 63% by weight at 100°C and 11% at 20°C. Purification has been carried out by means of several crystallizations from water, and the purity (ca. 100%) has been checked by potentiometric titration of the amine content. The APHA value<sup>11</sup> of the concentrated salt solution (30%) was equal to or less than 5.

**Hexamethylenediammonium Isophthalate (IH Salt).** IH salt was prepared according to the procedure used for the TH salt. Owing to the high solubility of the salt in water, a mixture of CH<sub>3</sub>OH/H<sub>2</sub>O (70/30 by volume) was used; in such a medium the solubility of the salt is about 130 g in 100 ml at 65°C. The salt was purified by crystallization in the presence of charcoal; several crystallizations were required in order to obtain a high-purity product.

### Polymerization

The monomer mixture, 25 g, dry-blended in a mortar, and 5 ml water were charged to a 0.1-liter autoclave heated electrically. The first step of the polymerization was carried out under nitrogen atmosphere at 260°C and under a pressure of 5 kg/cm<sup>2</sup> for 3 hr. The pressure was released and polymerization continued for additional 2 hr under reduced pressure (500 torr). Previous experiments showed that this mode of operation provides a final random copolymer or terpolymer.

Fifty-nine samples with different compositions were prepared. The polymers were extracted with water in a Soxhlet apparatus in order to remove oligomers and free monomers. Measurements of reduced viscosity (1%) in sulfuric acid (96%) showed that the materials were of high molecular weight.

### DTA Measurements

DTA curves were obtained by means of a du Pont 900 differential thermal analyzer, and the DSC cell was used for the measurements. The samples were dried at 100°C under vacuum for 16 hr. The previous thermal history was erased by heating the samples, at a rate of 15°C/min, up to 50–60°C

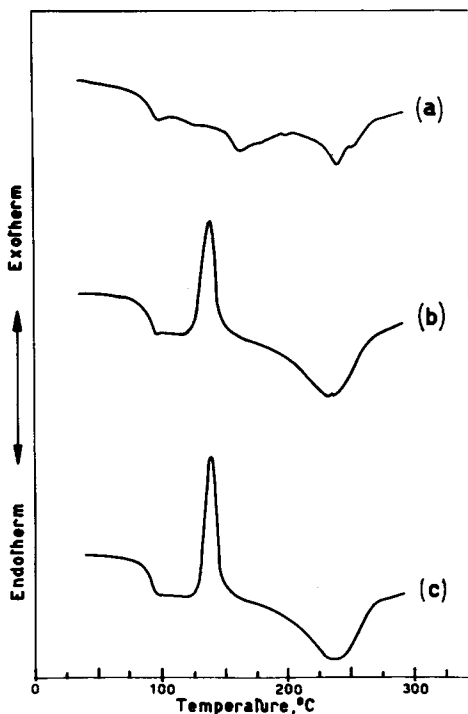


Fig. 1. Influence of thermal history on DTA results for the copolymer CL = 40, TH = 60: (a) 1st run, polymer as received; (b) 2nd run, cooled at 30°C/min and heated at 15°C/min; (c) 3rd run, experimental conditions as for 2nd run.

above their melting points, when decomposition did not occur. The samples were then cooled at about 30°C/min to room temperature. Further runs were then performed at 15°C/min.

Such a procedure was chosen because the DTA curve determined during the first run often shows very complex and nonreproducible behavior; results obtained from the second DTA run are quite reproducible (see Fig. 1). The DTA data which will be discussed were obtained in the second run, unless otherwise specified.

### RESULTS AND DISCUSSION

The DTA curves (Fig. 2) show that composition influences strongly the ability to crystallize and the crystallization rate of the terpolymers. It must be pointed out that most of the polymers appeared to be crystalline during the first DTA run; however, the supercooled melt in some cases crystallizes with great difficulty. It has been practically impossible in such cases to reobtain crystalline samples even though very long annealing periods at temperatures between  $T_m$  and  $T_g$  or very slow cooling rates were used.

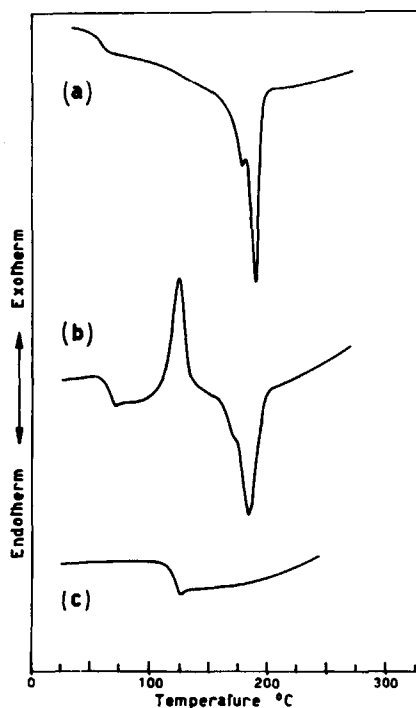


Fig. 2. Typical thermograms for (a) crystalline (CL = 90, TH = 10); (b) crystallizable (CL = 80, TH = 20); (c) amorphous terpolymers (CL = 10, IH = 90). Heating rate, 15°C/min.

The overall influence of composition on the ability to crystallize and on the crystallization rate is schematically shown in Figure 3 according to the following rough classification. The polymers were considered crystalline when the DTA curve showed only the melting peak and, with some difficulty, the glass transition temperature (Fig. 2a). Some other polymers, for which the cooling rate used in the first run is too high to allow crystallization, showed a thermal behavior like that reported in Figure 2b; the glass transition temperature  $T_g$ , the exotherm crystallization peak, and the melting peak were observed. These polymers were classified as crystallizable. Other samples displayed a completely amorphous behavior, like that shown in Figure 2c, where only the glass transition process can be detected.

On this basis, it is clear that such a classification is dependent on the experimental conditions used; in particular, the boundary between crystalline and crystallizable polymers can be shifted by changing the cooling rate. Figure 3 shows that amorphous terpolyamides may be more easily obtained with the introduction of the IH comonomer. All the polymers, lying on the CL-TH side, can indeed crystallize, but the crystallization rate and the maximum attainable crystallinity are dependent on the composition of the copolymer. The 50/50 by weight CL-TH copolymer

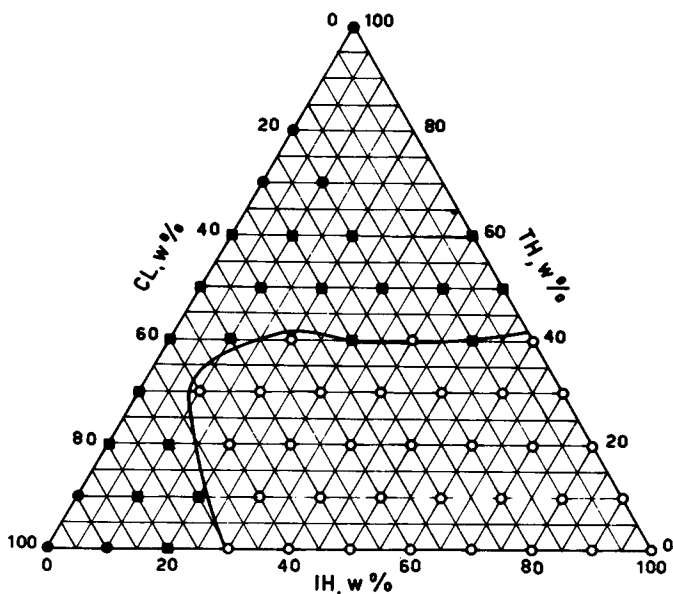


Fig. 3. Ternary diagram of the thermal behavior of CL-HI-TH system: (●) crystalline polymers; (■) crystallizable polymers; (O) amorphous polymers. Region of amorphous polymers is enclosed by continuous line.

shows the minimum crystallization rate, according to the ratio of the areas under the crystallization and the melting peaks.

### Melting Points

Sharp and well-defined melting peaks were observed for caprolactam-rich polymers; samples having a high TH content generally show a very broad melting range which often merges with the decomposition exotherm; in this case, the melting temperature could not be measured with sufficient accuracy. For these reasons the discussion will refer only to a restricted range of compositions. For the CL-TH copolymers, the experimental data as a function of TH content are reported in Figure 4. Good agreement between these results and literature data<sup>7</sup> has been found.

A minimum is evident at a TH molar fraction of 0.18 (31.5% by weight). Such a behavior is well known for other copolymeric systems,<sup>4,12</sup> and this could indicate that the TH unit is not isomorphous with the CL unit. This result could be confirmed by the trend of the DTA curves; the melting peaks, which remain sharp from pure polycaprolactam up to copolymers having a TH molar fraction of 0.18, become broad for TH contents above 0.235 on a molar basis (40% by weight). However, on the basis of the work of Tranter<sup>4</sup> and considering that all the CL-TH copolymers are crystalline, it should be admitted that TH units can arrange themselves in the crystalline lattice of polycaprolactam. On the other hand, an unsymmetric unit like that of IH can hardly enter the crystal structure of

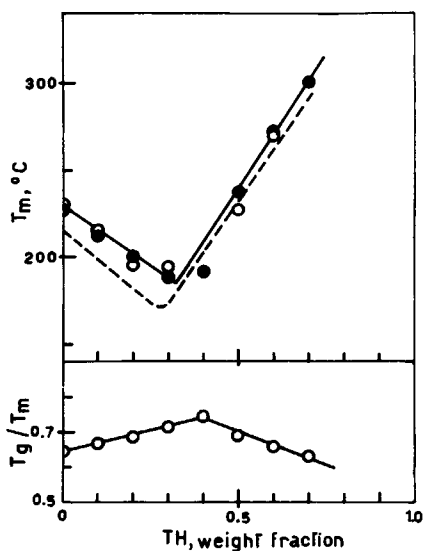


Fig. 4. Melting temperatures and  $T_g/T_m$  ratio as a function of weight fraction for CL-TH copolymers: (●) DTA; (○) heated microscope; (---) ref. 7.

nylon 6. The melting points decrease (Fig. 5), and so does the crystallinity; copolymers containing more than 30% by weight of IH are completely amorphous (the experimental melting point for the 70/30 composition could be determined only during the first DTA run). In Figures 4 and 5, the  $T_g/T_m$  ratios are also reported; this ratio is not a constant but is a function of the composition. Comparison between Figures 4 and 5 and Figure 6 indicates, in good agreement with other literature data,<sup>13,14</sup> a

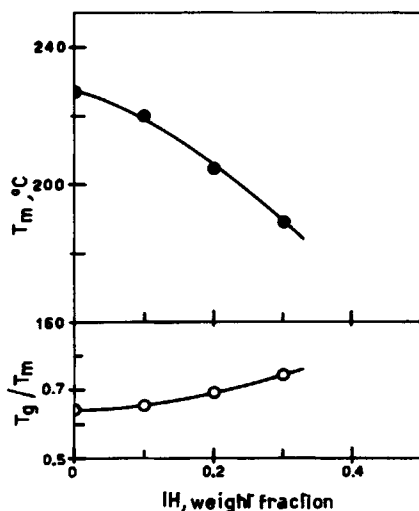


Fig. 5. Melting temperatures and  $T_g/T_m$  ratios as a function of weight fraction for CL-IH copolymers.

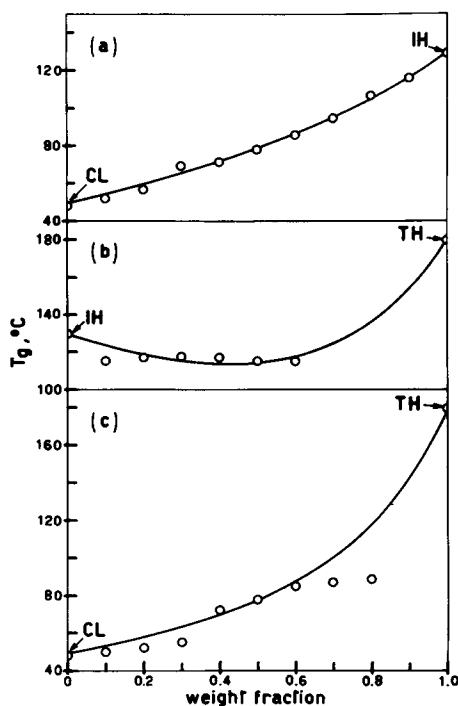


Fig. 6. Comparison between experimental data and calculated  $T_g$ -vs.- $w$ ; curves: (a) CL-TH copolymers, continuous line eq. (1); (b) IH-TH copolymers, continuous line eq. (4); (c) CL-TH copolymers, continuous line eq. (1).

poor relationship between  $T_m$  and  $T_g$  for polyamides in contrast with results generally found for other polymers.<sup>15</sup> The minimum found in  $T_m$ -versus-weight fraction curves is not reflected in a minimum in  $T_g$ -composition curves;  $T_g$  indeed varies monotonically with composition.

This means that parameters like chain stiffness, geometry, and intermolecular forces influence  $T_m$  and  $T_g$  in a quite different way. In particular, the last term, i.e., the hydrogen bonding in the case of polyamides, plays certainly a very important role in determining  $T_g$ , as shown, for example, by the constancy of  $T_g$  with increasing number of methylene units between amidic groups.<sup>14</sup>

#### Dependence of the Glass Transition Temperature on Composition

Several equations, based on different physical assumptions, have been proposed to describe the dependence of  $T_g$  on composition for random copolymeric systems.<sup>16-20</sup> Obviously, they can be easily extended to terpolymeric systems. In this work, the Gordon-Taylor (G-T)<sup>16</sup> equation will be used because of its simplicity. (It could be also pointed out that more sophisticated equations reduce to expressions formally identical to the G-T equation under some simplifying assumptions.) The influence

of the concentration on the glass transition temperature of a copolymer or a terpolymer is given by

$$\sum A_i w_i (T_g - T_{g,i}) = 0 \quad (1)$$

where  $A_i = (\beta_{l,i} - \beta_{g,i})$ ,  $\beta_{l,i}$  and  $\beta_{g,i}$  being the  $(dV/dT)$  coefficients of the liquid and glassy  $i$ th homopolymer;  $w_i$  is the weight fraction of the  $i$ th monomeric unit; and  $T_{g,i}$  is the glass transition temperature of the  $i$ th homopolymer. It must be pointed out that all the equations proposed are based on the assumption of completely amorphous materials. Inasmuch as some of the materials here studied are partially crystalline, the reliability of the results obtained by means of eq. (1) must be checked.

First of all, eq. (1) was used to fit the experimental  $T_g$  data obtained for the copolymeric systems CL-IH, IH-TH, and CL-TH. For CL-IH copolymers, a check of the applicability of the G-T equation can be done; copolymers, having  $w_{CL} < 0.8$ , display indeed a completely amorphous behavior; and if  $T_g$  is plotted against  $(T_{g,IH} - T_g)/(1 - w_{IH})$ , as suggested by Wood,<sup>17</sup> a straight line must be obtained; extrapolation to  $w_{IH} = 0$  would then give the glass transition temperature of amorphous nylon 6. Differences between extrapolated and experimental value of  $T_{g,CL}$  and any deviation of the points at low  $w_{IH}$  from a straight line should indicate an influence of the crystallinity on  $T_g$ . As shown in Figure 7, all the experimental data are well fitted by the G-T equation.  $T_{g,CL} = 49.3^\circ\text{C}$  (which compares quite well with the experimental value of  $48.7^\circ\text{C}$ ) and  $A_{IH}/A_{CL} = 0.577$  were calculated by means of the least-squares method. The correlation coefficient of the linear regression was found to be 0.9881.

The experimental data and the calculated  $T_g$ -versus- $w_{IH}$  curve are compared in Figure 6a. The conclusion that the crystallinity does not influence the glass transition of the polycaprolactam could appear to conflict with the results obtained by Takayanagi<sup>21</sup> by means of dynamic-mechanical experiments. It must be noted, however, that there is some evidence that the dynamic-mechanical  $\alpha$ -loss maximum may be attributed

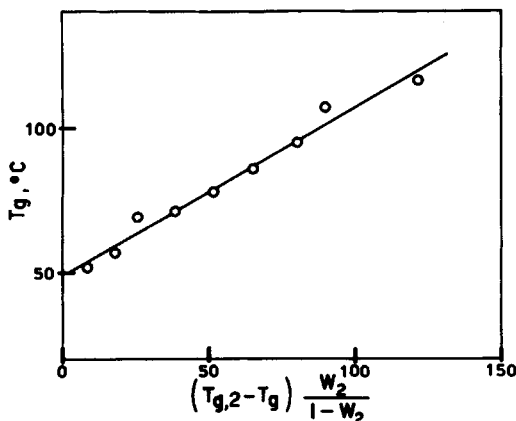


Fig. 7. Wood plot for CL-IH copolymers. Continuous line calculated by means of least squares.



not only to the glass transition process but also to some rearrangements in the crystalline phase.<sup>21</sup> Calorimetric measurements do not show evidence at all of such a process; the sensitivity of the apparatus is probably lower than the heat exchanged for this transition.

The trend of the experimental  $T_g$  data versus  $w_1$  for the IH-TH and CL-TH copolymers is such that they can hardly be fitted by the G-T equation. Such an equation cannot explain the presence of a minimum in the  $T_g$  curve for the IH-TH copolymers. This fact, although unexpected, is not unusual, and some examples of minima or maxima in the  $T_g$ -composition curves have been reported<sup>22,23</sup> for other copolymeric systems. As shown by Kanig,<sup>20</sup> such a behavior can be accounted for by assuming that the work required for the creation of a hole in a copolymer is not the arithmetic mean of the work for a hole in the pure homopolymers. Following the treatment suggested by Kovacs<sup>24</sup> for polymer-solvent mixtures, the G-T equation may be modified by introducing an excess volume  $V_e$ , to take into account the variation of the interactions between the two different monomeric units. Equation (1) can now be rewritten as follows:

$$\sum_i A_i w_i (T_g - T_{g,i}) - V_e = 0. \quad (2)$$

By convention,  $V_e$  is positive when the interaction is higher than the mean interaction between units of the same kind. Putting

$$V_e = k w_2 (1 - w_2) = \xi A_1 w_2 (1 - w_2) \quad (3)$$

and

$$(A_2/A_1) = K$$

and rearranging eq. (2), one obtains

$$T_g = \frac{(1 - w_2) T_{g,1} + K w_2 T_{g,2} + \xi w_2 (1 - w_2)}{[1 - w_2 (1 - K)]}. \quad (4)$$

For IH-TH copolymers,  $A_{TH}/A_{IH} = 0.477$  and  $\xi = -89.6$  were calculated by means of the iterative least-squares method, with  $T_{g,IH} = 129.5^\circ$  and  $T_{g,TH} = 180^\circ\text{C}$ . The residual<sup>25</sup>  $\sum (T_{g,calc} - T_{g,exp})^2$  was 96.6. The experimental data and the calculated curve are compared in Figure 6b. The value of the interaction parameter is  $k = \xi A_1 = -4.3 \times 10^{-2}$ , with the assumption<sup>15</sup> that  $A_1 \simeq 4.8 \times 10^{-4}$ . A negative value of  $k$  implies that the work for the creation of a hole is lower in the copolymer than in the corresponding homopolymers, or, in other words, the presence of an excess of nonoccupied volume.

A structure composed of IH and TH units indeed cannot be easily packed either for the presence of a bulky unsymmetric unit (IH) or for the stiffness of the aromatic structure. Moreover, a disordered and loosely packed structure should possibly hinder the formation of hydrogen bonds. As a consequence, even small fraction of IH are sufficient to lower dramatically the glass transition temperature of poly(hexamethylenediammonium terephthalate).

From the calculated ratios  $A_{IH}/A_{CL}$  and  $A_{TH}/A_{IH}$ , the ratio  $A_{TH}/A_{CL} = 0.257$  is univocally determined. The calculated G-T curve for CL-TH copolymers is compared in Figure 6c with the experimental data. The agreement is fairly good in the middle range of the composition, that is, for samples with low crystallinity. Generally, the points for the more crystalline samples fall below the calculated curve. The deviations from the calculated curve could be explained either by the influence of the crystallinity on  $T_g$ , or on the basis of the following arguments.

At high TH contents, the sudden drops of  $T_g$  could be accounted for by a reduction of chain stiffness through introduction of few units of caprolactam. At high  $w_{CL}$ , probably the introduction of the bulky terephthalic unit brings about an increase in nonoccupied volume with a consequent decrease in  $T_g$ . Careful dilatometric experiments could explain the observed behavior. Unfortunately, it was not always possible to obtain well-molded and completely amorphous specimens. It must be remembered that at high TH concentrations, degradation occurs before the melting point.

Owing to difficulties encountered in representing by means of the G-T equation the thermal behavior of copolymers, it was preferred to obtain a ternary map of  $T_g$  by means of a statistical analysis on the 59 experimental points. A nonlinear regression method has been used, and all the calculations were carried out on an UNIVAC 1108 computer. An iso- $T_g$  map, reported in Figure 8, was obtained; the mean deviation between calculated and experimental points was  $\pm 2.5^\circ\text{C}$ . A comparison between Figures 3 and 8 shows that the iso- $T_g$  curves have a smooth trend in the amorphous

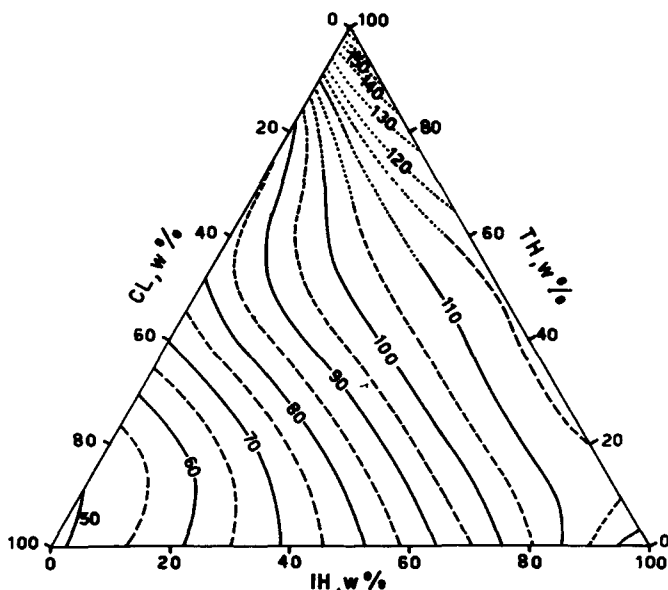


Fig. 8. Iso- $T_g$  ternary diagram for CL-IH-TH terpolymers.  $\Delta T_g$  between continuous and dashed lines,  $5^\circ\text{C}$ . Dotted lines relate to the zone where experimental data are not available.

zone, whereas noticeable variations of curvature are noted when passing to the semicrystalline zone where an influence of the crystallinity on  $T_g$  is to be expected. The plateau found in the  $T_g$  composition curve for the IH-TH copolymers is observed, in a large range of compositions, even for the terpolymers; in fact, for most compositions, at a constant CL content, the  $T_g$  is scarcely dependent on the IH:TH ratio; the influence of the TH comonomer is noticeable only at high weight fractions.

## CONCLUSIONS

The results obtained in this work point out that, in an extremely wide range of compositions, polyamides with the same  $T_g$  but with different crystallinity and possibly different physical and mechanical properties can be obtained. The effect on  $T_g$  and crystallinity due to the introduction of symmetric and unsymmetric isomers was shown. In particular, the unsymmetric isomer brings about difficulties in the packing of the polymeric chain. It was also shown experimentally that for polyamides a lack in the correlation between  $T_m$  and  $T_g$  actually exists.

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