Structure–Property Relationship and Thermal Behavior of Aliphatic and Semi-Aromatic Nylons

1. Background

Polymeric materials have been essential to human life since ancient times, serving basic needs such as clothing, food storage, shelter, and transportation. The evolution of polymer science and industry has closely paralleled the development of human civilization. From natural polymers like cotton, silk, and wood to synthetic fibers, plastics, and rubbers, scientists have continually designed, synthesized, and modified materials to meet practical needs and evolving demands.

Polyamides (PAs), commonly referred to as nylons, are polymers containing repeating amide groups (—CONH—) along their molecular chains. As one of the five major engineering thermoplastics, nylons exhibit excellent mechanical strength, wear resistance, chemical stability, and electrical insulation. These properties make them widely applicable in electronics, automotive components, aerospace systems, biomedical sciences, and industrial machinery.(1,2)

Polyamides are typically classified by chain structure into aliphatic, aromatic, or copolymerized polyamides. Aliphatic polyamides, formed from aliphatic diacids and diamines (or amino fatty acids), crystallize rapidly, exhibit high crystallinity, and possess balanced mechanical properties. Among these, nylon 11 (PA11) is a key representative (repeating unit shown in Figure 1).

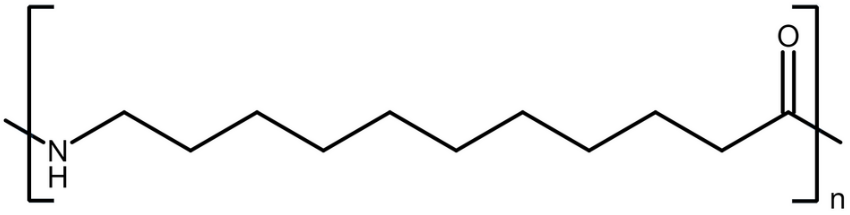

Figure 1: Structure of PA11

PA11 is synthesized from 11-aminoundecanoic acid, forming a semicrystalline polymer due to its strong intermolecular hydrogen bonding. The bulk polymer is a translucent, milky white solid with a density of 1.04 g/cm^3 and a melting range of 186–190°C. Its key properties include:

- ✓ High crystallinity
- ✓ Moisture resistance
- ✓ Thermal stability
- ✓ Wear and corrosion resistance
- ✓ Smooth surfaces

Semi-aromatic polyamides, such as poly(hexamethylene terephthalamide) (PA6T), are synthesized by reacting aromatic and aliphatic monomers. The chemical structure of PA6T, derived from terephthalic acid (PTA) and hexamethylenediamine (HMDA), is shown in Figure 2.

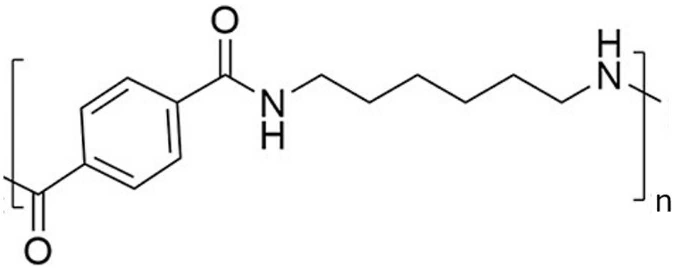

Figure 2: Structure of PA6T

PA6T retains some flexibility and crystallinity while gaining thermal stability and rigidity through aromatic ring incorporation. It exhibits:

- ✓ Higher mechanical strength and thermal resistance than aliphatic nylons
- ✓ Lower water absorption and superior dimensional stability
- ✓ Excellent chemical resistance

However, PA6T's high melting point (~370°C) exceeds its decomposition temperature (~350°C), requiring copolymer modification to reduce processing temperatures. For example, PA66/PA6T copolymers allow better processability due to structural similarity between monomers, enabling cocrystallization with minor lattice defects while preserving hydrogen bonding. The structure is shown in Figure 3.

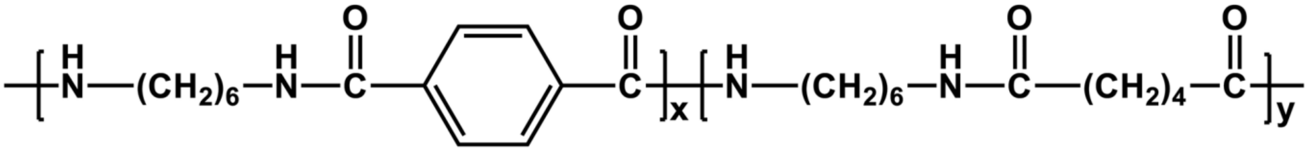

Figure 3: Structure of PA6T/66 copolymer

Key properties of PA6T-based nylons include:

- ✓ High melting points, glass transition temperatures, and crystallinity
- ✓ Low water absorption and minimal dimensional change
- ✓ Excellent chemical resistance
- ✓ Low thermal expansion
- ✓ Outstanding wear, fatigue, and creep resistance
- ✓ Excellent shape retention with minimal warping
- ✓ Strong weldability for dip or reflow soldering

Polymer crystallizability depends on molecular structure: polymers with simple, symmetric, flexible chains and small side groups tend to crystallize more easily. In nylons, amide groups form strong hydrogen bonds (-NH···O=C-) that promote two-dimensional sheets, which then stack into three-dimensional crystalline structures. Differences in hydrogen bond arrangements and stacking yield various polymorphs. Polyamides crystallize both during melt cooling and from the amorphous state. Imperfect crystals formed during initial cooling may undergo secondary crystallization. Upon reheating, these structures reorganize into more thermodynamically stable forms.

Crystallization in polymers involves two stages: nucleation and crystal growth. Nucleation may be homogeneous, occurring spontaneously within the melt, or heterogeneous, initiated at impurities or filler surfaces. In practice, heterogeneous nucleation dominates due to unavoidable impurities.

This study uses TGA (thermogravimetric analysis) and DSC (differential scanning calorimetry) to investigate the thermal stability and melting/crystallization behavior of two representative nylons: aliphatic PA11 and semi-aromatic PA6T.

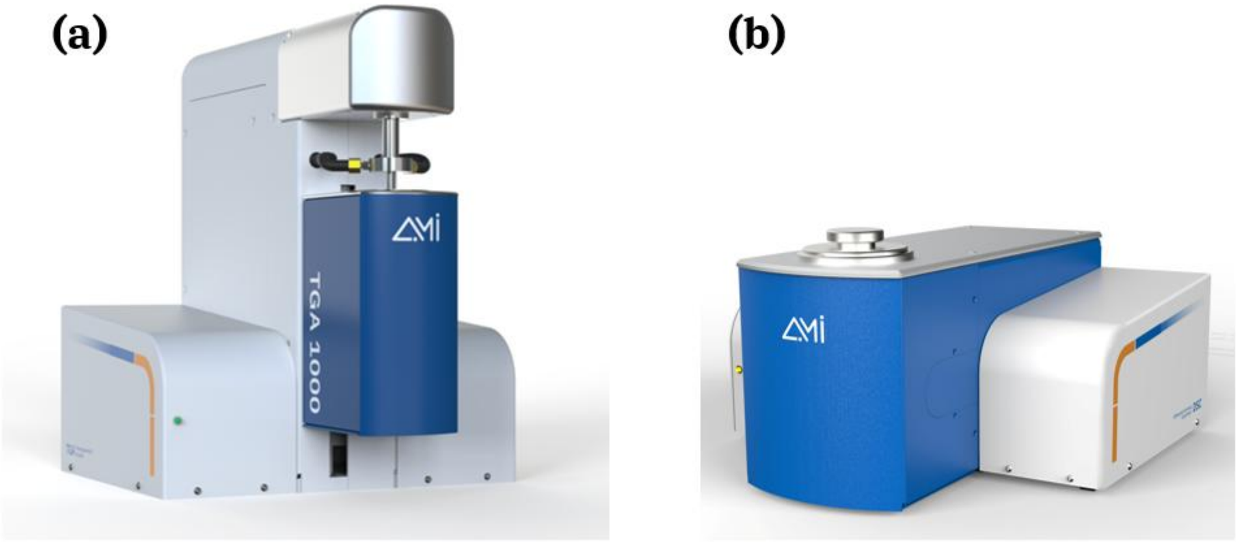

Figure 4: (a) ***TGA-1000*** *Thermogravimetric Analyzer and (b)* ***DSC-600*** *Differential Scanning Calorimeter*

2. Experimental Methods

Thermal properties were measured using the **TGA-1000** thermogravimetric analyzer and **DSC-600** differential scanning calorimeter, both developed by AMI. TGA was performed with high-purity nitrogen (99.999%) at 50 mL/min. About 15 mg of polymer was placed in ceramic crucibles and heated from 25 °C to 1000 °C at 10 °C/min. DSC was also performed with high-purity nitrogen at a flow rate of 30 mL/min. About 20 mg of PA11 was sealed in an aluminum crucible and heated from -90 °C to 300 °C at 20 °C/min. 5 mg of PA6T was similarly prepared and subjected to a heating-cooling cycle between 50 °C and 350 °C at 20 °C/min.

3. Results and Discussion

The TGA curves for PA11 and PA6T are shown in Figure 5. Both materials showed two-stage decomposition with minor weight losses from moisture evaporation at low temperatures and major decomposition due to random scission of C-C and C-N bonds at temperatures above 350 °C.

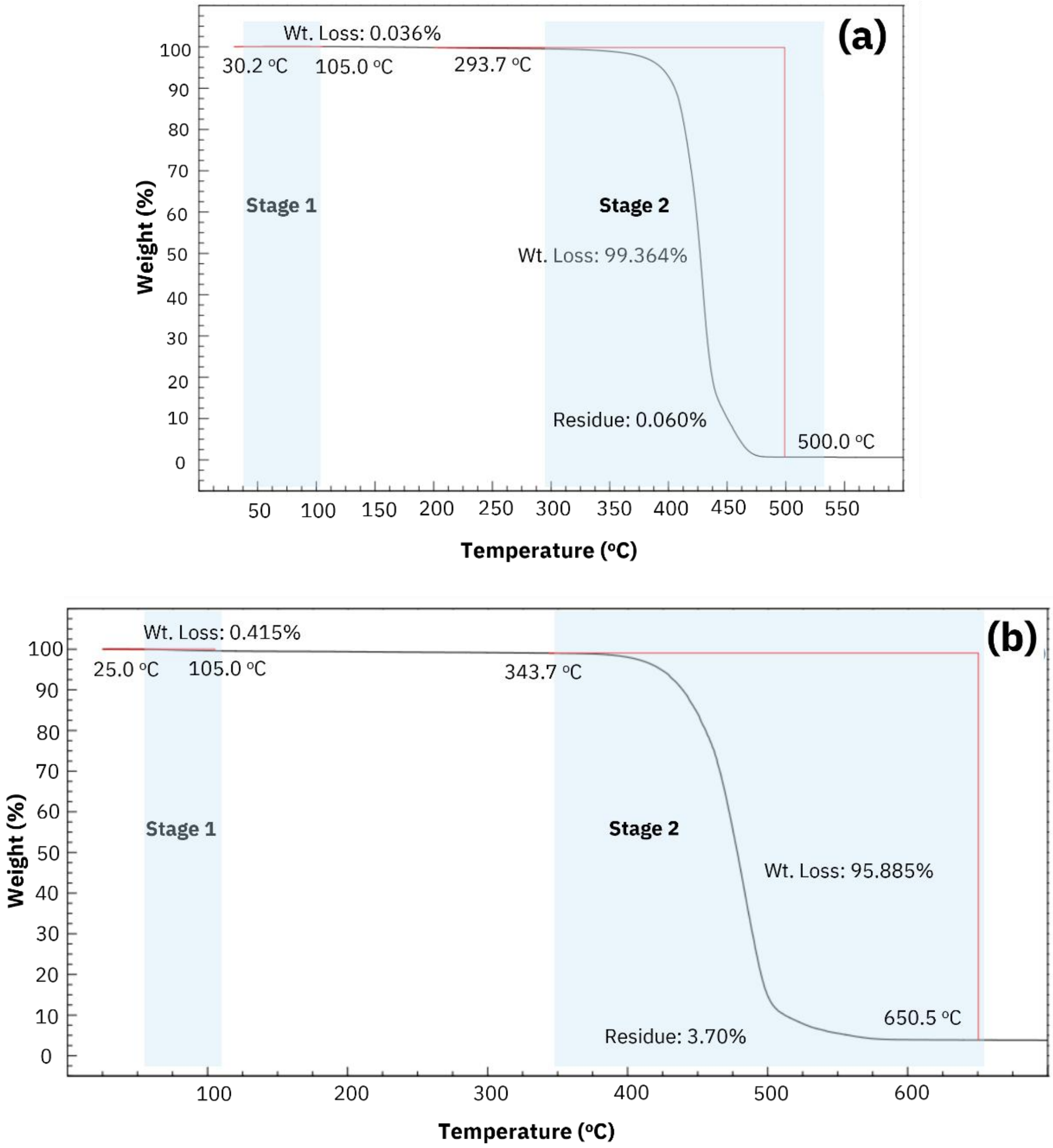

Figure 5: (a) TGA Curve of PA11, (b) TGA Curve of PA6T

Temperature range	PA11 wt. loss (%)	PA6T wt. loss (%)
30 – 105 °C (Stage 1)	0.036%	0.415%
345 – 650 °C (Stage 2)	99.364%	95.885%

Table 1: Percent weight loss during TGA for PA11 and PA6T nylons

The decomposition temperatures reflect material stability:

- ✓ PA11 (aliphatic): 293.7°C
- ✓ PA6T (semi-aromatic): 343.7°C

Increased thermal resistance in PA6T is attributed to aromatic ring content and stronger hydrogen bonding.

The DSC curve for PA11 is shown in Figure 6 and the thermal properties are shown in Table 2. The thermal stability was confirmed; decomposition (293.7 °C) occurs well above the melting point (188.13 °C).

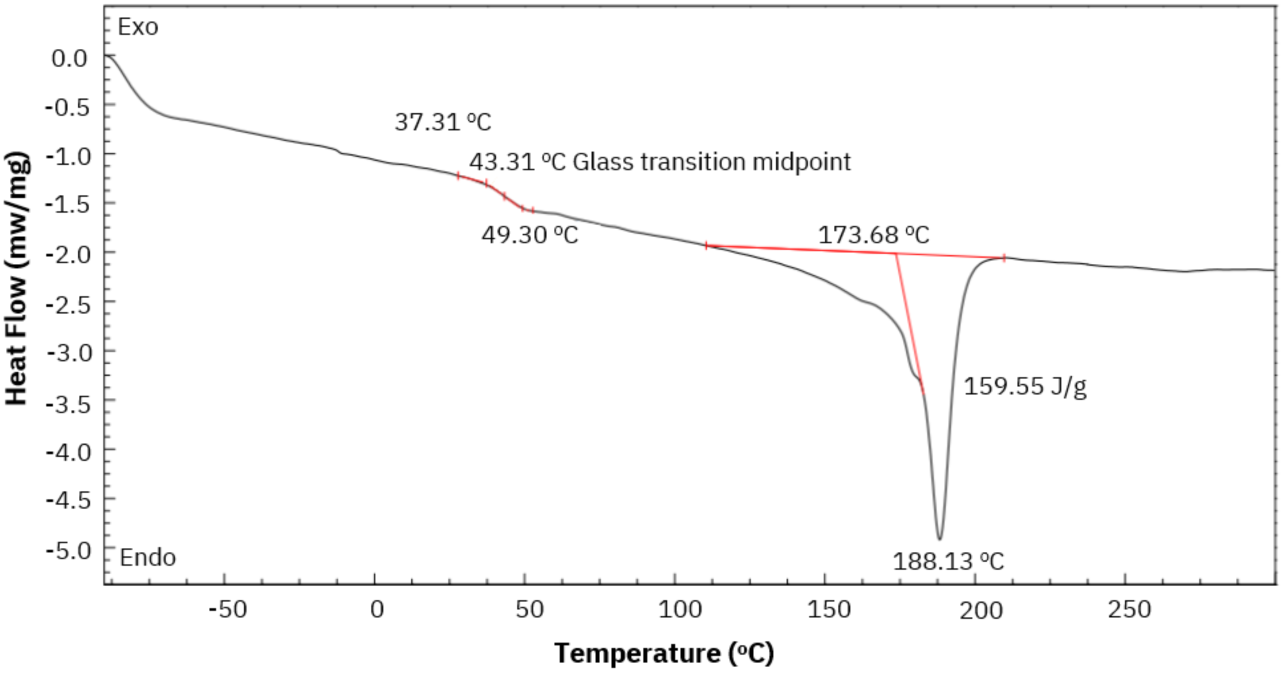

Figure 6: DSC thermogram of PA11

Glass transition		**Melting**		**Enthalpy of fusion (ΔH_m)**
Onset	**T_g**	**Onset**	**Melting peak**	
~37 °C	43.31 °C	173 °C	188.13 °C	159.55 J/g

Table 2: DSC results for PA11

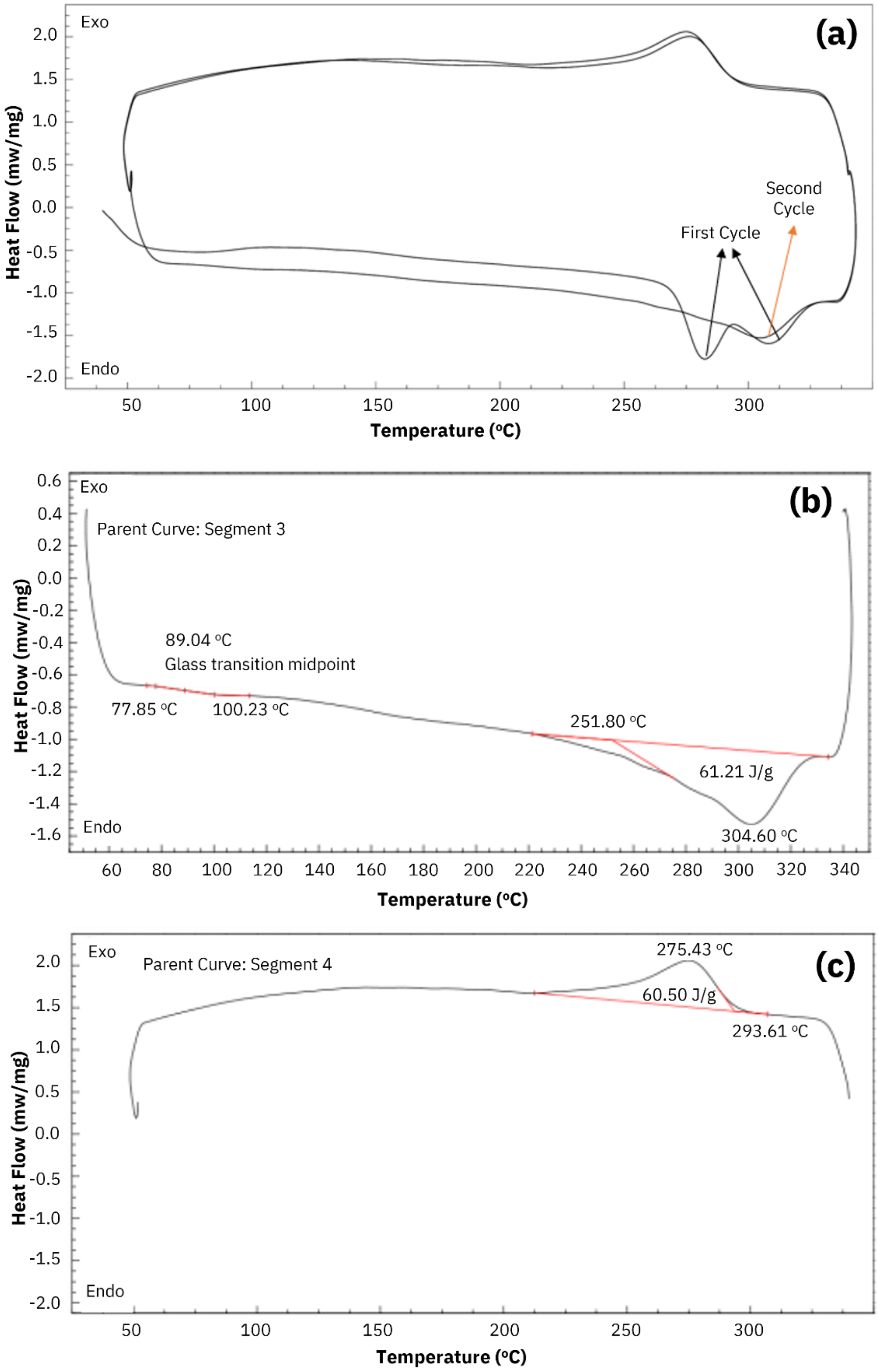

Figure 7: DSC thermogram of PA6T, temperature cycling between 50 °C to 350 °C (a), segment 3 of the parent curve (b), and segment 4 of the parent curve (c)

Finally, PA6T was cycled through 50 °C to 350 °C four times (Figure 7, Table 3). The first heating shows dual melting peaks, indicating recrystallization. The PA6T also showed higher glass transition (89°C) and crystallization temperatures (275.43°C) than PA11. Its superior thermal properties make PA6T ideal for high temperature environments.

Segment 3					Segment 4		
Glass transition		**Melting**			**Crystallization**		
Onset	**T_g**	**Onset**	**Melting peak**	**Enthalpy of fusion (ΔH_m)**	**Onset**	**T_c**	**Enthalpy of crystallization (ΔH_c)**
77.85 °C	89.04 °C	251.80 °C	304.60 °C	61.21 J/g	293.61 °C	275.43 °C	60.50 J/g

Table 2: DSC temperature cycling results for PA6T

4. Conclusions

This study examined the thermal stability and melting/crystallization behavior of aliphatic PA11 and semi-aromatic PA6T using TGA and DSC using the **TGA-1000** thermogravimetric analyzer and **DSC-600** differential scanning calorimeter from AMI.

Key findings include:

- ✓ Thermal decomposition:
    - PA11: 293.7°C
    - PA6T: 343.7°C
- ✓ Melting temperature:
    - PA11: 188.13°C
    - PA6T: 304.6°C

The aromatic structure in PA6T significantly improves thermal resistance and structural stability, making it well-suited for demanding engineering applications. These results highlight the critical role of molecular architecture in determining nylon performance across temperature-sensitive environments.

5. References

(1) Arioli, M.; Puiggali, J.; Franco, L. Nylons with applications in energy generators, 3D printing, and biomedicine. *Molecules*, **2024**, *29*, 2443.

(2) Pervaiz, M.; Faruq, M.; Jawaid, M.; Sain, M. Polyamides: Development and applications towards next-generation engineered plastics. *Curr. Org. Synth*. **2016**, *14*, 146-155.