Semicrystalline Copolyamides Based on the Renewable Monomer, 1,9-Nonane Diamine

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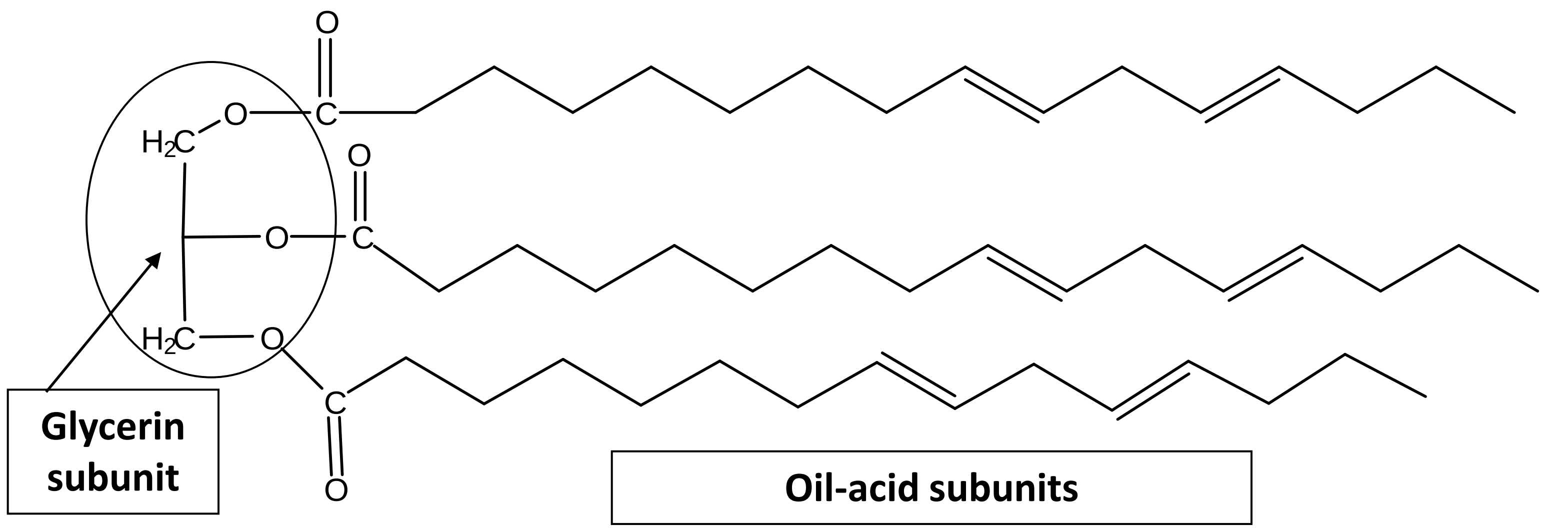
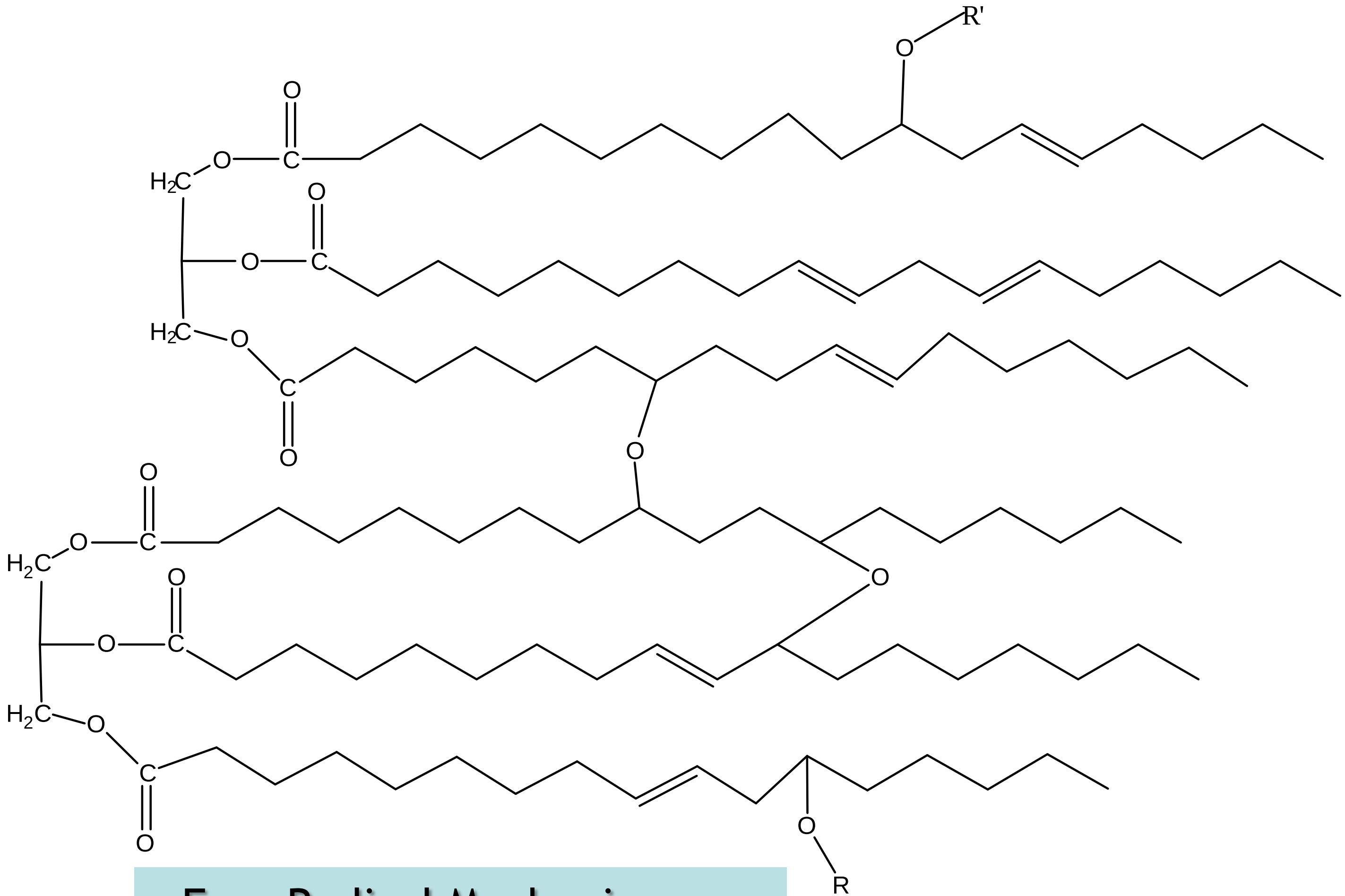
Vegetable Oils in Polymeric Materials



Arguably, vegetable oils have been the most useful of the renewable materials routinely used in coatings binders.

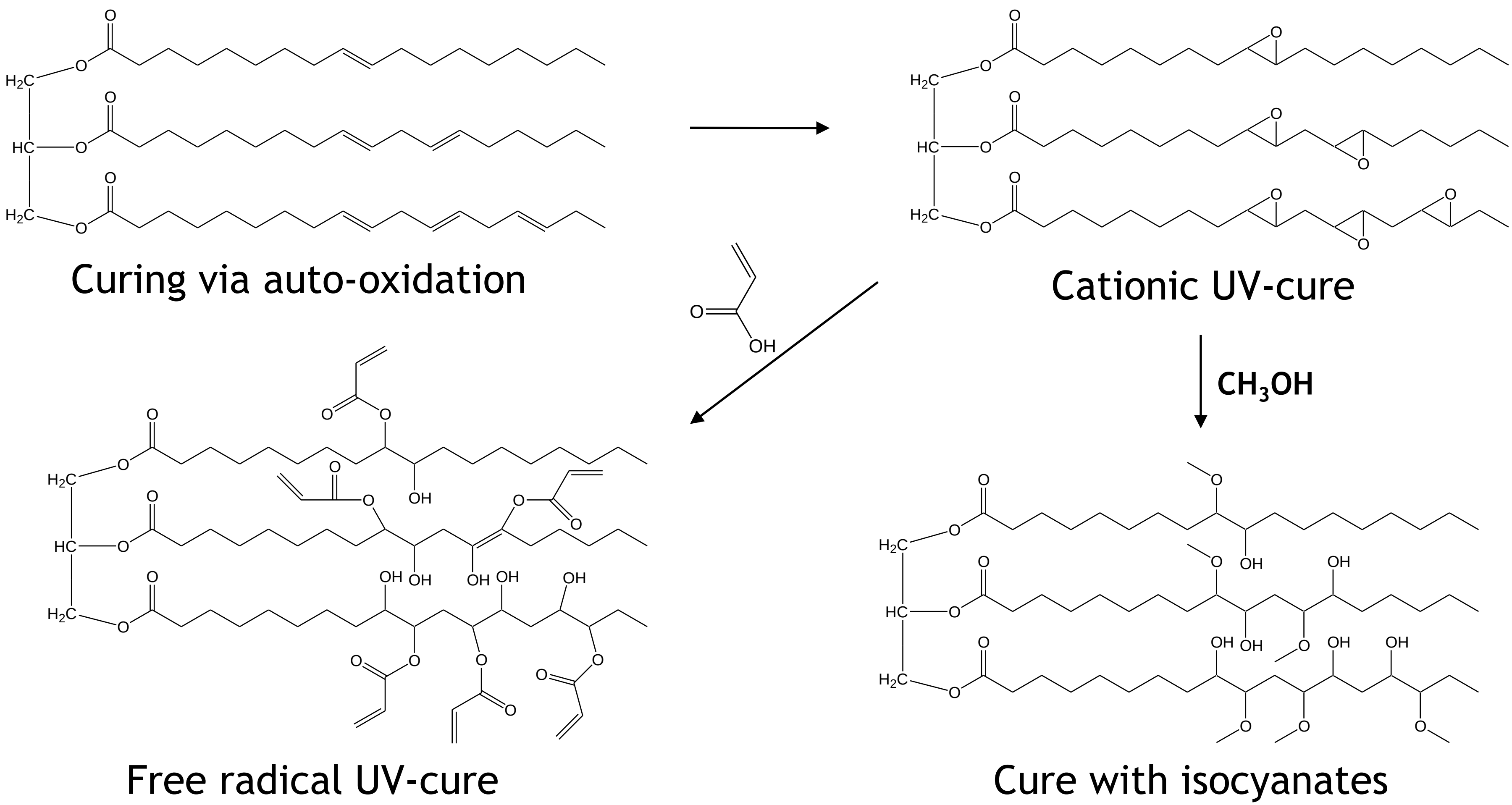
- Since 1000AD, vegetable oils have been used extensively as binders or additives in coatings.
- Reports of their use occurred at least 30,000 years ago, going back to the days of cave paintings.
- The primary use of vegetable oil in coatings is as a drying oil. These are highly unsaturated oils that will oligomerize or polymerize when exposed to the oxygen in air, usually in the presence of a catalyst.

Film Formation/Crosslinking via Auto-oxidation

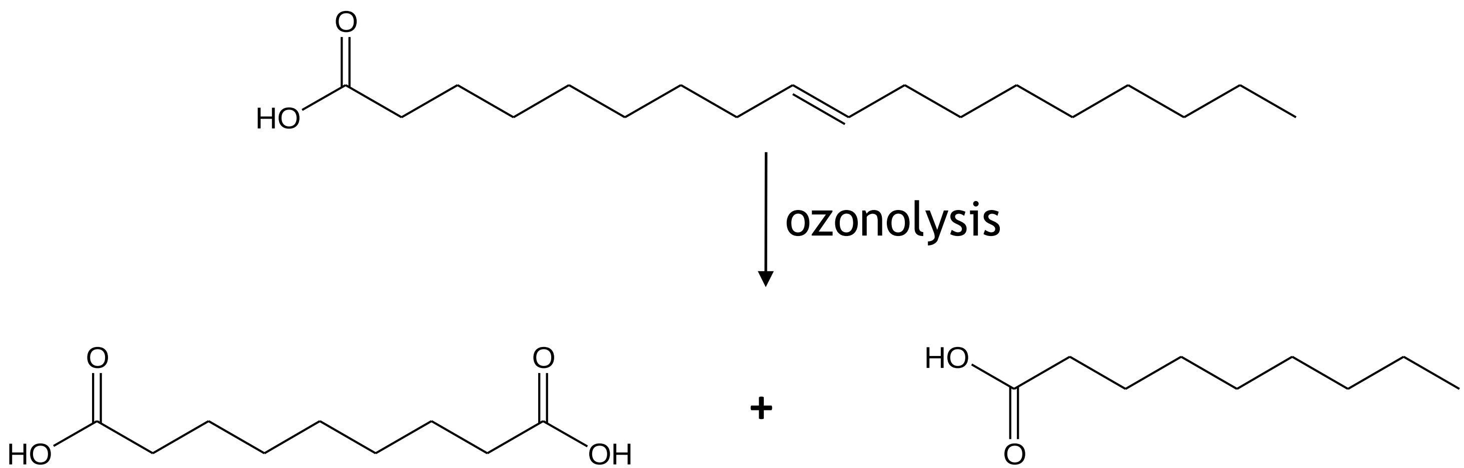


- Free Radical Mechanism
- Ambient Conditions
- Network Develops over Time

Derivatization of Vegetable Oils for other Cure Mechanisms

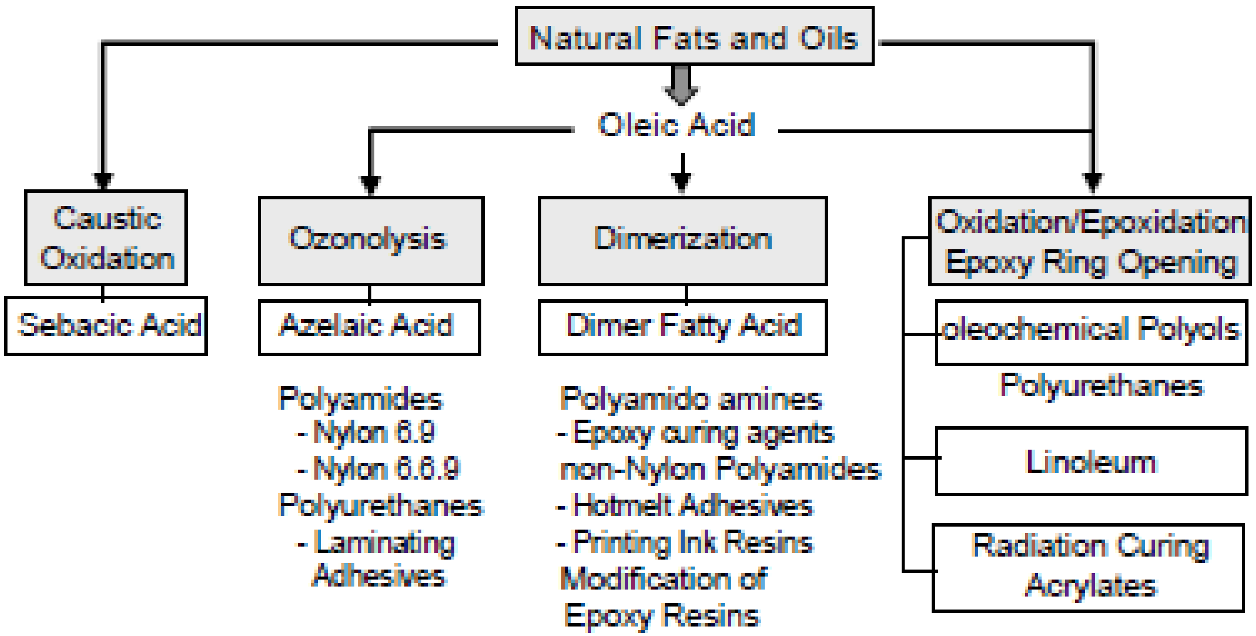


Oxidation to Produce Carboxylic Acids



Dicarboxylic Acid	Plant Oil Source
Adipic Acid, $HO_2C(CH_2)_4CO_2H$	Carrot seed, parsley seed
Suberic Acid, $HO_2C(CH_2)_6CO_2H$	Pot marigold
Azelaic Acid, $HO_2C(CH_2)_7CO_2H$	Olive, peanut, sesame seed, sunflower, safflower, corn
Sebacic Acid, $HO_2C(CH_2)_8CO_2H$	Castor seed
Brassylic Acid, $HO_2C(CH_2)_{11}CO_2H$	Crambe, rapeseed, wallflower seed, mustard seed

Current Uses for Long Chain Dicarboxylic Acids



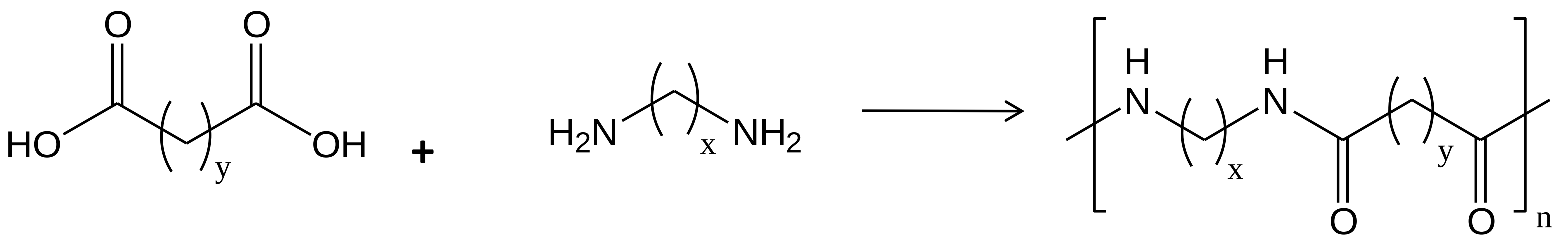
Properties imparted to polymers:

- elasticity
- flexibility
- impact strength
- hydrolytic stability
- hydrophobicity
- low glass transition temperature

K. Hill, *Pure Appl. Chem.*, vol. 72, 1255-1264 (2000)

Oleochemical-based dicarboxylic acids only make up about 0.5% of the total dicarboxylic acid market for polymers

Polyamides Based on Plant Oil Derived Dicarboxylic Acids



y = 7 = azelaic acid

y = 8 = sebacic acid

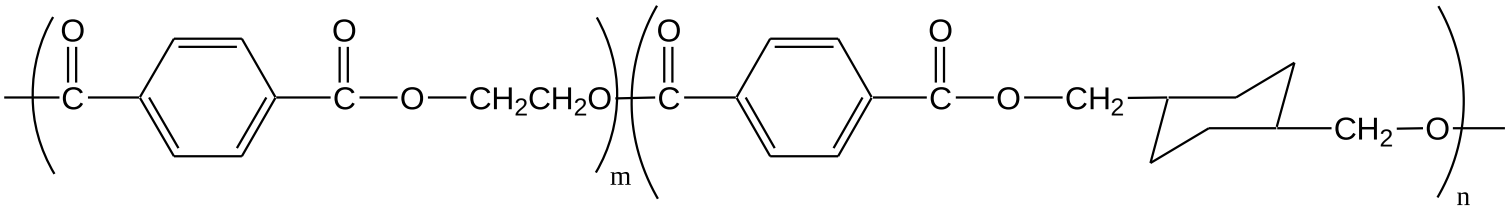
Y = 11 = erucic acid

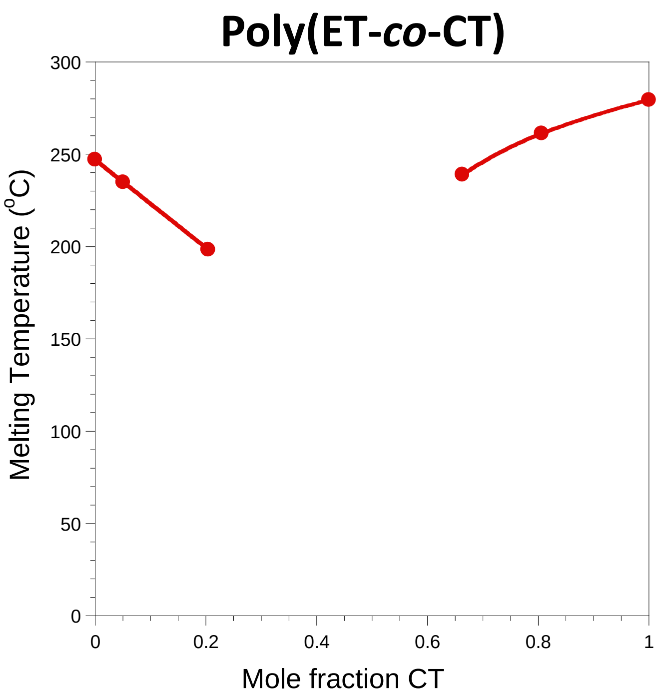
x,y	nylon ID	Tm	Tg
6,7	nylon 6,9	205	58
6,8	nylon 6,10	210	50
6,11	nylon 6,13	210	N/A
13,11	nylon 13,13	176	N/A
6,4	nylon 6,6	255	60

Aliphatic Polyamides Based on Plant-Oil-Derived Dicarboxylic Acids Have Relatively Low Melting Temperature and, Thus, Limited Utility

Typical Melting Point Depression Observed with Semi-crystalline Polymers

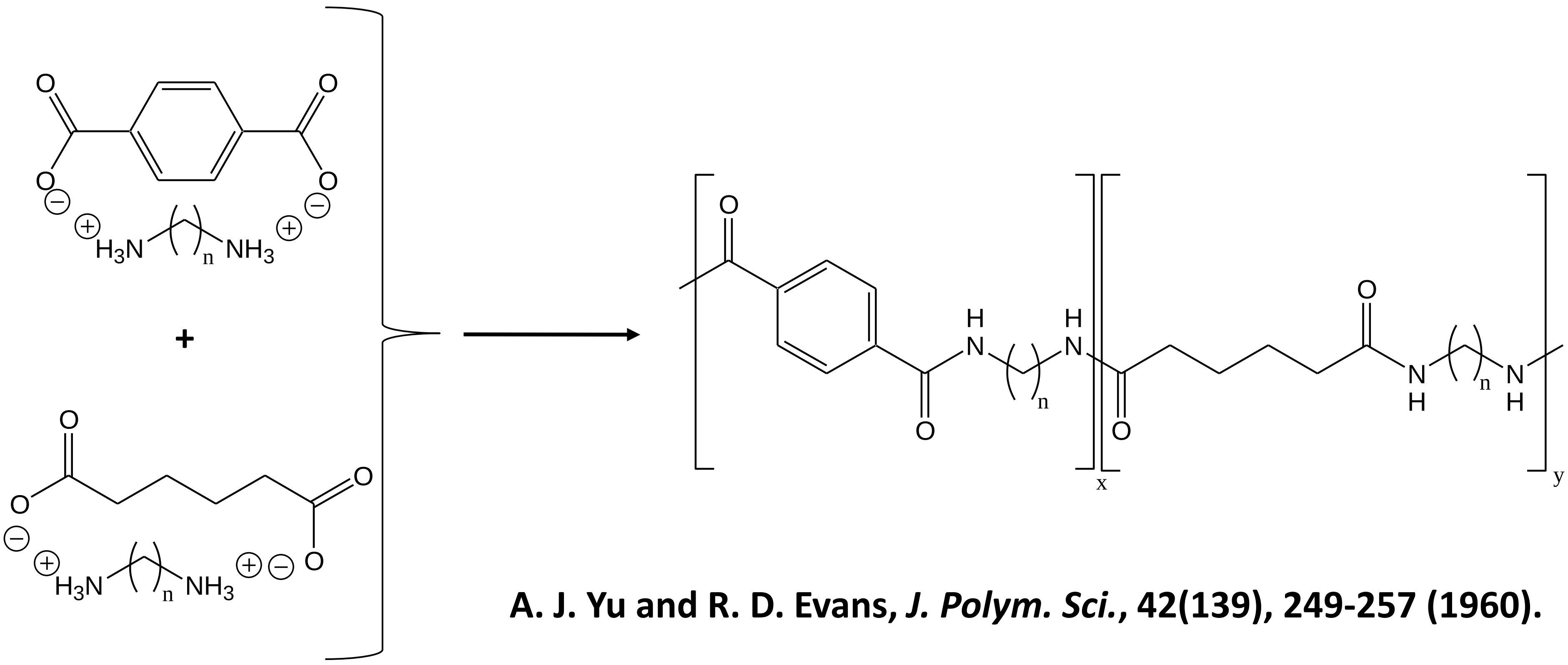
Example: Poly(ethylene terephthalate-*co*-1,4-cyclohexylene dimethylene terephthalate)





Reproduced from H. Y. Yoo, *Polymer*, 35(1), 117-122 (1994).

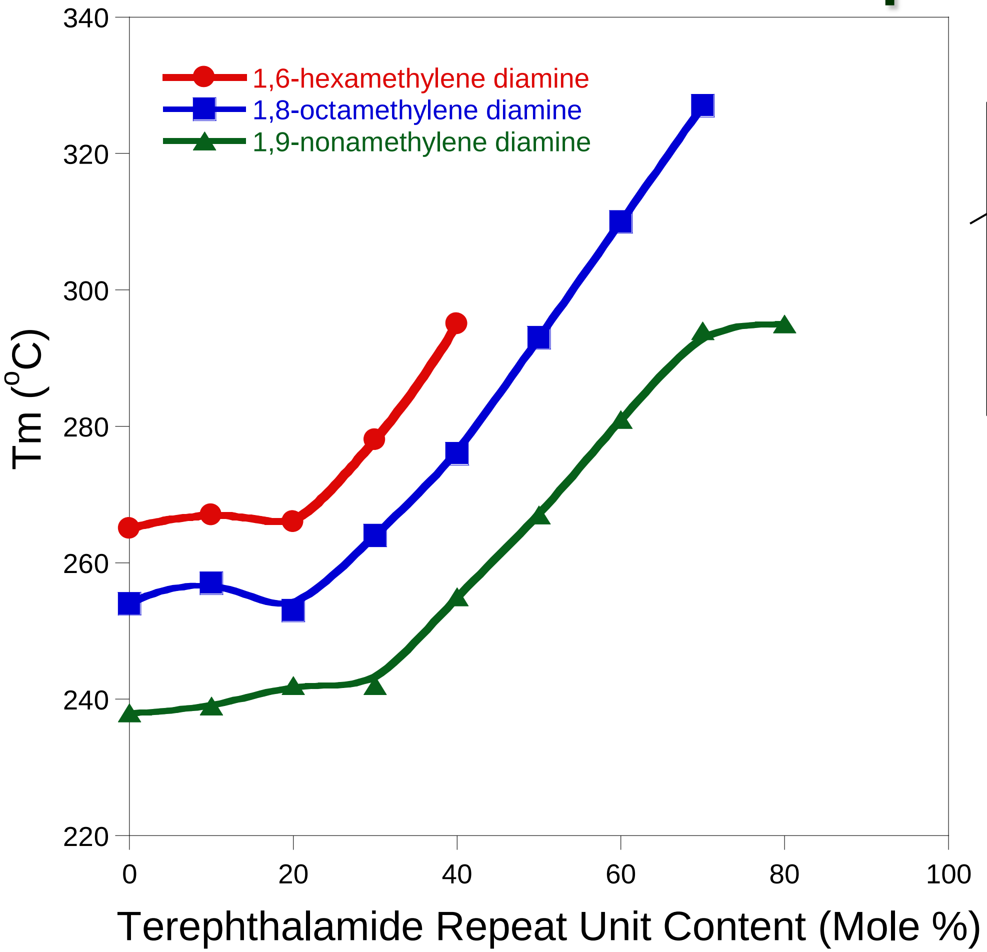
Semi-Aromatic Polyamides Exhibiting Isomorphism (i.e. Cocrystallization)

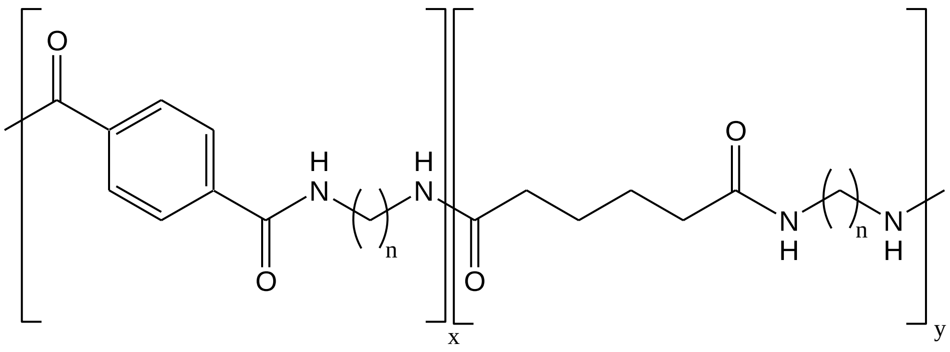


A. J. Yu and R. D. Evans, *J. Polym. Sci.*, 42(139), 249-257 (1960).

Similar Size of Repeat Unit x and Repeat Unit y Enables Cocrystallization (i.e. isomorphism)

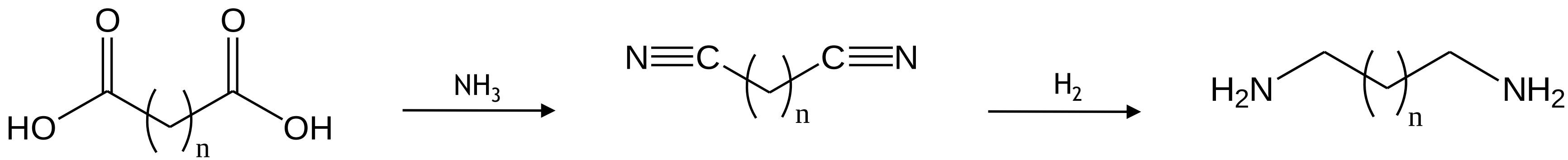
Melting Temperature as a Function of Composition

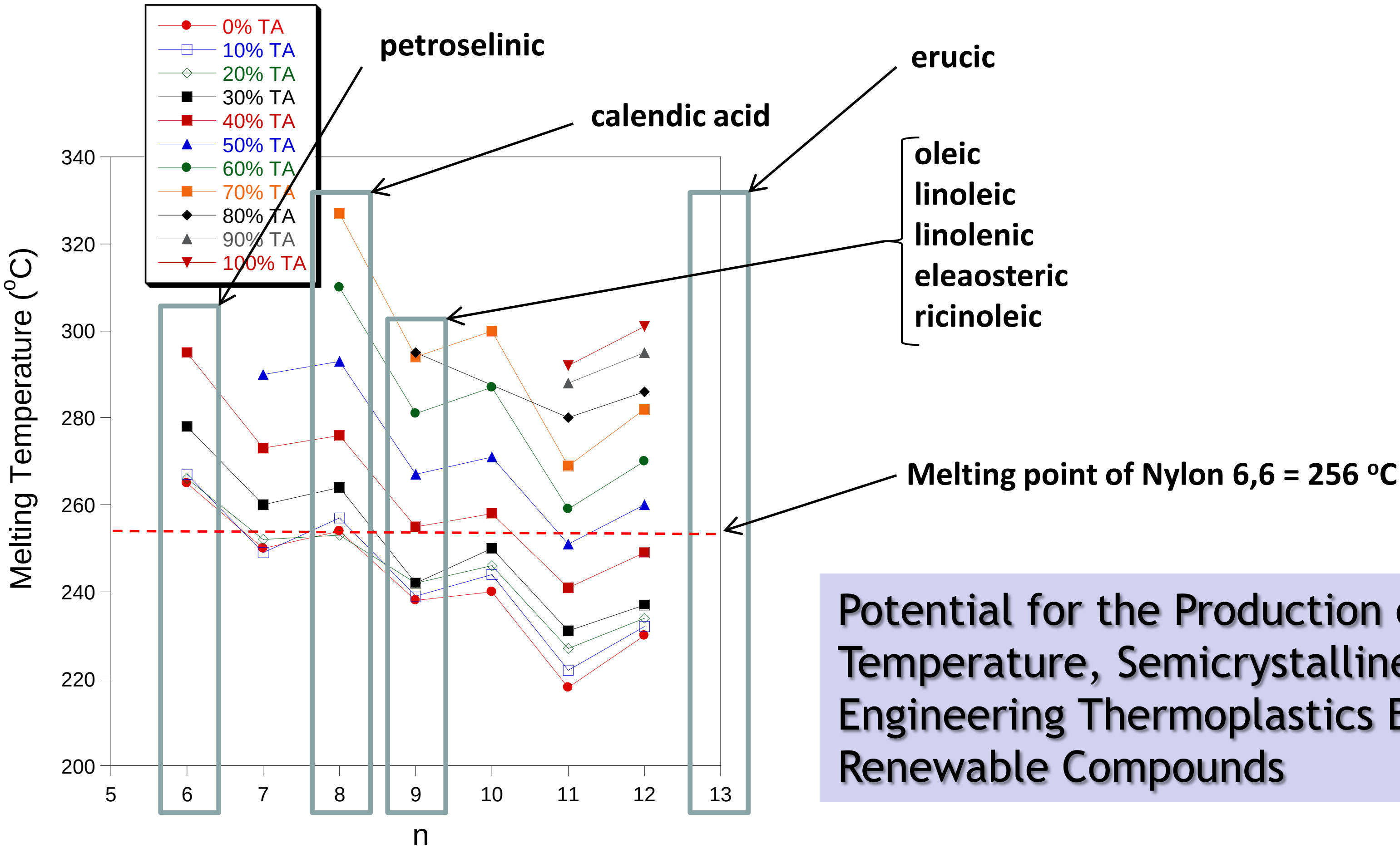




A. J. Yu and R. D. Evans, *J. Polym. Sci.*, 42(139), 249-257 (1960).

Copolyamides Based on Renewable Diamines

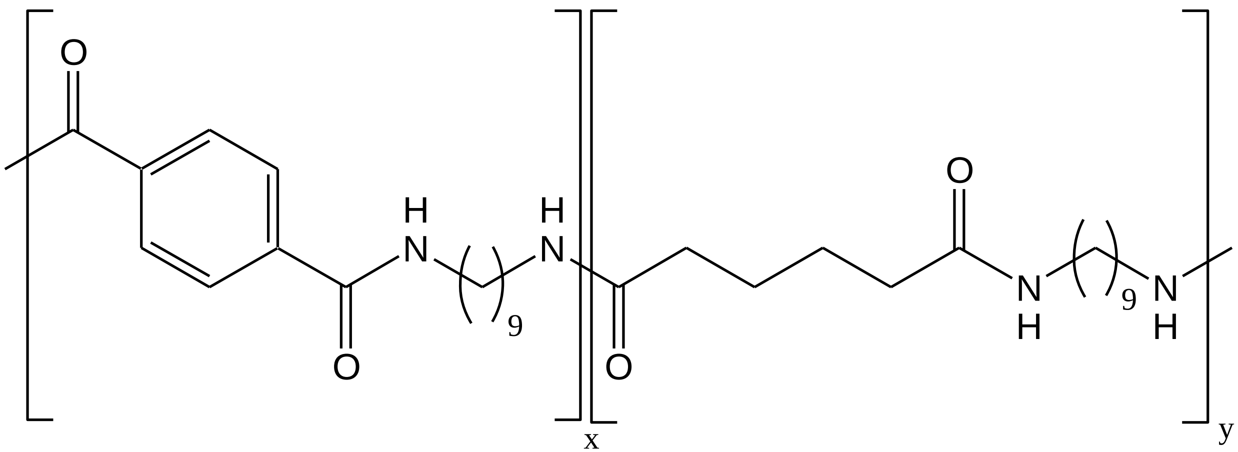




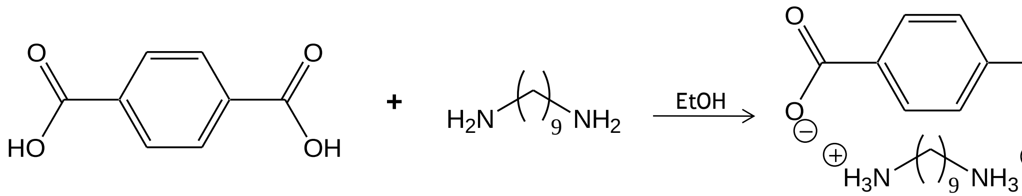
Potential for the Production of High Temperature, Semicrystalline Engineering Thermoplastics Based on Renewable Compounds

Research Objective

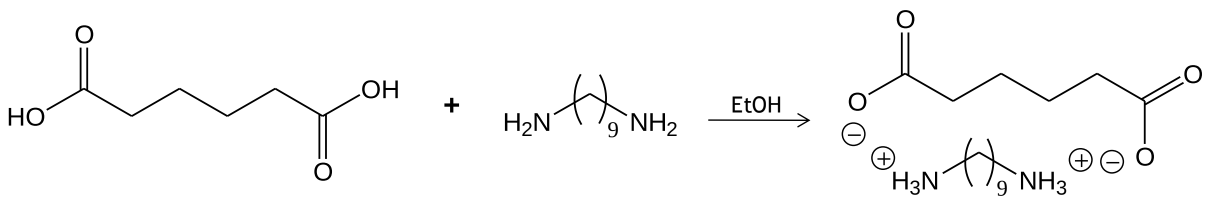
- Determine the utility of adipamide/terephthalamide copolymers for use as high-value engineering thermoplastics
- Compare properties to nylon 6,6
- Begin with copolymers based on 1,9-nonane diamine



Polymerization Process



9,T salt



9,6 salt

Dissolve 9,T and 9,6 Salts in H_2O

Distill Off H_2O Against Slight Pressure

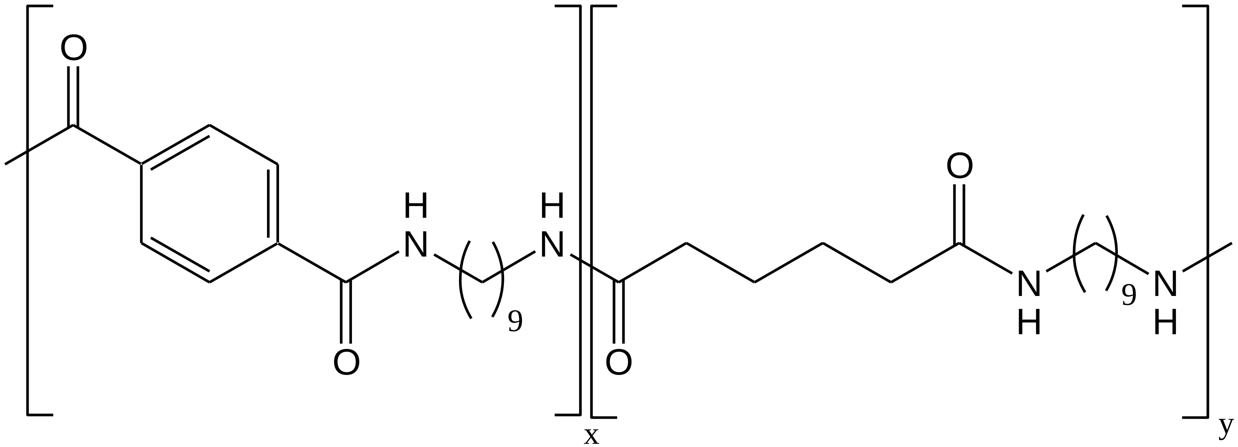
Heat to 250°C-300°C While Stirring

Reduce Pressure While Stirring

Cool Under Vacuum

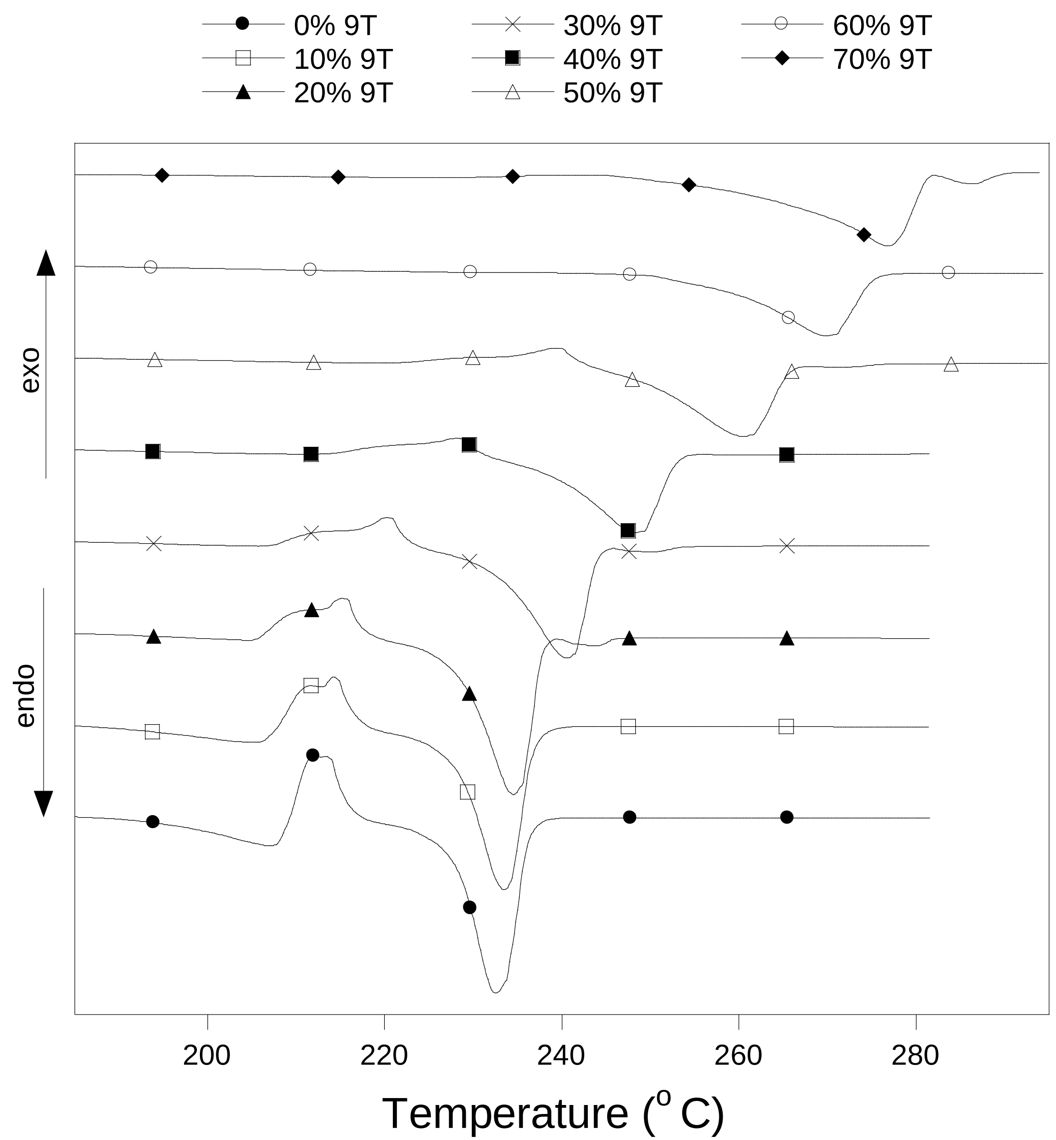
Two-Step Polymerization Process

Initial Study



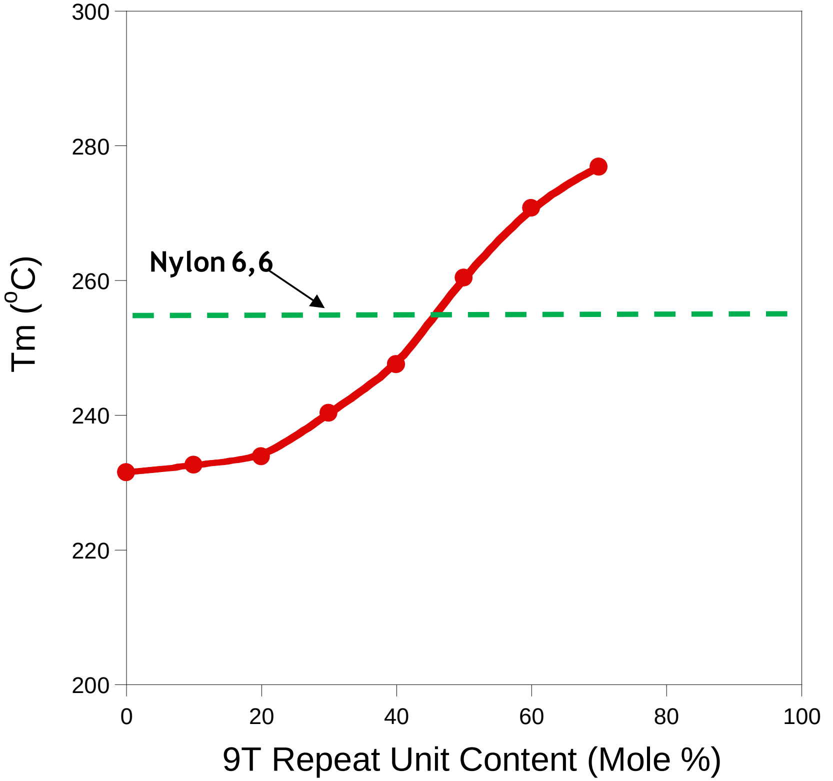
- Prepare ~2 g. samples of polymers varying in x/y content using test-tube reactor
- Determine basic thermal properties
  - melting temperature
  - glass transition temperature
  - thermal stability
  - crystallization temperature
  - isothermal crystallization kinetics
  - crystal structure

Melting Behavior

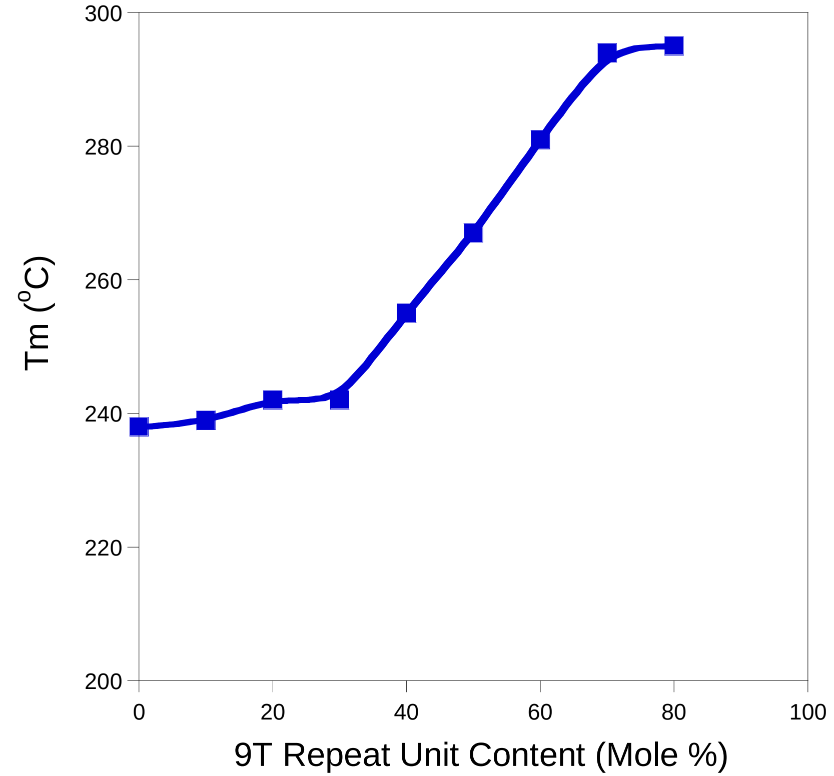


Melting Temperature

Our experimental data

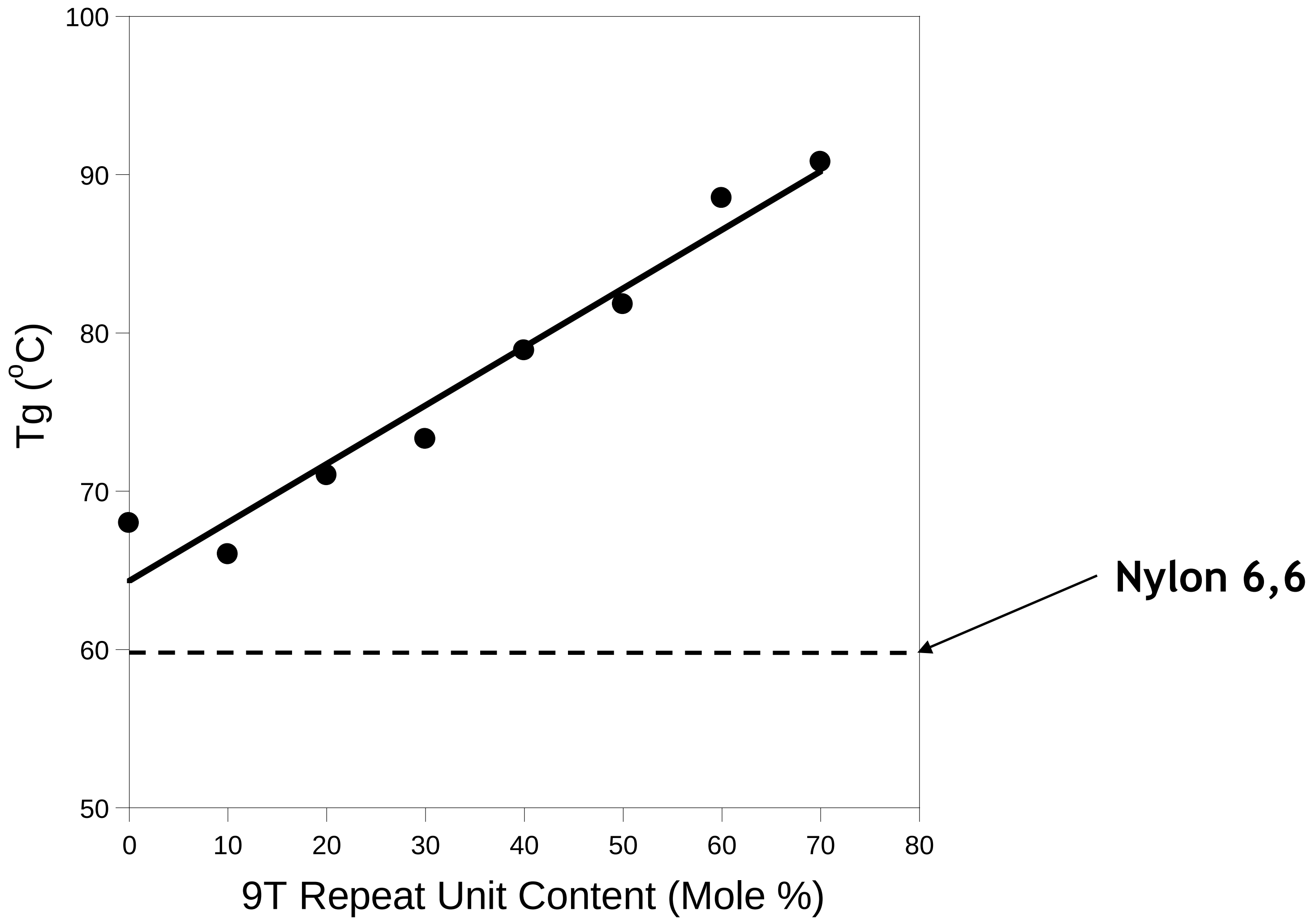


Data from Yu and Evans



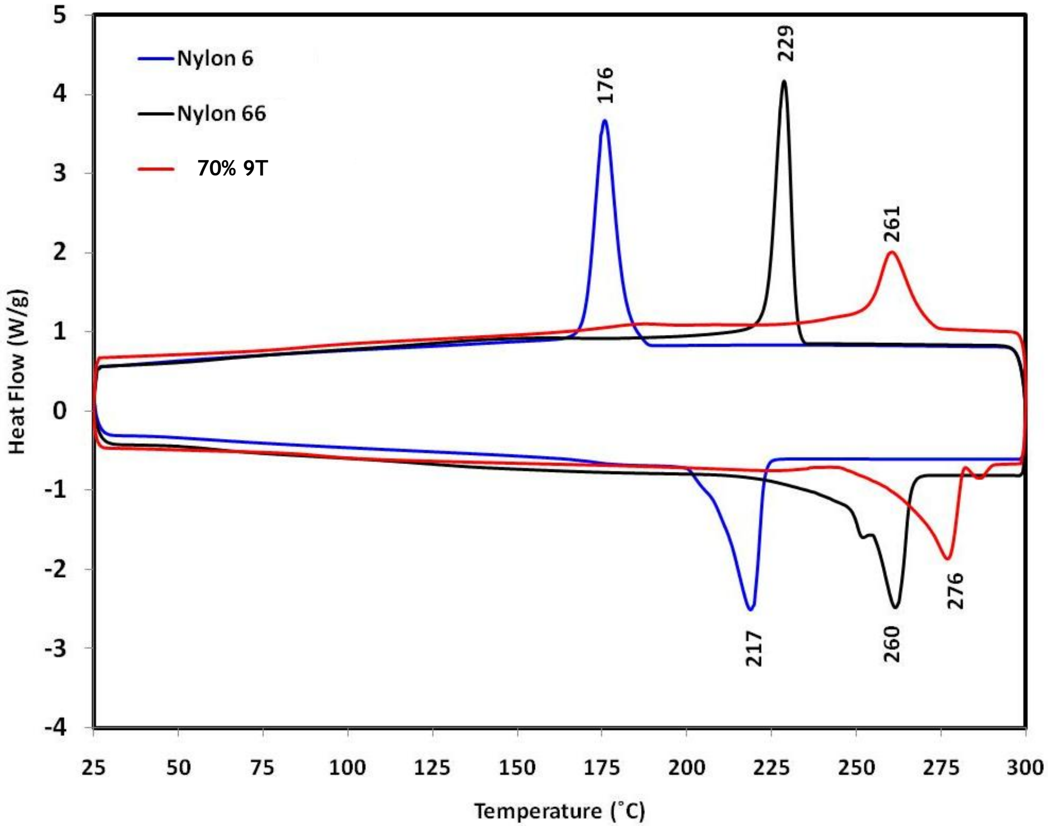
- Similar sigmoidal relationship between Tm and composition as observed in literature
- Absolute Tms are lower than literature most likely due to measurement method
- Copolymer with 45 mole % 9T content has similar Tm to Nylon 6,6

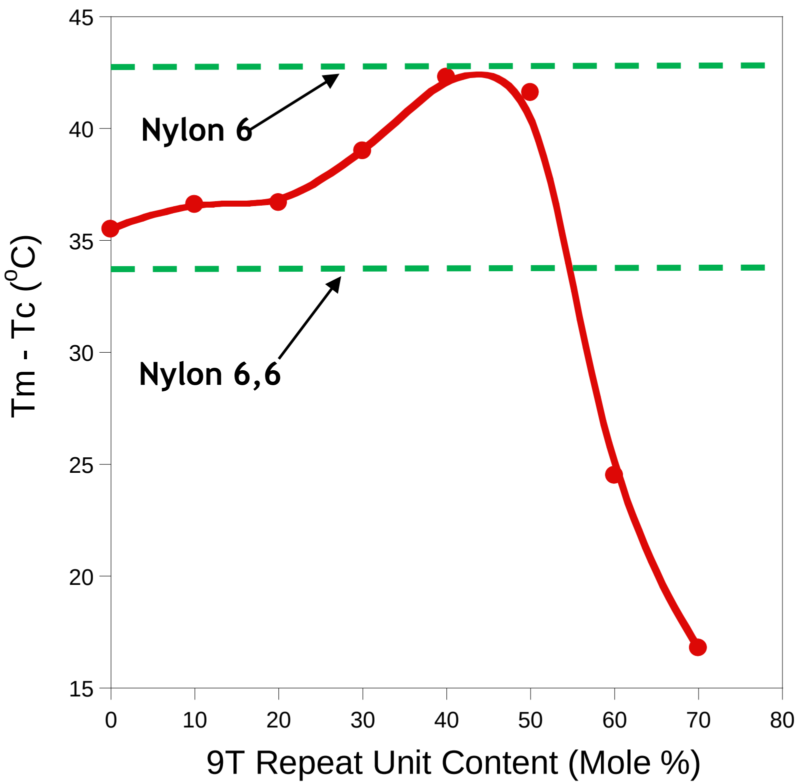
Glass Transition Temperature



Linear Increase in Tg with 9T Content

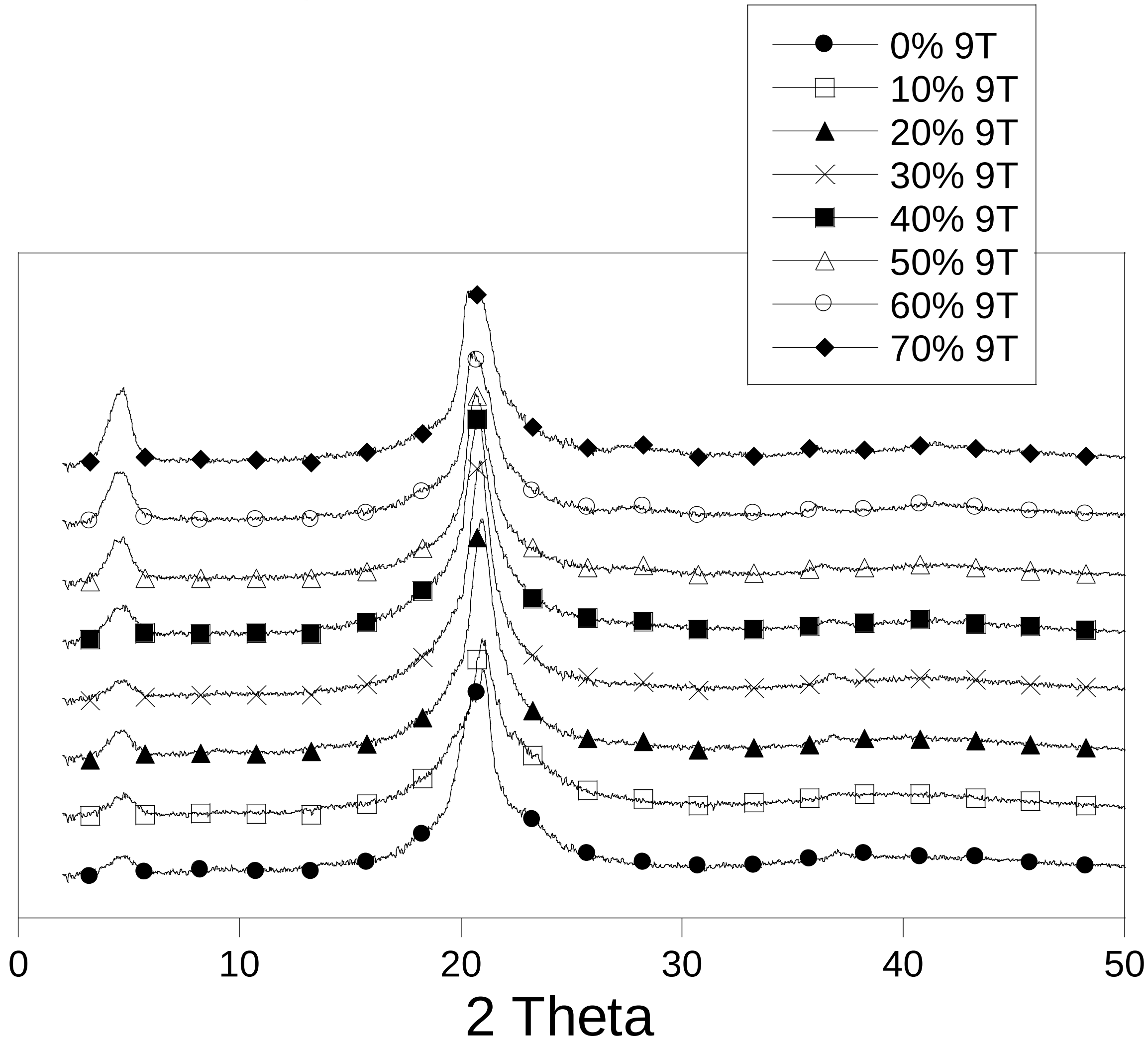
Non-Isothermal Crystallization





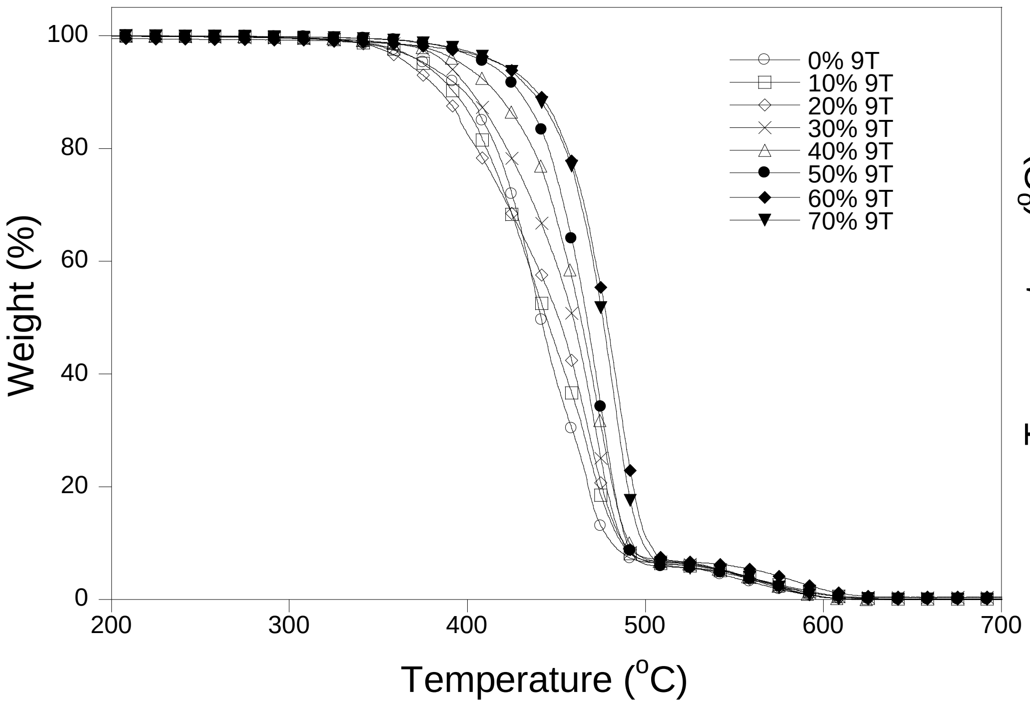
- Tm – Tc convenient way to compare relative crystallization rates
- Copolymers with 9T content above 50 mole percent crystallize remarkable fast!
- Polymer chain segments with long runs of 9T units may enable rapid homogeneous nucleation

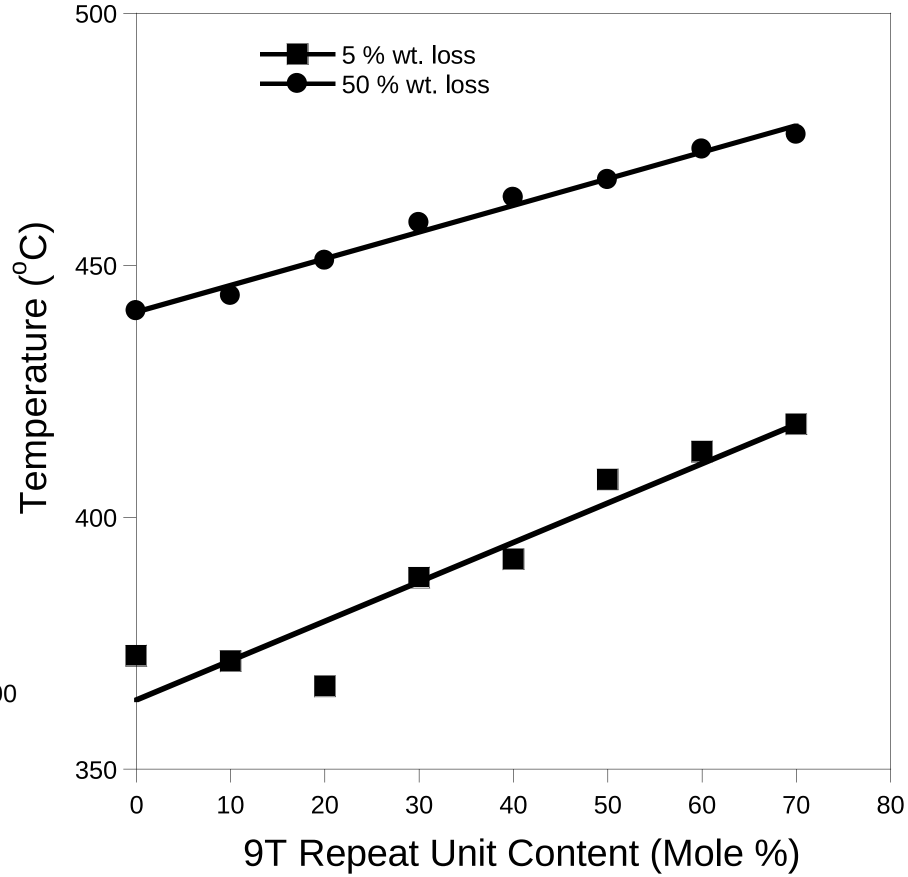
Crystal Structure



- Crystal Structure is Maintained over Entire Copolymer Compositional Range
- Diffraction Pattern Consistent with γ-form Crystalline Phase of Polyamides (Hexagonal Unit Cell)

Thermal Stability





Thermal Stability Increased With Increasing 9T Content

Comparison to nylon 6 and nylon 6,6

Polymer	Tg(°C)	Tm(°C)	Tm-Tc(°C)	T@5% wt. loss(°C)	T@50% wt. loss(°C)
Nylon 6	49.9	218.8	45.9	391.0	446.5
Nylon 6,6	59.1	261.3	32.8	410.5	470.5
0% 9T	68.0	231.5	35.5	372.5	441.0
10% 9T	66.0	232.6	36.6	371.5	444.0
20% 9T	71.0	233.8	36.7	366.5	451.0
30% 9T	73.3	240.3	39.0	388.0	458.5
40% 9T	78.9	247.5	42.3	391.7	463.5
50% 9T	81.8	260.4	41.6	407.5	467.0
60% 9T	88.5	270.7	24.5	413	473.0
70% 9T	90.8	276.8	16.8	418.5	476.0

Copolymer 60% 9T possesses higher Tm, Tg, and faster crystallization than nylon 6,6

Conclusions

- Confirmed Isomorphism
- Reproduced Sigmoidal Relationship Between Melting Temperature and Composition
- Tg Increased with Increasing 9T Content
- Thermal Stability Increased with Increasing 9T Content
- Crystallization Rate Increased Dramatically at 9T Contents Above 50 Mole %
- Copolymers Possessing a 9T Content Exceeding 50 Mole % 9T Possess Very Desirable Thermal Properties That Rival Nylon 6,6

Acknowledgement

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