Poly(amideimides) from Aliphatic Tricarboxylic Acids

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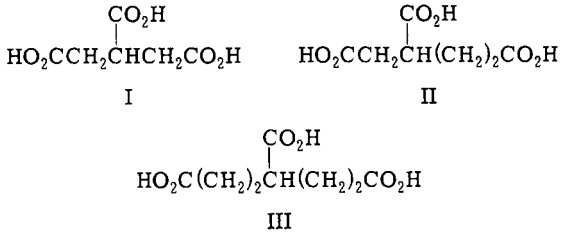
ABSTRACT: The conversion of aliphatic tricarboxylic acids and diamines to poly(amideimides) by melt polymerization of monomer mixtures is described. Monomer structure, stoichiometry, and reaction conditions were all found to affect polymer linearity. Homopolymers, obtained from diamine–tricarboxylic acid mixtures, were amorphous and had glass transition temperatures ranging from 50–200°C. Copolymers, derived from mixtures of tricarboxylic acids and adipic acid with 1,6-hexanediamine, were partially crystalline materials which could be converted into high-strength fibers and plastics having high impact resistance when equilibrated with atmospheric moisture.

The preparation of linear macromolecules from trifunctional monomers, having a single type of functionality, has not been reported frequently.[1] Poly(amideimides), potential polymerization products of this monomer class, have received considerable attention,[2–4] but have been produced primarily from more reactive carboxylic acid derivatives (e.g., anhydride acid chlorides) which are actually difunctional in the early stages of the polymerization. A number of years ago, the conversion of 1,2,3-propanetricarboxylic acid into poly(amideimides) by reaction with acyclic diamines containing two to ten carbon atoms was reported.[5,6] Very little characterization of the products of these melt polymerizations was disclosed.

To determine the effect of monomer structure and reaction conditions on polymer properties and linearity, a variety of poly(amideimides) were prepared[7] from three aliphatic tricarboxylic acids: 1,2,3-propanetricarboxylic acid (I), 1,2,4-butanetricarboxylic acid (II) and 1,3,5-pentanetricarboxylic acid (III). Their preparation and characterization is the subject of this paper.



I II

III

Results and Discussion

Polymerization Conditions. The polymers were prepared by conventional melt polymerization techniques involving nearly equimolar quantities of carboxylic acids and amines. Evidence that the products of these polymerizations exist as poly(amideimides) includes the following observations.

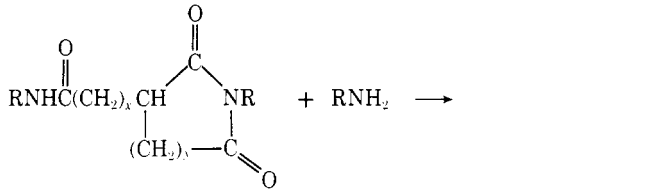
1. The ir spectra of these materials showed no carboxylic acid derived absorptions when η_{Inh} was 0.4 or greater. Lower molecular weight samples did show absorption at 2500–2700 and 910 cm^{-1}, probably resulting from carboxylic acid end groups.

2. The carbonyl absorption of these polymers shows the typical weak symmetrical (1760 cm^{-1})–strong asymmetrical (1650 cm^{-1}) band system characteristic of cyclic imides, as opposed to the strong symmetrical absorption normally observed with acyclic imides.[8]

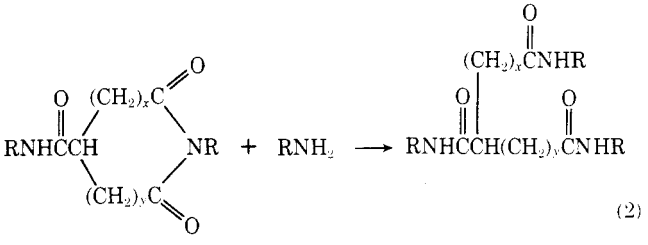
3. The fact that soluble, fusible polymers having a relatively high molecular weight (η_{Inh} 0.8) could be obtained from these polymerizations is compatible with the predominance of cyclic imide groups in these products, as opposed to acyclic (branched) imides.

Maintaining linearity, to the extent that reaction products were soluble and fusible, was found to be a major problem in the production of high molecular weight polymer. The final polymerization temperature had a substantial influence on this linearity, with 300°C being the maximum for use with I and 230°C for II. The presence of amine end groups late in the polymerization also contributed to nonlinearity. It was found that including a monofunctional carboxylic acid as an end-capping agent (e.g., 2 mol % acetic acid) or a small excess of the triacid, both gave high molecular weight products (η_{Inh} 0.8–1.2) which were soluble and fusible and which could be melt fabricated (e.g., spun into fibers) at elevated temperatures. Copolymerization of diamines with tricarboxylic and dicarboxylic acid mixtures, essentially reducing the concentration of imide rings in the resulting polymer, also favored the production of soluble, fusible polymer. When adipic acid was used as a comonomer with II and 1,6-hexanediamine, final polymerization temperatures as high as 275°C could be used to obtain soluble, fusible products in systems containing greater than 50 mol % adipic acid.

The apparent sensitivity of linearity to monomer structure, temperature, and end groups suggests that amine groups, when present at high temperatures in the latter stages of the polymerization, are reacting with cyclic imide groups to produce amide branches. In poly(amideimides) derived from I, where x and y = 1, only five- and six-membered ring imides can be present. Those obtained from II can contain five-, six-, and seven-membered ring structures and those derived from III have six- and eight-membered rings possible. These larger imide rings, having greater



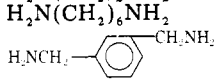
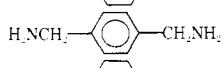
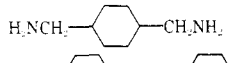
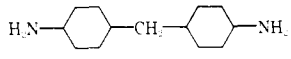
(1)



(2)

R = polymer radical, x and y = 1 or 2

Table I
Poly(amideimide) Homopolymers

Diamine	$HO_2CCH_2CH(CO_2H)CH_2CO_2H$ T_g, °C[a]	PMT, °C[b]	η_{Inh}[c]	$HO_2CCH_2CH(CO_2H)CH_2CH_2CO_2H$ T_g, °C[a]	PMT, °C[b]	η_{Inh}[c]
$H_2N(CH_2)_2NH_2$	130	190	0.15	87	140	0.12
$H_2N(CH_2)_6NH_2$	71	120	0.74	50	90	insol.
	141	205	0.56	110	160	0.56
	158	250	0.11	125	180	insol.
	149	230	0.37	114	170	0.26
	200	305	0.81	172	250	0.76

[a] Determined on premelted and quenched samples by DTA. [b] Polymer melt temperatures, no crystallinity detected by DTA. [c] Measured on 0.5% solutions in *m*-cresol at 30°C.

than six atoms, may contribute to nonlinearity in two ways. The lower entropy involved with their ring closure during imide formation may lead to more amide branches being produced directly. They should also undergo more facile ring-opening reactions with diamines (reactions 1 and 2) and more rapid interchange reactions with amide groups on adjacent polymer chains.

Structure–Property Relationships. The thermal transitions of poly(amideimides) prepared from I and II with a variety of aliphatic diamines are shown in Table I. All the polymers were obtained as clear glasses and did not evidence crystallinity by DTA. The glass transition temperatures (T_g) of polymers derived from I were about 30°C higher than those from II, because of the presence of one less methylene group in their repeat unit. Polymer melt temperatures[9] (temperatures at which polymer samples leave a trail when moved across a metal surface under moderate pressure), normally occurring 50–60°C above T_g in amorphous polyamides, averaged 55°C above T_g for the poly(amideimides) from II and 75°C above T_g for those from I. Poly(amideimides) derived from III were found to be insoluble and infusible in nearly all cases. A low molecular weight homopolymer was obtained from bis(4-aminocyclohexyl)methane and III (η_{Inh} 0.1, polymer melt temperature 215°C) by using a 2 mol % excess of the triacid.

The thermal transitions of copolymers prepared from mixtures of adipic acid and either I or II with 1,6-hexanediamine are plotted as a function of composition in Figures 1 and 2. Incorporation of I into poly(hexamethylene adipamide) (Figure 1) causes a steady decline in crystalline melting temperature (T_m) and a small increase in T_g. No crystallinity was observed in polymers having greater than 50 mol % I, the values shown in Figure 1 for these compositions being polymer melt temperatures of amorphous materials. When II was included in this poly(hexamethylene adipamide) polymer system (Figure 2), the decrease in T_m was more rapid than in similar copolymers derived from I, while T_g was affected to a lesser degree. Copolymers containing greater than 50 mol % II were amorphous. These tricarboxylic acids are very efficient disrupters of crystallinity in poly(amideimides). As little as 15 mol % can be used to obtain an amorphous polymer from dodecanedioic acid and bis(4-aminocyclohexyl)methane.[7]

Mechanical Behavior. The poly(amideimide) copolymers from mixtures of I and adipic acid with 1,6-hexanediamine were readily melt spun into fibers. A comparison of the copolymer from an 80/20 mol % mixture of adipic acid and I and the adipic acid homopolymer, poly(hexamethylene adipamide), is shown in Table II. Copolymers containing from 15 to 30 mol % I could consistently be drawn

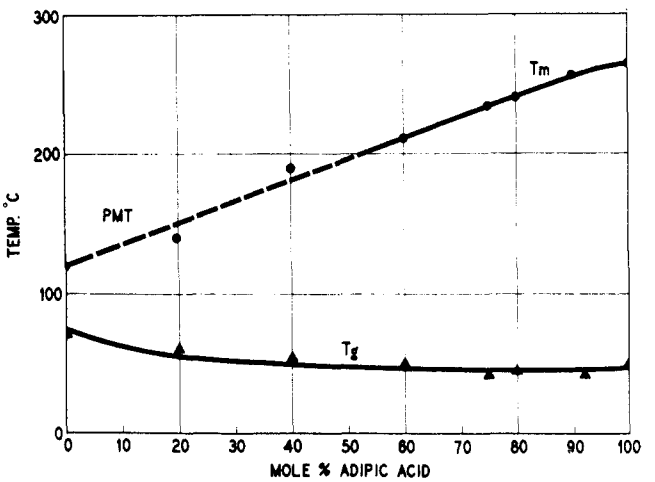


Figure 1. Thermal transitions of poly(amideimides) derived from mixtures of 1,2,3-propanetricarboxylic acid and adipic acid with 1,6-hexanediamine.

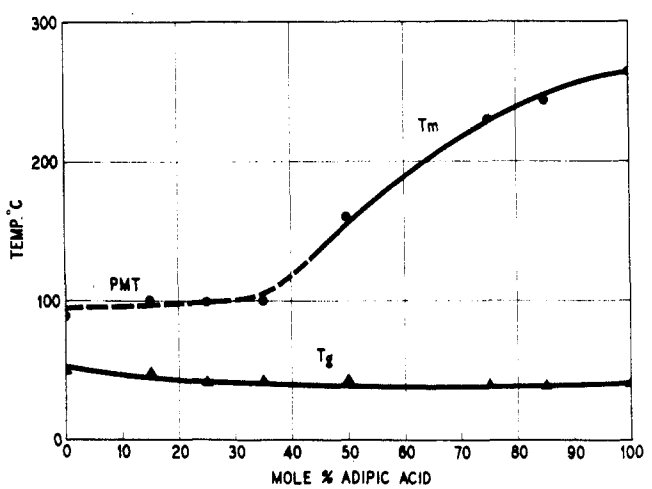


Figure 2. Thermal transitions of poly(amideimides) derived from mixtures of 1,2,4-butanetricarboxylic acid adipic acid with 1,6-hexanediamine.

at higher ratios than the homopolymer, resulting in slightly stronger (higher tenacity) fibers. Other fiber properties were not significantly affected. Boiling water shrinkage, even after annealing, remained quite high (20–30%) for the copolymers, making them of interest as the high-shrinkage component of a bicomponent fiber.

Table II
Fiber Properties of a Copoly(amideimide) from an 80:20 Mol% Mixture of Adipic Acid and 1,2,3-Propanetricarboxylic Acid with 1,6-Hexanediamine

	Mol % 1,2,3-propanetricarboxylic acid	
	0	20
η_{Inh}[a]	1.05	1.02
Extrusion temp, °C	280	250
Draw ratio[b]	5.5	6
Tenacity, gpd[c]	6.0	7.5
Elongation, %[c]	23	15
Initial modulus, gpd[c]	38	45
Boiling water shrinkage, %	3	20

[a] Measured on 0.5% solutions in *m*-cresol at 30°C. [b] Maximum operable ratio. [c] Determined according to ASTM 2256-69.

Copolymers derived from mixtures of adipic acid and II with 1,6-hexanediamine were not as easily melt spun into fibers because of voids in the extrudate and melt viscosity increases during spinning. In bulk molded form, however, they were found to exhibit exceptionally high impact strengths (Table III) when equilibrated with atmospheric conditions.

Experimental Section

Materials. 1,2,3-Propanetricarboxylic acid (Eastman) was triturated in refluxing diethyl ether and decolorized and recrystallized from water (mp 154–155°C). 1,2,4-Butanetricarboxylic acid was prepared by the nitric acid oxidation of 4-vinylcyclohexene[10] and recrystallized from ethyl acetate (mp 122–124°C). 1,3,5-Pentanetricarboxylic acid (Kay Fries) was decolorized and recrystallized from ethyl acetate (mp 113.5–114°C). Polymerization grade adipic acid (Rohm and Haas) was used as obtained. The diamines used were vacuum distilled and stored under nitrogen.

Polymerizations. The poly(amideimides) were prepared by conventional melt polymerizations conducted on a 10–50 mmol scale in glass reactors, prepared from ball/socket joint glass tubing, and on a 0.1–1.0 mol scale in a 316 stainless steel, 1-l. autoclave. Near equimolar mixtures of carboxylic acids and amines were placed in a reaction vessel and heated under a nitrogen atmosphere to temperatures ranging from 200 to 300°C for several hours. Initially, the systems were maintained under nitrogen pressure (70–140 kPa in glass, 1400–3500 kPa in steel) to prevent diamine loss. The final stage of the polymerization involved heating the mixture at the final temperature under a slow nitrogen flush at 0.1–3.0 kPa vacuum. The products were obtained in nearly quantitative yield.

Table III
Mechanical Properties[a] of Copoly(amideimides) from Mixtures of 1,2,4-Butanetricarboxylic Acid and Adipic Acid with 1,6-Hexanediamine

	Mol % 1,2,4-butanetricarboxylic acid		
	0	15	25
η_{Inh}[b]	1.35	1.08	1.05
Decomposition temp, °C[c]	417	445	420
Density, g/cm^3	1.15	1.15	1.17
Tensile strength,[d] MPa	74.6	69.3	47.6
Elongation,[d] %	72	29	3
Flexural modulus,[e] MPa	2770	2920	2270
Izod impact,[f] N m/m			
Dry	43	40	24
Conditioned[g]	107	284	465

[a] Determined on compression molded specimens. [b] Measured on 0.4% solutions in *m*-cresol at 30°C. [c] Intersection of the extrapolations of weight retention and loss straight-line portions of TGA curves. [d] ASTM D 638-68. [e] ASTM D 790-66. [f] ASTM D 256-66. [g] The homopolymer value was taken from a table in "Plastics Technology", 14, 276 (1968) on material equilibrated at 50% relative humidity; the copolymers were measured after equilibrating at 65% relative humidity.

Measurements. Inherent viscosities were measured in *m*-cresol at a concentration of 0.5 g of polymer per 100 ml of solution at 30°C. Polymer melt temperatures,[9] reported for amorphous polymers, were determined using a heated brass rod with a temperature gradient (modified "Dennis bar"). The DTA measurements were performed using a DuPont Model 900 instrument. Samples (10 mg) were premelted at 270°C for 3 min and quenched in liquid nitrogen. The heat up was carried out at 10°C/min under a nitrogen atmosphere using an empty pan reference. The heating rate for TGA measurements was 20°C/min.

References and Notes

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