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New High-Temperature Polymers. II: Ordered Aromatic Copolyamides Containing Fused and Multiple Ring Systems*

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Synopsis

Thermostable polymers and, more particularly, thermostable fibers and films are becoming more and more important as the demands of space-age technology increase. In the preparation of thermostable fibers having good tensile strengths and practical utility the processibility of the polymer is of great importance. Aromatic polyamides meet the two most important requirements: a high degree of thermal stability and an ease of preparation as viscous solutions that can be spun into fibers or cast into films.

The self-condensation of aromatic amino acids gives an A-B type of aromatic polyamide, and fiber properties have been reported (*1*,*2*). Another class of aromatic polyamide (AA-BB) is that formed by condensing aromatic diamines, such as *m*-phenylenediamine, with aromatic diacid halides, such as isophthaloyl chloride; fiber properties of poly(*m*-phenylene isophthalamide) have been reported (3). A third type of aromatic polyamide, from the polymerization of diacid halides with ordered diamines containing preformed carbonamide linkages, has been reported by us (*4*,*5*). This brief paper summarizes new work on the preparation of ordered diamines containing fused or multiple ring structures and their polymerization with diacid halides to high-molecular-weight polymers.

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Ordered diamines were made by the condensation of 1 mole of an aromatic diamine with 2 moles of *m*- or *p*-nitrobenzoyl chloride (either interfacially with dilute sodium hydroxide–tetrahydrofuran or wholly in solution in dimethylacetamide) and the reduction of the resulting dinitro compound to the diamine (catalytic hydrogenation or stannous chloride). Aromatic diamines used included *m*-phenylenediamine, *p*-phenylenediamine, benzidine, 1,5-diaminonaphthalene, and 2,7-diaminonaphthalene. Some properties of five ordered diamines are listed in Table 1.

TABLE 1

N,N′-Arylenebis(aminobenzamides)

Compound	Code	M.p., °C (uncorr.)	N, % Calcd.	N, % Found	
N,N′-*m*-phenylenebis(*m*-aminobenzamide (5)	MMM	213–214	16.14	16.13	16.08
N,N′-*m*-phenylenebis(*p*-aminobenzamide) (5)	PMP	227–228	16.14	15.93	15.89
N,N′-4,4′-biphenylene-bis(*m*-aminobenzamide)	MBM	332–334	13.27	13.32	13.36
N,N′-1,5-naphthylenebis (*m*-aminobenzamide)	MN5M	232–234	14.14	14.26	14.07
N,N′-2,7-naphthylenebis (*m*-aminobenzamide)	MN7M	298–300	14.14	14.14	14.33

These diamines were polymerized with isophthaloyl chloride, 4,4′-bibenzoyl chloride, and 2,6-naphthalenedicarbonyl chloride, to give the polymers listed in Table 2. Solution polymerization at −20 to 0°C, usually with the use of dimethylacetamide as solvent, gave high-molecular-weight products with number-average molecular weights up to about 60,000 by end-group analysis.

Fibers from the polymers prepared by polymerizing the diamine MMM with 4,4′-bibenzoyl chloride (polymer coded MMM-B) and with 2,6-naphthalenedicarbonyl chloride (polymer coded MMM-N6) were studied most. A typical set of properties for an unboiled-

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TABLE 2

Wholly Aromatic Ordered Copolyamides

Diamine (Table 1)	Acid chloride	η_{inh}[a]	PMT, °C[b]	DP, °C[c]	
MMM (5)	Isophthaloyl chloride (IC)	1.48	410	450	Strong films and excellent crystalline fibers
MMM	4,4′-Bibenzoyl chloride (BC)	2.38	420	490	Strong films and excellent crystalline fibers
MMM	2,6-Naphthalenedicarbonyl (NC)	2.42	430	490	Strong films and excellent crystalline fibers
PMP (5)	IC	1.27	475	490	Strong films and excellent crystalline fibers
PMP	BC	1.20	490	490	Strong films
PMP	NC	1.38	>500	500	Strong films
MBM	IC	0.58	470	500	
MBM	BC	0.60	480	>600	
MBM	NC	0.57	>500	500	
MN5M	IC	0.72	>500	>600	
MN5M	BC	1.13	400	430	
MN5M	NC	0.99	>500	480	
MN7M	IC	0.62	>500	490	
MN7M	BC	0.85	>500	450	
MN7M	NC	0.75	475	475	

[a] Inherent viscosity, 0.5% solution in 5% lithium chloride in DMAc at 30°C.

[b] Polymer melting temperature observed by DTA.

[c] Approximate decomposition temperature observed by TGA.

off sample of MMM-N6 are: tenacity 8.0 gpd, elongation 13% initial modulus 154 gpd, moisture regain (equilibrium moisture at 70°F and 65% RH) 4.5%, and density 1.35. Corresponding data for fibers of MMM-B were tenacity 5.9 gpd, elongation 16%, and initial modulus 93 gpd. When tested at elevated temperatures, fibers of MMM-N6 retained about 90% of their tenacity at 100°C, 75% at 200°C, 30% at 300°C, and 13% at 400°C. Fibers of MMM-N6 had great stability to the effects of prolonged exposure to dry heat in air at 300°C: originally, the fibers had a value for tenacity (gdp)/elongation (%)/initial modulus (gdp) of 5.5/25/90; after 9 days at

300°C the value was 1.2/2.5/53. That is, the fibers retained 21% of their tenacity after 9 days of exposure. The chemical resistance of these fibers to concentrated acids and bases was good.

Films of MMM-N6 were cast from solutions of the polymer in dimethylacetamide containing 5% dissolved lithium chloride. The inorganic salt readily leached out. The films had a breakdown voltage of 3000 V/mil at 180°C, compared with 2250 V/mil for poly(tetrafluorethylene) at 150°C and 120 V/mil for nylon at 150°C. Small 0.25-μF capacitances of aluminum foil/MMM-N6 film were still functioning at the end of 4 hr of use at 180°C; commercial aluminum–polyester condensers failed within 20 min under these conditions.

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