Excimer formation case iii, *i.e.*, between two chromophores belonging to two different polymer chains, should also be excluded by the following findings. Although in such a dilute solution as 10^{-3} mol/l. any intertwining of the polymer chains seems to be unlikely, in a solution as concentrated as 10^{-2} mol/l. no excimer emission was observed. Moreover, a model compound, EtCz, showed no excimer fluorescence in concentrated solution, in the molten state, and even in the solid state.

Consequently, in vinyl polymers having carbazole units, an excimer state can be formed only when the polymers have at least two carbazole rings connected to the main chain by a separation of three carbon atoms, *viz.*, the structure of case i.

Thus, we have obtained new information for excimer formation in aromatic vinyl polymers having large pendant π-electron systems. The study with the 1:1 alternating copolymers is a useful method for distinguishing between excimer formation cases i and ii. As mentioned above, the absence of excimer fluorescence even in concentrated solutions of EtCz is characteristic of the carbazole molecule. This leads us successfully to the above conclusion. Actually, the rule does not apply to pyrene derivatives because concentrated solutions of 1-ethylpyrene exhibit excimer fluorescence. Recently, we obtained the 1:1 alternating copolymer of 1-vinylpyrene and maleic anhydride, and observed excimer fluorescence of pyrene rings despite their separation by maleic anhydride units in the rigid skeleton. The details of this result will be reported elsewhere.

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Polyamides from Phenylenediamines and Aliphatic Diacids

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ABSTRACT: High molecular weight polyamides were made from *o*-, *m*-, and *p*-phenylenediamines and 4- to 12-carbon aliphatic diacid chlorides by interfacial and solution methods. Polymerization in cold tertiary amide solvents was preferred. The polymers were examined in terms of melting temperatures, solubility, and light stability. Melting temperatures increased in going from ortho to meta to para structures and as the chain length of the aliphatic diacid decreased. Solubility decreased in the above order. In solubility this group of polymers resembles both wholly aromatic polyamides and wholly aliphatic polyamides in that most members of the series dissolve in the basic amide solvents, at least in the presence of lithium chloride, and in acidic solvents such as *m*-cresol and trifluoroacetic acid. Polymers from aliphatic diamines and aromatic acids dissolve only in acids and phenols. Outstanding resistance to yellowing and degradation by ultraviolet light was demonstrated for several of the polymers in film and fiber form. Bright, strong fibers were prepared from poly(*m*-phenyleneadipamide). They could be obtained in an amorphous state and in a highly crystalline form. Matched pairs of para-linked aliphatic–aromatic and aromatic–aliphatic polyamides, such as poly(octamethyleneterephthalamide) and poly(*p*-phenylenesebacamide) had nearly coincident melting temperatures in several instances. Repeat spacings from X-ray diffraction patterns indicated that the polymer chain segments were fully extended in the crystalline state. However, the repeat spacing for the aliphatic–aromatic polymer was slightly less than that of the aromatic–aliphatic polymer in each pair.

There are numerous references to polyamides from aliphatic diamines with aromatic diacids and a far lesser number to polyamides from phenylene diamines with aliphatic diacids.[1,2] Two early references are those of Lum and Carlston[3] on poly(hexamethyleneisophthalamide) and Beaman and coworkers[4] on poly(*m*-phenylenesebacamide). Within the aliphatic–aromatic group of polyamides Shashoua and Eareckson[5] made one of the more extensive comparative studies of terephthalamides. This covered diamines with 2–7 chain-carbon atoms, as well as *N*-alkyl and some chain-alkyl substituents. Hopff and Krieger[6] prepared the polymers from 6-, 8-, and 10-carbon diamines and diacids with the complementary *o*-, *m*-, and *p*-phenylene intermediates. Recently Gorton[7] has explored a series of poly(methyleneisophthalamides). Bonner[8] has described the crystallization of poly(tetramethyleneisophthalamide) and poly(hexamethyleneisophthalamide), which were previously thought to be uncrystallizable.[2,3] Most of the unsubstituted aliphatic–aromatic polyamides which have been reported are listed in Table I. For brevity only selected references are noted.

Of this group poly(hexamethyleneterephthalamide) has received the most attention. Not only has it been prepared in a number of ways but it has been the subject of extensive spinning studies and characterization in fiber form.[5,12-14]

Probably the reason that aliphatic–aromatic polyamides

Table I
Polyamides from Aliphatic Diamines and Aromatic Acids

Diamine, carbon atoms in chain	*o*-Phthalamide[a]		Isophthalamide			Terephthalamide		
	Softening or melt temp, °C	Ref	η_{inh},[b] dl/g	Softening or melt temp, °C	Ref[c]	η_{inh}, dl/g	Softening or melt temp, °C	Ref[c]
2			0.94	292–310	7	1.00[d]	455[f]	5
3			0.72	240–288	7	1.70[d]	399[f]	5
4			1.05	230–245	*7*, 8	1.20[d]	436[f]	5
5						2.00[d]	353[f,k]	5
6	150	6	0.68	170–230	3, 6, *7*, 8–10	0.9[d]	371[f]	*5*, 6, 11–16
7						0.69[e]	327[g,h,l]	5, *17*
8	123	6		123[i]	6		186[j]	6
9						1.03[e]	309[g]	17
10	115	6	0.79	166–194	6, *7*, 10	0.86[e]	316[g]	6, *17*
12						0.77[e]	290[g]	17

[a] No viscosity data. [b] *m*-Cresol at 30°. [c] Italics indicate reference from which data are taken. [d] H_2SO_4 at 30°. [e] Dichloroacetic acid at 25°. [f] DTA; polymers were medium to highly crystalline. [g] Vicat penetrometer test. [h] Reference 5 gives 341°; DTA; high crystallinity. [i] This work, 150–200°; η_{inh} 1.00. [j] This work, 322–333°; η_{inh} 0.93. [k] This work, 356°; DTA, 354°; η_{inh} 1.07 (*m*-cresol). [l] This work, 330°; DTA, 330°; η_{inh} 1.11 (*m*-cresol).

Table II
Polyamides from Phenylenediamines and Aliphatic Diacid Chlorides[a]

Diacid unit		*o*-Phenylenediamine		*m*-Phenylenediamine		*p*-Phenylenediamine	
Name	Carbon atoms	η_{inh}, dl/g[b]	Yield, %	η_{inh}, dl/g[b]	Yield, %	η_{inh}, dl/g[b]	Yield, %
Succinyl	4	0.19[c]	79	0.33	98	0.40	85
Glutaryl	5	0.26[c]	76	0.81	100	0.72	84
Adipyl	6	0.26	84	1.66	100	0.80	85
Pimelyl	7	0.59	93	0.57	76	0.85	94
Suberyl	8	0.70[c]	96	1.42	100	1.27[c,d]	95
Azelayl	9	0.23	100	0.80[c]	100	0.77[c]	92
Sebacyl	10	0.62[c]	95	1.20	100	1.03	100
Undecanoyl	11			0.19	84		
Dodecanoyl	12	0.40[c]	83	1.10	100	0.94	100

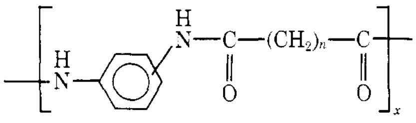
[a] Synthesized by method B described in the Experimental Section. [b] Determined in *m*-cresol at 0.5% concentration and 30° except as noted. [c] Determined in 96–98% H_2SO_4. [d] With highly purified acid chloride a polymer with η_{inh} of 2.06 was obtained.

have been studied in greater detail than the aromatic–aliphatic polyamides is that many of the former group can be made by melt and plasticized melt methods[3,17] or by standard interfacial procedures.[5,7,11] The aromatic–aliphatic polyamides, on the other hand, when prepared by melt methods, frequently are discolored and may have branched or network structures. Only polymers from selected diamines, such as 4,4′-diaminodiphenylmethane, are readily made.[18] The usual interfacial procedures are not generally satisfactory. The intermediates may be considered to be more difficult to purify and store, although this is not truly a major problem.

The purpose of this paper is to describe the preparation and properties of a group of unsubstituted aromatic–aliphatic polyamides prepared by low-temperature procedures, to compare properties within the group, and to make appropriate comparisons with the aliphatic–aromatic polyamide series. The range of polymers synthesized is shown in Table II. In addition to several references given in the introduction, a U.S. Patent sets forth some of the data presented here.[19]

Discussion and Results

Polymerization Methods. Unsubstituted homopolyamides of the aromatic–aliphatic type illustrated can be prepared only with difficulty by melt polycondensation. Balanced salts are not readily prepared and the diamines tend to sublime. The uncatalyzed reaction is slow and serious discoloration and branching side reactions are encountered.



Interfacial polycondensation can be applied with some modifications. Weak bases should be used as acid acceptors to minimize acid chloride hydrolysis. The usual solvents should be replaced by solvents with higher polarity to accelerate the reaction and increase polymer swelling. The use of chlorobenzene, acetophenone, and cyclohexanone is illustrated in the Experimental Section.

Simple solution polymerization in a halogenated hydrocarbon and a tertiary amine acid acceptor can be used with fair success (method A). By far the most useful method (B) employs a tertiary amide (dimethylacetamide, *N*-methylpyrrolidone, or hexamethylphosphoramide) as the solvent medium and acid acceptor. The polymerizations are carried out with cooling and stirring. The polymers remain dissolved in the reaction media and thus have an opportunity

Table III
Solubility of Phenylene Polyamides[a]

Polyamide: Diamine	Polyamide: Diacid	TFA	*m*-Cresol	Formic acid	$CHCl_3$–formic acid (70:30)	NMP–5% LiCl	DMAc–5% LiCl	DMAc	DMSO	DMF
p-Phenylene	4	-	-	-	-	+	+	-	-	-
	5	-	s	-	-	+	+	-	-	-
	6	-	-	-	-	+	+	-	-	-
	7	++[b]	s	-	-	++	++	-	+	-
	8	s	-	-	-	+	+	-	-	-
	9	++[b]	+	-	-	++	++	-	+	-
	10	++[b]	-	-	-	++	++	-	++	-
	12	++	-	-	-	++	++	-	++	-
m-Phenylene	4	++	++	s	-	++	++	++	++	++
	5	++	++			++	++	++	++	++
	6	++	++	++	++	++	++	++	++	++
	7	++	++	++	++[b]	++	++	++	++	++
	8	++	++	++	++[c]	++	++	++	++	++
	9	++[c]	++	++	++	++	++	++	++	++
	10	++[c]	++	++	++	++	++	++	++	++
	11	++	++	++	++[b]	++	++	++	++	++
	12	++	++	+[b]	++[b]	+	+	+	+	+
o-Phenylene	4	+	s	-	s	+	+	s	+	s
	5	++	++	++	++	++	++	+	+	+
	6	++	+	+	++	+	+	+	+	+
	7	++	++	++	++	++	++	+	+	+
	8	++	++	+	++	++	++	+	+	+
	9	++	++	++	++	++	++	+	+	+
	10	++	++	+	++	++	++	+	+	+
	12	++	++	+	++	++	++	+	+	+

[a] Polymers were those listed in Table II. Solubility was determined at 3% concentration. ++, soluble at room temperature; +, soluble with heat up to boiling point if needed; s, swollen noticeably; -, insoluble. [b] Two phases. [c] Cloudy.

to reach maximum molecular weight. In some cases an extra increment of several tenths of a viscosity unit has been gained by adding equivalents of diethylaniline or triethylamine to the system. The synthesis and thermal behavior of polyamides from *o*-phenylenediamine is discussed in more detail in a later section.

Polymer Crystallinity. The as-prepared polyamides were amorphous when isolated in small amounts (5 g) and not heated excessively in the presence of water. Likewise, films and fibers prepared by melt or solvent methods were amorphous if only water extracted and air dried. Crystallinity in the range of intermediate to high degree could be induced in many of the *m*- and *p*-phenylene polymers or their shaped structures by heating in steam. In drying granular, alcohol–water wet polymer in quantity at 80–100°, crystallinity was frequently induced. It should be noted that crystallinity has been induced in fibers of poly(terephthalamides)[5] and poly(isophthalamides)[8] by drawing in steam.

Further comments on crystallinity are found in the sections on solubility and fibers.

Polymer Solubility. Unsubstituted polyamides from aliphatic diamines and aromatic diacids dissolve only in such solvents as sulfuric acid, trifluoroacetic acid and *m*-cresol. In this respect they resemble the wholly aliphatic polyamides.

Unsubstituted polyamides from aromatic diamines and aliphatic acids have a much wider range of solubility. Many of them dissolve not only in the acidic solvents but also in various polar, slightly basic solvents such as the tertiary amides and dimethyl sulfoxide. The addition of certain salts, that is, lithium chloride or calcium chloride, may assist solubility in the amide solvents. Solubility in amide solvents (with or without salts) is characteristic of many wholly aromatic polyamides.[1]

Table IV
Effect of Solvent on the Inherent Viscosity Value for Several Samples of Poly(*m*-phenyleneadipamide)[a]

m-Cresol	H_2SO_4	Dimethylacetamide	Dimethyl sulfoxide
1.20	1.14	0.89	0.88
1.66	1.61	1.37	1.14
1.73			1.27

[a] All polymers were made by method B in dimethylacetamide.

All of the polymers reported in Table II were soluble in concentrated sulfuric acid. Table III gives some solubilities in other acidic and basic solvents. The *o*-phenylene and *m*-phenylene polyamides had broad solubility in both types of solvents. Borderline solubility was encountered with poly(*m*-phenylenedodecanediamide), poly(*m*-phenylenesuccinamide), and poly(*o*-phenylenesuccinamide). In the *p*-phenylene series there are interesting limits in solubility. The whole series lacks solubility in formic acid, chloroform–formic acid mixtures, and dimethylformamide. *m*-Cresol dissolves or swells only the polymers from odd-numbered diacids. All of the polymers derived from diacids of less than nine carbon atoms have little or no solubility in the remaining solvents tested. This effect is probably related to the relatively high energy required to separate the polymer chains, which is further reflected in the high softening temperatures of these polymers (>345°; Table V).

Table IV shows the effect of varying the solvent on the

Table V
Softening and Melting Temperatures of Phenylene Polyamides[a]

	o-Phenylenediamine		*m*-Phenylenediamine		*p*-Phenylenediamine	
Diacid unit, carbon atoms	Softening temp,[b] °C	Melt temp,[c,d] °C	Softening temp,[b] °C	Melt temp,[c] °C	Softening temp,[b] °C	Melt temp,[c] °C
4		195		325 dec		>400 dec
5	168	180	198	212		~410 dec
6		145	324	344		400 dec
7		135		174	360	373
8	134	140[e]	288	302		372
9		~110	155	184	330	348
10	115	135	245	258	322	332
11				150[d]		
12		~ 75		220	310	323

[a] Determined on polymers described in Table II with dry powdered samples on a temperature gradient bar. See section on Test Methods.[20] [b] Point of initiation of softening under light sliding pressure. [c] Point at which polymer leaves a molten or waxy trail adhering to the metal surface of the bar. [d] The melting point of these polymers is affected by the low molecular weight of the samples. [e] Alcohol extracted.

Table VI
Comparison of Some Thermal Properties of Selected Pairs of *m*- and *p*-Arylene Polyamides

Polymer[a]	Softening temp,[b] °C	Melting temp,[b] °C	DTA endotherms,[b,c] deg T_g	DTA endotherms,[b,c] deg T_m	T_g/T_m, °K
3-T				399[d]	
P-5		~410 dec	135	398	0.61
4-T				436[d]	
P-6		400 dec	133	399	0.60
5-T		356	137	354	0.65
P-7	360	373	133	372	0.63
6-T		367	125[e]	371	0.62
P-8		372	138	374	0.64
7-T		330	110	330	0.64
P-9	330	348	130	345	0.65
8-T	322	333	123	335	0.65
P-10	322	332	125	334	0.66
10-T	316				
P-12	310	323			
4-I	230	245	141	262	0.77
M-6	324	344	140		
6-I	180	195[f]	124[g]	200	0.84
M-8	288	302	118		
8-I	150	200	105		
M-10	245	258	113		

[a] I, isophthaloyl; T, terephthaloyl; M, *m*-phenylene; P, *p*-phenylene. [b] See Test Methods. [c] Determined under nitrogen at a heating rate of 20°/min. [d] Data from ref 5. [e] Reference 12 gives T_g as 180°. [f] Undrawn fiber heated in 12 psi steam for 1 hr. [g] Reference 3 gives 113° from heat distortion temperature.

inherent viscosity of poly(*m*-phenyleneadipamide) samples. The viscosity data indicate that dimethylacetamide and dimethyl sulfoxide interact less strongly than sulfuric acid or *m*-cresol. Yet the amide and sulfoxide will dissolve 25 to 35% or more (by weight) of polymer to form excellent spinning solutions. High crystallinity can reduce ease of dissolution. For the amides of this class the effect can be overcome in tertiary amide solvents by addition of suitable salts.

Thermal Characteristics. Table V summarizes softening and melting temperatures determined on powdered polymers on a gradient temperature bar, using the polymer samples listed in Table II. Clearly the softening temperatures increase in going from ortho to meta to para diamine segments in the polymers. Likewise the melting temperatures are increased as the chain length of the aliphatic segment is shortened. For the meta series there is a definite alternation of melting points up and down with even and odd numbers of carbon atoms in the diacids, although coincident variation in molecular weights and crystallinity may make contributions here. A plot of melting temperatures for the para series shows a zig-zag line even though a polymer from an odd-membered acid may melt no lower than the next higher even-membered polymer. These effects parallel those found in the aliphatic–aromatic classes of polyamides. While these relationships are somewhat crudely derived on bulk polymer, similar effects should be apparent from DTA endotherms (Table VI), crystalline melting points by X-ray diffraction, and related measurements.

The polyamides derived from *p*-phenylenediamine are noteworthy for having quite sharp melting points, all above 300°. The *o*-phenylene polyamides softened broadly over a wide and low temperature range. They were amorphous or very low in crystallinity.

When pairs of polymers from aromatic–aliphatic and aliphatic–aromatic series which have equal numbers of chain atoms between the rings are compared (Table VI), the melting temperatures are found to be similar for the *p*-arylene group. However, for the *m*-arylene group the isophthalamides are consistently much lower melting. Whether this difference in the behavior of meta and para types is a real structural effect is uncertain, since there could be contributions from differences in crystallinity, molecular weight, and molecular weight distribution.

Calculation of the T_g/T_m ratio from DTA endotherms (Table VI) in degrees Kelvin gave values between 0.61 and 0.66 for ten polymers of the *p*-arylene type. This approximates the two-thirds rule proposed by Beaman.[21]

Films and Fibers. Flexible, self-supporting films were readily prepared from polymers with inherent viscosities of about 0.6 or above. For strong fibers somewhat higher viscosities are desirable.

For a typical fiber evaluation poly(*m*-phenyleneadipamide) was selected because of its ready preparation in high molecular weight, intermediate thermal characteristics, and good solubility. Fibers were prepared by both melt and dry spinning. Some test results on dry-spun fibers are given in Table VII along with others for the suberamide and sebacamide.

Table VII
Preparation and Properties of Fibers from *m*-Phenylene Polyamides

	Adipamide	Suberamide	Sebacamide
Polymer η_{inh} (*m*-cresol)	1.38	1.24	1.10
Spinning solvent	Dimethyl sulfoxide	Dimethylacetamide	Dimethylacetamide
Drawing	4.3× in 12 psi steam 1.1× at 200°, hot plate	3.25× at 85° dry[b]	3× at 80° dry[b]
Denier/filament[a]	3.0	11	15
Tenacity, gpd	5.4	1.3	1.7
Break elongation, %	31	117	144
Initial modulus, gpd	75		
Flex life	5 × 10^5 cycles		
X-Ray diffraction			
orientation angle	16[c]	30[d]	20[d]
crystallinity: amount	High	Low	Low
perfection	High	Medium	Medium
Stick temp, °C	236	198	153
Zero strength, °C	297	244	200

[a] Properties determined after scouring in a relaxed state and conditioning at 21° and 65% R.H. Tensile tests made with Instron tensile tester with 1-in. gage-length filament samples and a rate of extension of 60%/min. Before the scour T–E–M_i–Denier were 6.2:13:98:2.5 for the adipamide. [b] Solvent tenaciously held by fiber. [c] Type 2 pattern. See Figure 1. [d] Type 1 pattern. See Figure 1. After treating drawn fiber in taut conditions with steam at 50 psi for 30 min.

All of the fibers were amorphous as spun, but they could be crystallized by drawing in a steam atmosphere. The adipamide was found to yield different X-ray diffraction patterns with changes in yarn processing (Figure 1). All patterns had essentially the same d spacings and it is therefore believed that the difference in patterns arises from the relation of crystal angle to the fiber axis.

The tenacity, elongation, modulus values for poly(*m*-phenyleneadipamide) and poly(*p*-phenylenesuberamide) fibers were comparable to those of fibers from aliphatic poly(isophthalamides) and poly(terephthalamides) reported in the literature.[5,8,12,17]

Films of several *m*- and *p*-arylene polymers were solvent cast, washed and dried, and then hot drawn as 1.5–3-mm strips over a gradient temperature bar. The casting solvents were trifluoroacetic acid, dimethylacetamide, or dimethylacetamide–lithium chloride (see Table III for solubilities). Table VIII shows the results of examination by X-ray diffraction. All of the compositions, both odd and even chained, attained a medium degree of crystallinity and good orientation. The layer line spacings for the *p*-arylene polymers combined with model measurements indicated that the longitudinal dimension of the unit cells contained one repeat unit in a fully extended conformation. Films or fibers of *p*-phenylene polyamides were crystalline and oriented after hot drawing, but as indicated above *m*-phenylene polyamides required steam treatment taut for attainment of appreciable crystallinity.

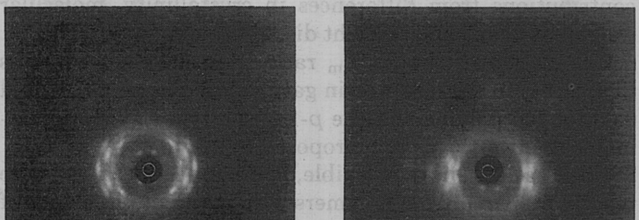


Figure 1. X-Ray diffraction patterns of fibers from poly(*m*-phenyleneadipamide). (Left) Drawn 3.4 times in 12 psi steam and then 1.2 times over a 222° hot plate (Type 1). (Right) Drawn 4.3 times in 12 psi steam and then 1.1 times over a 200° hot plate (Type 2).

Comparison of the X-ray diffraction patterns of pairs of polymers, such as 8-T and P-10 or 6-T and P-8 (Table VIII), shows that the terephthalamides have somewhat shorter repeat distances than the corresponding *p*-phenylenediamine polymers. This is confirmed by measurements on models in an extended regular conformation. Mixtures of some of these polymer pairs cast into films appeared to be compatible as judged by film clarity.

The densities of drawn films of 6-T and P-8 were 1.2447 and 1.2408 whereas the density of M-8 was 1.2293. X-Ray diffraction patterns of M-6, M-8, and M-10 indicate that the chains of these polymers are not fully extended in the crystalline regions. A more extensive examination is needed to relate crystalline form, unit cell arrangements, and densities.

Light Stability. Films of several polyamides were exposed to ultraviolet light in a Fade-Ometer (Table IX). They showed no visible discoloration in the times noted. The degree of stability in terms of molecular weight retention is excellent for polyamides containing no added stabilizers or pigments. Drawn, crystallized fibers of poly(*m*-phenyleneadipamide) exposed in a Fade-Ometer for 200 hr retained 80% of the filament tenacity and had a tenacity half-life of 425 hr. The tenacity half-life of clear, unstabilized filaments of 6-6 nylon is about 200–250 hr under similar conditions.

Prolonged exposure of films (Table IX), beyond the 400–500-hr range, led to gradual yellowing and either cross-linking or appreciable molecular weight loss, which were apparent from solubility changes, embrittlement, and η_{inh} loss. The casting or spinning solvent had an appreciable influence on light stability. Amide solvents yielded the most stable shaped products whereas acid solvents, such as trifluoroacetic acid, frequently greatly reduced the light stability in spite of careful washing and drying.

Hydrolytic Stability. Drawn fibers of poly(*m*-phenyleneadipamide) with intermediate crystallinity were unchanged in regular tensile properties by 30 min immersion in boiling water or 1% aqueous sodium hydroxide. There was 25% loss in tenacity after a like treatment with 1% aqueous hydrochloric acid.

Water Absorption. The water absorption of amorphous

Table VIII
X-Ray Examination of Drawn Films

Polymer[a]	Drawing conditions	Crystallinity: Amount	Crystallinity: Perfection	Orientation: d spacing	Orientation: Angle, deg	Layer line spacing, Å	Fully extended model repeat distance, Å[b]
5-T	3.4×, 325°	Medium	Low	4.27 Å	30	14.1[c]	13.8
P-7	4.2×, 300°	Medium	Medium	4.04	20	14.7	14.6
6-T	3.0×, 350°[e]	Medium	Medium	3.92	21	15.6	15.5
P-8	4.3×, 365°	Medium	Medium	3.95	17	16.3	16.1
8-T	3×, 292°	Medium	Low	3.93	21	17.9	18.0
P-10	4.5×, 300°	Medium	Medium	4.08	21	18.5	18.4
P-12	4.5×, 295°	Medium	Medium	4.09	16	21.2	20.8
M-6[d]	4.3×, 94.4° 1.1×, 200°	High	Medium	4.06	19	11.8[f]	25[g]
M-8	3.25×, 90° Taut, 30 min in 50 psi steam	High	Medium	3.46	18	13.0	29[g]
M-10	3.0×, 80° Taut, 30 min in 50 psi steam	High	Medium	3.52	~30	14.9	33[g]

[a] T, terephthaloyl; P, *p*-phenylene; M, *m*-phenylene. [b] Corey–Pauling–Koltun (CPK) precision molecular models, The Ealing Corp., Cambridge, Mass. [c] Livingston and Gregory[22] report 13.3 Å for 5-T and 11.4 Å for 3-T. [d] Fiber drawn in steam, Table VII. [e] Then heated 40 min relaxed in boiling water. [f] Type 1 pattern. [g] Two structural units.

Table IX
Stability to Ultraviolet Light in a Fade-Ometer

Polymer	Film[a]: Casting solvent	Film[a]: Thickness, mils	Exposure time, hr	Inherent viscosity (*m*-cresol): Before	Inherent viscosity (*m*-cresol): After
o-Phenylenesebacamide	Dimethylacetamide–2% LiCl	0.4	240	0.6	0.5
m-Phenylenesebacamide	Dimethylacetamide	0.4	250	0.80	0.85
			425	0.80	1.35
			600	0.80	Partly insoluble
p-Phenylenesebacamide	Dimethylacetamide–5% LiCl	0.3	100	0.78[b]	0.70[b]
			260	0.78[b]	0.76[b]
m-Phenyleneadipamide	*N*-Methylpyrrolidone	0.5	100	1.53	1.25
			200	1.53	1.07
			500	1.53	0.82
			1000	1.53	0.64

[a] Films were dry-cast on glass, washed thoroughly with water, and redried at 90–100° under vacuum. [b] Sulfuric acid.

Table X
Dissociation Constants for Phenylenediamines

Diamine	K_1 (H_2O at 20°)	K_2 (H_2O at 20°)	*N*-Monobenzoyl (50% aq MeOH at 25°)
Ortho	3.2×10^{-10}	0.16×10^{-12}	1.9×10^{-11}
Meta	7.6×10^{-10}	3.2×10^{-12}	8.1×10^{-11}
Para	123×10^{-10}	14.1×10^{-12}	17×10^{-11}

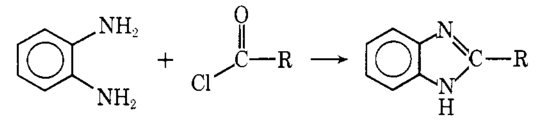
poly(*m*-phenyleneadipamide) film was 9.1% after a 24-hr soak.

Films of poly(*o*-phenylenesebacamide) were brittle when soaked in water, but became flexible again when dried. This possibly indicates a type of swelling in which the structure stiffens as in the formation of a gel.

Polymers from *o*-Phenylenediamine. Although meta- and para-oriented aromatic diamines have been successfully used in many polyamide syntheses, several considerations make ortho aromatic diamines seem unpromising intermediates for polyamide formation. The proximity of the amine groups could introduce steric hindrance to acylation of the second amine group. The base strength of the second amine group, and therefore its reactivity, is reduced by the neighboring polar group. The orientation of the amine groups appears to favor benzimidazole formation.

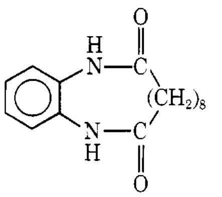
The differences in base strengths of the *o*-, *m*-, and *p*-phenylenediamines have been determined by Kuhn and Zumstein[23] and Kraiman[24] examined the monobenzoyl derivatives (Table X). The base strengths differ in the expected order, but not enough to exclude the possibility of easy polymer formation by the *o*-phenylenediamine.

Ortho phenylenediamines will form benzimidazoles[25–27] with acylating reactants. The ring closure requires high temperature for high yields. However, only a small propor-

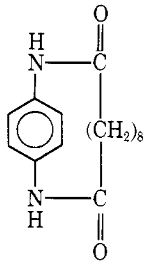


tion of this reaction would interfere with high polymer formation. Howlett, Butler, and Low[28] disclosed the use of *o*-phenylenediamine to control the molecular weight of 6 and 6-6 nylons in melt polycondensations.

That many complementary difunctional compounds will condense in dilute solution to yield macrocyclic structures has been known since the work of Ruggli.[29] Stetter and coworkers[26,30,31] studied the formation of macrocyclic diamides from phenylenediamines and aliphatic diacid chlorides. At reactant concentrations in the optimum range of 0.01–0.02 *M*, the compounds below were obtained in the yields indicated. Clearly the *o*-phenylenediamine has a high ring-forming tendency with sebacyl chloride. This side reaction could cause serious loss in materials. However, chain termination would not result and therefore polymerization is not precluded.



87%



35%

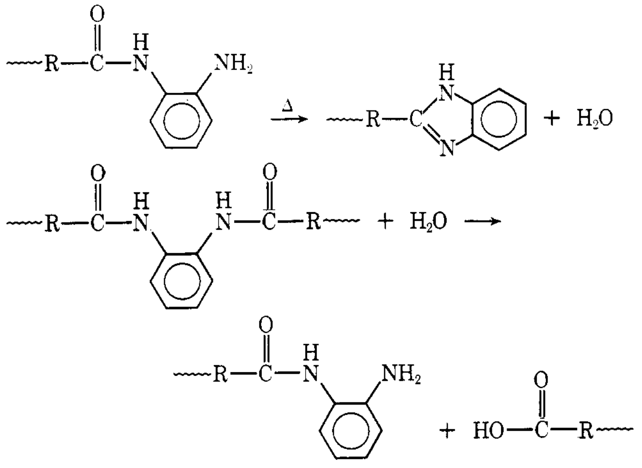
The conditions which favor polymer formation are (1) use of polar solvents to raise the reaction rate, (2) use of high concentrations of reactants to avoid cyclization, and (3) lowering the temperature to reduce side reactions. The medium should preferably dissolve the polymer.

Polymerizations were carried out in hexamethylphosphoramide, a polymer solvent, at 5–10° and 0.25–0.66 *M*. *o*-Phenylenediamine formed polymers with inherent viscosities up to 0.7 after a limited number of experiments (Table II). Higher molecular weights can no doubt be attained by more careful purification of the intermediates and variation of polymerization techniques. The yields were high in all cases.

A sample of poly(*o*-phenylenesuberamide) (η_{inh} 0.62) was alcohol extracted 20 hr to yield a residue with η_{inh} of 0.62 and 5.4% of extract with η_{inh} of 0.06. The extract presumably consisted of linear and cyclic oligomers (mp 255–265°). The extracted polymer showed no weight loss in thermal gravimetric analysis up to 275° (20°/min under nitrogen).

In a melting experiment at 210° for 20 min under nitrogen a dough-like mass formed and the η_{inh} dropped to 0.33. Part of this drop could result from equilibration of a less than random molecular weight distribution arising from the low-temperature synthesis. At 220° a brown, uniform melt was obtained. After 15 min, η_{inh} was 0.15 and at 30 min η_{inh} was 0.06. Long, brittle fibers were pulled from the cooling melt.

A mechanism whereby this continued degradation could occur would be the formation of a benzimidazole unit at an amine-terminated end. The by-product water might then hydrolyze an amide link, yielding a new amine end and start the cycle anew. Analogous degradative behavior would be expected from poly(*o*-phthalamides) which would yield low molecular weight imides.



Directions for greater thermal stability in *o*-phenylenediamine polyamides would be to avoid amine chain termination, as by capping with acyl groups, removal of all adsorbed water before melting, and rapid removal of any water from benzimidazole formation or polyamidation.

Experimental Section

Intermediates. The phenylenediamines were purified by one to three vacuum sublimations through coarse filter paper or a layer of silica gel. The purified diamines remained white and undegraded for many months when stored in brown bottles in a nitrogen atmosphere.

The acid chlorides were used as purchased or were synthesized from the diacid and thionyl chloride. See ref 1, p 476, for physical constants.

Amide solvents were purified by distillation from toluene diisocyanate or 4,4′-diisocyanatodiphenylmethane through a spinning band column under vacuum and stored over molecular sieves. Isocyanates react with the common impurities, water, amines, and acids.

Polymer Preparation. A. Solution Polymerization of Poly(*m*-phenylenesebacamide). In a home style blender was placed a solution consisting of 3.242 g (0.03 mol) of *m*-phenylenediamine, 9.16 ml (0.06 mol plus 10% excess) of triethylamine, and 120 ml of washed and dried chloroform. Stirring was begun and a solution of sebacyl chloride (6.40 ml, 0.03 mol) in 44 ml of chloroform was added rapidly. The resulting precipitate was stirred for 7 min, cooled to about 25°, and filtered. The polymer was washed with 3% aqueous hydrochloric acid, water, and acetone–water (1:1 by volume). The yield of polymer was 86% and inherent viscosity was 0.62 (*m*-cresol).

B. Modified Solution Polymerization of Poly(*m*-phenyleneadipamide). In a 500-ml round-bottomed flask equipped with a stirrer, nitrogen-inlet tube, and $CaCl_2$ drying tube was placed 10.814 g (0.1 mol) of *m*-phenylenediamine and 75 ml of dimethylacetamide. The solution was cooled with ice to about 10° and 14.7 ml (0.1 mol) of adipyl chloride was added. The resulting mixture was stirred for 1 hr at about 10–15° and for 1 hr at about 25°. The polymer was precipitated by adding water and was washed several times with water and alcohol. After drying in a vacuum oven, the polymer had an inherent viscosity of 1.66 (*m*-cresol) and the yield was 100%.

For *o*-phenylenediamine another variation was used. Diamine (1.08 g) was dissolved in 15 ml. of hexamethylphosphoramide in a stoppered 50-ml Erlenmeyer flask, containing a Teflon-coated bar magnet. Some warming was used to hasten solution and then the flask was cooled in a small ice bath on a magnetic stirrer. Suberyl chloride (1.70 ml) was added from pipette over a period of 3 min with rapid stirring. The mixture became quite viscous in 15 min at which time a small drop of acid chloride was added. At 20 min another drop was added. At 25 min the mixture was hazy and stiff. It was diluted with 5 ml of solvent and one more drop of acid chloride was stirred in manually. The system was left overnight, diluted with an equal volume of dimethylacetamide, and then poured into water in a blender. The polymer was washed thoroughly and dried under vacuum at 80°. The yield was 96% and the η_{inh} 0.70 (H_2SO_4).

Another sample of the polymer was extracted 20 hr with absolute ethanol in a Soxhlet extractor and dried. It was then dissolved in dimethylacetamide–3% LiCl, precipitated in water, washed, and dried. The η_{inh} was 0.60. *Anal.* Calcd for $C_{14}H_{18}N_2O_2$: C, 68.27; H, 7.37; N, 11.37. Found: C, 68.51; H, 7.46; N, 11.46. The infrared spectrum was consistent with a polyamide structure.

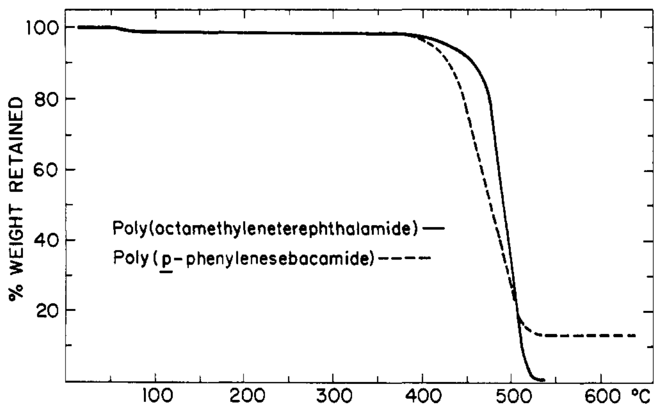


Figure 2. TGA in nitrogen (heating rate 20°/min).

C. Interfacial Polymerization of Poly(*m*-phenylenesebacamide). A solution of 2.00 g (0.0185 mol) of *m*-phenylenediamine, 1.48 g (0.037 mol) of sodium hydroxide, and 182 ml of water was placed in a home style blender. While the latter was being stirred, a solution of 3.95 ml (0.0185 mol) of sebacyl chloride in 17 ml of chlorobenzene was poured in. The mixture was stirred for 7 min and the polymer was collected. The polymer was washed with water and alcohol several times. The inherent viscosity of the polymer was 0.40 and the yield was 87%.

In a home style blender was placed a solution of 2.00 g of *m*-phenylenediamine, 1.48 g of sodium hydroxide, and 182 ml of water. Stirring was begun and 3.95 ml of sebacyl chloride in 100 ml of acetophenone was added. The mixture was stirred for 3 min. The polymer was washed with 200 ml of 3% aqueous hydrochloric acid, water, and acetone–water (1:1). The inherent viscosity of the polymer was 0.85 (*m*-cresol) and the yield was 84%.

D. Modified Interfacial Polymerization of Poly(*m*-phenylenesebacamide). *m*-Phenylenediamine (3.243 g), 6.36 g of sodium carbonate, 40 ml of water, and 60 ml of freshly distilled cyclohexanone were placed in a 1-quart blender jar. A solution of 6.42 ml of sebacyl chloride in 50 ml of cyclohexanone was added as rapidly as possible to the rapidly stirred diamine solution. A small portion of solvent (10 ml) was used to rinse in residues of acid chloride. The mixture was stirred 10 min and then diluted with 400 ml of water. The polymer was collected on a filter, washed thoroughly and dried. The yield was 97% and the inherent viscosity was 0.78 (*m*-cresol).

Test Methods. Softening and Melting Temperatures. Many polymers which are not highly crystalline do not melt sharply and such melting behavior is often reported as a temperature range. In this study samples of dry powdered polymer were tested on a chrome-plated gradient temperature bar.[20] Two temperatures were noted: (1) the initiation of softening under moderate sliding pressure, and (2) the point at which the polymer left a molten or waxy trail adhering to the bar. The latter value approximates the melting temperature determined by DTA endotherms (Tables I, V, and VI).

Differential Thermal Analysis. Analyses were made on a Du Pont 990 Thermal Analyzer with a standard cell (DSC) in nitrogen at a heating rate of 20°/min. T_m values were obtained from dried crystalline samples and the first heating cycles. The T_g values were determined on samples with minimum crystallinity and were taken from the second or third heating cycle. These values are the temperatures at the point formed by extension of the base line and the back extrapolation of the low temperature side of the endotherm step.

Fiber Stick Temperature. The temperature at which fibers stick for 2 sec to a brass block upon release of a light pressure is the sticking temperature.[32] The tension on the fibers was 0.1 g/denier.

Zero Strength Temperature. The zero strength temperature was determined as the breaking temperature of a fiber or film passing over a heated rod under a load of 0.1 g/denier.

Density. Density was determined in a density gradient tube containing heptane–carbon tetrachloride at 25°.

X-Ray Diffraction. Wide angle X-ray diffraction patterns were obtained with a Warhus pinhole camera and Phillips X-ray generating unit No. 12045 having a copper fine-focus diffraction tube and a nickel β filter. The distance from sample to film was 50 mm. The arc length in degrees between the half-maximum intensity points of a principal equatorial diffraction spot is reported as the orientation angle of the sample.

The degree of crystallinity was estimated by visual examination and use of the terms in Chart I.

Chart I

Degree of crystallinity	Sharpness of spots	Diffuse scatter
Low	Broad	Considerable
Medium	Intermediate	Some
High	Narrow and sharp	Essentially absent

Light Stability. Films and fibers were exposed in a Model FDA-R Fade-Ometer (Atlas Electric Devices Co., Inc., Chicago, Ill.) operated in accordance with ASTM method D506-55 for dyed textiles except for mounting of samples. Films were stapled to the face of a cardboard (91 lb white Bristol Index) and part of the sample was covered by additional cardboard to serve as a control for possible thermal effects. Fibers were wound on the cardboard in the shorter direction in a single layer and otherwise treated the same as film.

Dilute Solution Viscosity. The inherent viscosity number [$\eta_{\text{inh}} = 2.3 \log (\eta_{\text{rel}})/c$] was determined at 30° on solutions containing 0.5 g of polymer per 100 ml of solvent with a Cannon-Fenske viscometer. Results are reported in deciliters per gram.

Acknowledgment. We wish to acknowledge the excellent technical assistance of W. F. Dryden, Jr., and P. Lopez, the preparation of fibers by C. E. Smullen, and the preparation and analysis of X-ray diffraction patterns by H. G. Thielke.

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