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Aromatic-Aliphatic Azomethine Ether Polymers and Fibers

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ABSTRACT: Three series of melt-spinnable thermotropic aromatic-aliphatic poly(azomethine ethers) containing two, three, or four consecutive azomethine-linked aromatic rings per rigid segment have been prepared by reaction of 1,2-bis(4-formylphenoxy)ethane, terephthalaldehyde, or 4,4′-biphenyldicarboxaldehyde, respectively, with 1,*n*-bis(4-amino-3-methylphenoxy)alkanes where *n* = 1-10, 12, 14, and 16. Polymer properties determined include melt temperatures and anisotropic-isotropic transition temperatures. The terephthalaldehyde series has been melt spun, and fibers have been characterized by tensile properties, wide-angle X-ray analysis, and density. Polymer and fiber properties have been correlated with the length of aliphatic segments.

Introduction

Recent papers by Morgan, Pletcher, and Kwolek describe the preparation and properties of a variety of wholly aromatic melt-anisotropic poly(azomethines) and their fibers.[1,2] Only a few main-chain aliphatic-aromatic examples were reported, and fiber properties were not correlated with the length of aliphatic segments. In other studies, aromatic-aliphatic poly(azomethine ethers) having systematic variations in structure were prepared, but properties of the mesophases only were reported.[3,4] Recent reviews of the preparation, properties, and applications of liquid crystal polymers containing main-chain flexible segments indicate that relatively little has been reported correlating systematic changes in the length of flexible segments with fiber properties.[5,6]

The present work extends that of Morgan et al. by describing the synthesis of three series of fusible, aromatic-aliphatic poly(azomethine ethers) featuring systematic variations in the length of both segments. The length of flexible aliphatic segments is correlated with melt and anisotropic-isotropic transition temperatures for each series and observed fiber properties for one melt-spun series.

Results and Discussion

Monomer Preparation. Diamines used for poly(azomethine ether) preparation are 1,*n*-bis(4-amino-3-methylphenoxy)alkanes (4), where *n* = 1-10, 12, 14, and 16. They were prepared according to Scheme I. Two equivalents of 3-methyl-4-nitrophenol (1) was reacted with 1,*n*-dibromoalkanes **2a** for *n* = 1-10 and 12 or 1,*n*-ditosylalkanes **2b** for *n* = 14 and 16 in refluxing acetone containing anhydrous potassium carbonate to give 1,*n*-bis(3-methyl-4-nitrophenoxy)alkanes **3**. Dinitro ethers **3** were reduced to diamino ethers **4** by using iron in acidic isopropyl alcohol or by catalytic hydrogenation using Raney nickel in methyl alcohol. The preparative methods, yields, and physical properties of all dinitro compounds and diamines are summarized in Table I. Diamine melting points generally fell with increasing length of the *n*-alkane chain. Diamines with an odd number of methylene units between rings usually melted lower than adjacent diamines having an even number. The diamino ethers **4** are coded 3,3′-DMePO*n*OP, where *n* represents the number of methylene units between aromatic rings.

Scheme I

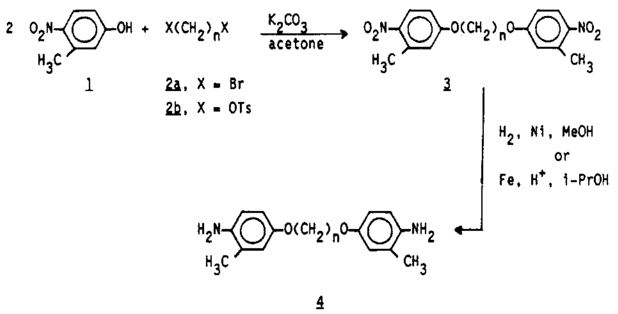
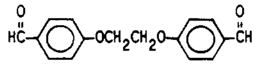


Table I
Preparation, Yields, and Melting Points of Dinitro Ether 3 and Diamino Ether 4

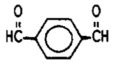
	dinitro ether 3		method of reduction	diamino ether 4	
n	mp, °C	% yield		mp, °C	% yield
1	140-141	23	*a*	78-80 bp 218 (1 mmHg)	70
2	188-190	34	*a*	106-107	65
3	141-142	59	*a*	108.5-109.5	68
4	126.5-127.5	61	*a*	108-110	70
5	100-101	44	*a*	69-72 bp 242 (0.4 mmHg)	75
6	128-129	72	*a*	103-104	76
7	119-120	84	*a*	71-72.5	87
8	123-124	53	*a*	90-91	78
9	100-104	92	*b*	65-68	82
10	93-94	81	*a*	79-82 bp 260 (0.5 mmHg)	68
12	77.5-79	90	*a*	93-94	75
14	71-75	87	*b*	80-86	78
16	81-84	75	*b*	94.5-96.5	93

[a] H_2, Raney nickel, MeOH. [b] Fe, H^+, *i*-PrOH.

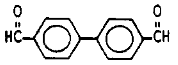
The dialdehydes used for polymer preparation are 1,2-bis(4-formylphenoxy)ethane (**5**), terephthalaldehyde (**6**), and 4,4′-biphenyldicarboxaldehyde (**7**), coded FPE, TA, and DBA, respectively. **5** was prepared by reducing the dimethyl ester of 1,2-bis(4-carboxyphenoxy)ethane with lithium aluminum hydride to the corresponding diol, 1,2-bis(4-(hydroxymethyl)phenoxy)ethane, which was then oxidized to **5** with ceric ammonium nitrate. **7** was prepared similarly from the dimethyl ester of 4,4′-biphenyldicarboxylic acid.



5 FPE



6 TA



7 DBA

Polymer Synthesis for Melt Anisotropy Studies. Poly(azomethine ethers) for anisotropy studies were prepared by allowing equivalent amounts of diamine and dialdehyde to react at room temperature in anhydrous *N,N*-dimethylacetamide containing 5% anhydrous lithium chloride and 0-7% 4-aminoacetanilide as a capping agent. When polymers displayed low inherent viscosities of ca. 0.1-0.2 dL/g, solid samples were heated in nitrogen at 220 °C for up to 10 min, resulting in inherent viscosities of ca. 0.5-1 dL/g. Final inherent viscosities determined in

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Table II
Properties of 3,3′-DMePO*n* OP–FPE Polymers

composition	η_{inh},[a] dL/g	PMT,[f] °C	DTA melt endotherm,[g] °C	anisotropic melt range,[h] °C	DTA A → I endotherm,[i] °C
3,3′-DMePO*1*OP–FPE	*b*	235	238	232 (isotropic)	
3,3′-DMePO*2*OP-FPE	0.46	270	255	251–335	360
3,3′-DMePO*3*OP–FPE	0.56	185	195	177–258	252
3,3′-DMePO*4*OP–FPE	0.64	180	178	178–378	375
3,3′-DMePO*5*OP–FPE	0.67	200	203	192–270	267
3,3′-DMePO*6*OP–FPE	0.26	270	277	279–298	287
3,3′-DMePO*7*OP–FPE	0.70	180	184	179–252	252
3,3′-DMePO*8*OP–FPE	0.30	200	201	193–263	253
3,3′-DMePO*9*OP–FPE	0.98[c]	210	197	192–243	245
3,3′-DMePO*10*OP–FPE	0.31	175	188	175–241	225
3,3′-DMePO*12*OP–FPE	0.31	200	160	164–245	243
3,3′-DMePO*14*OP–FPE	0.49[d]	170	157	165–223	206
3,3′-DMePO*16*OP–FPE	0.49[e]	175	164	154–216	212

[a] In methanesulfonic acid, 0.5%, 30 °C. [b] Decomposed. [c] After solution preparation, polymer isolated and heated at 220 °C for 10 min in flowing N_2. [d] After solution preparation, polymer isolated and heated at 220 °C for 5 min in flowing N_2. [e] After solution preparation, polymer isolated and heated at 220 °C for 4 min in flowing N_2. [f] Polymer melt temperature on gradient hot bar, ref 7. [g] Differential thermal analysis. [h] Initial flow temperature–clearing temperature by microscopic thermal analysis. [i] Anisotropic to isotropic transition (clearing) temperature determined by DTA on polymer.

Table III
Properties of 3,3′-DMePO*n* OP–TA Polymers

composition	η_{inh},[a] dL/g	PMT,[d] °C	DTA melt endotherm,[e] °C	anisotropic melt range,[f] °C	polymer A → I endotherm,[g] °C	fiber A → I endotherm,[h] °C
3,3′-DMePO*1*OP–TA	*b*	255	257	255–316	303	305
3,3′-DMePO*2*OP–TA	0.41	270	273	261–400+	400+	400+
3,3′-DMePO*3*OP–TA	0.46	250	240	250–350	328	338
3,3′-DMePO*4*OP–TA	0.37	230	229	225–400+	400+	400+
3,3′-DMePO*5*OP–TA	0.49	240	230	237–329	317	325
3,3′-DMePO*6*OP–TA	0.43	260	259	260–357	342	355
3,3′-DMePO*7*OP–TA	0.99	130	130	130–306	315	309
3,3′-DMePO*8*OP–TA	1.14	200	175	178–317	314	314
3,3′-DMePO*9*OP–TA	0.53	130	136	130–268	275	279
3,3′-DMePO*10*OP–TA	0.31	175	176	174–256	242	272
3,3′-DMePO*12*OP–TA	0.49	210	211	210–254	250	257
3,3′-DMePO*14*OP–TA	0.40[c]	145	152	145–200	190	na[i]
3,3′-DMePO*16*OP–TA	0.35	160	166	159–205	205	na[i]

[a] In methanesulfonic acid, 0.5%, 30 °C. [b] Decomposed. [c] After solution preparation, polymer isolated and heated at 220 °C for 8 min in flowing N_2. [d] Polymer melt temperature on gradient hot bar, ref 7. [e] Differential thermal analysis. [f] Initial flow temperature–clearing temperature by microscopic thermal analysis. [g] Anisotropic to isotropic transition (clearing) temperature determined by DTA on polymer. [h] Anisotropic to isotropic transition (clearing) temperature determined by differential scanning calorimetry on as-spun fibers in Tables V and VI. [i] na = not available.

Table IV
Properties of 3,3′-DMePO*n* OP–DBA Polymers

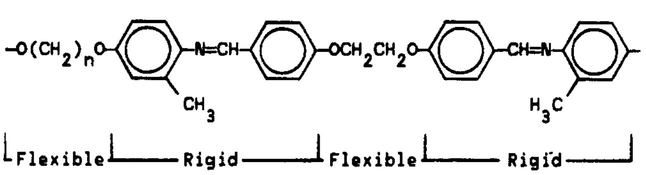
composition	η_{inh},[a] dL/g	PMT,[c] °C	DTA melt endotherm,[d] °C	anisotropic melt range,[e] °C	DTA A → I endotherm,[f] °C
3,3′-DMePO*1*OP–DBA	*b*	275	286	274–400+	400+
3,3′-DMePO*2*OP–DBA	0.41	275	303	299–400+	400+
3,3′-DMePO*3*OP–DBA	0.73	275	204	203–400+	400+
3,3′-DMePO*4*OP–DBA	0.24	215	232	221–400+	400+
3,3′-DMePO*5*OP–DBA	0.72	210	175	171–400+	400+
3,3′-DMePO*6*OP–DBA	0.37	230	240	226–400+	400+
3,3′-DMePO*7*OP–DBA	0.60	200	171	175–400+	400+
3,3′-DMePO*8*OP–DBA	0.62	200	212	200–400+	400+
3,3′-DMePO*9*OP–DBA	0.40	150	152	150–400+	400+
3,3′-DMePO*10*OP–DBA	0.40	200	200	184–400+	400+
3,3′-DMePO*12*OP–DBA	0.62	170	180	174–375	377
3,3′-DMePO*14*OP–DBA	0.35	170	167	160–322	310
3,3′-DMePO*16*OP–DBA	0.24	170	160	150–337	324

[a] In methanesulfonic acid, 0.5%, 30 °C. [b] Decomposed. [c] Polymer melt temperature on gradient hot bar, ref 7. [d] Differential thermal analysis. [e] Initial flow temperature–clearing temperature by microscopic thermal analysis. [f] Anisotropic to isotropic transition (clearing) temperatures determined by DTA on polymer.

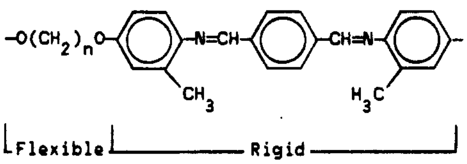
methanesulfonic acid ranged from 0.24 to 1.14 dL/g (Tables II–IV). Polymers prepared from 3,3′-DMePO*1*OP gave very low inherent viscosity values due to the facile acid-catalyzed cleavage of the acetal linkage in methanesulfonic acid. Unacceptable decomposition of all polymers was noted in concentrated sulfuric acid.

Polymer Structure and Color. Polymer structures are illustrated in Figure 1. The FPE, TA, and DBA series

3,3'-DMePOnOP-FPE



3,3'-DMePOnOP-TA



3,3'-DMePOnOP-DBA

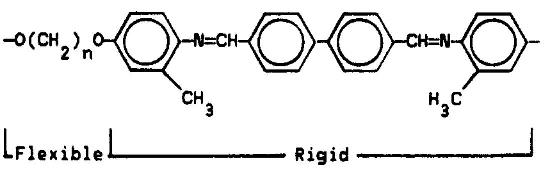


Figure 1. Structure of poly(azomethine ethers) prepared from the diamines 3,3'-DMePO*n*OP (4) and the dialdehydes FPE (5), TA (6), and DBA (7).

contained two, three, and four aromatic rings per rigid segment, respectively. The increasing length of the conjugated aromatic system resulted in increasing polymer color; the FPE series was off-white, while the TA and DBA series were distinctly yellow.

Polymer Thermal Stability. Thermogravimetric analyses (TGA) in nitrogen showed no weight loss below 425 °C. Decomposition exotherms obtained by differential thermal analysis (DTA) in nitrogen occurred at ca. 400 °C.

Polymer Melting Temperature Relationships. A general discussion of melting temperature relationships in poly(azomethines) has been given.[1b,c] The inclusion of methyl substituents on the diamine aromatic rings ensured melting points below decomposition temperatures.

Polymer melting points were measured as endotherms on a differential thermal analyzer, polymer melt temperatures (PMTs) on a temperature gradient bar,[7] and initial flow temperatures on a hot-stage microscope. The melting point of a given poly(azomethine) composition has been noted to vary considerably depending upon preparative and testing methods.[1b,c] For the methods used here, melting points determined by all procedures were generally in agreement. Polymer melting data are summarized in Table II–IV, and initial flow temperatures are plotted vs. the number of methylene units *n* in Figures 2–4.

Correlations between melting point and *n* can be noted. As *n* increases, the melting point is progressively lowered within each series. An odd–even *n* zigzag pattern is observed in the DBA series, which contains the longest rigid segments, and the tendency toward this pattern is less marked in the less rigid TA and FPE series. Lower melting points of the odd-*n* systems suggest poorer molecular packing in the solid.

Optical Anisotropy in Poly(azomethine ethers). The observation of optical anisotropy in poly(azomethines),

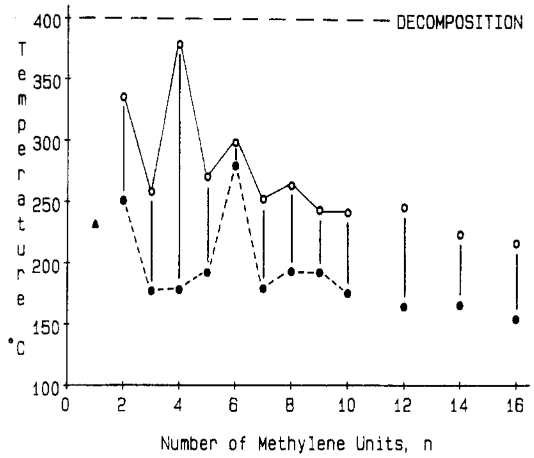


Figure 2. Changes in the initial flow (anisotropic ●, isotropic ▲) and clearing (○) temperatures with the number of methylene units *n* in 3,3'-DMePO*n*OP-FPE polymers determined by microscopic thermal analysis.

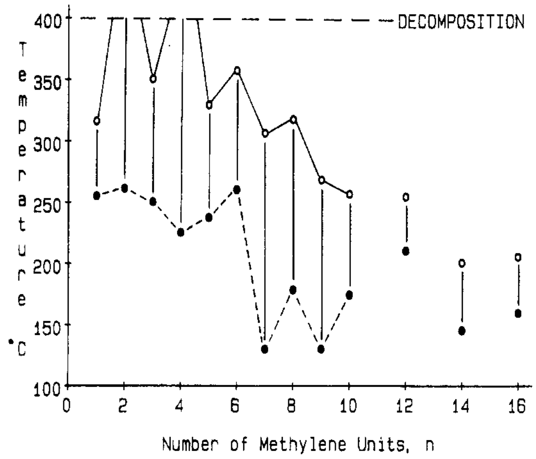


Figure 3. Changes in the initial flow (anisotropic ●) and clearing (○) temperatures with the number of methylene units *n* in 3,3'-DMePO*n*OP-TA polymers determined by microscopic thermal analysis.

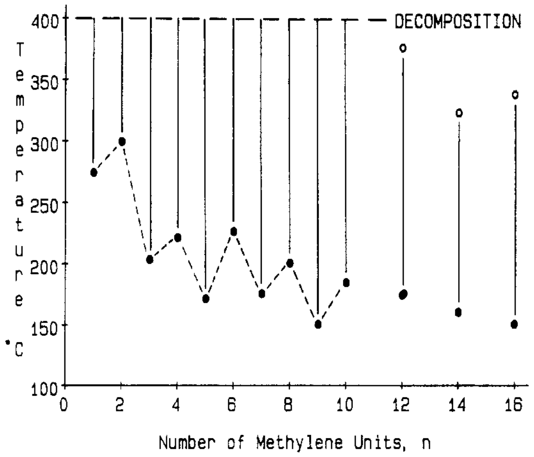


Figure 4. Changes in the initial flow (anisotropic ●) and clearing (○) temperatures with the number of methylene units *n* in 3,3'-DMePO*n*OP-DBA polymers determined by microscopic thermal analysis.

including a discussion of measurements of melt anisotropy, has been described.[1b,c] Measurements in the present study were made microscopically by heating polymer while measuring light transmission through crossed polarizing filters, termed the thermal optical test.[1c,2] This allowed determination of the initial flow temperature, light

Table V
Polymer, Spin, and Fiber Data for 3,3′-DMePO*n*OP–TA with Even *n*

	polymer		polymer plug		fiber					
n	η_{inh},[a] dL/g	PMT,[b] °C	molding temp, °C	PMT,[b] °C	spin temp, °C	WUS,[e] ypm	DSC endotherm,[f] °C	fiber staged heat treatment time, h; temp, °C	fiber properties[g] T/E/Mi/Den	fiber type[h]
2	0.69	*c*	220	280	300	600	271	as-spun	4.5/2.0/321/7.6	AS
								1, 170; 3, 240	7.5/3.1/377/8.1	HS
								1, 170; 1, 250; 3, 280	24.5/2.9/839/10.6	HS
								1, 170; 1, 250; 3, 300	8.3/3.9/281/9.7	HW
4	0.46	220	283	na[d]	300	500	226	as-spun	4.8/3.7/229/7.5	AS
								7, 220	9.9/5.0/246/6.8	HS
								6, 245	7.6/4.9/135/8.0	HW
								1, 220; 3, 260	5.0/5.6/117/8.4	HW
								1, 220; 3, 280	6.7/8.9/113/8.1	HW
6	0.23	260	230	280	315	600	267	as-spun	3.0/3.6/165/11.6	AS
								1, 160; 1, 200; 6, 230	5.7/4.7/169/14.7	HS
								1, 190; 6, 250	5.8/6.4/151/10.1	HW
								1, 220; 3, 290	3.4/17.9/34/7.9	HW
8	2.02	190	160	210	245	75	189	as-spun	4.4/6.7/111/31.5	AS
								4, 170	6.7/4.5/167/32.0	HS
								4, 190	6.4/7.9/101/32.7	HW
								2, 155; 5, 220	6.5/30.2/19/32.1	HW
10	1.04	200	160	200	205	600	190	as-spun	1.4/2.1/97/6.1	AS
								4, 170	3.0/2.5/143/6.3	HS
								2, 160; 5, 190	2.0/5.6/76/7.2	HW
								1, 190; 3, 205	fiber decomposes	HW
12	1.10	*c*	230	240	240	400	213	as-spun	3.9/5.0/118/16.1	AS
								4, 170	4.6/4.5/116/18.4	HS
								4, 190	5.3/5.6/107/18.2	HS
								1, 170; 5, 215	3.5/13.2/50/16.0	HW
								2, 160; 5, 225	1.6/56/10/21.1	HW

[a] 0.5% in methanesulfonic acid, 30 °C. [b] Polymer melt temperature on gradient hot bar, ref 7. [c] Rapid viscosity increase observed. [d] Not available. [e] Windup speed in yards per minute. [f] Differential scanning calorimetry melting endotherm. [g] T = tenacity in g/denier.[9] E = % elongation at break. Mi = initial modulus in g/denier.[9] Den = Denier of filaments. [h] AS = as-spun. HS = heat-strengthened. HW = heat-weakened.

transmission through the melt, and anisotropic–isotropic transition (clearing) temperature at which light transmission fell to a base-line value, indicating the melt became isotropic. Endotherms observed in the DTA and DSC (differential scanning calorimetry) scans of polymer and as-spun fiber, respectively, agreed with clearing temperatures determined microscopically.

All poly(azomethine ethers) in this study, with one exception (3,3′-DMePO*1*OP–FPE), were anisotropic at their flow temperature. Many turned isotropic at still higher temperatures, while others decomposed below the clearing temperature. Polymer flow temperatures, clearing temperatures, and anisotropic ranges for the three sets of poly(azomethine ethers) are given in Tables II–IV and plotted vs. the number of methylene units *n* in Figures 2–4.

Within a given series, the clearing temperatures generally fall as *n* increases. The clearing temperatures display an odd–even zigzag effect, the magnitude of which decreases as *n* increases. The odd-*n* polymers generally display the lower temperatures. Since the magnitude of the clearing temperature is a measure of stability of the anisotropic phase in the melt, less stability in the odd systems is indicated, probably caused by structural differences. When the three series are compared with one another, the clearing temperatures for the DBA series are generally higher than those for the TA series, which are in turn higher than those for the FPE series. These latter observations support the hypothesis that polymers with the most rigid chains display the greatest tendency toward liquid crystallinity. Anisotropy is observed in all series with 18 total units in the flexible segment (*n* = 16), which extends the previously reported 14 units.[1,3]

Polymer Preparation for Melt Spinning. Fibers were prepared from the terephthalaldehyde series only. Preparation of poly(azomethine ethers) at room temperature in high-boiling amide solvent yielded polymer suitable for melt anisotropy studies, but for satisfactory melt spinning a more volatile solvent was preferred. Complete solvent removal was necessary; otherwise, vaporization in the spinneret cell resulted in gas bubbles that disrupted spinning continuity. Thus, terephthalaldehyde was reacted with ca. 5% excess diamine in refluxing benzene with azeotropic removal of water. Excess diamine served as capping agent, and the amount was adjusted as needed for individual samples. This was important since the more forcing conditions of the azeotropic procedure made control of polymer molecular weight during preparation more difficult than for the milder conditions of the amide solvent procedure. As a result, inherent viscosities were generally higher and showed a wider range (0.23–2.02 dL/g, Tables V and VI) for the benzene-prepared polymers. Excess diamine also prevented excessive chain growth and viscosity increases during spinning. However, too much excess diamine inhibited increases in tensile properties during heat strengthening of fibers by inhibiting molecular weight increases at that time (vide infra).

Polymer Spinning. Preparation and testing of fibers from poly(azomethines) have been discussed by Morgan et al.,[1] and similar methods were used here.

Polymer powders were molded into small plugs and extruded as filament from a single-hole spinneret usually at temperatures significantly higher than PMTs, but within the anisotropic melt range. In the case of 3,3′-DMePO*12*OP–TA, the spinneret temperature was raised above the clearing temperature during spinning. Polymer extrusion ceased with an accompanying increase in pressure in the spinneret cell. This reflected a much higher viscosity of the isotropic melt relative to that of the anisotropic melt. Lowering the temperature of the melt below the clearing temperature resulted in resumed smooth

Table VI
Polymer, Spin, and Fiber Data for 3,3′-DMePO*n*OP–TA with Odd *n*

	polymer		polymer plug		fiber					
n	η_{inh},[a] dL/g	PMT,[c] °C	molding temp, °C	PMT,[c] °C	spin temp, °C	WUS,[d] ypm	DSC endotherm,[e] °C	fiber staged heat treatment time, h; temp, °C	fiber properties[f] T/E/Mi/Den	fiber type[g]
1	*b*	270	220	280	278	600	263	as-spun	3.2/10.5/43/11.9	AS
								7, 208	5.0/9.9/46/11.9	HS
								1, 165; 3, 243	5.0/11.0/45/11.7	HS
								1, 165; 3, 260	4.2/10.4/47/12.4	HS
								0.5, 200; 0.5, 250; 2, 275	1.6/6.7/42/12.2	HW
3	1.05	250	220	260	287	480	251	as-spun	1.2/10.7/36/6.4	AS
								3, 170	3.2/10.4/57/4.9	HS
								1, 170; 3, 225	2.5/8.6/38/6.0	HW
								1, 170; 3, 255	3.3/17.1/31/7.0	HW
5	0.73	240	225	240	260	600	230	as-spun	0.9/5.9/36/10.5	AS
								4, 170	2.1/1.8/127/9.3	HS
								1, 170; 3, 210	1.8/1.7/101/10.2	HW
								1, 170; 6, 225	2.9/3.7/84/10.9	HW
								1, 170; 3, 245	0.6/6.2/19/10.9	HW
7	1.94	130	150	180	290	150	163	as-spun	3.9/15.1/39/13.3	AS
								3, 150	4.0/12.3/37/13.4	HS
								3, 180	3.9/48.9/7/12.5	HW
9	0.56	120	80	100	145	150	140	as-spun	1.0/21.6/13/120	AS

[a] 0.5% in methanesulfonic acid, 30 °C. [b] Decomposed. [c] Polymer melt temperature on gradiant hot bar, ref 7. [d] Windup speed in yards per minute. [e] Differential scanning calorimetry melting endotherm. [f] T = tenacity in g/denier.[9] E = % elongation at break. Mi = initial modulus in g/denier.[9] Den = denier of filaments. [g] AS = as-spun. HS = heat-strengthened. HW = heat-weakened.

Table VII
X-ray Data and Densities of 3,3′-DMePO*n*OP–TA Fibers

n	crystallite size, Å	crystallinity index	orientation angle[a]	density, g/cm^3	fiber type[b]
1	139	52	11	1.2366	AS
2	30	22	24	1.2098[f]	AS
3	24	17	~70	1.1694	AS
4	na[d]	na[d]	24	1.1906	AS
5	25	13	~50	1.1673[f]	AS
6	36	16	23	1.1659	AS
7	26	15	~55	1.1338	AS
8	26	19	24	1.1391	AS
9	NC[e]	NC[e]	NO[e]	1.1097	AS
10	47	52	15	1.0996	AS
12	99	69	19	1.1226	AS
4	170	48	16		HS[g]
5[c]	169	43	15		HS[h]
12	NC[e]	NC[e]	NO[e]		HW[i]

[a] In degrees, 2θ. [b] AS = as-spun. HS = heat-strengthened. HW = heat-weakened. [c] Polymer prepared in amide solvent and spun by pulling from a molten polymer pool; not oriented as-spun, T/E/Mi/Den = 1.3/7.8/38/3.7; heat-strengthened 4.4/3.3/178/3.9. [d] Not available; a different but similar spin as in Table V gave fiber with crystallite size 30 Å, crystallinity index 16, and orientation angle 25°. [e] NO = not oriented. NC = not crystalline. [f] Fibers from different but similar spins as those in Tables V and VI. [g] Maximum heat treatment temperature, 220 °C. [h] Maximum heat treatment temperature, 195 °C. [i] Maximum heat treatment temperature, 225 °C.

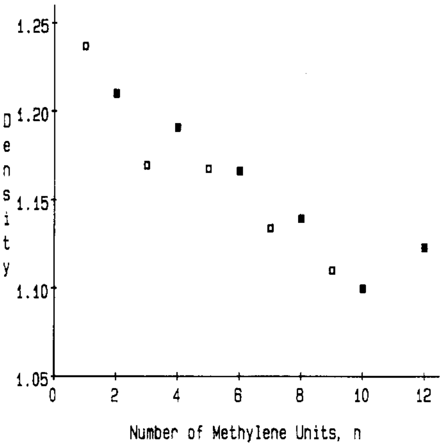


Figure 5. Changes in density (g/cm^3) with the number (even ■, odd □) of methylene units *n* in 3,3′-DMePO*n*OP–TA as-spun fibers.

fiber spinning. Spinning continuity was good for all fibers, and air-cooled filaments were collected on bobbins at windup speeds ranging from 75 to 600 yd/min. Polymer spin data are summarized in Tables V and VI. Fiber tensile properties were not optimized.

Fiber Heat Treatment. Tensile properties of as-spun fiber can be improved substantially by staged heating in the relaxed state at progressively higher temperatures, referred to as heat strengthening.[1,2] Since heat-strengthening conditions are empirically determined for individual samples, fibers were heated at maximum temperatures below and above the DSC melting endotherms of the as-spun fibers. Heating beyond maximum heat-strengthening temperatures did not result in loss of the fiber form by melting, but in adverse effects on tensile properties, here termed heat weakening. The present study determined the effect of flexible segments on tensile properties of heat-treated fibers. Heat-treatment conditions are summarized in Tables V and VI.

Fiber X-ray Data. For each as-spun and several heat-treated fibers, wide-angle X-ray diffraction patterns were obtained, and crystallinity index (representative of degree of crystallinity on a scale of 0–100) and crystallite size and orientation angle (OA) were measured (Table VII). All fibers with even *n* gave similar patterns, as did those with odd *n*, but the even and odd patterns were not the same, indicating fundamentally different structures. As-spun fibers with *n* = 1, 10, and 12 were very highly crystalline and oriented relative to those with *n* = 2–8, while those having *n* = 3, 5, 7, and 9 were very poorly oriented. Heat-strengthened fibers displayed substantial increases in crystallinity and improved orientation over as-spun fibers. The heat-weakened fiber (*n* = 12) displayed loss in crystallinity and orientation. X-ray determination of fiber structure when *n* = 1 and 12 is in progress.

Fiber Density. Densities of the as-spun fibers described in Tables V and VI are reported in Table VII and are plotted vs. *n* in Figure 5. Densities fall as *n* increases.

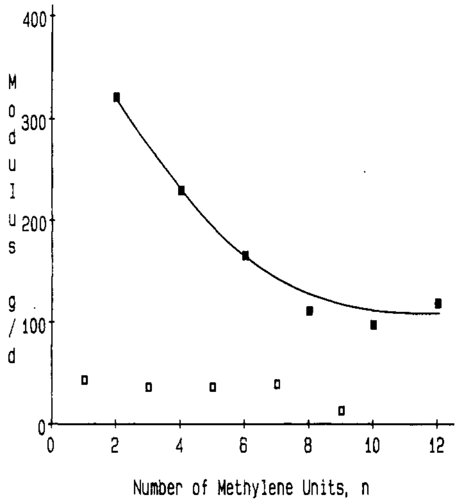


Figure 6. Changes in initial modulus (g/denier) with the number (even ■, odd □) of methylene units n in 3,3′-DMePOnOP–TA as-spun fibers.

The densities of poorly oriented fibers ($n = 3$, 5, 7, and 9) are low relative to the densities of fibers with higher crystallinity and/or better orientation.

Modulus of As-Spun Fibers. Initial modulus of as-spun fiber is reported in Tables V and VI, and changes with n are graphically illustrated in Figure 6. The fibers divide into two categories: those where n is odd have a low modulus, i.e., less than ca. 50 g/denier,[9] and those where n is even have a high modulus, i.e., ca. ≥ 100 g/denier. For the latter, modulus is highest for low values of n, i.e., 321 g/denier for $n = 2$, and drops linearly to ca. 100 g/denier as n increases toward 12. These observations correlate with polymer chain rigidity and/or fiber orientation. Fibers with low n and OA have the highest modulus, which decreases as either value increases. Fiber modulus might be expected to fall as chains become less rigid and/or crystallites align more poorly with the fiber axis. The fiber with $n = 1$ is an exception since it has high chain rigidity and is oriented, but displays low modulus. The same structural differences between odd and even systems that affect melting and clearing temperatures may be affecting tensile properties also. High degress of molecular order aid in the achievement of high tensile properties. Odd n systems contain an uncancelled bend in each flexible segment that may make this more difficult than in even-n systems. This difficulty in achieving order would be most pronounced in low-odd-n cases where conformational mobility is poorest due to highest chain rigidity. A better understanding of the structure of these fibers at the molecular level is needed.

Modulus of Heat-Strengthened Fibers. Initial modulus values achieved on heat strengthening are reported in Tables V and VI, and maximum observed values are plotted vs. n in Figure 7. The data can again be divided for fibers with even and odd n.

Even-n fibers with the lowest n values show the largest increases, i.e., to 839 g/denier for $n = 2$ and no increase for $n = 12$. Fibers with low n values have high melting points allowing high heat-treatment temperatures. Low-n fibers also have more reactive sites, i.e., imine bonds, which can undergo transimination, per given length of polymer chain than high-n fibers. These factors facilitate the molecular processes that cause chain growth and improved ordering resulting in increased modulus.

Fibers with odd-n values do not show similar modulus increases relative to n upon heat treatment. The moduli of fibers having $n = 1$ and 7 remain essentially unchanged, while fibers with $n = 3$ and 5 show increases that are small and moderate, respectively. The fiber with $n = 1$ did not show modulus increases on heat treatment because very high as-spun orientation and crystallinity left little room for improvement; odd-n chain structure may also play a role. The absence of improvement in the fiber with $n = 7$ is probably due to its low melting point, which prevents adequately high heat-treatment temperatures. If this is correct and the fiber with $n = 7$ could be heat treated at high temperatures, the odd- and even-n curves in Figure 6 would merge beyond $n = 5$.

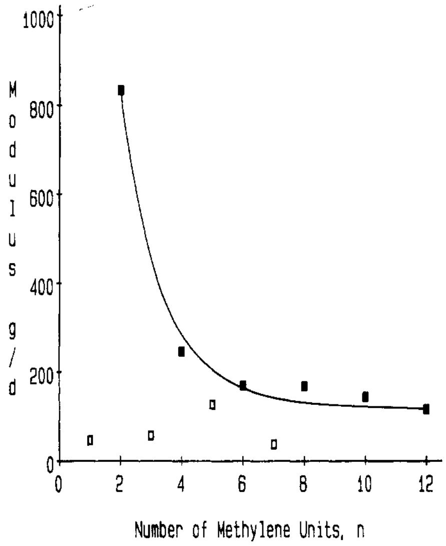


Figure 7. Changes in initial modulus (g/denier) with the number (even ■, odd □) of methylene units n in 3,3′-DMePOnOP–TA heat-strengthened fibers.

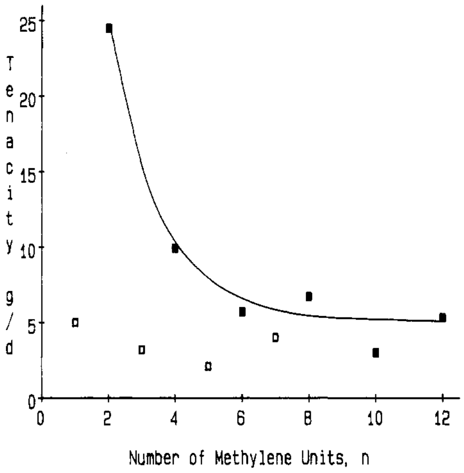


Figure 8. Changes in maximum observed fiber tenacity (g/denier) with the number (even ■, odd □) of methylene units n in 3,3′-DMePOnOP–TA heat-strengthened fibers.

Tenacity of As-Spun and Heat-Strengthened Fibers. Fiber tenacities are reported in Tables V and VI. As-spun fiber tenacities were uniformly low (1–5 g/denier). Tenacities frequently increased substantially on heat strengthening, and maximum values are plotted vs. n in Figure 8. Again the fibers can be divided for odd and even n. When n is even, the largest increases are observed for the lowest n values, i.e., from 4.5 to 24.5 g/denier for $n = 2$, and only ca. 1 g/denier for $n = 12$. The same factors discussed above play a role here, especially the need for high heat-strengthening temperatures to improve orientation and particularly molecular weight, which is necessary for high tenacity. Data in Table VIII illustrate that the highest heat-strengthening temperatures result in the

Table VIII
Inherent Viscosity Changes on Spinning and Heat-Strengthening 3,3′-DMePOnOP–TA Fibers

	temp, °C		η_{inh},[a] dL/g		
				fiber	
n	spin	heat-strengthening max	unspun polymer	as-spun	heat-strengthened
2	300	280	0.69	2.19	insol
5	260	170	0.73	0.88	1.33
6	315	230	0.23	1.40	insol
10	205	170	1.04	0.97	1.21

[a] 0.5% in methanesulfonic acid, 30 °C.

highest molecular weights as reflected by inherent viscosity. When n is odd, fibers display only ca. 1–2 g/denier increases above as-spun values, resulting in uniformly low heat-strengthened tenacities of $\leqslant 5$ g/denier. Again, more information is needed for a better understanding of the odd-n fiber.

Elongation of As-Spun and Heat-Strengthened Fibers. Elongation is low (ca. 6% or less) for high-modulus fibers and higher (generally ca. 10% or more) for low-modulus fibers as summarized in Tables V and VI.

Tensile Properties of Heat-Weakened Fibers. Tensile properties of heat-weakened fibers are reported in Tables V and VI. Initial modulus decreased to below as-spun values for even- and odd-n fibers. For fibers with even n, the decrease was smooth as n increased. Tenacities were generally lower than for heat-strengthened fibers, and elongation was frequently substantially higher, the magnitude of which increased as n increased. The heat-weakened fiber with $n = 2$ was strong (8 g/denier) and retained a high modulus (281 g/denier) in spite of the relatively severe final heating conditions of 3 h at 300 °C.

Heating to high temperatures causes fiber softening, which relaxes structure. This results in loss of orientation (Table VII) and hence tenacity and modulus with an accompanying increase in elongation. The possibility exists that a low level of cross-linking contributes to the retention of fiber form, high elongation, and insolubility of heat-treated fibers (Table VIII). The fiber with $n = 2$ probably remained oriented, due to its high chain rigidity, which accounts for its retention of high tensile properties.

Fiber Heating under Tension. Heat treatments discussed so far were performed on fibers in a relaxed condition; however, as-spun fibers with n = 1, 3, 5, 7, 10, and 12 were also heated under tension. Such treatment of conventional fibers normally results in hot drawing, which is characterized by a substantial increase in length, and improved orientation and tensile properties. This was not the case for fibers in this study. Fibers with odd values for n increased slightly in length, especially at higher values of n. In contrast, fibers with even values for n decreased in length very slightly. Fibers with odd n values were generally less oriented in contrast to the improved orientation of fibers with even n values. Tensile properties did not show substantial changes for odd-n fibers, but even-n fibers displayed modulus increases corresponding to orientation improvements (cf. Tables V, VI, and IX).

Fiber Spinning from Isotropic Melts. Morgan et al.[1b] have observed that the tendency of aromatic poly(azomethines) to orient is great and that fibers with high tensile properties can be obtained by spinning from liquid crystalline pools of molten polymer. In the present study, fibers of 3,3′-DMePO*12*OP–TA, which has a clearing temperature of 254 °C, were obtained by pulling polymer from molten polymer pools with forceps. Fibers spun at 240 °C (anisotropic region) displayed T/E/Mi/Den (tenacity/elongation/initial modulus/denier of filaments) of 2.2/2.2/141/8.6, while fibers similarly spun at 290 °C (isotropic region) had T/E/Mi/Den of 2.1/2.8/126/6.8. Passage of this molten isotropic polymer through the cooler anisotropic region during spinning resulted in tensile properties essentially equivalent to those of filament spun from the anisotropic pool. Molecular ordering was more rapid than the rate of fiber spinning.

Table IX
Results of Heating 3,3′-DMePOnOP–TA Fibers under Tension

n	max heating temp, °C	length change, %	X-ray orientation angle[a]		T/E/Mi/Den[b] after heating
			before	after	
1	180	+0.2	11	~16	4.5/9.4/49/13.5
3	80	+6.9	~70	NO[c]	1.5/13.6/34/6.7
5	180	+17.1	~50	NO[c]	1.7/8.6/50/10.0
7	110	+14.5	~55	~40	3.9/16.4/34/11.9
10	150	−0.2	15	8	1.7/1.7/155/8.3
12	160	−1.4	19	13	3.9/3.7/122/27.0

[a] In degrees, 2θ. [b] T = tenacity in g/denier.[9] E = % elongation at break. Mi = initial modulus in g/denier.[9] Den = denier of filaments. [c] NO = not oriented.

Polymers and Fibers from Highly Rigid Azomethines. Polymers and fibers of the 3,3′-DMePOnOP–TA series with fewer than three units per flexible segment were not prepared in this study; however, such highly rigid systems of closely related structure have been prepared. Their polymer and fiber properties are in agreement with trends observed here.[8]

Summary and Conclusions

Three series of thermotropic aromatic–aliphatic poly(azomethine ethers) have been prepared by reaction of 1,2-bis(4-formylphenoxy)ethane, terephthalaldehyde, or 4,4′-biphenyldicarboxaldehyde with 1,n-bis(4-amino-3-methylphenoxy)alkanes where n = 1–10, 12, 14, and 16. The polymers decomposed at ca. 400 °C. As the length of the flexible aliphatic segments increased, both melting points and clearing temperatures decreased. Polymers with an odd number of methylene units generally had lower melting and clearing temperatures than adjacent polymers in the same series with an even number, indicating poorer molecular packing in the solid and weaker chain alignment in the melt for the odd systems.

Fibers were melt spun from the terephthalaldehyde series. As-spun fibers with odd n values displayed lower modulus than even-n fibers. Fibers with low even n values achieved high tenacity and modulus upon heat treatment due to increases in molecular weight and orientation; fibers with low odd n values did not. Fibers with high n values could not be heat treated at temperatures high enough to develop high tensile properties due to low polymer melting points. Fibers did not hot draw; therefore, processing other than that examined is needed to obtain high tensile properties from fibers with odd or high even n values. Fibers heated in stages to temperatures above those for maximum heat strengthening displayed retention of fiber form, substantial decreases in tenacity and modulus, and substantial increases in elongation, possibly aided by a low level of cross-linking. Fiber density fell with increasing number of flexible units and rose with improved fiber orientation and crystallinity. The length of flexible segment relative to rigid segment at which poly(azomethine ethers) give only isotropic melts and fibers that behave like conventional fibers remains unknown. A better understanding of structure of these fibers, especially with odd n values, at the molecular level is needed; X-ray determination of fiber structure is in progress.

Experimental Section

Terephthalaldehyde (TA). Terephthalaldehyde was purified by sublimation at reduced pressure giving 99+% purity by gas chromatographic analysis.

4,4′-Biphenyldicarboxaldehyde (DBA). 4,4′-Biphenyldicarboxaldehyde was prepared according to the method of Morgan, Pletcher, and Kwolek.[1c]

1,2-Bis(4-formylphenoxy)ethane (FPE). A 3-L, three-necked, round-bottom flask was equipped with nitrogen flow, drying tube, and a modified Soxhlet extractor which dripped extract back into the reaction continuously. The flask was charged with 1 L of dry tetrahydrofuran (THF) and 15.5 g (0.4 mol + 2 wt % excess) of lithium aluminum hydride (LAH), and the extractor thimble was charged with 66.1 g (0.2 mol) of the dimethyl ester of 1,2-bis(4-carboxyphenoxy)ethane. This was extracted into the LAH slurry during 4 h of refluxing. Stirring at room temperature was continued overnight. The reaction mixture was ice-cooled and hydrolyzed with 15.5 mL of water, 15.5 mL of 15% aqueous sodium hydroxide, and 46.5 mL of water. It was filtered, and the solid product was washed three times with 20 mL of THF and finally Soxhlet-extracted with THF. The filtrate, extract, and washings were combined, and volatiles were removed on a rotary flash evaporator to yield 97% 1,2-bis(4-(hydroxymethyl)phenoxy)ethane: mp 175–176 °C.

In a 5-L, three-necked, round-bottom flask equipped with stirrer, dropping funnel, condenser, and thermometer was dissolved 106.3 g (0.39 mol) of 1,2-bis(4-(hydroxymethyl)phenoxy)ethane in 2000 mL of glacial acetic acid at 80–85 °C. A 2000-mL solution containing 904.0 g of 98.7% ceric ammonium nitrate was added dropwise over 1 h at 85 °C. The solution was stirred for 1 h at 92 °C during which time a red-to-yellow color change occurred. The solution was cooled to room temperature and poured onto ice. The resulting precipitate was filtered, washed with water, and dried under nitrogen. The crude product was dissolved in benzene and washed once with 250 mL of 1.5 N potassium hydroxide and three times with water. The benzene solution was dried over magnesium sulfate, filtered, and reduced in volume by distillation. Petroleum ether was added to precipitate the dialdehyde, which was recrystallized from methylene chloride/petroleum ether: mp 113–114 °C, yield 85%.

1,*n*-Ditosylalkanes (2b). 1,14-Tetradecanediol or 1,16-hexadecanediol (0.043 mol) and 50 mL of dry pyridine were placed in a three-necked round-bottom flask fitted with stirrer, thermometer, and nitrogen inlet tube. The flask was cooled to below 10 °C, and freshly purified *p*-toluenesulfonyl chloride (17.5 g, 0.092 mol) was added in portions, keeping the temperature below 10 °C. The mixture was stirred for 6 h at below 10 °C and stored in the freezer overnight. It was then diluted with 200 mL of cold water and acidified with concentrated hydrochloric acid. The resultant white solid was collected and sucked as dry as possible on a Büchner funnel. Recrystallization from ethanol gave white needles. The ditosylate prepared from hexadecanediol melted at 79–82 °C.

1,*n*-Bis(4-nitro-3-methylphenoxy)alkanes (3). A mixture of 3-methyl-4-nitrophenol (0.6 mol), dibromo-*n*-alkane **2a** or ditosylate **2b** (0.3 mol), anhydrous potassium carbonate (84 g, 0.6 mol), and reagent grade acetone (600 mL) was refluxed and protected from moisture for 48 h. Acetone was removed under reduced pressure, and the solid residue was triturated with aqueous sodium carbonate. The product was dried over phosphorus pentoxide in a vacuum desiccator, leaving tan crystals that were usually pure enough for further use. The product may be recrystallized from ethanol. Yields and melting points are given in Table I. IR and NMR spectroscopy confirmed structure.

1,*n*-Bis(4-amino-3-methylphenoxy)alkanes (4). The dinitro ethers **3** were reduced by one of two methods detailed below. The method of reduction, yield, and melting points of products are given in Table I. Acceptable elemental analysis or mass spectral peak matching of parent ions was obtained for all diamino ethers. IR and NMR spectroscopy confirmed structure.

Reduction by Catalytic Hydrogenation. Dinitro ether **3** was hydrogenated at 1000–1500 psi in methanol at 70 °C or higher in the presence of Raney nickel catalyst. The product was dissolved in hot methanol, treated with decolorizing charcoal, and filtered hot under nitrogen. The product crystallized on cooling, was collected by suction filtration under nitrogen, and dried in a vacuum desiccator. It was usually pure enough to use directly. The diamino ethers did not sublime, could sometimes be vacuum-distilled, and could be recrystallized from ethanol, but heating in solvent in air resulted in rapid discoloration.

Reduction by Iron. In a three-necked, 1-L flask flushed with nitrogen and fitted with a reflux condenser and overhead stirrer were placed isopropyl alcohol (225 mL), dinitro ether **3** (23 mmol), concentrated hydrochloric acid (1.5 mL), water (3 mL), and powdered iron (30 g). The mixture was refluxed overnight under nitrogen with stirring. Aqueous sodium hydroxide (50%, 1.5 mL) was added followed by hot filtration through Celite under nitrogen. The product usually crystallized on cooling and was collected by filtration under nitrogen, dried in a vacuum desiccator, and used directly. If it failed to crystallize, isopropyl alcohol was removed under reduced pressure, and the product was recrystallized from ethyl alcohol under nitrogen.

Polymer Preparation. For Melt Anisotropy Studies. In a dry 25-mL, single-necked flask were placed *p*-aminoacetanilide (0–7 mol %), diamino ether 4 (0.005 mol), and dry *N*,*N*-dimethylacetamide (10 mL) containing 5% dry lithium chloride. When solids were dissolved, dialdehyde (0.005 mol) was added, the flask stoppered, and the mixture stirred overnight at room temperature. Water was added with thorough mixing to precipitate the polymer. The polymer was collected by suction filtration, washed with water, ethanol, and ether, and dried in a vacuum oven at 80 °C. Yields were generally quantitative.

For Melt Spinning. A 500-mL, round-bottom, three-necked flask was fitted with an overhead stirrer, a Dean–Stark trap, and a nitrogen inlet. In it were placed diamino ether 4 (0.015 mol + 5% excess), Neozone A antioxidant (0.03 g), and 200 mL of benzene. The mixture was warmed until solution occurred, and then terephthalaldehyde (0.015 mol) was added. The mixture was stirred and refluxed for 6 h with azeotropic removal of water followed by standing at room temperature overnight. The polymer was collected by filtration as a yellow powder and dried in a vacuum desiccator at room temperature.

Fiber Preparation. Spinning. The polymer (6 g) was first molded at temperatures usually below the PMT under hydraulic pressure into a short rod with a diameter to fit the preheated spinning cell. Pressure was applied to the cell by a hydraulically driven piston, and heating was applied primarily in a melt zone approaching and at the spinneret. This limited heating reduced the amount of polymerization and increased control and ease of spinning. The molten polymer was extruded through a series of fine screens and a single 9-mil hole. The fiber was collected by cooling in air and passing through guides and rollers to the collecting bobbin. The rate of windup and the amount of yarn attenuation varied with the extrusion rate and characteristics of the polymer melt. A spin stretch factor of five or more was common (ratio of windup rate to linear extrusion speed). Data for individual samples are in Tables V and VI.

Heat Treatment. Fibers were wound on a bobbin padded with a layer of refractory fibrous material sold under the name Fiberfrax. Heat treatment was accomplished by staged heating of these fibers under flowing nitrogen at various temperatures to maxima below and above the fiber melting point indicated by its DSC endotherm. Fibers heated above the DSC endotherm sometimes adhered slightly to the bobbin. Actual conditions for specific fibers are given in Tables V and VI.

Heating under Tension. Forty-two centimeters of as-spun filament was placed on a uniformly heated bar with a 1-g weight suspended from one end. The hot bar temperature was raised gradually at a constant rate to just below the point of fiber breakage. Afterward, length changes, X-ray orientation angles, and tensile properties were measured.

Characterization Tests. Differential Thermal Analysis. DTA measurements were made with a Du Pont 990 differential thermal analyzer in conjunction with a DSC cell. Samples were run at a heating rate of 20 °C/min in an atmosphere of flowing nitrogen. Data were obtained from the first heating of the sample.

Thermogravimetic Analysis. TGA measurements were made with a Du Pont Model 950 thermogravimetric analyzer. Samples were run at a heating rate of 20 °C/min in an atmosphere of nitrogen.

Dilute Solution Viscosity. Inherent viscosity values were measured in methanesulfonic acid at 30 °C as described in ref 1c.

Thermal Optical Test. The thermal optical test is described in ref 1c and 2.

X-ray Data. Wide-angle X-ray diffraction patterns were obtained from fiber bundles by using Ni-filtered Cu Kα radiation and a vacuum flat-plate camera with a 5.0-cm sample-to-film distance. An orientation angle and crystallite size for each fiber were obtained from angular and radial densitometer scans through a principal equatorial reflection. The orientation angle is taken to be the half-width of the angular scan. The crystallite size was obtained by using the Scherrer equation and the half-width of the radial scan. The crystallinity index was calculated from a ratio of the crystalline and amorphous areas of the radial scan.

Fiber Tensile Properties. Fiber tensile properties were measured as described in ref 1c.

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Registry No. **3** (n = 1), 106780-72-7; **3** (n = 2), 106780-73-8; **3** (n = 3), 106780-74-9; **3** (n = 4), 106780-75-0; **3** (n = 5), 106780-76-1; **3** (n = 6), 106780-77-2; **3** (n = 7), 106780-78-3; **3** (n = 8), 106780-79-4; **3** (n = 9), 106780-80-7; **3** (n = 10), 106780-81-8; **3** (n = 12), 106780-82-9; **3** (n = 14), 106780-83-0; **3** (n = 16), 106780-84-1; **4** (n = 1), 106780-85-2; **4** (n = 2), 106780-86-3; **4** (n = 3), 106780-87-4; **4** (n = 4), 61594-64-7; **4** (n = 5), 106780-88-5; **4** (n = 6), 106780-89-6; **4** (n = 7), 106780-90-9; **4** (n = 8), 106780-91-0; **4** (n = 9), 106780-92-1; **4** (n = 10), 106780-93-2; **4** (n = 12), 61594-66-9; **4** (n = 14), 106780-94-3; **4** (n = 16), 106780-95-4; (**4**, n = 1)(**5**) (copolymer), 106781-34-4; (**4**, n = 1)(**5**) (SRU), 106780-96-5; (**4**, n = 2)(**5**) (copolymer), 106781-35-5; (**4**, n = 2)(**5**) (SRU), 106780-97-6; (**4**, n = 3)(**5**) (copolymer), 106781-36-6; (**4**, n = 3)(**5**) (SRU), 106780-98-7; (**4**, n = 4)(**5**) (copolymer), 106781-37-7; (**4**, n = 4)(**5**) (SRU), 106780-99-8; (**4**, n = 5)(**5**) (copolymer), 106781-38-8; (**4**, n = 5)(**5**) (SRU), 106781-00-4; (**4**, n = 6)(**5**) (copolymer), 106798-76-9; (**4**, n = 6)(**5**) (SRU), 106781-01-5; (**4**, n = 7)(**5**) (copolymer), 106781-39-9; (**4**, n = 7)(**5**) (SRU), 106781-02-6; (**4**, n = 8)(**5**) (copolymer), 106798-79-2; (**4**, n = 8)(**5**) (SRU), 106781-03-7; (**4**, n = 9)(**5**) (copolymer), 106781-40-2; (**4**, n = 9)(**5**) (SRU), 106781-04-8; (**4**, n = 10)(**5**) (copolymer), 106798-77-0; (**4**, n = 10)(**5**) (SRU), 106781-05-9; (**4**, n = 12)(**5**) (copolymer), 106781-41-3; (**4**, n = 12)(**5**) (SRU), 106781-06-0; (**4**, n = 14)(**5**) (copolymer), 106781-42-4; (**4**, n = 14)(**5**) (SRU), 106781-07-1; (**4**, n = 16)(**5**) (copolymer), 106781-43-5; (**4**, n = 16)(**5**) (SRU), 106781-08-2; (**4**, n = 1)(**6**) (copolymer), 106781-44-6; (**4**, n = 1)(**6**) (SRU), 106781-09-3; (**4**, n = 2)(**6**) (copolymer), 106781-45-7; (**4**, n = 2)(**6**) (SRU), 106781-10-6; (**4**, n = 3)(**6**) (copolymer), 106798-78-1; (**4**, n = 3)(**6**) (SRU), 106781-11-7; (**4**, n = 4)(**6**) (copolymer), 61594-65-8; (**4**, n = 4)(**6**) (SRU), 61601-76-1; (**4**, n = 5)(**6**) (copolymer), 106781-46-8; (**4**, n = 5)(**6**) (SRU), 106781-12-8; (**4**, n = 6)(**6**) (copolymer), 106781-47-9; (**4**, n = 6)(**6**) (SRU), 106781-13-9; (**4**, n = 7)(**6**) (copolymer), 106781-48-0; (**4**, n = 7)(**6**) (SRU), 106781-14-0; (**4**, n = 8)(**6**) (copolymer), 106781-49-1; (**4**, n = 8)(**6**) (SRU), 106781-15-1; (**4**, n = 9)(**6**) (copolymer), 106781-50-4; (**4**, n = 9)(**6**) (SRU), 106781-16-2; (**4**, n = 10)(**6**) (copolymer), 106781-51-5; (**4**, n = 10)(**6**) (SRU), 106781-17-3; (**4**, n = 12)(**6**) (copolymer), 106781-52-6; (**4**, n = 12)(**6**) (SRU), 106781-18-4; (**4**, n = 14)(**6**) (copolymer), 106781-53-7; (**4**, n = 14)(**6**) (SRU), 106781-19-5; (**4**, n = 16)(**6**) (copolymer), 106781-54-8; (**4**, n = 16)(**6**) (SRU), 106781-20-8; (**4**, n = 1)(**7**) (copolymer), 106781-55-9; (**4**, n = 1)(**7**) (SRU), 106781-21-9; (**4**, n = 2)(**7**) (copolymer), 106781-56-0; (**4**, n = 2)(**7**) (SRU), 106781-22-0; (**4**, n = 3)(**7**) (copolymer), 106781-57-1; (**4**, n = 3)(**7**) (SRU), 106781-23-1; (**4**, n = 4)(**7**) (copolymer), 106781-59-3; (**4**, n = 4)(**7**) (SRU), 106781-24-2; (**4**, n = 5)(**7**) (copolymer), 106781-60-6; (**4**, n = 5)(**7**) (SRU), 106781-25-3; (**4**, n = 6)(**7**) (copolymer), 106781-61-7; (**4**, n = 6)(**7**) (SRU), 106781-26-4; (**4**, n = 7)(**7**) (copolymer), 106781-62-8; (**4**, n = 7)(**7**) (SRU), 106781-27-5; (**4**, n = 8)(**7**) (copolymer), 106781-63-9; (**4**, n = 8)(**7**) (SRU), 106781-28-6; (**4**, n = 9)(**7**) (copolymer), 106781-64-0; (**4**, n = 9)(**7**) (SRU), 106781-29-7; (**4**, n = 10)(**7**) (copolymer), 106781-65-1; (**4**, n = 10)(**7**) (SRU), 106781-30-0; (**4**, n = 12)(**7**) (copolymer), 106781-66-2; (**4**, n = 12)(**7**) (SRU), 106781-31-1; (**4**, n = 14)(**7**) (copolymer), 106781-67-3; (**4**, n = 14)(**7**) (SRU), 106781-32-2; (**4**, n = 16)(**7**) (copolymer), 106781-68-4; (**4**, n = 16)(**7**) (SRU), 106781-33-3.

References and Notes

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(8) The poly(azomethine ether) prepared from methyl-*p*-phenylenediamine and bis(4-formylphenyl) ether contains one flexibilizing unit between rigid segments. It displayed an anisotropic melt with flow and clearing temperatures of 258 and 375 °C, respectively. As-spun and heat-strengthened (7 h at 190 °C) fibers displayed T/E/Mi/Den of 1.2/27.0/18/23 and 2.1/19.1/20/41, respectively. X-ray analysis indicated the as-spun fiber was not crystalline or oriented, the heat-strengthened fiber displayed medium crystallinity and a 60° orientation angle, and the diffraction pattern resembled that of the odd n fibers in this paper. Data kindly supplied by Stephanie L. Kwolek. The wholly aromatic poly(azomethine) prepared from methyl-*p*-phenylenediamine and terephthalaldehyde contains no flexibilizing units; polymer and fiber properties are reported in ref 1.

(9) Pounds per square inch equals grams per denier (fiber density in grams per cubic centimeter) (12800); decinewtons per tex equals grams per denier (0.8826); gigapascals equal decinewtons per tex ((fiber density in grams per cubic centimeter)/10).