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Aromatic Azomethine Polymers and Fibers[1]

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ABSTRACT: The synthesis of a variety of fusible aromatic poly(azomethines) by solution and melt methods is described. The aromatic amine–aldehyde reaction is very rapid, and end-capping is necessary to control molecular weight and restrain polymerization during melt processing. A useful range of melting or softening points (200–350 °C) was attained by ring substitution, copolymerization, and/or introduction of limited chain flexibility. Many of the poly(azomethines) yielded liquid crystalline melts, which were readily spun into oriented, high-tenacity, high-modulus fibers. These fibers were further strengthened by heat treatment in a relaxed state at temperatures near but below the flow temperature. One of the more fully characterized polymers was that from methyl-1,4-phenylenediamine and terephthalaldehyde. This polymer was spun into fiber with tenacity/initial modulus of 7.3/916 g/denier as spun. The heat-treated fiber had a tenacity/initial modulus of 38/1012 g/denier (average values).

Introduction

The literature of polymeric azomethines (Schiff bases) is extensive.[2-6] It is one of those segments of polymer chemistry in which researchers have tried repeatedly to prepare polymers with high molecular weight but in general have failed because of low solubility or infusibility of the products. In part this was due to the selection of compositions that had a low potential for tractability or ease of preparation. In some cases low to intermediate solution viscosities have been reported or molecular weights have been estimated from elemental or end-group analyses. There have been only a few reports of the successful formation of films or sintered disks.[7,8] Within this field there have been many studies of thermal stability and electrical properties of metal chelated and nonchelated products.

The first poly(azomethines) were prepared by Adams and co-workers[9] from terephthalaldehyde and benzidine and dianisidine. The products were insoluble and infusible. In the period from 1950 to 1959 Marvel and coworkers prepared a number of polyazines and poly(azomethines) from aromatic dialdehydes with hydrazine and *o*-phenylenediamine and examined their chelate formation and thermal stability.[10] Cotter and Matzner[3] have provided a summary of the literature and a table of compositions synthesized up to early 1967, and D'Alelio[2] has written a review, primarily on his work in the 1967–1968 period.

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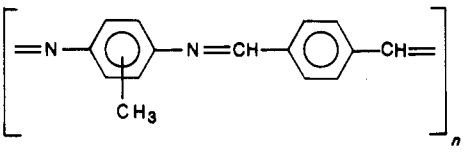
The present work describes the successful synthesis of a variety of aromatic poly(azomethines) and copoly(azomethines) by solution and melt methods. The key objective was to prepare polymers with rodlike chain structures which might be converted to high-strength fibers. The achievement of tractability has been accomplished by lowering the melting points through modification and selection of polymer structures in several ways, for example, by unsymmetrical substitution of aromatic ring units.



The above composition, coded MePPD–TA, has been studied extensively and used to prepare fibers with exceptionally high tensile properties.

Following publication of this research in patents,[11] there has appeared a series of papers by Millaud and co-workers[12] in which MePPD–TA and related polymers have been examined in terms of viscosity–light scattering molecular weight relationships, persistence length, light absorption spectra, and the formation of lyotropic solutions in sulfuric acid.

Results and Discussion

Synthetic Routes. Aromatic poly(azomethines) are very readily prepared by several routes described in the literature, the most direct being the reaction of a diamine with a dialdehyde (eq 1). The diamine will react with

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$$H_2N—R_1—NH_2 + OHC—R_2—CHO \rightarrow [=N—R_1—N=CH—R_2—CH=]_n + H_2O \quad (1)$$

$$H_2N—1,4\text{-}C_6H_4—NH_2 + (RO)_2CH—1,4\text{-}C_6H_4—CH(OR)_2 \rightarrow [=N—1,4\text{-}C_6H_4—N=CH—1,4\text{-}C_6H_4—CH=]_n + ROH \quad (2)$$

$$H_2N—1,4\text{-}C_6H_4—NH_2 + R—N=CH—1,4\text{-}C_6H_4—CH=N—R \rightarrow [=N—1,4\text{-}C_6H_4—N=CH—1,4\text{-}C_6H_4—CH=]_n + RNH_2 \quad (3)$$

$$RCH=N—1,4\text{-}C_6H_4—N=CHR + OHC—1,4\text{-}C_6H_4—CHO \rightarrow [=N—1,4\text{-}C_6H_4—N=CH—1,4\text{-}C_6H_4—CH=]_n + RCHO \quad (4)$$

dialdehyde derivatives such as an acetal or an azomethine to evolve a mono alcohol or amine (eq 2 and 3). The dialdehyde can react with a bis(azomethine) derived from the diamine (eq 4). And finally azomethine exchange can take place so that two complementary bis(azomethines) will yield a polymer.

An important feature in the application of these polymerization reactions is that the equilibrium should favor polymer formation or that there be a mechanism for selectively removing the low molecular weight byproduct, as by distillation.

Another characteristic of the poly(azomethine) system apparent from the above synthetic routes is that, since polymer is in equilibrium with byproducts and monomers, the reactions are reversible at elevated temperatures and should yield a random molecular weight distribution when the system is homogeneous. Further, copolymers will have random distribution of components when prepared under equilibrium conditions.

D'Alelio and co-workers[2] in applying these and other reactions used strenuous conditions of 320 or 400 °C and usually produced highly discolored to black products which were probably partially decomposed.

Polymerization Methods. Several methods of preparing poly(azomethines) are illustrated in the Experimental Section and also in a number of the tables.

The reaction between aromatic diamines and dialdehydes is rapid at room temperature. Polymerization can be initiated in solution in water-free solvents, such as dimethylacetamide, ethanol, or benzene. Appreciable polymerization occurs before the polymer begins to precipitate, and the reaction continues more slowly in the suspension or pasty state. No catalysts are necessary but removal of water expedites polymerization. In the amide solvents anhydrous lithium chloride or other water-absorbing agents increase the molecular weight. Water may also be removed by direct or azeotropic distillation.

The poly(azomethines) may be obtained in high yield with low to intermediate molecular weights (η_{inh} values up to two) by solution methods. Such polymers are prone to continue polymerization in any thermal processing. Some control of thermal polymerization can be attained by adding a monofunctional intermediate or capping agent, by using an excess of one of the intermediates, or by confining the polymerization byproducts in the system. The capping agent should be chosen so as to have low volatility in order to retard its loss during polymer processing.

Higher molecular weights are attained by conducting the reaction at elevated temperature in a solid or molten state. As implied above, polymerization may be begun in a solvent in a first stage and then continued in a molten state, optionally at reduced pressure. For preparations in the molten state the reaction of diamines with bis(azomethines) is a convenient and well-controlled process that yields polymer with high molecular weight.

Table I
MePPD-TA Melt Polymerization

reaction time,[a] min	η_{inh}, dL/g in H_2SO_4	reaction time,[a] min	η_{inh}, dL/g in H_2SO_4
13	1.55	50	3.77
20	1.73	60	3.93
30	2.71	90	4.11
40	3.50		

[a] Reaction of equivalents of 2-methyl-1,4-phenylenediamine and *N,N'*-1,4-xylylidenebis(aniline) at 260 °C and about 760 Torr with distillation of byproduct aniline. Timing was begun at point of complete melting of intermediates.

Table I gives an example of the reaction of 2-methyl-1,4-phenylenediamine with *N,N'*-1,4-xylylidenebis(aniline) at 260 °C (see eq 3). The rate of aniline removal controls the polymerization rate. The yield of polymer is essentially quantitative.

Other examples of this polymerization are given in Tables VII and VIII under Fiber Preparation.

Selection of Polymer Compositions. Mono- and bis(azomethines) from para aromatic units bearing suitable terminal functional groups have long been known to form liquid crystalline melts. On the other hand, most previously known aromatic poly(azomethines), whether para-linked or not, did not melt below their decomposition temperatures. In order to obtain meltable poly(azomethines) with sufficient linearity and stiffness to form liquid crystalline melts, several structural modifications were employed, separately and in combination. A range of typical polymers is given in Tables II and III. All of these polymers except the first in Table II yielded optically anisotropic (liquid crystalline) melts.

The basic homopolymers are derived from ring units with para or parallel and oppositely directed chain-extending bonds, thus creating a structure or structural segments with rodlike character, that is, having appreciable persistence length.[12]

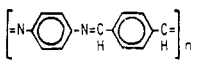
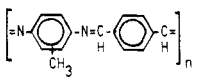
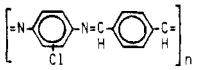
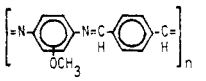
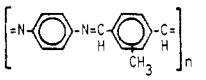
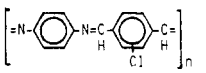
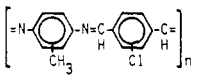
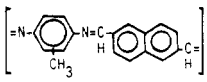
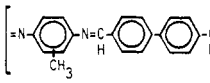
The polymers in Tables II and III are illustrative of the variety of structures that may be prepared to yield optically anisotropic melts. Many others have been examined, including those from substituted 4-aminobenzaldehydes and their copolymers with AA–BB compositions. Some of these will be described in future publications.

Melting Temperature Relationships. Discussion of melting temperature relationships is complicated by the marked increase in melting temperature with molecular weight and the tendency of many polymers to increase rapidly in molecular weight on heating. Also, the melting temperature may be altered by residues of strongly held solvents or polymerization byproducts and the presence of a nonrandom molecular weight distribution.

Different methods of melting point determination give differing results. The highest melting temperatures are those for formation of melts from which fibers can be drawn. The lowest values are from DSC determinations. Intermediate values are obtained by observing the temperature of polymer flow on a microscope hot stage or by PMT (polymer melt temperature) determinations on a gradient temperature bar. The temperature at which the polymer powders could be compressed into films or rods for spinning was much below the PMT.

In spite of these difficulties some qualitative structural effects on melting temperatures can be pointed out.

Table II
Aromatic Azomethine Homopolymers

polym no.	polym structure	prep method	η_{inh},[a] dL/g	PMT,[b] °C
1		amide–LiCl	0.99	400
2		amide–LiCl	2.0[c]	255[c]
3		amide–LiCl	1.75	310
4		melt (dianil)	1.1	285
5		amide–LiCl	0.70[d]	270
6		amide–LiCl	0.56	350
7		amide–LiCl	0.48	275
8		amide–LiCl	1.0	265[e]
9		amide–LiCl	1.22[f,g]	250[e]

[a] In concentrated sulfuric acid; c = 0.5%, 30 °C. [b] Reference 14. [c] When 1,4-diacetylbenzene was used in place of terephthalaldehyde, η_{inh} was 0.5 dL/g and PMT was 370 °C. [d] Capped by 4-acetamidobenzaldehyde. [e] Unsubstituted polymer does not melt at 400 °C. [f] Capped by 4-aminoacetanilide. [g] c = 0.1%.

Substituents. Unsubstituted, para-linked poly(azomethines) are unmeltable below the decomposition temperature. Meltability is achieved by introduction of unsymmetrically placed ring substituents. Single substituents, chloro, methoxy, and methyl, on the 1,4-phenylene unit lower the melting point in that order. Chloro and methyl substituents on the terephthalaldehyde unit are less effective (Table II; polymers 2–6). When a single substituent is placed on both the diamine and dialdehyde, the effect is not additive (Table II; polymer 7). This lack of additive depressing effect may result from some degree of ordered placement of substituents along the polymer chain arising from reactivity differences in the monomer functions having ortho substituents. Substituting the diketone 1,4-diacetylbenzene for terephthalaldehyde in combination with 2-methyl-1,4-phenylenediamine results in a considerable increase in melting temperature. Rather surprisingly, replacing terephthalaldehyde with 2,6-naphthalenedicarboxaldehyde or 4,4′-biphenylenedicarboxaldehyde in combination with 2-methyl-1,4-phenylenediamine resulted in polymers having similar melting temperatures (polymers 8 and 9). Comparison at identical molecular weights might provide a greater distinction.

Angular Units. Angular units, such as bis(4-aminophenyl) ether or the corresponding dialdehyde, tend to raise the melting temperatures when fully replacing the 1,4-phenylene unit (Table III; polymers 10–12). However, in intermediate copolymers there can be a pronounced melting point depression.

Flexible Chain Units. 1,2-Ethylene units and related longer flexible chains between phenylene rings lower the melting temperature (Table III; polymers 13, 14, and 18–20), as does copolymerization with linear aliphatic diamines (polymer 17). Large proportions of flexible chain units can be present without loss of ability to form optically anisotropic melts. However, the poly(azomethine) from hexamethylenediamine and terephthalaldehyde forms only an isotropic melt at 195 °C (ref 15 reports 200 °C). This polymer is colorless.

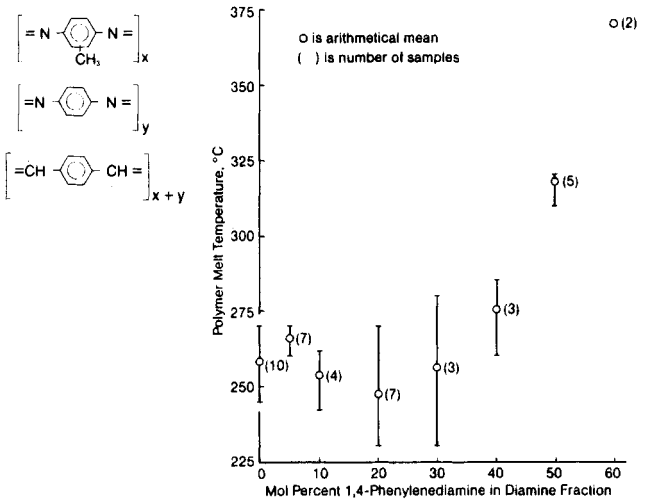
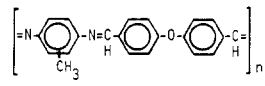
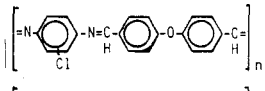
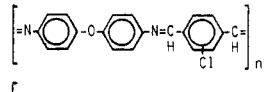
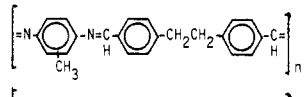
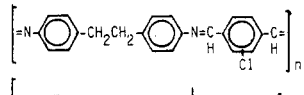
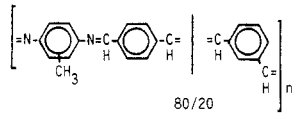
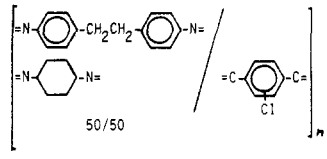
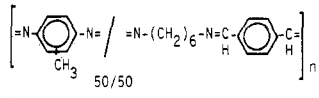
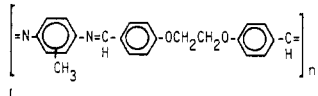
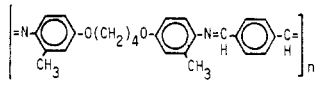
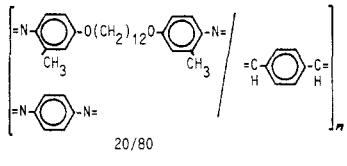


Figure 1. Relation of polymer melt temperature and composition for a series of copoly(azomethines) from 2-methyl-1,4-phenylenediamine, 1,4-phenylenediamine, and terephthalaldehyde; numbers in parentheses indicate the number of different polymer preparations and open circles indicate the arithmetical mean of the melt temperatures.

Guillon and Skoulios[16] have described a poly(azomethine) derived from benzidine and 4,4′-diformyl-α,ω-diphenoxydodecane which is reported to be thermotropic above 300 °C, demonstrating the possibility of obtaining a liquid crystalline melt with a high proportion of flexible chain segments without the use of ring substitution.

Copolymers. Figure 1 shows the melting ranges for a series of copoly(azomethines) derived from 2-methyl-1,4-

Table III
Aromatic Poly(azomethines) Polymers with Flexible Units and Copolymers

polym no.	polym structure	prep method	η_{inh},[a] dL/g	PMT,[b] °C
10		amide–LiCl	0.73	288
11		amide–LiCl	0.64	305
12		amide–LiCl	0.51[c]	320
13		amide–LiCl	1.2[d]	175
14		melt (dialdehyde)	0.94	260
15		toluene at reflux	1.9	260
16		amide–LiCl	0.6[d]	272
17		benzene at reflux	0.7[d]	150
18		tetrahydrofuran at 50 °C diphenyl ether at 200 °C	1.67	253
19		benzene at reflux	0.46[e]	220
20		amide–LiCl	0.49	220

[a] In concentrated sulfuric acid; c = 0.5%, 30 °C. [b] Reference 14. [c] Capped with methyl 4-aminobenzoate. [d] Capped with 4-aminoacetanilide. [e] In methanesulfonic acid.

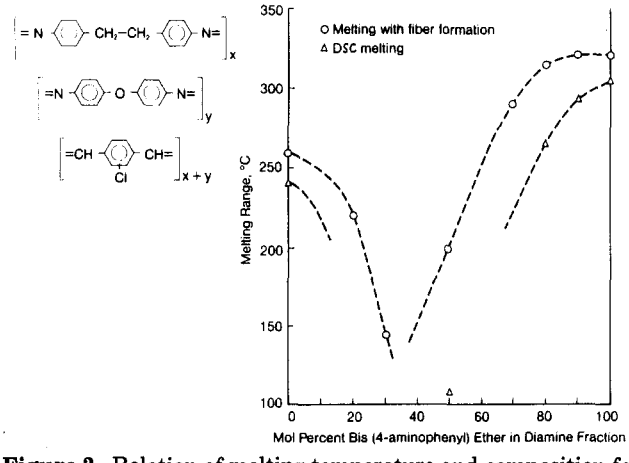
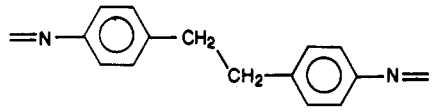


Figure 2. Relation of melting temperature and composition for a series of copoly(azomethines) from 1,2-bis(4-aminophenyl)-ethane, bis(4-aminophenyl)ether, and 2-chloroterephthalaldehyde: (O) melting with fiber formation; (Δ) DSC melting endotherm.

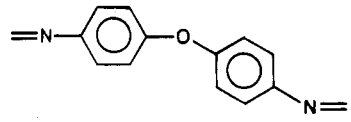
phenylenediamine and 1,4-phenylenediamine. Each composition is represented by a group of polymers from different preparations and having different inherent viscosities. The temperatures reported were PMT values, that is, the lowest temperature at which a trail of molten polymer forms on a gradient temperature bar. From the average melt temperature there is a modest minimum in melting temperature at the 80/20 composition. For unknown reasons there appears to be a slight elevation of the melt temperature for the 95/5 composition. Polymers with greater than 60 mol % unsubstituted 1,4-phenylenediamine units were unmeltable.

Figure 2 illustrates the marked melting temperature depression obtained when the comonomer units are quite different in structure. 1,2-Bis(4-aminophenyl)ethane provides flexible chain units, whereas bis(4-aminophenyl) ether units enforce bends in the polymer chain. The data in the figure also show the wide difference between DSC endotherms and melting temperatures to form fibers.

Thermal Behavior of MePPD–TA by DSC. The melting profile of MePPD–TA is complicated and, generally, exhibits a multiplicity of peaks. Furthermore, the thermal behavior is modified by the method of polymer preparation and the molecular weight and thermal history of the sample. Heat treatment of polymers and fibers at



1,2-bis(4-iminophenyl)ethane unit



bis(4-iminophenyl) ether unit

175–250 °C for as little as 1 min has a marked effect on the melting behavior.

For example, a sample made by low-temperature polymerization in an amide solvent (η_{inh} = 1.48) showed endotherms at 230 and 248 °C (Figure 3). When the sample was cooled after heating to only 300 °C, there was an exotherm at 174 °C due to some crystallization. On a second heating cycle there was then only one endotherm at the low temperature of 219 °C. After a new sample of this polymer was first annealed at 240 °C for 20 min, the DSC curve showed one sharp endotherm at 247 °C (Figure 4).

The proposed explanation of this behavior is that the polymer contains one crystalline form which is present in several populations having different degrees of perfection or crystalline size and therefore different melting points. The possibility of several polymorphic forms was eliminated by X-ray diffraction studies.

Figure 5 shows the changes in the position of three DSC peaks with time of heat treatment at 204 °C for five samples of MePPD–TA polymer prepared from equivalents of intermediates by consecutive solution and melt polymerization (η_{inh} = 4.67). Preheating the samples for 2 min at 200 °C eliminated a lower peak at 205 °C. In this case the initial peak at 220 °C showed extensive growth and was shifted to 237 °C; the 235 °C endotherm gradually shifted to higher temperatures and was eventually eliminated or overlapped by the 255 °C peak. The latter was little changed by the 204 °C treatment.

After a sample of this polymer was heated at 228 °C for 240 min, the DSC plot had only a single endotherm at about 255 °C. With isothermal heating of a group of samples at 254 °C the 255 °C peak disappeared in about 15 min while a new endotherm appeared above 255 °C and moved to 280 °C with 240 min of heating. Upon continued heating or heating at higher temperatures polymer samples may become unmeltable. This may result from crosslinking or an extreme degree of polymerization.

From DSC curves for a wide range of polymer and fiber samples of MePPD–TA, the heat of fusion varied from 0.7 to 2.0 kcal/mol. A heat of fusion value, ΔH_u, of 1.5 kcal/mol for 100% crystalline MePPD–TA was obtained from a plot of $1/T_m$ vs. log percent aromatic diamine for a series of MePPD/6-TA copolymers. The heat of fusion for the polymer described in Figures 3 and 4 varied with sample history from 0.73 to 0.93 kcal/mol.

Structure and Color of Azomethines. Aromatic poly(azomethines) are naturally colored yellow, orange, red, and sometimes brown. Deeper coloration and brown tones may develop from heat treatment, exposure to light and air, or from impurities in the intermediates. Acids, particularly strong acids such as sulfuric acid or trifluoroacetic acid, produce dark browns and red. The relatively low coloration is explained by the lack of coplanarity of the aromatic ring structures with the azomethine units and the consequent low conjugation of double bonds along the polymer chain. This conclusion is supported by data on monomeric azomethines as outlined below.

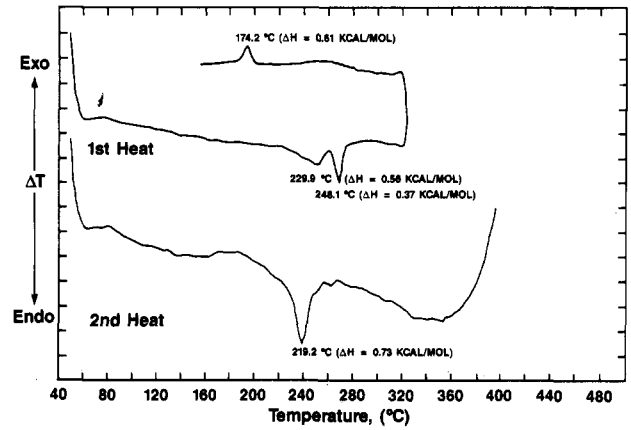


Figure 3. Thermal behavior of MePPD–TA by DSC: heating rate 20 °C/min under nitrogen; polymer prepared by solution method in amide solvent; η_{inh} = 1.48 dL/g.

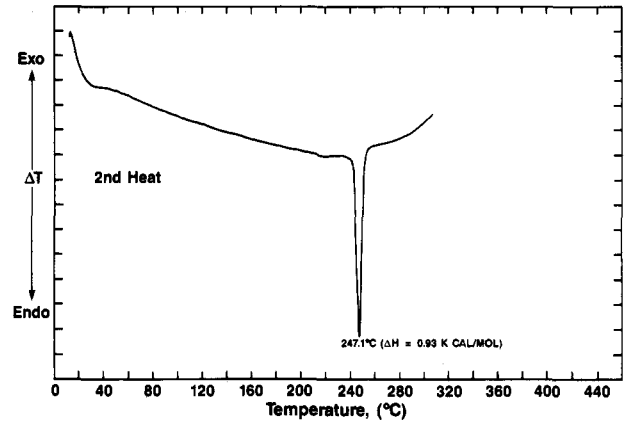


Figure 4. DSC for MePPD–TA after isothermal heating for 20 min at 225 °C; polymer same as described in Figure 3.

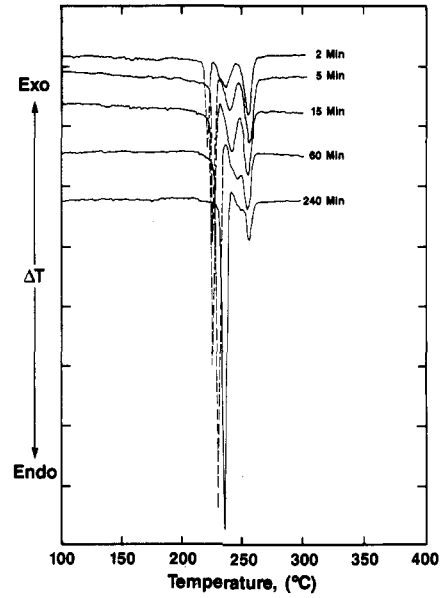
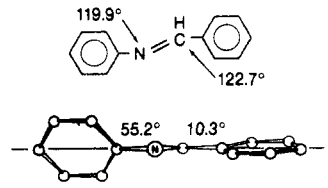


Figure 5. DSC response of MePPD–TA samples to heat treatment for various times at 204 °C, samples preheated for 2 min at 175 °C to remove a low endotherm at 174 °C. Polymer prepared by consecutive solution and melt process; η_{inh} = 4.67 dL/g.

Measurement of dipole moments on monomeric aromatic azomethines from aldehydes has indicated that they have a trans configuration.[17] In solid benzylidineaniline X-ray evidence shows that the aniline ring is twisted out

Configuration of Benzylideneaniline



Adapted from Bürgi and Dunitz, *Helv. Chim. Acta* **1970**, *53*, 1747.

of the C—N=C—C plane by 55°; the benzylidine ring is twisted in the opposite direction by 10°. Bürgi and Dunitz[18] also determined the angles in the azomethine unit to be such that the deviation from parallel extension is only 2.8°. Substituents in the para positions change the angles somewhat. This is an appreciably lower deviation from parallel than has been found for the bonds in the amide group in benzanilides.

van der Veen and Grobben[19] synthesized a series of ortho-methyl-substituted azomethines and found that the melting points were depressed and the nematic liquid crystalline range was reduced relative to values for the unsubstituted azomethines. They assumed that the methyl group increased the twist angle of the aromatic rings. It also stiffened and broadened the molecule, yet the liquid crystal propensity was retained. The structure broadening presumably made crystal lattice packing less favorable and resulted in lower melting points and lower stability of the liquid crystalline phase.

Observation of Optical Anisotropy. Optical anisotropy in the polymer melts is easily observed as a pearlescent appearance in the polymer melts during preparation while the reaction mixture is stirred or as a stirred melt on a gradient temperature bar. A more acceptable evaluation is the observation of light transmission by the melt when seen on a microscope stage between crossed polarizers[20] and examination of the texture and other characteristics.

Another procedure, the thermal optical test[11] (TOT, outlined briefly in the Experimental Section), is a useful characterization test carried out with a polarizing microscope, a hot stage, and a temperature recorder. In this test one can observe the beginning of polymer flow, the presence of optical anisotropy, and the transition to an isotropic state or the occurrence of decomposition. Figure 6 gives a representative plot of the recorded light transmission through a polymer sample between crossed polarizers as the temperature is raised rapidly (ca. 50 °C/min). The level of light transmission should be at least twice the background transmission to indicate optical anisotropy. There is often a flash of light from disturbance of the melt at the nematic–isotropic transition.

Table IV lists TOT results for a number of poly(azomethines). As with other melting test methods, the flow temperature, fluid mobility, and optical anisotropy range vary somewhat among polymer samples of the same chemical composition but from differing sources. The small sample size and rapid heating rate make this test a valuable adjunct to other thermal characterizations.

The flow temperature is sometimes different from the beginning of anisotropy, partly because it is observed on a separate sample and because the required fluidity may not coincide with ordering of the polymer chains. The flow temperature of a sample by the thermal optical test may be higher than the polymer melt temperature because the sample has been polymerized some in making the required film. Heating for film preparation is made as short as possible.

Thermal Optical Test on a Polyazomethine

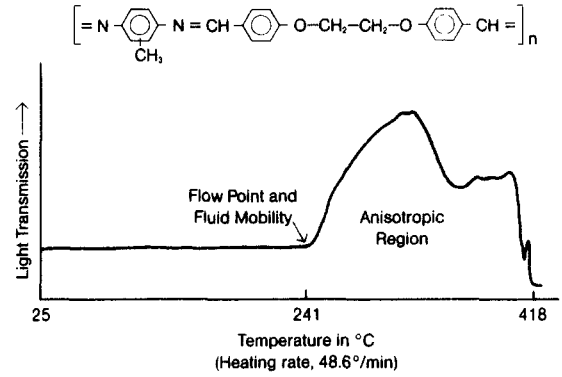


Figure 6. Thermal optical test on the poly(azomethine) from 2-methyl-1,4-phenylenediamine and 1,2-bis(4-formylphenoxy)-ethane. Particles pressed at 250 °C; heating rate 48.6 °C/min.

Liquid Crystalline Solutions. Many aromatic poly(azomethines) that form anisotropic melts also form optically anisotropic (lyotropic) solutions in concentrated sulfuric acid, methanesulfonic acid, chlorosulfonic acid, and hydrogen fluoride. Compositions that are unmeltable, such as the poly(azomethine) from 1,4-phenylenediamine and terephthalaldehyde, likewise yield anisotropic solutions. Because these solutions may undergo appreciable degradation with time, accurate determinations of critical concentrations and of exactly defined ranges of anisotropy are difficult. Millaud, Thierry, and Skoulios[21] have reported on concentration ranges for optically anisotropic solutions of MePPD-TA.

When concentrated solutions of aromatic poly(azomethines) in sulfuric acid are extruded into cold water and other aqueous solutions, the color changes from very dark red to orange and severe degradation occurs.

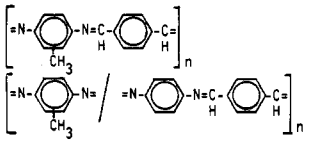
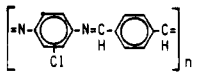
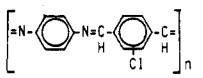
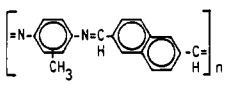
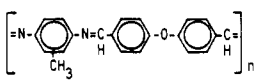
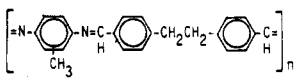
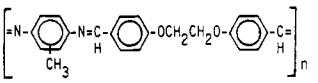
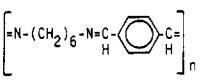
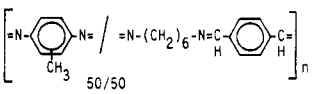
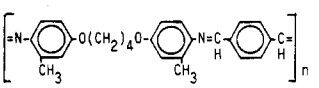
Fiber Preparation and Properties. High-strength fibers have been melt-spun from many different thermotropic poly(azomethines) (Table V and ref 11). The examples in the table are chosen to show different compositions, a range of initial inherent viscosities, and a range of melting temperatures.

Because the polymers are prepared as powders or granules, the first step toward small-scale spinning is usually compaction or molding into a rod. This is followed by spinning (extrusion of molten polymer through fine holes) and then by a heat-strengthening step. The fibers cannot be hot-drawn as is done with conventional fibers from flexible-chain polymers such as aliphatic polyamides.

In the earlier discussion of molecular weight control, the strong tendency of the poly(azomethines) to polymerize thermally was pointed out. Experience has shown that there is frequently an inherent viscosity gain at each stage of fiber preparation. For example, the following data in Table V are cited as a possible progression leading to high-tenacity fibers. The initial inherent viscosity may be lower or much higher than illustrated, and the molecular weight changes will vary with the polymer and how its processing is conducted. The gain in molecular weight upon molding and spinning is not essential since the starting molecular weight can be set as desired. However, molecular weight gain during heat treatment is an important factor in attaining the maximum increase in fiber strength.

The extruded polymer melts are in a liquid crystalline state in which the polymer chains are aligned in more or less parallel arrays. As a result, the as-spun fibers have quite a high degree of molecular orientation (Figure 7, top) and a useful level of tensile properties. This ease of ori-

Table IV
Melting and Optical Anisotropy Ranges for Selected Poly(azomethines) by the Thermal Optical Test

polym structure	η_{inh}, dL/g	flow temp, °C	anisotropic melt range, °C
	2.20	256	256 to >420
95/5	1.36	216	251 to >420
90/10	2.07		245 to >420
70/30	0.97	317	317 to >420
60/40	1.44	357	357 to >420
	0.69	298	296 to ~405 dec
	0.30	334	334–400
	1.0	288	288 to >410
	0.69	283	283–418[a]
	1.9	208	204 to >420
	0.48	275	275–418
	1.05	195	none[b]
	0.57	150	174 to ~320 dec
	0.46[c]	230	230–400

[a] Isotropic melt above 418 °C. [b] Isotropic melt above 195 °C. [c] In methanesulfonic acid.

Table V
Changes in Polymer Solution Viscosity during Processing

stage of processing	η_{inh}, dL/g	stage of processing	η_{inh}, dL/g
polymer as prepared	1.2	as-spun fibers	3.2
molded rod	1.6	heat-treated fibers	7.5

entation can be shown in a simple experiment of drawing strong oriented fibers from a melt pool.

As an example, the polymer from 2-methyl-1,4-phenylenediamine and *N,N'*[2,6-naphthylenebis(methylidyne]bis(aniline) (η_{inh} = 1.0; melting at 265 °C) was melted on a gradient temperature bar to form a small pool of polymer. Fibers in 2-ft lengths were spun by withdrawing forcep tips from the melt in a steady rapid motion. Good tensile properties were achieved by this simple method of spinning (Table VI). The denier is higher and less regular than one obtains from machine-controlled spinning.

Table VIII shows the effect of increasing polymer inherent viscosity of as-spun fibers when other variables are held essentially constant. A comparison with the first as-spun fiber example (MePPD–TA) in Table VII where the η_{inh} was 6.0 shows a similar high result with a somewhat higher modulus.

Upon fiber heat treatment the tensile properties are increased. The gain is accompanied by increases in molecular weight, molecular orientation, and crystallinity (Figure 7, bottom). Heat-treatment conditions for the fibers in Table VII are not related in any systematic way

Table VI
Fibers from a Melt Pool of a Poly(azomethine)

fiber[a]	tenacity, g/denier	elongation, %	modulus, g/denier	denier/filament
as-spun (4 breaks)	3.2	1.1	300	67
heat-treated (3 breaks)[b]	9.8	1.3	764	15

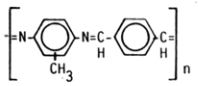
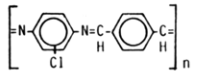
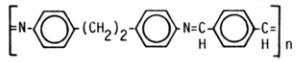
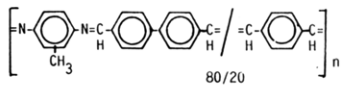
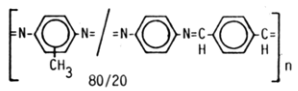
[a] Polymer from 2-methyl-1,4-phenylenediamine and *N,N'*-[2,6-naphthylenebis(methylidyne)]bis(aniline). [b] Heated on a bobbin for 6 h at 240 °C under nitrogen.

and show that different treatments may yield similar results. If the fiber is heat sensitive because of a low softening temperature, then a gradual or stepwise rise in treating temperature is desirable. In general, the higher the final treatment temperature in the absence of melting or decomposition, the higher the property level.

The MePPD–TA example illustrates an oustanding, and reproducible, fiber for which the average tenacity is 38 g/denier with a single break at 44 g/denier. From another spin of a similar polymer, heat-treated fibers were obtained with T/E/Mi/Den of 43.6/4.8/944/3.2 (average of 10 breaks) with a single break at 46 g/denier. Heat treatment in this case was on a bobbin, 1 h to 160 °C, 1 h at 160 °C, 1 h to 245 °C, 4 h at 245 °C. These are the highest tenacity values that have been reported for a fiber from a condensation polymer.

In Table IX are presented some data on varying the preparation of MePPD–TA from *N,N'*-1,4-xylylidenebis-

Table VII
Fibers from Several Poly(azomethines)

polym structure	prep method	polym η_{inh},[a] dL/g	polym PMT,[b] °C	fiber	tenacity, g/denier	elongation, %	initial modulus, g/denier	denier	OA,[c] 2θ
	benzene and melt	6.0	260	AS:[d]	7.3	1.1	916	4.0	
				HT:[e]	38	4.4	1012	3.7	
	amides and LiCl[f]	0.8[g]	310[g]	AS:	7.4	1.3	683	11	22
				HT:	15.3	1.9	844	11	10
	amides and LiCl[h]	0.4[i]	256	AS:	3.6	1.3	400		25
				HT:[j]	21.4	4.3	447		9
	CH_2Cl_2 azeotrope[k]	1.13	190	AS:	5.8	0.9	729	7.6	24
				HT:[l]	14.8	3.4	508	8.9	15
	benzene azeotrope	1.07	260	AS:	4.2	1.0	554	4.2	
				HT:[m]	26.1	3.8	775	3.7	10

[a] In concentrated sulfuric acid, c = 0.5%, 30 °C. [b] Reference 14. [c] See Experimental Section for definitions. [d] AS = as spun; HT = heat treated. [e] Heat treatment as suspended fibers: 40 min to 165 °C; 1 h to 230 °C; 7.6 h at 232–234 °C. [f] Capped with 4-acetamidobenzaldehyde. [g] The fiber inherent viscosity was 4.46, and PMT was 320 °C. [h] Capped with 4-aminoacetanilide. [i] Inherent viscosity of as-spun fiber was 1.05. [j] Heat treatment was 2 h, 150 °C; 2 h, 260 °C. [k] 5 mol % excess diamine and 5 mol % 4-aminoacetanilide. [l] Heat treatment was 16.5 h, 115 °C; 2 h, 150 °C; 3 h, 175 °C; 3 h, 200 °C. [m] Heat treated 6 h, 225 °C; 6 h at 200 °C gave tenacity of 28.8 g/d.

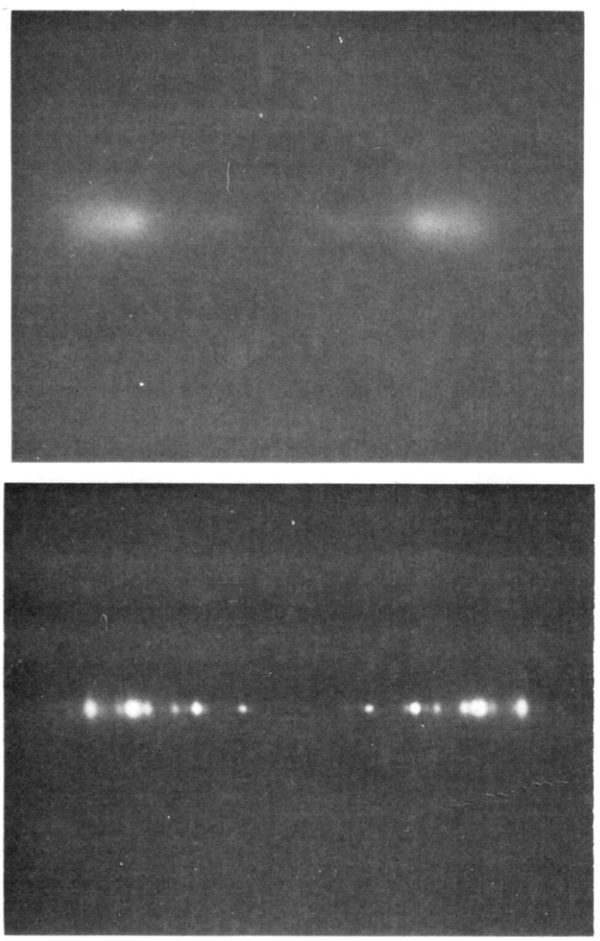


Figure 7. Wide-angle X-ray diffraction patterns of MePPD–TA fibers: (top) as-spun fibers, orientation angle 22°; (bottom) heat-treated fibers, orientation angle 11°.

(aniline) so as to change the end-group balance in the polymer sample. The inherent viscosities are in the range 3.4–4.7. They may have influenced the properties of the as-spun fibers, as already pointed out, but this is not the dominant factor during heat treatment. Excess dianil seems to have restricted initial polymer formation, reduced the tenacity of as-spun fiber, and in turn reduced the tenacity and modulus of heat-treated fiber (Table IX). The fiber from a polymer prepared from equivalents of reactants has excellent properties, while those fibers in

Table VIII
As-Spun Fibers of MePPD–TA from Polymer with Varied Inherent Viscosity[a]

reaction conditions ~760 Torr	reaction conditions 0.25 Torr	polym η_{inh}, dL/g	T/E/Mi[b] as spun
10 min	10 min	2.57	3.3/1.2/737
10 min	20 min	3.34	4.2/1.1/700
10 min	40 min	4.77	7.4/1.3/749

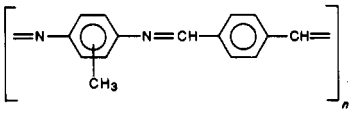
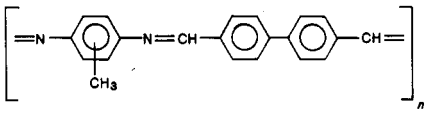
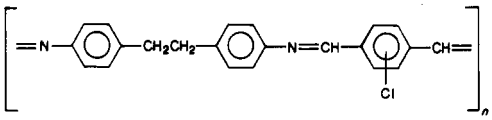
[a] Prepared from equivalents of 2-methyl-1,4-phenylenediamine and *N,N'*-1,4-xylylidenebis(aniline). Aniline distilled during reaction in the melt at 260 °C. [b] T = tenacity in g/denier; E = % elongation at break; Mi = initial modulus in g/denier.

Table IX
Influence of Monomer Balance on Properties of Fibers from MePPD–TA[a]

reaction conditions	polym η_{inh}, dL/g	T/E/Mi[b] as spun	T/E/Mi[b] heat treated[c]
equivalence of reactants			
20 min, ~760 Torr	4.73	6.3/1.3/744	16.2/1.1/975
40 min, 0.25 Torr			
3 mol % excess dianil			
20 min, ~760 Torr	3.44	3.0/1.1/833	9/0.9/637
40 min, 0.25 Torr			
3 mol % excess diamine			
20 min, ~760 Torr	4.72	7.5/1.4/735	19.8/2.5/908
25 min, 0.25 Torr			
8 mol % excess diamine			
20 min, ~760 Torr	3.57	5.7/1.2/648	30/1.8/868
10 min, 0.25 Torr			

[a] Polymer from 2-methyl-1,4-phenylenediamine and *N,N'*-1,4-xylylidenebis(aniline). Reaction in the melt at 260 °C. [b] T = tenacity in g/denier; E = % elongation at break; Mi = initial modulus in g/denier. [c] Yarns wrapped on Fiberfrax covered bobbins and heated in flowing nitrogen to 150 °C, held 3 h, and then heated at 260 °C for 1 h and cooled to room temperature in oven.

Table X
Densities of Oriented, Crystalline Fibers

fiber composition	density, g/cm³
	1.225
	1.234
	1.297
poly(ethylene terephthalate)	1.390
poly(1,4-phenyleneterephthalamide)	1.44
high-tenacity cellulose	1.524

which there is an excess of amine-terminated polymer chains provide an even greater response to heat treatment. Presumably the required gain in molecular weight is produced more readily by an amine–azomethine interaction than an azomethine–azomethine exchange with evolution of aniline.

Fiber Densities. The measured densities of heat-treated fibers of poly(azomethines) are appreciably lower than the values for other linear ring-containing polymers such as poly(ethylene terephthalate), poly(1,4-phenyleneterephthalamide), and cellulose. Typical values are shown in Table X. This property may reflect the effect of lateral substituents and the out-of-plane twist of successive rings along the polymer chain on chain packing.

Orientation and Crystalline Order. Typical wide-angle X-ray diffraction patterns for MePPD–TA are given in Figure 7. They show a high degree of lateral order in the polymer crystallites. Other polymers have shown three-dimensional order in the crystallites of oriented fibers.

Experimental Section

Polymer Intermediates. In general, intermediates were from commercial sources and were purified by known procedures of distillation, sublimation, and crystallization. High purity and careful storage and handling are necessary for attainment of high molecular weight polymers.

2-Methyl-1,4-phenylenediamine. This diamine was purchased in an impure form as the dihydrochloride or the sulfate. The free diamine is exceptionally air and light sensitive.

The diamine was obtained as the free base by treating the salt with aqueous concentrated ammonium hydroxide, separating the diamine as an oil, distilling the oil from granular zinc (5–10 mol %) through an efficient column, and collecting the water-white diamine in 50-mL flasks for storage in a drybox in low light. The flasks were opened and used only in the nitrogen-filled drybox. The pure diamine has a melting point of 64 °C and a boiling point of 274 °C (760 Torr).

4,4′-Diaminodiphenylethane. The diamine was purchased from Eastman Chemical Co. and sublimed at 140 °C and 0.25 Torr prior to use: mp 138–140 °C.

Terephthalaldehyde. Terephthalaldehyde was purchased from Aldrich Chemical Co. and purified by sublimation at reduced pressure. The melting point was 115 °C, and the purity by vapor pressure chromatography (VPC) was 99.4–99.6%.

2-Chloroterephthalaldehyde. 2-Chloroterephthalaldehyde was prepared from 2-chloro-*p*-xylene as described by Naylor[22] for dihalogeno-substituted terephthalaldehydes. The intermediate chloroterephthalaldehyde tetraacetate, recrystallized from methanol, melted at 105–108 °C. The acetate was hydrolyzed with sulfuric acid in aqueous ethanol. The aldehyde was recrystallized from *n*-hexane and melted at 79–80.5 °C.

In an alternative preparation 2-chloro-*p*-xylene was chlorinated in carbon tetrachloride by irradiation with ultraviolet light. The 2-chloro-*p*-xylylene dichloride was allowed to react with hexamethylenetetramine to form a salt in chloroform. The salt (584 g) was heated at reflux with 180 mL of 37% aqueous formaldehyde for 16 h. The yellow sludge was washed with cold water and heated with 400 g of sodium bisulfite in 2 L of water for 1 h on a steam bath, and then 400 mL of concentrated hydrochloric acid was added. After 4 h more of heating, the aldehyde separated as an oil. After cooling, it solidified and was dried and recrystallized from hexane.

2-Methylterephthalaldehyde. 2-Methyl-α,α'-1,4-xylenediol (mp 78–81 °C) was prepared by reducing 2-methylterephthaloyl chloride with lithium aluminum hydride by the general procedure of Nystrom and Brown.[23] The diol was then oxidized to the dialdehyde with aqueous 1 N ceric ammonium nitrate by the procedure of Trahanovsky et al.[24] The aqueous reaction mixture was extracted with ether twice and methylene chloride once. The combined organic layers were washed with aqueous sodium bicarbonate and water and then dried over magnesium sulfate. The latter solid was filtered off and the filtrate evaporated to a soft solid, which was sublimed at 65 °C to yield a white powder: mp 70–71 °C. The powder was crystallized from water to give 2-methylterephthalaldehyde: mp 71–72 °C.

4,4′-Biphenyldicarboxaldehyde. The dimethyl ester of 4,4′-dibenzoic acid was reduced with lithium aluminum hydride in tetrahydrofuran at about 5 °C to the bibenzyl alcohol: mp 190–192 °C. The alcohol was oxidized to the dialdehyde with ceric ammonium nitrate in glacial acetic acid/water.[24] The crude product was obtained in 95% yield. It is readily oxidized in air to the mono-and diacids. The product was purified by washing a methylene chloride solution repeatedly with a 1.5 N aqueous potassium hydroxide solution and then many times with water. The isolated aldehyde melted at 142–147 °C. After sublimation at 135 °C (0.3 Torr), the melting point was 143–145 °C.

4,4′-Oxybis(benzaldehyde). This dialdehyde was prepared by conversion of bis(4-chloromethylphenyl) ether to the bis(hydroxymethylphenyl) ether as described by Trapp and Doedens.[25] The latter compound was then oxidized to the dialdehyde as described for 4,4′-bibenzaldehyde above.[24] The 4,4′-oxybis(benzaldehyde melted at 61–63 °C. The overall yield was about 80%.

***N,N′*-1,4-Xylylidenebis(aniline).** The dianil of terephthalaldehyde was prepared according to the procedure of D'Alelio.[26]

***N,N′*-[2,6-Naphthylenebis(methylidyne)]bis(aniline).** 2,6-Naphthalenedicarbonyl chloride (50.6 g; 0.02 mol) in ethylene glycol dimethyl ether (150 mL) was reduced with lithium tri-*tert*-butylaluminum hydride (103 g) in 700 mL of ethylene glycol dimethyl ether. To the stirred diacid chloride solution at −70 °C, under nitrogen, the reducing agent was added dropwise over 4 h, after which the mixture was stirred overnight and allowed to warm to room temperature.

The reaction mixture was poured into ice, and the precipitated product was collected and, while still damp, treated with boiling ethanol. Residual solid was separated from the alcohol, and the alcohol was evaporated to leave crude dialdehyde (mp 162–190 °C). The crude product (4 g) was dissolved in 200 mL of alcohol. Aniline (6 mL) was added and the solution refluxed for 8 h. When this solution was cooled, the dianil formed a yellow precipitate: mp 180–182 °C.

Terephthalaldehyde Bis(diethyl acetal). The procedure of Ehrlichmann and Friedrich[27] was used with a reaction time of 3 h. The acetal was distilled through a spinning band column with the principal fraction obtained at 116–117 °C, 0.09 Torr.

Polymerization Methods. Solution Polymerization in Amide Solvents. 2-Methyl-1,4-phenylenediamine (4.40 g; 0.036 mol), bis(4-aminophenyl) ether (0.80 g; 0.004 mol), and 4-acetamidobenzaldehyde (0.4 g) were dissolved in an anhydrous mixture of hexamethylphosphoramide (25 mL) and *N*-methylpyrrolidone (25 mL) containing 2.0 g of lithium chloride. To this solution was added terephthaldehyde (5.36 g; 0.04 mol) with stirring. After 16 h at room temperature, the reaction mixture was unstirrable. The reaction mixture was combined with water in a blender. The product was collected, washed well with water and alcohol, and

dried under vacuum at 80 °C. The yield was 9.2 g (100%), η_{inh} = 1.1 dL/g, and the PMT was 306 °C.

Polymer from Diamine Salt. For many small polymerizations a 150-mL resin kettle, equipped with a 3-necked head, was used. A glass paddle stirrer was mounted through the central neck, and nitrogen was introduced through one side neck and exited through the third neck.

In a flask of this type was placed 19.5 g (0.1 mol) of 2-methyl-1,4-phenylenediamine dihydrochloride in 75 mL of *N*-methylpyrrolidone together with 7.4 g of lithium carbonate. To this stirred mixture at room temperature was added 13.4 g (0.1 mol) of terephthalaldehyde. The solution was viscous and starting to form a precipitate in 15 min. At this point 0.20 g of 4 -aminoacetanilide was added. At 16 h a very viscous paste had formed. The product and solvent were stirred in excess water. The polymer was collected on a filter and washed repeatedly with water and methanol and then dried in a vacuum oven at 80 °C. The orange powder weighed 21.5 g and had a PMT of 255 °C and η_{inh} = 2.1 dL/g.

Consecutive Polymerization in a Solution and a Melt. 2-Methyl-1,4-phenylenediamine (47.5 g; 0.39 mol) and 0.875 g of phenyl-1-naphthylamine were dissolved in 200 mL of boiling ethanol under nitrogen. Terephthalaldehyde (50 g; 0.373 mol) was dissolved in another 200 mL of ethanol in a 1-L resin kettle equipped with a helical stirrer. The diamine solution was added quickly to the aldehyde solution with stirring, giving a dark cherry red mixture. An orange color formed in 2 min followed in 4 more min by conversion of the solution to a gummy mass which exhibited stir opalescence. Stirring was stopped at 15 min when the mass solidified. After 60 min the mass was collected, washed with ethanol, broken up, and dried at 80 °C under vacuum for 16 h. Further grinding and drying gave a 100% yield of pale orange polymer.

The polymer was passed through a 1-in. screw extruder at 275 °C with a residence time of about 3 min. The tough product had an η_{inh} of 5.19 dL/g (c = 0.1% in sulfuric acid).

Polymerization by an Azeotropic Method. In a 500-mL round-bottomed flask equipped with stirrer, nitrogen inlet tube, distillate trap, condenser, and drying tube, there were combined 10.26 g (0.0804 mol) of 2-methyl-1,4-phenylenediamine, 0.176 g of phenyl-1-naphthylamine, 0.600 g of 4-aminoacetanilide, and 300 mL of methylene chloride. When solution occurred, 16.82 g (0.08 mol) of 4,4′-biphenyldicarboxaldehyde was added. The reaction mixture was heated to reflux by an oil bath for 3 h while water–methylene chloride azeotrope gradually distilled out and the water was separated. Polymer began precipitating at about 30 min. The mixture was cooled and filtered. The washed and dried product weighed 20.8 g (88%) and had an η_{inh} of 1.66 dL/g (c = 0.1% in sulfuric acid).

Melt Polymerization of a Diamine with a Dialdehyde. 4,4′-Diaminodiphenylethane (4.24 g; 0.02 mol) and 2-chloroterephthalaldehyde (3.36 g; 0.02 mol) were placed in a 250-mL, three-necked, round-bottomed flask equipped with stirrer, nitrogen inlet, and distilling head. The temperature was increased to 275 °C over a 34-min period while the reaction mixture was stirred and byproduct water collected. The polymer melt was cooled to room temperature. The solid was removed from the flask, ground in a laboratory mill, washed with acetone, and dried in a vacuum oven at 80 °C. The orange-colored polymer, obtained in a 93% yield, had an η_{inh} of 0.94 dL/g and a PMT of 260 °C.

Melt Polymerization with a Dianil. 2-Methyl-1,4-phenylenediamine (0.02–0.2 mol) and equivalent *N*,*N*′-1,4-xylylidenebis(aniline) were placed in a 250-mL, three-necked, round-bottomed flask equipped with a stirrer, a nitrogen inlet, and a distilling head. The flask was lowered, while the dry ingredients were stirred, into an oil bath preheated to 260 °C. The byproduct aniline was collected at atmospheric pressure until about 80% had been evolved (10–20 min). Then the pressure was reduced to 0.25–0.15 Torr, and reaction was continued for up to 40 min. The melts were opalescent during stirring by the end of the atmospheric stage. At completion the stirrer was removed and the mass was allowed to cool. The saucer-shaped polymeric product usually did not adhere to the glass and was retrieved by carefully breaking the flask. The mass was broken up and pulverized in a Wiley laboratory mill. The yields of orange polymer were over 90%. See Tables VII and VIII for some typical reaction times and viscosity results.

Polymerization of a Diamine with a Bisacetal. In a tall 1-in. test tube were placed 2-methyl-1,4-phenylenediamine (12.2 g; 0.1 mol), terephthalaldehyde bis(diethyl acetal) (25.6 g; 0.09 mol), and 0.5 g of 4-carboxybenzaldehyde. The mixture was heated at 70 °C in an oil bath while it was stirred by nitrogen bubbles from a capillary tube. The system evolved ethanol and remained clear and fluid for 15 min. The temperature was raised to 205 °C for 30 min, during which time the mixture became solid. The product was removed and stirred with water in a blender, washed well with water and methanol, and dried at 80 °C under vacuum. There was obtained 19.2 g of granular orange polymer, η_{inh} of 1.06 dL/g and PMT of 260 °C.

Caution must be observed in this preparation not to heat too vigorously once a precipitate forms since evolving alcohol may cause eruption.

Polyketimine from 1,4-Diacetylbenzene. 2-Methyl-1,4-phenylenediamine (2.44 g; 0.02 mol) and 1,4-diacetylbenzene (3.24 g; 0.02 mol) were well mixed in a 12-in. polymer tube in which was inserted a fine capillary for introduction of nitrogen. The mixture was heated under nitrogen flow at 156 °C for 1 h and then at 205 °C for 2 h. The sintered orange mass was collected, broken up, washed in a blender separately with water and methanol, and dried under vacuum at 80 °C. The yield of polymer was 4.32 g. The η_{inh} was 0.5 dL/g, and the PMT was 370 °C.

Fiber Preparation. Spinning. Fibers were prepared on a small scale by extruding the molten polymer through a series of fine screens and a multiple-hole spinneret. The polymer (5–15 g) was first molded into a short rod with a diameter to fit the preheated spinning cell. Pressure was applied by a hydraulically driven piston, and heat was applied primarily in a melt zone approaching the spinneret and at the spinneret. This limited heating reduced the amount of polymerization and increased control and ease of spinning. The fiber was collected by cooling in air or nitrogen and passing it through guides and rollers to the collecting bobbin. The rate of windup and the amount of yarn attenuation varied with the extrusion rate, spinneret hole size, and characteristics of the polymer melt. A spin stretch factor of five or more was common (ratio of windup rate to linear extrusion speed).

Heat Treatment. Strengthening of fibers was often possible by heating the fibers in a relaxed state at various temperatures up to within about 20 °C of the flow temperature. The maximum possible treatment temperature without fiber sticking often was shifted upward as heat treatment progressed, probably because of polymerization and a consequent rise in softening temperature. The treatment may be done on suspended fibers, skeins of yarn, or fibers wound upon a bobbin padded with a layer of refractory fibrous material sold under the name Fiberfrax. Treatments can be carried out also on taut fibers and on fibers passed continuously through a heated tube or oven. The treatments may be at a series of successively higher temperatures or at a single temperature, and the time may be seconds to several hours. Usually, not more than 8 h is needed for maximum effect. Specific examples are given with the fiber properties.

Characterization Tests. Dilute Solution Viscosity. Inherent viscosity, $\eta_{inh} = \ln(\eta_{rel})/c$, values were determined in 96–98% sulfuric acid at 30 °C and a concentration, c, of 0.5 g of polymer per 100 mL of solution, unless otherwise noted.

Because many of the poly(azomethines) were found to degrade in concentrated sulfuric acid when exposed to light, the determinations were conducted as much as possible in the dark or subdued light. The polymer sample or fiber, sulfuric acid, and an equal volume of 3-mm Teflon tetrafluoroethylene fluorocarbon pellets were placed in a closed bottle in a shaking machine for a minimum time to form a solution, usually 10–25 min. This step was done in the dark. A Cannon-Fenske viscometer was filled by inversion technique in subdued light and placed in a constant-temperature bath consisting of a saturated water solution of potassium dichromate. Three consecutive flow times were measured immediately. If the solution flow times decreased with successive measurements, the longest time was used for the calculation of inherent viscosity, expressed in deciliters per gram.

Thermal Optical Test. This test provides an instrumental means of determining the optical anisotropy of molten polymers and at the same time observing the onset of flow and melting of

the polymer sample. A detailed description is given in patents.[11] An outline is presented here. The apparatus is similar to that described by Kirshenbaum et al.[28]

The equipment consists of a high-quality microscope equipped with Polaroid polarizers and a heating stage capable of being heated to 500 °C. A photodetector is attached at the top of the microscope barrel, and a slider permits transfer of the image from the eyepiece to the photodetector. The photodetector signal is amplified and fed to the *Y* axis of a recorder, and a stage thermocouple is connected to the *X* axis. A second thermocouple from the stage goes to a temperature controller which is programmed to raise the temperature at a rate of about 50 °C/min.

Duplicate polymer film samples are prepared in a prescribed way from polymer particles pressed between pairs of cover slips at a temperature 10 °C above the temperature at which a particle of polymer has been observed to begin to flow. The films should have a thicknes from 4 to 6 μm. One of the films is used to observe the *flow temperature*, the temperature at which the edges of the film change contour. The second sample is placed so that essentially all of the light intercepted by the photodetecter passes through the film, and the light transmission vs. temperature is recorded. A typical recording is sketched in Figure 6.

Optically anisotropic melts commonly give light transmission two or more times the background transmission. Isotropic melts (sample should be fully melted) give transmission equal to or less than the background. Polymers yielding anisotropic melts may become optically isotropic because of decomposition or because of a thermal transition to the disordered isotropic state.

Polymer Melt Temperature. Polymer melting was determined on dry powdered polymer on a chrome-plated gradient temperature bar[14] and is noted as the temperature at which the polymer under moderate sliding pressure leaves a molten or waxy trail adhering to the bar.

X-ray Orientation Angle. Wide-angle X-ray diffraction patterns were obtained with a Warhus pinhole camera and Phillips generating unit Model 12045 having a copper fine-focus diffraction tube and a nickel β filter. The distance from the sample to the 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.

Fiber Tensile Properties. Tensile strength (T) (grams per denier), percent elongation at break (E), and the initial modulus (Mi) (grams per denier) were determined on an Instron tensile tester (Instron Engineering Corp., Canton, MA). The fibers were conditioned for at least 16 h at 21 °C and 65% relative humidity. Single filaments were broken with 1-in. initial jaw separation. Results are reported as the average of at least three breaks. Denier (the weight in grams of 9000 m of filament) was determined for each filament by a resonance method described in ASTM D1577-66, part 25, 1968.

Thermal Analysis. DSC measurements were made with Du Pont 900 series thermal analyzers in conjunction with a DSC cell. Samples were run at a heating rate of 20 °C/min in an atmosphere of flowing nitrogen.

Safety Considerations. Hexamethylenephosphoramide has been found to be an experimental carcinogen in rats (health risks determined by Du Pont). It should be used with extreme caution in handling and disposal. Other amide solvents should be used with care, avoiding skin contact and inhalation of vapors. Skin contact and breathing of dust from aromatic diamines should be avoided.

2-Chloro-1,4-phenylenediamine has been found to decompose violently during distillation or sublimation. Vessels should not be heated above 90 °C, and only small quantities of diamine should be processed at a time. Similar precautions are advisable with other halogenated aromatic diamines.

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Registry No. 1 (copolymer), 25280-01-7; 1 (SRU), 28157-08-6; 2 (copolymer), 61594-45-4; 2 (SRU), 61674-11-1; 3 (copolymer), 61594-46-5; 3 (SRU), 61674-05-3; 4 (copolymer), 106781-69-5; 4 (SRU), 89962-77-6; 6 (copolymer), 61594-60-3; 6 (SRU), 61674-06-4; 7 (copolymer), 61594-59-0; 7 (SRU), 61674-08-6; 8 (copolymer), 61594-56-7; 8 (SRU), 61674-15-5; 10 (copolymer), 61594-47-6; 10 (SRU), 61674-19-9; 11 (copolymer), 106781-70-8; 11 (SRU), 106780-08-9; 14 (copolymer), 61594-61-4; 14 (SRU), 61674-21-3; 15 (copolymer), 61594-62-5; 15 (SRU), 61674-10-0; 18 (copolymer), 61594-89-6; 18 (SRU), 61674-23-5; 19 (copolymer), 61594-65-8; 19 (SRU), 61601-76-1; 20 (copolymer), 61594-67-0; $C_6H_5NH_2$, 62-53-3; *N,N'*-[2,6-naphthylenebis(methylidyne)]bis(aniline), 61594-55-6; 2,6-naphthalenedicarbonyl chloride, 2351-36-2; (terephthalaldehyde)(2-methyl-1,4-phenylenediamine dihydrochloride) (copolymer), 106781-72-0; (2-methyl-1,4-phenylenediamine)(1,4-diacetylbenzene) (copolymer), 61594-93-2; (1,4-diacetylbenzene)(2-methyl-1,4-phenylenediamine) (SRU), 61674-13-3; (2-methyl-1,4-phenylenediamine)(*p*-phenylenediamine)(terephthalaldehyde) (copolymer), 61594-54-5; (hexamethylenediamine)(terephthalaldehyde) (copolymer), 29036-87-1; (hexamethylenediamine)(terephthalaldehyde) (SRU), 31987-41-4; (4,4'-biphenyldicarboxaldehyde)(2-methyl-1,4-phenylenediamine)(terephthalaldehyde) (copolymer), 61594-68-1; (2-methyl-1,4-phenylenediamine)(*N,N'*-1,4-xylylidenebis(aniline)) (copolymer), 106781-74-2.

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