

A Polyamide from Bisacid A2 and *p*-Phenylenediamine: Synthesis, Properties, and Fiber Formation

RUDOLPH S. LENK,* JAMES L. WHITE, and JOHN F. FELLERS,
Department of Chemical and Metallurgical Engineering, The University of Tennessee, Knoxville, Tennessee 37916

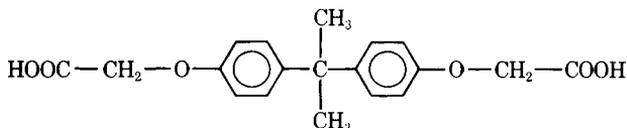
Synopsis

The synthesis, characterization, and processing of a new polyamide which is formed from bisacid A2 and *p*-phenylenediamine are reported. The polymer is synthesized using low-temperature solution polycondensation methods. The conditions for producing high molecular weight polymer are described. The polymer produced is amorphous, but lower molecular weight varieties may be crystallized with a formic acid treatment. Differential scanning calorimetry indicates a transition in the range of 180–190°C. Mechanical properties of films are measured. Fibers have been produced by both melt and wet spinning.

INTRODUCTION

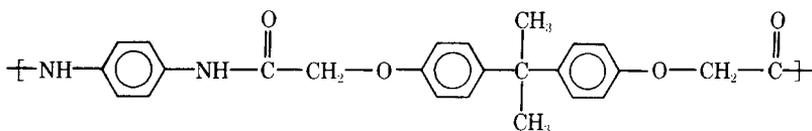
Aliphatic polyamides have been well known and characterized since the 1930's and 1940's when nylon 66 and nylon 6 were developed. During the 1960's, there was rapid development of wholly aromatic polyamides and related polycondensates, notably in industrial laboratories, which led to the commercial development of Nomex and Kevlar aromatic polyamides by du Pont and of similar materials on a pilot plant scale by Monsanto.¹⁻⁵ The *p*-linked aromatic polyamides were of special interest because of their high modulus and strength.

In 1971, Lenk⁶ reported the preparation of essentially pure bisacid A2:



and made kilogram quantities of it. This monomer was at first applied by Lenk⁷ to prepare crosslinkable polyesters. More recently, aliphatic polyamides such as the polymer with hexamethylenediamine have been prepared.^{8,9} In this paper, we present a study of the preparation and evaluation of the polymer formed from bisacid A2 and *p*-phenylenediamine having the repeat unit

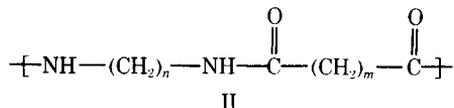
* Permanent address: Polytechnic of the South Bank, London SE1 0AA, England.



I

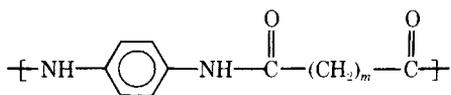
We choose to call this polymer *bisparamid A2*.

We need to discuss in more detail the character of the polyamide with which we are dealing. Generally, polyamides of form



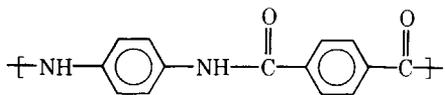
II

are considered *wholly aliphatic*. Black and Preston¹ classify polyamides of the type made by Shashoua and Earecksen¹⁰



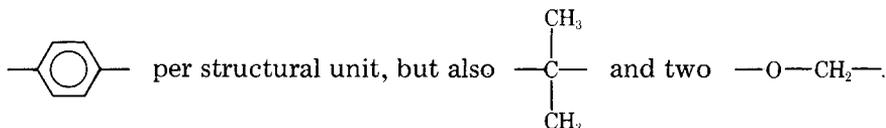
III

as being *aliphatic-aromatic*. They classify polyamides of form



IV

as being *wholly aromatic*. As one can see, our polyamide I is intermediate in aromatic character between III and IV. It has three



It is similar to Black and Preston's¹ wholly aromatic polyamide #47. It seems reasonable to consider the structure I as being *largely aromatic*.

The methods of synthesis of such polyamides require attention. It was not until 1959 that Shashoua and Earecksen¹⁰ reported the formation of high molecular weight polyterephthalamides with aliphatic diamines using acid chlorides and interfacial polymerization.¹¹ Five years later, Morgan and Kwolek¹² reported a detailed study of the formation of a piperazine polyterephthalamide made with a homogeneous low-temperature solution polycondensation. Morgan¹³ shortly thereafter published a monograph on these two techniques. The low-temperature solution polymerization method is described in the patent literature as the method of synthesis for fully aromatic polyamides.¹⁴⁻¹⁶

This paper continues earlier studies in our laboratories on wholly and largely aromatic polyamides and their copolymers. Earlier papers have dealt with the low-temperature solution polymerization of wholly aromatic polyamides and the formation of block copolymers¹⁷ and wet spinning.¹⁸

SYNTHESIS

Preparation and Purification of Reactants

Bisacid A2 reacts readily with thionyl chloride (SOCl_2). The acid (250 to 300 g) is gradually solubilized as it converts to the acid chloride by gentle warming and eventual refluxing in an excess of thionyl chloride (500 to 600 ml). Reagent-grade thionyl chloride is suitable. The bisacid A2 chloride produced is purified as follows. Excess SOCl_2 is recovered by distillation and may be used again. Vacuum is applied, and the temperature of the mixture is raised to 165°C . Three 10-ml portions of dry toluene are added and distilled off in turn, finishing with an internal temperature (under vacuum) of 180° , 183° , and 192°C , respectively. The first portion is slightly yellow after distillation and obviously contains some residual SOCl_2 ; the second may still be faintly yellow; but the third should be water white. After cooling, the mixture is extracted with 2×200 ml *n*-hexane (a nonsolvent for the acid chloride) to remove any traces of toluene and the bottom layer of acid chloride is transferred to the distillation flask, 200 ml CCl_4 is added, and the latter is distilled off, finishing with vacuum and an internal temperature of 198°C . In this way, all the solvents are removed. At no time should the temperature be allowed to exceed 200°C .

This cumbersome purification technique is made necessary by the fact that bisacid A2 is a viscous, brown oil which neither crystallizes nor vacuum distills without decomposition. Excessive heating causes decomposition accompanied by foaming and charring. The oil sets to a glass at low temperature.

The *p*-phenylenediamine (reagent grade) was purified by sublimation in vacuo and stored under dry N_2 in a stock jar kept in a desiccator over solid KOH.

The solvents used were generally a 2:1 v/v mixture of dimethylacetamide (DMA) and hexamethylphosphoramide (HMPA) or N-methylpyrrolidone (NMP). DMA was received at a stated purity of 99+ (Aldrich Chemical Company). It was first treated with a few crystals of terephthaloyl or isophthaloyl chloride to decompose any dimethylformamide (assumed to be the principal impurity), filtered through glass wool, treated with barium oxide, and filtered again to remove excess BaO and Ba salts. This was followed by three successive redistillations, collecting the fraction boiling between 163° and 166°C . Reagent-grade HMPA was redistilled twice, collecting the fraction boiling between 235° and 240°C . N-Methylpyrrolidone (received 98% pure) was redistilled three times, collecting the fraction boiling between 201° and 204°C . Triethylamine was tried in one experiment. Like all the other solvents, it was stored in a dark glass bottle under dry N_2 and over molecular sieves.

Polymerization Method

The method was essentially analogous to that for the low-temperature solution technique for fully aromatic polyamides of isophthalic and terephthalic acids, but with minor modifications which were made necessary by the fact that bisacid A2 chloride is a viscous oil. The most convenient procedure was as follows.

(i) An aliquot of pure bisacid A2 chloride was accurately weighed into a dry 100-ml round-bottomed flask fitted with a small rubber-capped side arm and a ground-glass stopper, the flask having been thoroughly dried and purged with

TABLE I
Inherent Viscosities of Batches of Polymer Made Under Conditions Approaching or
Equalling Effective Stoichiometry^a

Batch no.	Theor. diamine deficiency, %	Theor. moles bischloride A2 × 10 ³	Moles diamine × 10 ³	Concn. during initial reaction, %	Final concn., %	Temp. at addition, °C	η_{inh}
59	-9.1 (excess)	85.00	92.80	24.6	24.3	-10	0.35
55	2	53.95	52.87	21.0	19.2	-10	0.70
66	4	47.50	45.60	18.2	15.0	-25	0.76
60	5	55.43	52.65	14.5	12.2	-30	0.83
65	6	43.05	40.47	18.7	13.9	-25	1.62
72	6½ ^b	57.72	57.72	20.2	10.3	-45	2.03
64	7	53.46	49.71	19.8	14.8	-25	1.40
61	8	69.21	63.67	20.6	13.4	-27	1.23
67	9	45.35	41.27	17.1	13.4	-25	0.93
62	11	48.38	43.06	16.5	15.2	-25	0.44
74	6½ ^b	14.81	13.85	16.1	12.5	-30	1.08
75	6½ ^b	16.05	15.01	15.9	12.2	-30	0.94
76	6½ ^b	14.14	13.22	16.3	11.5	-40	1.21
77	7	14.56	13.61	20.1	13.4	-30	1.03
79	6½ ^b	14.42	13.48	18.6	12.6	-30	1.51

^a Solvent: #55 to #62: DMA/HMPA, 2:1 by volume; others, NMP.

^b Effective isostochiometry = 6½% theoretical diamine deficiency.

dry N₂ beforehand. A small amount of CCl₄ (dry toluene is an acceptable alternative) is added to reduce the viscosity and make it readily pourable through the side arm later on.

(ii) The precise mole equivalent of *p*-phenylenediamine which corresponds to the aliquot of acid chloride is calculated and weighed into a dry N₂-purged round-bottomed flask of 250 to 1000 ml capacity (depending on batch size) which is fitted with a stirrer, N₂ inlet, and drying tube outlet. The diamine is dissolved in a 2:1 (v/v) mixture of DMA and HMPA with slight warming to facilitate complete dissolution. The amount of total amide solvents is calculated to give a solution, eventually, of between 16% and 22% polyamide.

(iii) After cooling the solution of diamine in a bath of Dry Ice and isopropanol to some subzero temperature at which it becomes cloudy due to crystallization of diamine, the acid chloride solution is quickly added with fast stirring, transferring the rinsings with small amounts of CCl₄ (or toluene, as the case may be) quantitatively to the reaction flask. The polyamide forms rapidly and gives a viscous solution which may become highly viscoelastic—almost rubbery. Generally, the bath temperature is taken down to -40°C which takes care of the substantial exotherm, whereupon it is allowed to regain room temperature naturally. (The highly exothermic nature of the polycondensation reaction is illustrated by the fact that 15.820 g (0.0400 theoretical moles) of bisacid A2 chloride, dissolved in 6 ml CCl₄ and subsequently rinsed in with an additional 3 ml CCl₄ and 4.330 g (0.0400 mole) *p*-phenylenediamine in 22 ml HMPA and 44 ml DMA, gave a peak temperature of 61° within 3 min of adding the reactant solutions together at 26°C with stirring.)

(iv) The polymer solution may be diluted with DMA to adjust the concen-

TABLE II
Inherent Viscosities of Batches of Bisparamid A2 Made Under Conditions
of Theoretical Stiochiometry^a

Batch no.	Conditions ($\eta_{inh} \geq 0.50$)				
	Bisacid A2 chloride	Moles reactants $\times 10^2$	Temp. at addition, °C	g Reactants + ml solvents	η_{inh}
4		2.50	<-20	63	0.67
5		5.00	<-20	172	0.73
6		5.00	<-20	225	0.50
7	in situ production	5.00	<-20	100	0.78
8	from aliquots of	2.50	<-20	46	0.65
9	bisacid A2; dis-	2.50	<-20	43	0.63
11	solved in DMA	5.00	<-20	61	0.54
12		2.00	<-20	39	0.54
16		2.00	<-20	49	0.60
17		2.00	<-20	48	0.66
27		1.87	<-20	44	0.93
	Ex stock dissolved in CCl ₄				
28		2.81	<-20	64	0.65
30		2.15	<-20	48½	0.67
32		2.42	<-20	56	0.55
34		3.33	-10	73	0.63
35	Ex stock dissolved	3.26	+14	70	0.75
36	in CCl ₄	4.30	+20	100	0.72
37		3.89	+20	90	0.68
38		4.44	+25½	103	0.63
39		4.00	+26	95	0.70
44		8.40	-5	171	0.60
45		14.30	-8	268	0.58
46		14.77	-40	262	0.71
47		16.16	-25	289	0.60

^a Solvent: DMA/HMPA = 1/2 by vol., except for 47, where it was 4/3 by vol.

tration and is precipitated as pearls by slowly dripping it from a dropping funnel into a large volume of water which is agitated by a magnetic stirrer. It is left to coagulate fully and diffuse out solvents and salts for a minimum of 24 hr, preferably with a change of water, resuspended in methanol with agitation for at least a further 24 hr, filtered, and dried in vacuo up to 60°C for at least 24 hr.

Investigation of Polymerization Variables

The influence of polymerization variables on the molecular weight was investigated. Inherent viscosities η_{inh} were used to estimate molecular weights. The η_{inh} is determined at 25°C, the solvent being a 5% solution of LiCl in DMA and the solution having a concentration of 0.5% with respect to the polymer. A check of the intrinsic viscosity proved this to be close to η_{inh} . Numerous batches were made in which the importance (or otherwise) of a number of variables was studied. These were summarized in Tables I-III.

The polymerization variables studied will now be described.

TABLE III
Inherent Viscosities of Batches of Bisparamid A2 Made Under Conditions
of Theoretical Stoichiometry^a

Batch no.	Conditions ($\eta_{inh} \leq 0.5$)				
	Bisacid A2 chloride	Moles reactants $\times 10^2$	Temp. at addition, °C	g Reactants + ml solvents	η_{inh}
2		2.50	-20	53	0.29
10	in situ production	5.00	<-20	61	0.31
14	from aliquots of	2.00	<-20	39	0.27
15	bisacid A2 dis-	2.00	<-20	49	0.47
25	solved in DMA	2.00	<-20	100	0.40
26		2.58	<-20	62½	0.48
31	Ex stock dissolved	3.70	-25	64	0.43
48	in CCl ₄	7.97	-40	169	0.47

^a Solvent: DMA/HMPA = 1/2 by vol., except for 47, where it was 4/3 by vol.

(i) Variation of stoichiometry of reactants was studied. This proved to be the crucial variable. A full investigation of effective stoichiometry involved the preparation of polyamides with increasing weight fractions of acid chloride (increasing theoretical deficiency of diamine) and the determination of the inherent viscosities of the products. The result is shown in a plot of reactant proportions versus η_{inh} (Fig. 1). It is seen that "effective stoichiometry" is attained at an apparent amine deficiency of 6½%, from which an "effective molecular weight" of bisacid A2 chloride was calculated and found to be 407.5 compared to the theoretical value of 381. Polymer made with reactants in "effectively stoichiometric" ratio produced a pseudo-gel within 2-5 min at con-

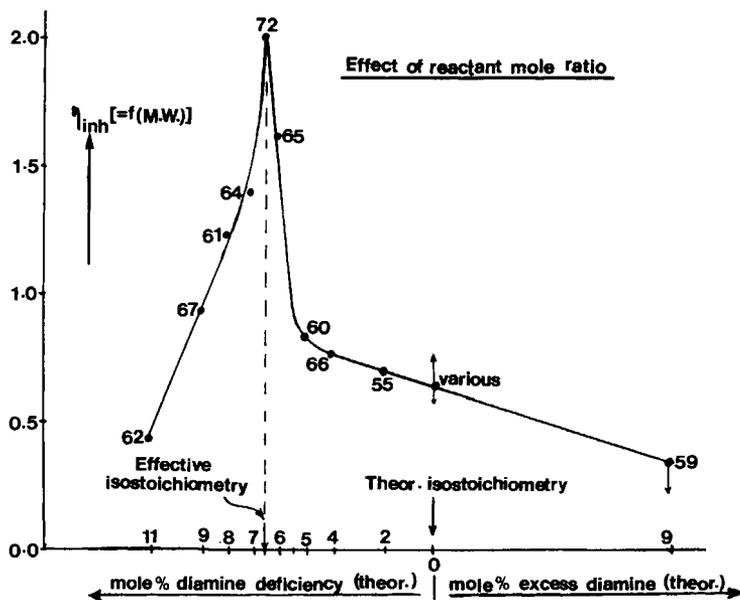


Fig. 1. Inherent viscosity as a function of reactant proportions.

centrations in the 15–20% range. The variables investigated were as follows:

(ii) The method of SOCl_2 pretreatment before use in converting bisacid A2 to the acid chloride was studied. This was found to have no effect on the quality of the reaction product, SOCl_2 of good reagent grade, recovered SOCl_2 , or SOCl_2 purified by other methods being equally suitable.

(iii) Reactant concentration did not appear to be highly critical so long as the concentration of the resulting resin solution was between 15% and 20%.

(iv) Reaction temperature at the point of addition and the subsequent thermal schedule were studied. Again, this was not found to be highly critical, so long as the exotherm was dissipated.

(v) The order of addition of reagents was considered. Since the diamine solution constitutes the bulk of the liquid, it is logical to add the acid chloride to it, rather than vice versa. The latter is conveniently introduced after dissolving it in about 20% v/w of CCl_4 or toluene in order to reduce the viscosity. Quantitative transfer is ensured by addition of three successive CCl_4 rinsings.

(vi) Rate of addition. Fast addition is recommended with rapid stirring. Dropwise addition may result in polymer of low molecular weight.

(vii) Solvent system. NMP is the preferred solvent, but 2:1 mixtures (DMA/HMPA) are equally good.

(viii) Solvent for the acid chloride. DMA can be used, but CCl_4 (or toluene) are preferred since these may be regarded as truly inert and unlikely to react with the solute.

Polymer Molecular Weights

Molecular weights of the polymer may be calculated from the intrinsic or inherent viscosities of the polymers using an appropriate Mark-Houwink equation between $[\eta]$ and molecular weight, i.e.,

$$[\eta] = KM^a \quad (1)$$

Values of K and a for this polymer are not available. However, we would expect these to be of the same order as those obtained by Burke¹⁹ on an amide hydrazide and an aromatic polyamide. Burke gives a K value of 6.15×10^{-5} and an a value of 1.06 for the p -linked amide hydrazide (Monsanto X500) and values of 4.5×10^{-5} and 0.77 for the polyamide. From eq. (1), Burke's amide hydrazide polymer with η_{inh} of 0.5 has a molecular weight of 5000; that of 1.0 has a molecular weight of ~ 9500 ; and that of 2.0 has a molecular weight of 18,500. For the polyamide, an η_{inh} of 0.5 corresponds to a molecular weight of 9000; an η_{inh} of 1.0, to 22,000; and an η_{inh} of 2.0, to 54,500.

The polymer chain is more flexible than Burke's amide hydrazide, and one would expect the $[\eta]$ to correspond to higher molecular weights. These might not be as high, though, as the values for his aromatic polyamide. We intend further investigation leading to correct values of K and a appropriate to this polymer system.

CHARACTERIZATION OF BULK POLYMER

General Appearance

The initial polymer precipitates were an off-white color. The films prepared by precipitation from dimethylacetamide solutions are clear yellow to amber

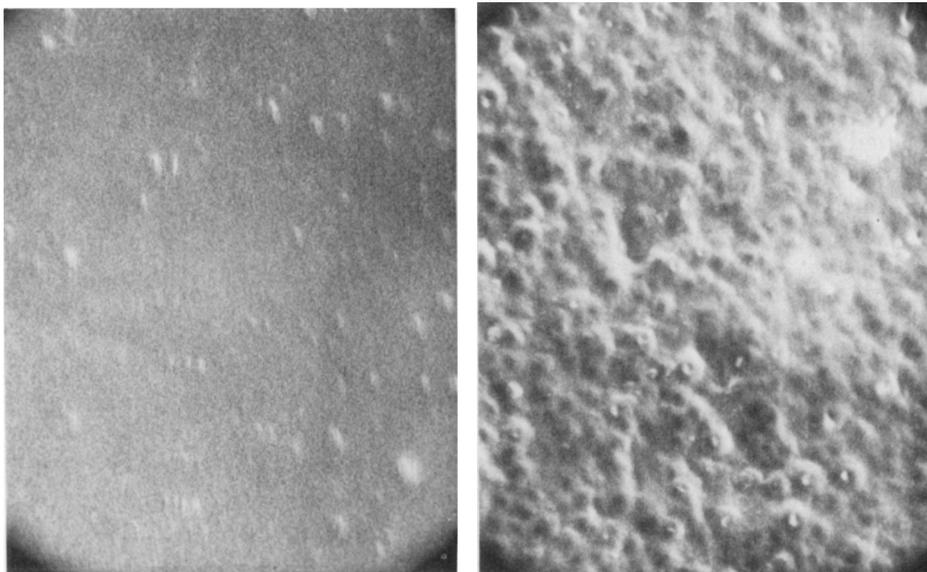


Fig. 2. Scanning electron microscopy (SEM) photomicrographs of effect of formic acid on film, $\times 5000$.

in color. It becomes white and opaque on exposure to formic acid (see Fig. 2).

Wide-Angle X-Ray Scattering (WAXS)

A 10% to 15% solution of polymer in dimethylacetamide (DMA) was cast onto plate glass and dried, giving a clear film which could be readily detached on immersion in water. Some of the film was treated with formic acid (which instantaneously caused the film to become opaque) followed by washing and drying (see Fig. 2). WAXS measurements were then carried out using a Philips Norelco x-ray generator and a pinhole camera. All untreated film was found to be amorphous, irrespective of the η_{inh} of the polymer. Formic acid-treated film of low η_{inh} , however, proved to be crystalline (Fig. 3), while similarly treated film cast from a polymer of high η_{inh} was not. Similar observations have been made by Sweeny¹⁵ for poly(*m*-phenyleneisophthalamide).

From the WAXS pattern of low- η_{inh} formic acid-treated film, it was possible to calculate the d spacings using Bragg's law to give the results summarized in Table IV. We also list the reflections of poly(*p*-phenyleneterephthalamide) and its interpretation in terms of indexed reflections from a monoclinic unit cell by Northolt.²⁰

Differential Scanning Calorimetry (DSC)

A Perkin-Elmer differential scanning calorimeter was used to study these polymers in the temperature range of 60° to 400°C at a scan rate of 10°/min.

The most notable feature was the consistent appearance of an exothermic transition between 180° and 190°C for both high- and low-molecular weight polymers. It is worth noting that the same observation also applied to polymers

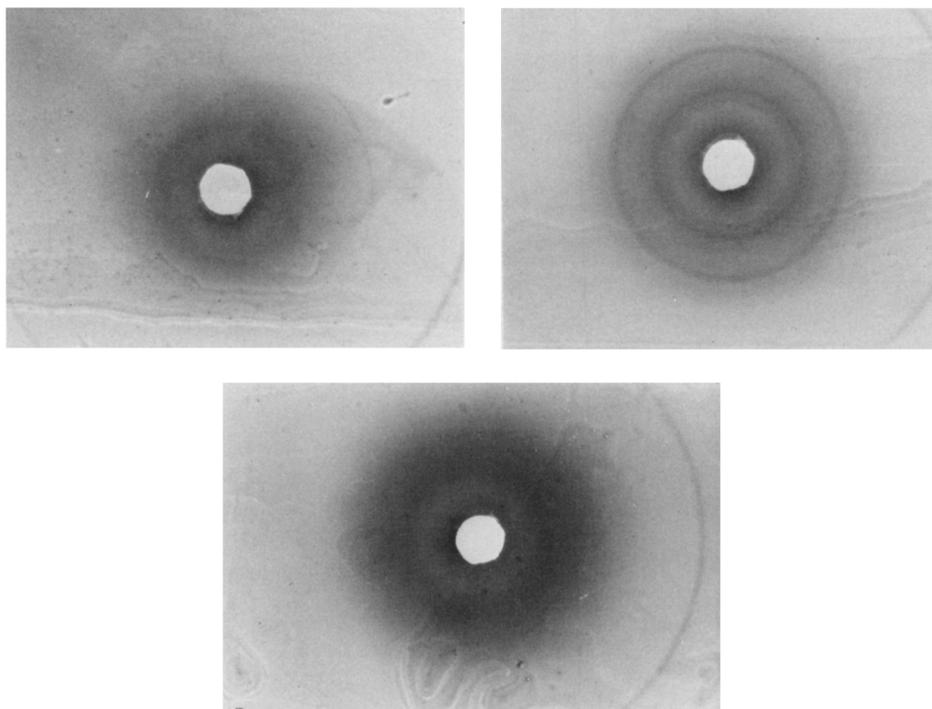


Fig. 3. WAXS patterns of formic acid-treated polymer.

from analogous aromatic diamines, such as *m*-phenylenediamine and ring-substituted phenylenediamines, which will be the subject of a subsequent paper.

It is more important to note that the small peak at 180–190°C could never be obtained when formic acid-treated polymer film was run. The temperature traverse across the 180–190°C region produces a transition in untreated polymer, but not in formic acid-treated polymers (see Fig. 4). At higher temperatures (320–380°C), the polymers show an endothermic Δc_p shift and degrade.

TABLE IV
WAXS of Formic Acid-Treated Film of Low MW and of
Poly(*p*-phenyleneterephthalamide)

Line no.	$l/2$	Intensity	d spacings, Å	d spacings, Å, and (in parentheses) crystal planes of poly(<i>p</i> -phenyleneterephthalamide)
1	0.971	medium	6.33	6.424 (002)
2	1.122	strong	5.53	4.715 (011)
3	1.301	weak	4.81	4.134 (111)
4	1.562	weak	4.07	3.864 (200)
5	1.741	strong	3.70	3.239 (013)
6	1.956	weak	3.35	3.084 (211)
7	2.100	weak	3.15	— —

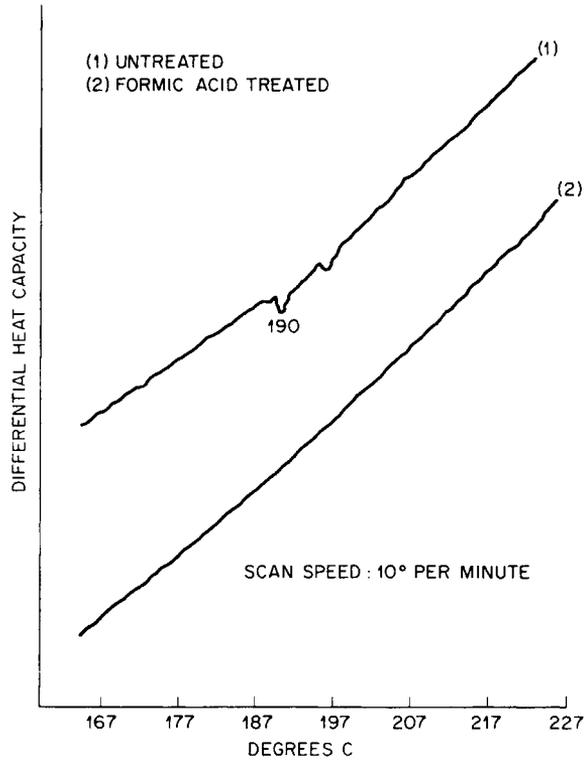


Fig. 4. DSC traces of untreated film and formic acid-treated film in the transition region.

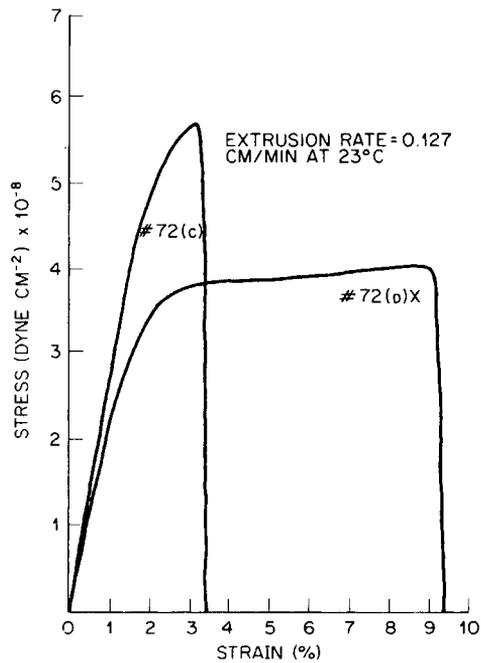


Fig. 5. Typical stress-strain curves of film in tension; #72(C), as cast; #72(D)X, formic acid treated.

Mechanical Properties of Film

The mechanical properties of the film cast from DMA solutions were measured in an Instron tensile testing machine. Samples of approximately initial length 6 to 7 cm and width 0.8 cm were used, and a cross-head speed of 0.127 cm/min was applied. A typical stress-strain curve is shown in Figure 5. Strains at break of 3% were obtained. Tensile strengths of $(5-6) \times 10^8$ dynes/cm² were obtained.

Cast films which had been treated with formic acid were also tested. The formic acid treatment increases elongation to break about 8%, especially in the high molecular weight material. The tensile strength is, though, generally reduced about 30%. It would seem to "toughen" the polymer.

Discussion

We form the view that the polymer is an amorphous glassy material at room temperature. Low to moderate molecular weight polymers may be crystallized in formic acid but not high molecular weight polymers. A DSC transition is observed in films not treated with acid. Treatment with acid removes the transition and toughens the polymers. The structural meaning of this is not clear. However, recent infrared spectral measurements²¹ show that formic acid treatment permanently changes the hydrogen bonding of these polymers.

FABRICATION

Melt Processing

Visual observations and Instron capillary rheometry showed that the polymer softens, becomes leathery, and attains a quasi-melt condition in the temperature range of 220–250°C. Extrusion would seem possible at 230°C and above. Polymer granules were compressed between the cold platens of a molding press in order to squeeze out as much air as possible and were then kept in a vacuum oven at 60°C for three days in order to ensure removal of any traces of moisture that may have been picked up from the atmosphere. Finally, the material was stored in polyethylene bags over dry nitrogen in a desiccator containing anhydrous CaSO₄ prior to charging into the extruder barrel.

An Instron capillary rheometer was used to extrude and melt spin the fibers. The melt was extruded through a cylindrical die with diameter of 0.135 cm and length/diameter (L/D) ratio of 9.7. Generally the extrudate swell was large, achieving values up to twice the die diameter.

The pressure drops Δp were used to estimate viscosities using the expression²²

$$\eta = \frac{D\Delta p/4L}{\frac{32Q}{\pi D^3} \left(\frac{3n' + 1}{4n'} \right)} \quad (2a)$$

with

$$n' = \frac{d \log D\Delta p/4L}{d \log 32Q/\pi D^3} \quad (2b)$$

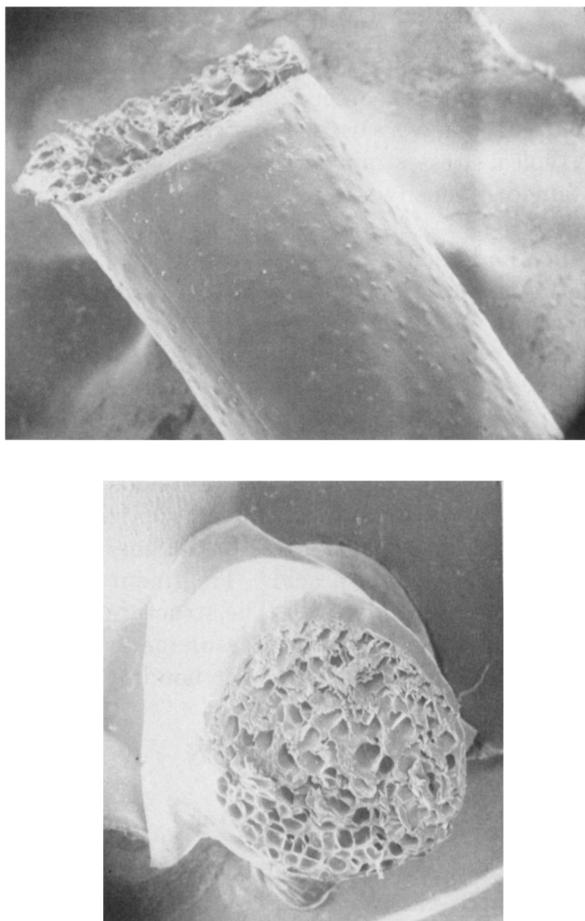


Fig. 6. Scanning electron (SEM) photomicrograph of extrudate (Batch 74/75).

and found to be of order 10,000 to 80,000 poises. The viscosity decreases as the shear rate increases and generally tends to a Newtonian constant viscosity region at low shear rates. These results are, of course, only approximate because of the neglect of entrance pressure drops.

The η_{inh} of the resulting extrudates was measured. Considerable degradation was found to occur during extrusion. Thus, polymers with η_{inh} of 0.65 and 1.02 degraded to values of 0.36 and 0.68, respectively. In an extreme case, a polymer (η_{inh} of 2.0) gave an extrudate η_{inh} of 0.50. It is clear that the realization of satisfactory "melt" extrusion of the polymer and related polyamides, as indeed of conventional polyamides, depends upon appropriate stabilization, which has not so far been attained for this polymer.

Some of the polymer studied in this extrusion experiment was melt spun into fiber and was taken up on a motor-driven rotating roll at a distance of about 10 cm from the spinneret. The apparatus is similar to that described by White, Dharod, and Clark,²³ only the spinline length was shorter. The take-up speed was between 150 and 200 meters per minute. The melt-spinning process yielded a clear amber-colored monofilament of a diameter of 0.030 ± 0.015 cm.

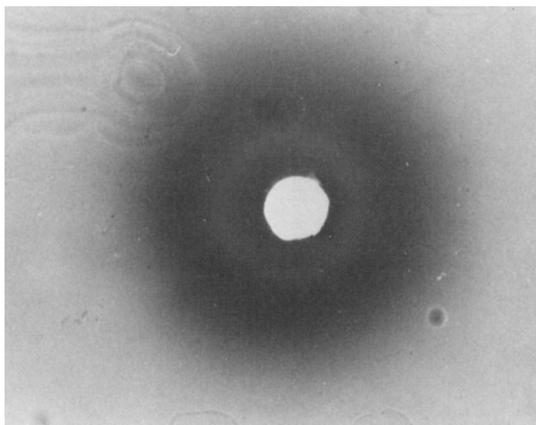


Fig. 7. WAXS pattern of melt-spun fiber.

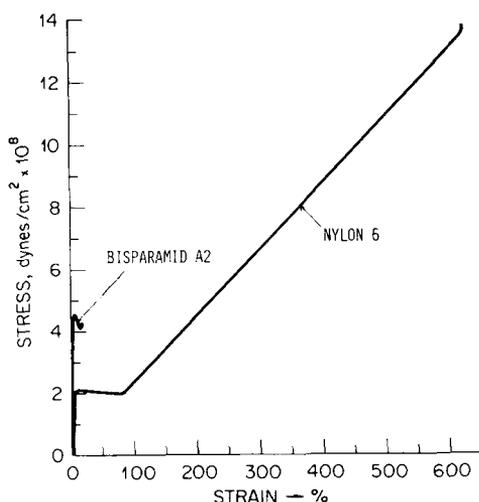


Fig. 8. Stress-strain curve for typical "melt" spun fiber.

A scanning electron microscope (SEM) photomicrograph of the melt-spun fiber is shown in Figure 6. (For a discussion of the apparatus in our laboratories and techniques, see Sze, Spruiell, and White¹⁸ and Hancock, Spruiell, and White.²⁴) The fiber showed a thin outer skin without holes and an internal columnar cellular structure of great uniformity throughout the cross section. The cells are long and parallel to the filament axis. Fibrillation at the frayed ends of a break is seen. The cellular voids are probably the result of gaseous decomposition products, especially since the value of η_{inh} after extrusion was found to be substantially lower than before extrusion.

WAXS measurements show the melt-spun fiber to be amorphous (see Fig. 7).

The mechanical properties of drawn-down melt-spun polymer were determined on an Instron tensile testing machine. A typical stress-strain curve is shown in Figure 8 where it is compared to a nylon 6 fiber melt spun and charac-

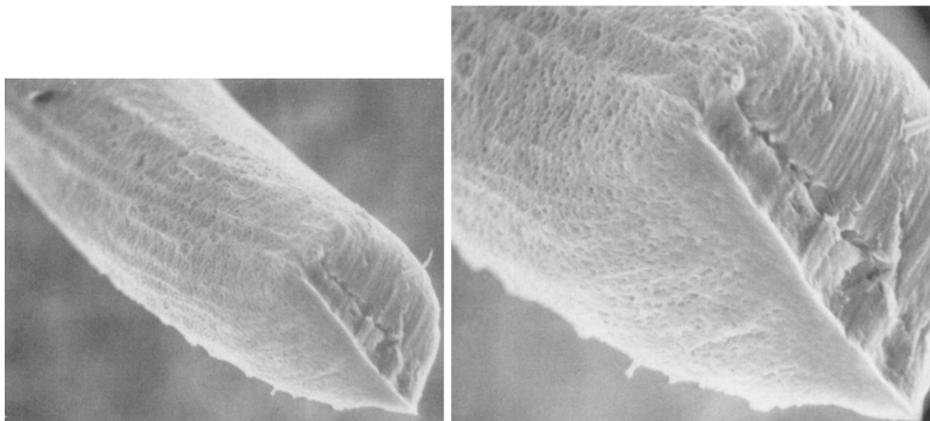


Fig. 9. SEM photomicrograph of fiber "pulled" from dimethylacetamide solution.

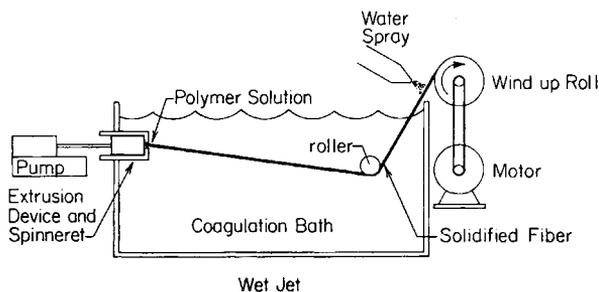


Fig. 10. Wet-spinning apparatus.

terized by Bankar, Spruiell, and White.²⁵ The filament obtained has a substantially higher modulus and tensile strength. This comparison cannot serve as a basis for quantitative evaluation because of degradation during processing and the structure of the extrudate as seen in the SEM and optical micrographs. If the cross section were not porous, the modulus and yield value would be substantially higher and the elongation to break considerably greater. The results are thus quite promising.

Solutions and Pulling Fibers from Solutions

Solutions of the polymer in dimethylacetamide (DMA) were prepared. The solutions did not seem to be anisotropic and liquid crystalline in the sense described by Kwolek¹⁶ for other aromatic polyamides (see also the discussion of Hancock, Spruiell, and White¹⁸ and Ciferri²⁶).

The solutions of the polymer appear to be highly viscoelastic. If a solution of the polymer in DMA is heated on a glass plate during the preparation of cast film, it is possible to draw highly elastic and exceedingly fine thread from the concentrated polymer solution. Evaporation and perhaps atmospheric moisture quickly causes the polymer to precipitate and the thread to turn white at the surface. In this condition, it can be pulled to give even greater elongation before

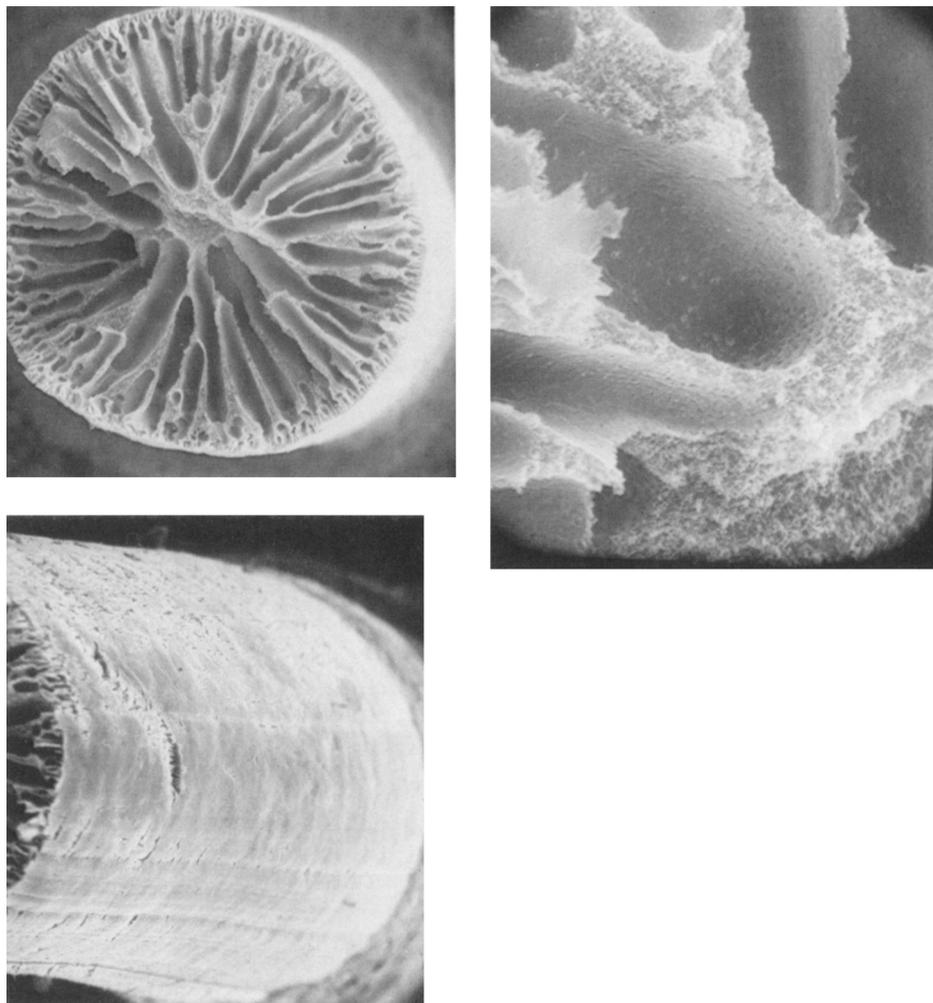


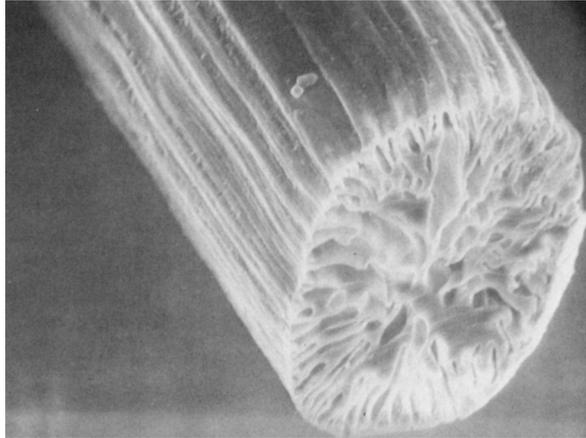
Fig. 11. SEM photomicrograph of wet-spun fiber.

finally dropping it into water to wash out the solvent. This suggests that solution spinning should be a good method for making these fibers.

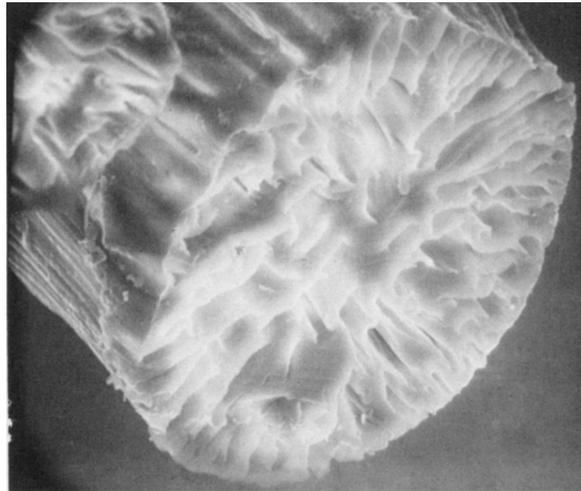
Scanning electron microscopy photomicrographs of these fibers are shown in Figure 9.

Wet Spinning

The polymer was wet spun from the DMA solution using the equipment and technology developed previously in our laboratories by Hancock, Spruiell, and White¹⁸ for other polyamide solutions. This is shown in Figure 10. The wet spinning of fiber from these DMA spinning dopes proved to be quite easy. A coagulation bath of water at room temperature was used. The coagulated spun fiber was strong enough to be reeled up without break, provided that η_{inh} was close to and preferable above unity.



(a)



(b)

Fig. 12. SEM photomicrograph of wet-spun and drawn fiber at 200°C: (a) 500X; (b) 1000X.

Figure 10 shows scanning electron micrographs of fibers obtained by wet spinning. Looking at Figure 11, it is seen that while the skin appears to be quite smooth and uniform (apart from longitudinal extrusion marks caused by the die) at low magnification (center), it is clearly porous as seen at higher magnification (right top, right bottom). In section a, a "grapefruit" pattern is revealed made up of septa and voids (top left). However, the voids are not continuous channels parallel to the fiber axis but merely elongated cavities of finite length.

WAXS measurements show the wet-spun fibers to be amorphous.

Hot Drawing Wet-Spun Fibers

Hot drawing of the polymer was readily accomplished at 200°C by means of a manual tensile stretching device in a metallurgical oven. The fiber was drawn

to twice its original length. It was found that the tensile strength and modulus were greatly increased.

Scanning electron micrography (Fig. 12) shows the surface and cross section topography of the hot-drawn fibers. Figure 11 shows that, apart from a great contraction in diameter which is obviously the result of the drawing process, the structure itself is only slightly affected. There is certainly no sign of fusion; the surface, having contracted onto the core, has become much more ribbed and is perhaps fibrillated as suggested by earlier studies in our laboratories on other fibers.²⁵

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