

"Bishydrazid A2": A New Semiaromatic Film and Fiber-Forming Polymer Based on Bisacid A2

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Synopsis

We report the preparation of the dihydrazide of bisacid A2 (bisdihydrazide A2²). Its composition and structure have been verified by elemental analysis and by means of infrared and NMR spectra. This material was then converted into a polyhydrazide ("bishydrazid A2²") by low-temperature solution polymerization with the acid chloride of bisacid A2 ("bischloride A2²") in an HCl-accepting solvent. The polymer was converted to fiber by wet spinning the dope obtained during the polycondensation reaction without prior neutralization or dilution. Film was cast from a solution of the precipitated and washed polymer which had an inherent viscosity of about 0.8; mechanical tests on the film—both before and after treatment with formic acid—were carried out. Differential scanning calorimetry showed an α/β transition comparable to that shown by bisacid A2 polyaramides and described in preceding papers.^{1,2} Wide-angle x-ray scattering showed that the polymer is amorphous. Scanning electron micrographs revealed the physical structure of wet-spun fiber and the probable mechanism of fiber formation by dope extrusion into a water bath.

INTRODUCTION

Earlier communications in this series^{1,2} have reported the preparation and initial evaluation of polyamides from bisacid A2 and *p*- and *m*-phenylenediamines ("bisparamid A2²" and "bismetamid A2," respectively). These polymers were of interest because they combined the rigidity of benzene rings with the flexibility of oxymethylene groups in the main chain. In this paper, the synthesis and initial evaluation of "bishydrazid A2²" are reported. This polymer is prepared by the same low-temperature solution technique, using isostoichiometric quantities of the diacid chloride of bisacid A2 (bischloride A2) and the dihydrazide of bisacid A2 (bisdihydrazide A2).

Hydrazides react with acid chlorides to give compounds with —CO—NH—NH—CO— linkage. The same structure can be generated by reaction of hydrazine directly with acid chloride. Polymeric compounds with such linkages have been investigated in the past ten years. Randall, Morrison, and Preston³ have characterized the oligomers formed by reacting terephthaloyl chloride with excess *p*-aminobenzhydrazide, and Culbertson and Murphy⁴ have described the synthesis of aromatic amide/hydrazide polymers. Frazer and Wallenberger⁵ reported preparation of aromatic polyhydrazide fibers and their conversion to oxadiazole fibers. Holsten and Lilyquist⁶ reported the preparation of a polymer

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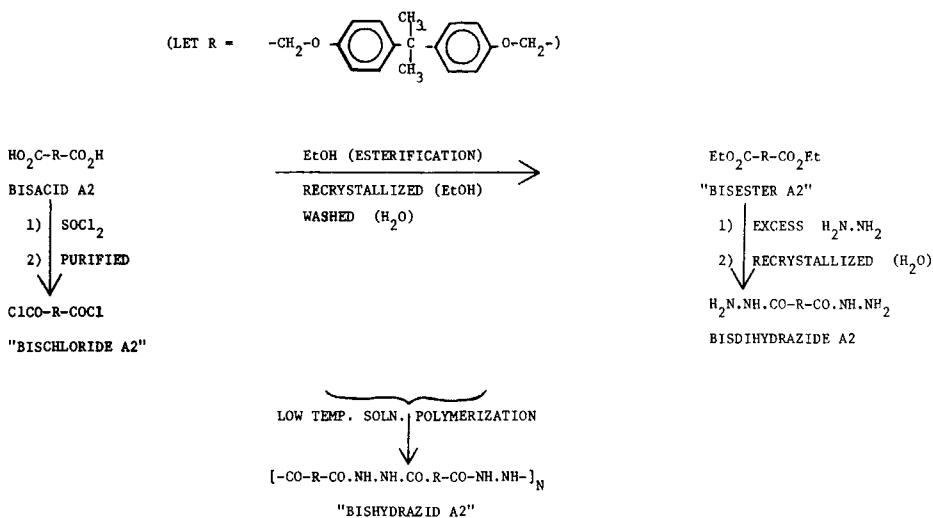


Fig. 1. Flow chart for the preparation of the homopolyhydrazide of bisacid A2 ("bishydrazid A2").

from the acid chloride and the dihydrazide of terephthalic acid and the modification of the polymer by cyclocondensation so that it contained aromatic triazole units. Morrison, Preston, Randall, and Black⁷ discussed the chemical order in amide/hydrazide polymers. A sizeable patent literature covers polyhydrazides.^{8,9,10} The field has been reviewed by Preston, Black, and Hofferbert.¹¹ Indeed, an entire symposium was devoted to polyhydrazides and poly(amide/hydrazides) and their fibers.¹²

The present work deals with a unique structure which is not derived from phenylenediamines or aromatic amide-hydrazides. This new polymer derives its aromatic chain elements from 2,2-diphenylpropane moieties introduced as bisacid A2 derivatives; elements of flexibility, specifically oxymethylene units, are simultaneously introduced. Thus, this new polymer contains a peculiar aromatic/aliphatic structure, promising an interesting combination of properties.

EXPERIMENTAL RESULTS AND OBSERVATIONS

As shown in Figure 1, the diacid chloride plus dihydrazide reaction was utilized for polyhydrazide formation. This route was chosen over the diacid chloride plus hydrazine alternative route for several reasons, including lower heat of polymerization, less evolved HCl, and more nearly equal weights needed for stoichiometric reaction. Additionally, availability of the dihydrazide and experience with its homopolymerization should allow ready extension of this work to the preparation of ordered copolyhydrazides.

Bisdihydrazide A2

The previously unreported dihydrazide of bisacid A2 (bisdihydrazide A2) was obtained by refluxing the diethyl ester in ethanol in the presence of a threefold excess of hydrazine and was purified by recrystallization from water. The ester

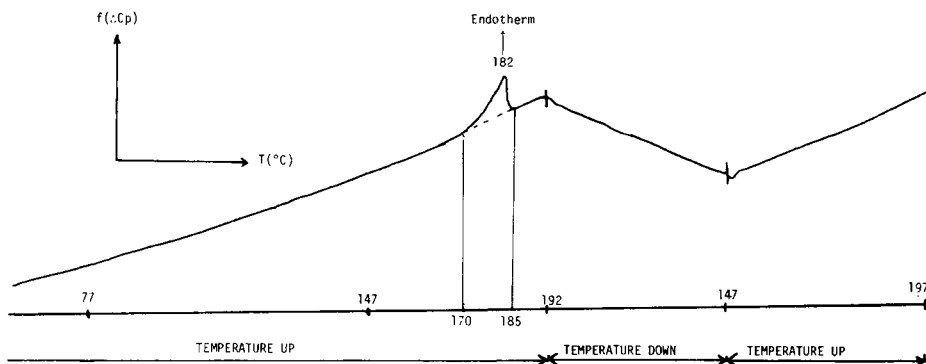


Fig. 2. DSC trace of bisdihydrazide A2, showing irreversibility of fusion peak. Scanning rate, $10^\circ/\text{min}$; sensitivity, 16.

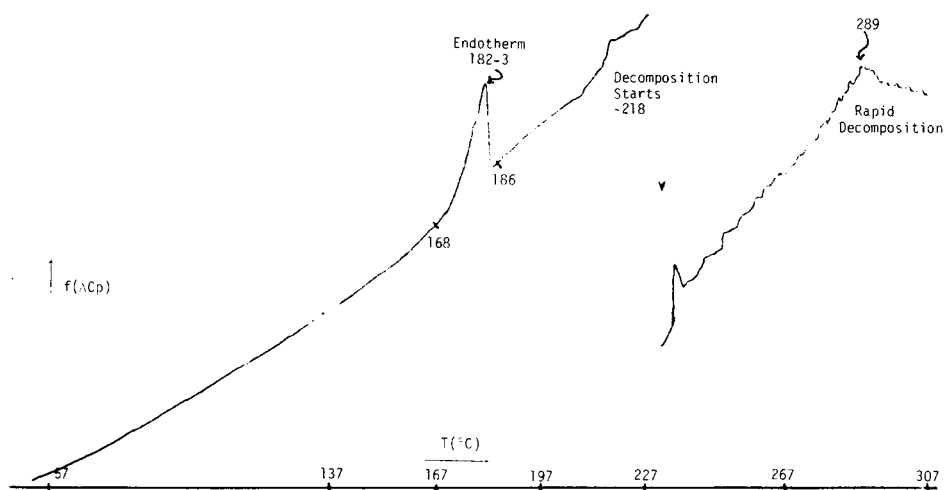


Fig. 3. DSC trace of bisdihydrazide A2 in the range of 57° to 307°C . Scanning rate, $10^\circ/\text{min}$; sensitivity, 8.

was obtained from bisacid A2 by standard methods and recrystallized (needles) from ethanol. Bischloride A2 was prepared according to reference 11.

Differential scanning calorimetry (DSC) shows that bisdihydrazide A2 undergoes irreversible melting in the range of 170 – 185° (Figs. 2 and 3). This is reminiscent of the melting behavior of bisacid A2 itself,¹³ which is believed to form a polyanhydride as it melts and sets to a glass on cooling. The bisdihydrazide A2 could likewise condense by loss of hydrazine and/or ammonia. The melt of bisdihydrazide A2 forms a clear and colorless glass upon cooling.

Elemental analysis of bisdihydrazide A2 gave the following results:

ANAL. Calcd for $\text{C}_{19}\text{H}_{24}\text{N}_4\text{O}_4$: C, 61.28%; H, 6.50%; N, 15.04%; O, 17.18%. Found*: C, 61.29%; H, 6.58%; N, 14.76%; O, 17.37%.

The bisdihydrazide A2 is further characterized by the infrared spectrum shown in Figure 4 and the nuclear magnetic resonance spectrum shown in Figure 5. Principal infrared bands include NH stretching (3.0 – 3.2μ), CH stretching

* Average of two determinations (0 by difference); Galbraith Laboratories, Knoxville, Tennessee.

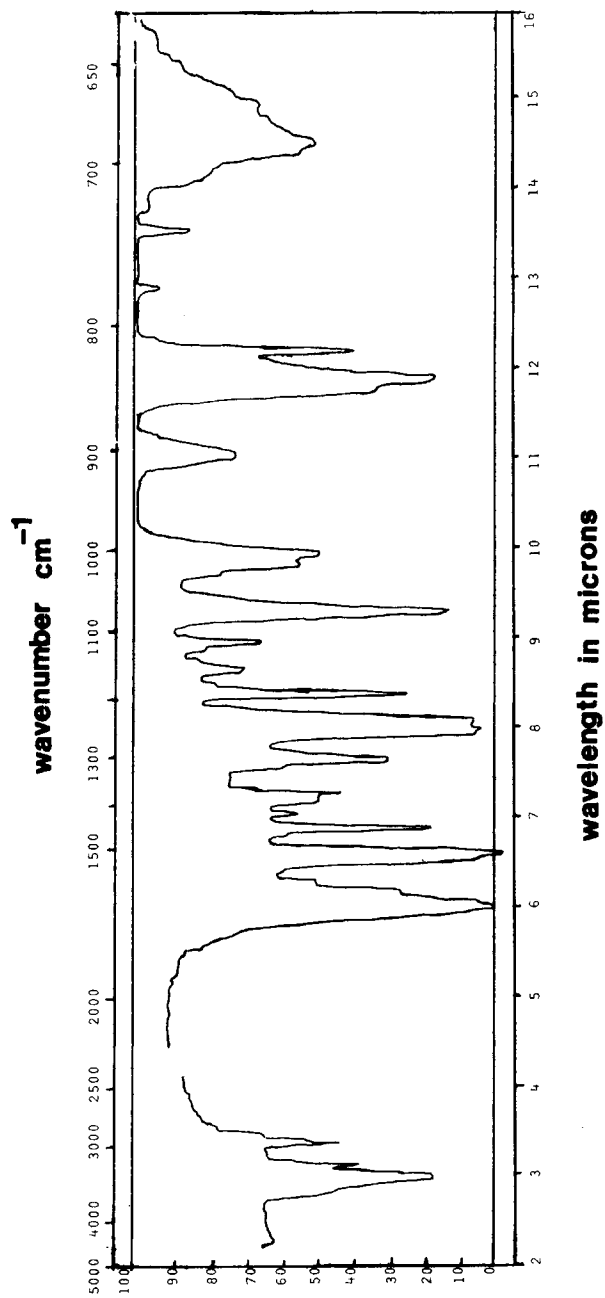


Fig. 4. Infrared spectrum of bisdihydrazide A2.

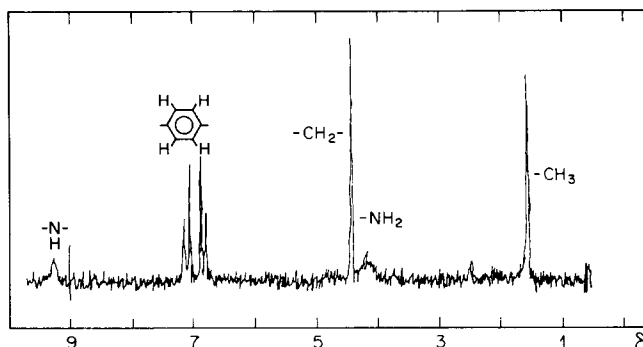


Fig. 5. NMR spectrum of bisdihydrazide A2.

(3.2–3.5 μ), C=O ($\sim 6 \mu$), skeletal aromatic ring deformation (6.2–7.0 μ), the amide II band as a shoulder on the 6.6 μ absorption, CH bending (6.8, 7.2–7.3 μ), the amide III band at $\sim 8 \mu$, O—Ar stretching (9.3 μ), O—CH₂ stretching ($\sim 10 \mu$), and the p-disubstituted ring pattern at $\sim 11.9 \mu$. The NMR spectrum was obtained in DMSO-*d*₆ at room temperature, using a Varian HA 1000 spectrometer. Resonance assignments are given on the spectrum.

Bisdihydrazide A2 is readily soluble in amide-type solvents such as dimethylacetamide (DMA), hexamethyl phosphoramide (HMPA), and N-methylpyrrolidone (NMP), as well as in dimethyl sulfoxide (DMSO). The yield from recrystallization in water was only 50–60%; the material remaining in the mother liquor did not crystallize upon concentration. When heated to dryness, it evolved hydrazine and/or ammonia; this mass, upon cooling, formed a clear amber-colored, brittle resin.

Bishydrazid A2 Polymer Formation

Polymerization according to Figure 1 occurs readily. The bisdihydrazide A2 is dissolved in NMP and cooled to -25°C . Bischloride A2, containing a viscosity reducing agent such as CCl₄, is added.¹ (The solvent mixture is $\sim 92\%$ NMP, the final polymer concentration is $\sim 20\%$.) A substantial viscosity increase occurs within a few minutes. The pale-yellow solution is allowed to come to room temperature with continued stirring.

For example, batch 203 was prepared by adding 13.981 g (0.03431 "effective" moles) bischloride A2 in 7 ml CCl₄ (including rinsings) all at once to 12.763 g (0.03431 theoretical mole) bisdihydrazide A2 in 91 ml NMP at -25° . The solution was maintained at -25° for 20 min, then allowed to warm to room temperature (20 min), and stirring was continued for an additional 10 min.

The bishydrazid A2 polymer can be precipitated in pearl form by dropping the polymerization solution from a funnel into water with stirring. Alternatively, the polymerization solution can be used directly as a spinning dope without neutralization, concentration, or dilution. It was found that the "effective" molecular weight of bischloride A2 is 407.5 as opposed to the theoretical molecular weight¹ of 381.3. The bisdihydrazide molecular weight, calculated as 372.4, is correct. This is substantiated by the close match of calculated and determined elemental compositions. Also, it was observed that bishydrazid A2 polymer of highest inherent viscosity was obtained when isostoichiometric proportions of

reactants were calculated based upon the "effective" molecular weight of bis-chloride A2 and on the theoretical molecular weight of bisdihydrazide A2. These findings are consistent with the assumption that a dimer-type impurity in the acid chloride is produced in its preparation from the acid and is not due to an impurity in the acid itself. Interestingly, even bishydrazid A2 polymers prepared under stoichiometrically imbalanced conditions (e.g., batch 205, mole ratio dihydrazide to acid chloride of 1.07:1.00; and batch 204, mole ratio dihydrazide to acid chloride of 1.085:1.00) formed continuous films when cast from DMA solution.

Dishydrazid A2 Polymer Characterization

The inherent viscosity, η_{inh} , of batch 203 was 0.77, while batches 205 and 204 each exhibit η_{inh} of 0.61 (η_{inh} obtained in DMA containing 5% LiCl at 25°C, 1/2% concentration). Even for the polymer prepared under isostoichiometric conditions, these values are lower than those observed for the bisaramid polymers. This is a logical result: the new "bishydrazid A2" polymer has a somewhat lower aromatic content than the polybisaramids and a higher proportion of oxy-methylene units per unit polymer chain length. It would, therefore, be expected to have greater chain flexibility and lower inherent viscosity in solution while the molecular weight is still high enough to afford good wet-spinnability from solution. Indeed, it is a considerable advantage in that solutions of very high concentrations (~20%) can be spun with ease. Importantly, the bishydrazide A2 polymer wet spins quite as excellently as the polyaramides, producing, moreover, a clear colorless strong film on casting from DMA solution. The cast film becomes opaque (white) on treatment with formic acid.

DSC traces of bishydrazide A2 polymers showed an exothermic α/β transition analogous to that of the bisacid A2 polyaramides, but at a slightly lower temperature (165–170°C), while the formic acid-treated film failed to show this transition—also analogous to the polyaramides.¹ Both untreated and formic acid-treated materials appeared to fuse at about 290°, and each decomposed with extensive evolution of gaseous decomposition products, without charring or carbonization, some 10–20° above this temperature (Fig. 6).

Scanning electron microscopy (SEM) shows quite a different fiber structure for bishydrazid A2 than for the bisaramids.^{1,2} The skin is free from porosity—no evidence for it showing up at a 5000-fold magnification (Fig. 7, top right). Consequently, solvent can only transfer to the water bath by a slow process of diffusion based on an adsorption/desorption mechanism. There are, therefore, no powerful radial streams of solvent pouring through skin holes to the exterior and leaving a "grapefruit" pattern. Instead, coaxial fronts move toward the periphery in waves which presumably relate to the osmotic gradient. This causes a "tree trunk" pattern (Fig. 7, top left) and tends to leave coaxial rings or partial rings of voids and even a central void in place of the macrofoam which is so characteristic for the wet-spun bisaramids. An untypical piece of fiber with holes in the skin due to (presumably) rough handling during spinning is worth noting. In that portion of fiber (Fig. 7, bottom right), the "grapefruit" pattern is clearly seen in the section nearest to the holes while the opposite side shows the "tree trunk" pattern.

It may be due to the high concentration of the spinning solution (19–20%) and perhaps also partly to the less hydrophilic nature of the dope compared to

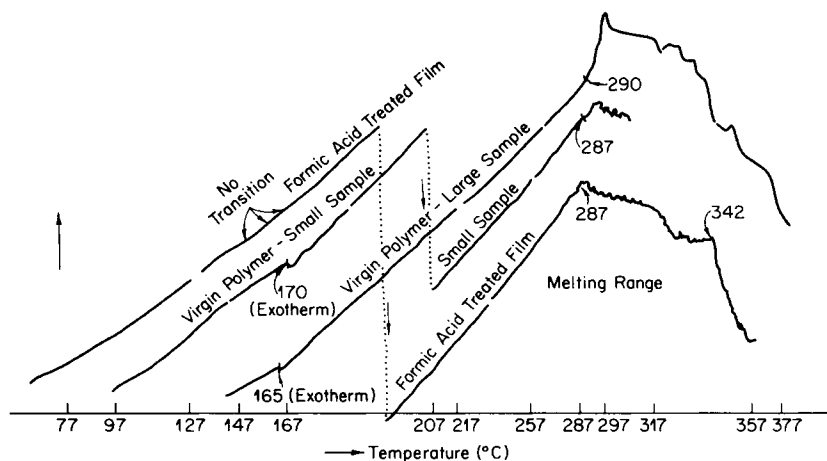


Fig. 6. DSC traces of bishydrazid A2 (Batch 203). Scanning rate, $10^{\circ}/\text{min}$; sensitivity, 8. (1) The transition blip at 165° – 170°C in the virgin polymer and its absence in the formic acid-treated film. (2) Similarity in melting behavior: no carbonization, limited stability above the melting point (287 – 290°C), followed by decomposition (gaseous products).

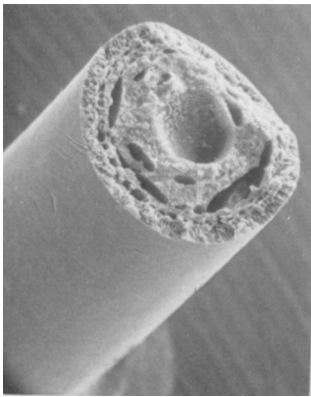
bisaramid dopes that the skin is not perforated by the streams of solvent which are generated by the osmotic pressure gradient. Thus, a stout skin is formed quickly as the dope hits the coagulating bath, and subsequent elution must perform by diffusion only. It is also possible that the presence of HCl and the absence of LiCl play a part.

The mechanical properties of the polymer were determined on the as-cast and formic acid-treated films after conditioning at 23°C and 65% relative humidity. The tests were carried out on an Instron tensile tester at strain rates of 0.508 and 2.54 cm/min. The results are shown in Table I.

At each strain rate, the as-cast films failed in a brittle manner and the formic acid-treated films failed in a tough manner; i.e., the latter yielded and exhibited considerable elongation before breaking. Thus, the formic acid treatment converted an otherwise brittle film into a tough film. The strain rate was not increased sufficiently to force the formic acid-treated film to behave as a brittle material. Interestingly, examination of the formic acid-treated film by wide-angle x-ray scattering (WAXS) showed it to be amorphous. For both materials, the maximum stress and the initial modulus were higher at the lower testing speed, as observed for the bisacid A2 polyaramides.² Evidently, the relaxation time of the polymer allows, at the lower testing rate, better gradual conversion of the polymer into an oriented material with greater strength.

SUMMARY AND CONCLUSIONS

The dihydrazide of bisacid A2 (“bisdihydrazide A2”) was prepared and was found on elemental and spectral analysis to have the composition expected by theory. This proved, once again, that the bisacid A2 itself was a pure starting material for this work. The subsequent low-temperature solution polymerization with “bischloride A2”—using the “effective” molecular weight of the latter rather than the theoretical value in calculating isostochiometry—proved that the notion of an “effective” molecular weight for bischloride A2 is correct. Indeed, this was the key to the successful production of the bisaramid A2 polymers reported in



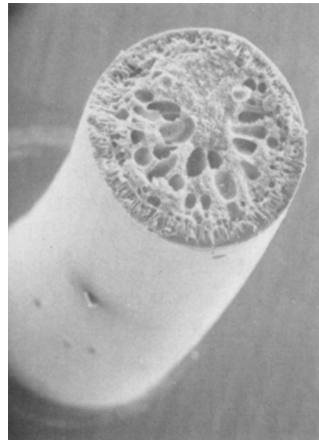
TREE TRUNK PATTERN INDICATES
SLOW CIRCUMFERENTIAL DIFFUSION



TYPICAL SURFACE, FREE FROM HOLES



x5000 CORE STRUCTURE



x100 UNTYPICAL SURFACE WITH A FEW
LARGE DEFECTS CAUSING RADIAL SOLVENT
SURGE ("GRAPEFRUIT" PATTERN)

Fig. 7. Bishydrazid A2 wet-spun fiber (#203).

references (1) and (2) and is clearly equally applicable to our present type of polymer.

An α/β transition was observed when running DSC traces. The results of tensile tests showed a similar pattern to that observed in bisaramid A2 films (q.v., loc. cit.): As-cast film was quite strong (but brittle), while formic acid-treated film had lower strength and modulus, but was tough and had much higher elongation at break, a tendency which has also been observed in the bisaramids.

We have not observed crystallinity in the film—even after formic acid treat-

TABLE I
Tensile Tests on Bishydrazid A2 Films (Batch 203, $\eta_{inh} = 0.77$)^a

	203 ^b	203X	203	203X
Strain rate, cm/min	2.54	2.54	0.508	0.508
Maximum stress dyne/cm ² × 10 ⁻⁸	1.96 bk	1.30 yd	3.27 bk	2.79 yd
Mean S.D.	0.19	0.20	0.44	0.49
Strain at yield or break, %	2.34 bk	5.29 yd	2.17 bk	6.40
Mean S.D.	0.46	1.81	0.40	0.90
Initial modulus, dyne/cm ² × 10 ⁻¹⁰	1.02	0.36	1.77	0.84
Mean S.D.	0.09	0.03	0.25	0.17
Number of specimens	7	9	10	8

^a bk = Break, yd = yield, S.D. = standard deviation.

^b Sample designation; × denotes formic acid-treated film.

ment—or in the wet-spun fiber, but we are not ruling out the possibility of inducing crystallinity under conditions which would presumably involve a high degree of orientation (hot drawing, annealing, “melt” spinning of suitably stabilized polymer). The differences in the physical structure of wet-spun fiber compared with that found in bisaramide polymers and the probable causes of these differences have been discussed.

It is thought that the new polymer may well prove to be a useful addition to the growing number of aromatic and semiaromatic amide and hydrazide polymers which are currently being evaluated for use as fiber.

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