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AFWAL notice, 3 Nov 1983

AFML-TR-74-199

SYNTHESIS OF HIGH MOLECULAR WEIGHT "PARA"-PHENYLENE PBI

TECHNICAL REPORT AFML—TR—74—199

NOVEMBER 1974

AIR FORCE MATERIALS LABORATORY
AIR FORCE SYSTEMS COMMAND
WRIGHT—PATTERSON AIR FORCE BASE, OHIO 45433

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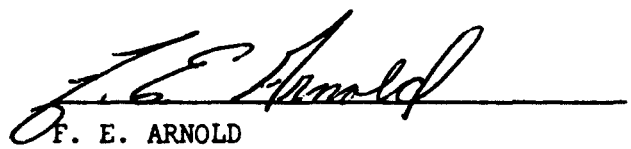

F. E. ARNOLD
Project Monitor

FOR THE COMMANDER

R. L. VAN DEUSEN, Chief
Polymer Branch
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A new class of aromatic polyamide materials has recently become commercially available which exhibit super mechanical properties. The properties are primarily connected to the all-"para" aromatic structure of these polyamides. This report is concerned with the synthesis of an all-"para" aromatic heterocyclic polymer system.

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A study has been conducted on the use of various monomers and polymerization conditions to obtain high molecular weight poly[1,7-dihydrobenzo[1,2-d:' 4,5-d] diimidazole -2, 6-diyl)-1, 4-phenylene]. The polycondensation of 1,3-diamino -4, 6-(p-toluenesulfamido) benzene with terphthalic acid and also the homopolymerization of a series of AB-monomers has resulted in a polymer with intrinsic viscosities as high as 5.0. The resulting high molecular weight rod-like all-"para" PBI, with its high temperature capability and its ability to crystallize, shows great promise as a thermally stable material which should exhibit superior mechanical properties.

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734004, "Synthesis of Novel Polymer Materials for High Temperature Resin Applications." It was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. F.E. Arnold as the AFML Project Scientist. This report describes work conducted from December 1972 to December 1973.

The work described in this report was conducted in the Polymer Branch laboratory by Dr. R.L. Kovar of the University of Dayton Research Institute and Dr. F.E. Arnold. The manuscript was released by the author in August 1974 for publication as a Technical Report.

SUMMARY

A new class of aromatic polyamide materials which exhibit super mechanical properties has recently become commercially available. The properties are primarily connected to the all-"para" aromatic structure of these polyamides. This report is concerned with the synthesis of an all-"para" aromatic heterocyclic polymer system.

A study has been conducted on the use of various monomers and polymerization conditions to obtain high molecular weight poly[1,7-dihydrobenzo[1,2-d:4,5-d]diimidazole-2,6-diyl)-1,4-phenylene]. The polycondensation of 1,3-diamino-4,6-(p-toluenesulfamido)benzene with terphthalic acid and also the homopolymerization of a series of AB-monomers has resulted in a polymer with intrinsic viscosities as high as 5.0. The resulting high molecular weight rodlike all-"para" PBI, with its high temperature capability and its ability to crystallize, shows promise as a thermally stable material which should exhibit superior mechanical properties.

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SECTION I

INTRODUCTION

Advanced aircraft and aerospace systems demand lighter weight structures and these are dependent upon the availability and effective utilization of superior structural materials. The material requirements are not only for superior mechanical properties but also for evidence that the material possesses a high degree of thermal oxidative stability.

A series of new organic fibers has recently appeared in the literature (References 1 through 3) which exhibits exceptionally high strength and high modulus. Their modulus values approach those of boron and graphite, while their tenacity (specific tensile strength, 20 g/den) values far surpass those of any other known fibers. The density (1.41-1.46 g/cc) of these fibers is significantly lower than for any other reinforcing fiber.

The unique fibers are derived from the wet spinning of optically anisotropic aromatic polyamide dopes. The anisotropic solutions are obtained from the group of aromatic polyamides whose chain-extending bonds from each aromatic nucleus are essentially coaxial or parallel and oppositely directed in liquid media. For a given polyamide/liquid medium below a particular polyamide concentration, the dope is isotropic. As the concentration of the polyamide increases, the viscosity of the dope increases. At a critical concentration point, there is a sharp discontinuity in the slope of the viscosity vs concentration curve as the dope changes from isotropic to anistropic, and it is accompanied by a decrease in viscosity of the slope. This unusual solution property characteristic allows an evaluation of its potential as a fiber prior to the actual spinning operation.

Although the aromatic polyamides are found to exhibit very superior mechanical properties, they do not meet the thermal requirements needed for all Air Force and Aerospace systems. The objective of work in this field has been to synthesize polymer systems which would be expected to exhibit the desired superior mechanical properties and also the needed high degree of thermal oxidative stability. This report describes a phase of the current effort toward attaining these goals.

SECTION II

DISCUSSION AND REPORTS

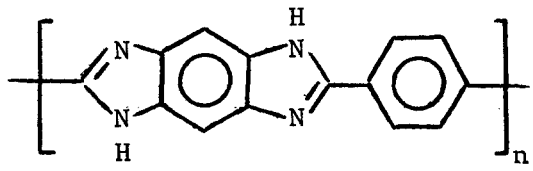
The published literature has left the feeling that the following structural criteria are required to obtain materials with a high degree of tensile strength, and an abnormally high stiffness.

a. Polymer structures which are "para" oriented for maximum orientation and crystallinity.

b. Planar structures for optimum packing of chains devoid of bulky side groups.

c. Structures that exhibit a high degree of interchain hydrogen bonding and π bond overlap.

A polymer which would meet all the above structural criteria and would also have good thermal oxidative stability is the a+l "para" oriented polybenzimidazo polymer, poly[1,7-dihydrobenzo[1,2-d:4,5-d]diimidazole-2,6-diyl)-1,4-phenylene] I.

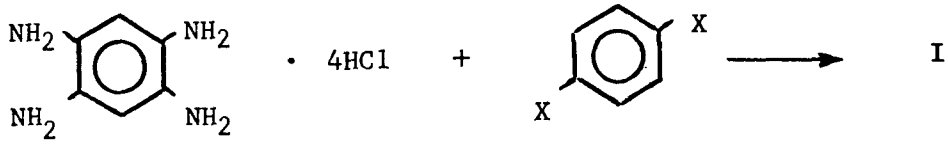


I

Polymer I was first prepared by Vogel and Marvel (Reference 4) from the melt polycondensation of diphenylterphthalate with 1,2,4,5-tetraaminobenzene, and also by an interfacial polycondensation employing terephthalyl chloride. The synthetic methods resulted in a low molecular weight polymer of limited solubility. It was assumed that the difficulty in synthesis was due to the sensitivity of the aromatic tetraamine

to oxidation, and because the basicity of the amino groups was insufficient for an interfacial synthetic method. Although the polymer was of low molecular weight, it exhibited a high degree of order and good thermal oxidative stability.

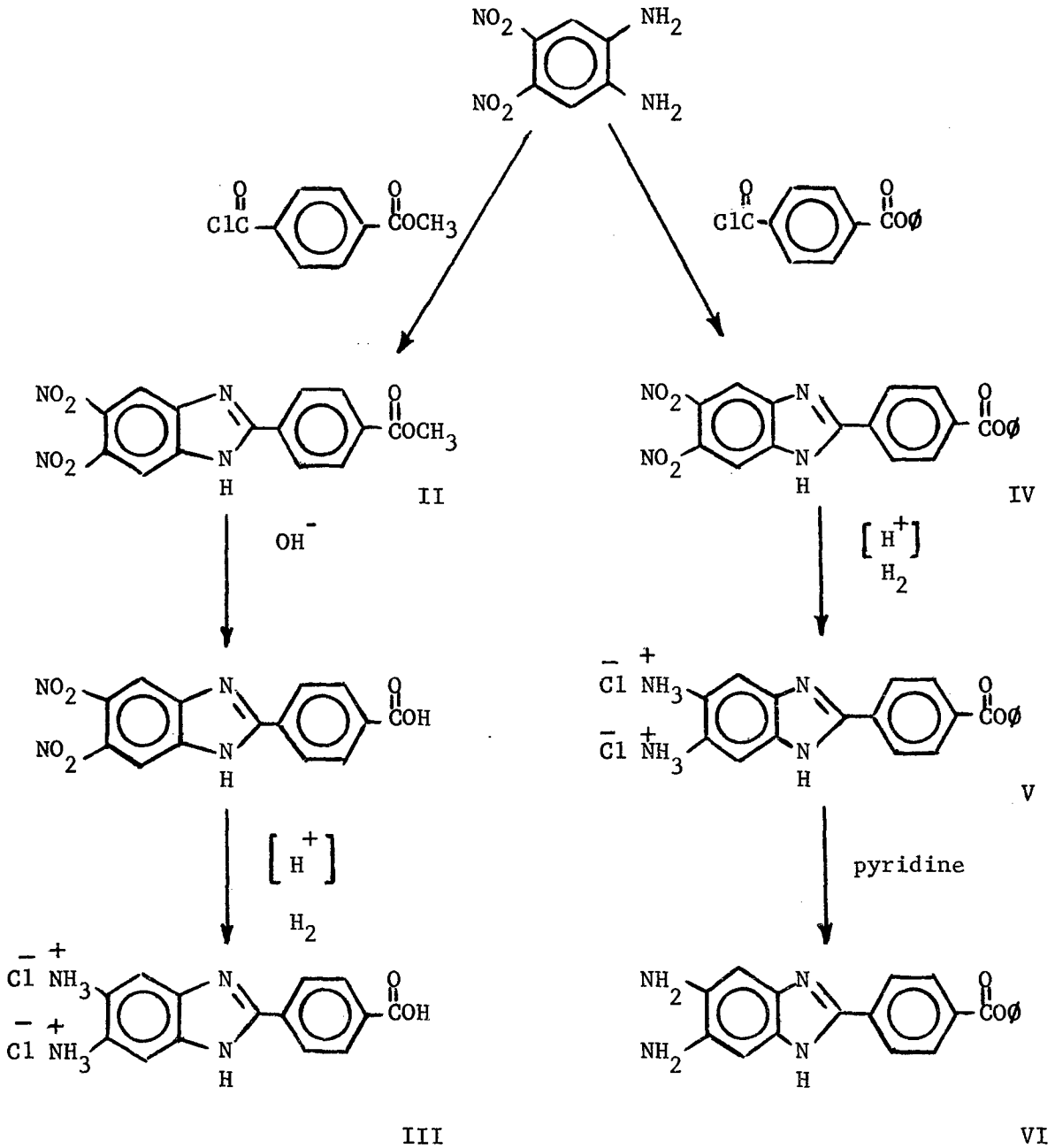
High molecular weight polybenzimidazoles, other than polymer I, have been prepared (Reference 5) from 3,3'-diaminobenzidine and various aromatic dicarboxylic acids or their acid derivatives, using polyphosphoric acid (PPA) as the polymerization solvent. PPA is an excellent polymerization solvent since it is a dehydrating agent with high temperature capability and offers the advantage of using the more oxidatively stable amine hydrochlorides as monomers. Several polymerizations were carried out using the hydrochloride salt of TAB with terephthalic acid in PPA; however, in all cases the resulting materials were completely insoluble, even in strong acidic solvents. Other acid derivatives such as esters, amides, and nitriles were also employed as monomers with the same results.



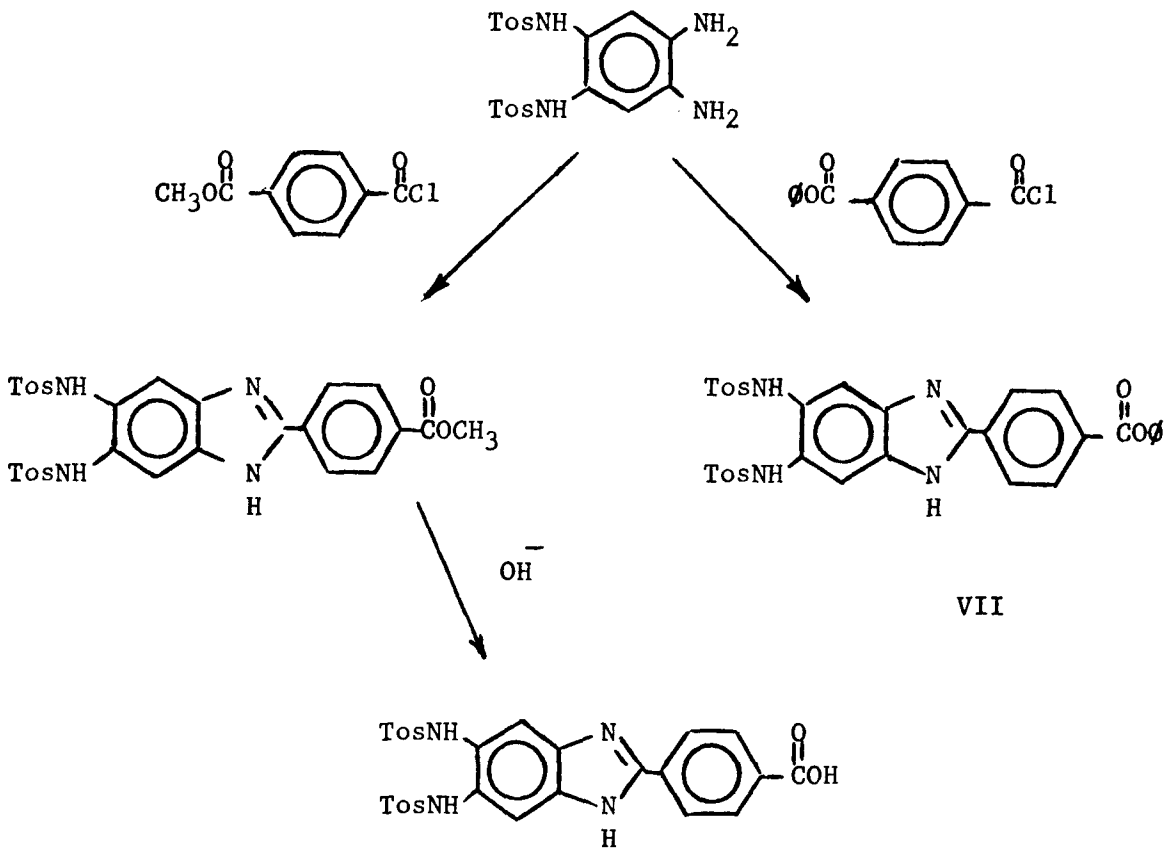
$$X = -CO_2H,\ -CO_2\phi,\ -CO_2NH_2,\ -CN$$

A series of AB-monomers were prepared in an effort to circumvent problems associated with the oxidative instability of TAB. The monacid chloride of methyl terphthalate was condensed with 1,2-diamino-4,5-dinitrobenzene to give 2-[p-carboxyphenyl]-5,6-dinitrobenzene II. Basic hydrolysis of II followed by catalytic reduction in a methanol hydrochloric acid

medium gave the AB-monomer, 2-[p-carboxyphenyl]-5,6-diaminobenzimidazole hydrochloride III. In an analogous fashion the monacid chloride of phenyl terphthalate reacted with 1,2-diamino-4,5-dinitrobenzene gave the dinitrobenzimidazole IV, which was subsequently reduced to give 2-[p-carboxyphenyl]-5,6-diaminobenzimidazole-dihydrochloride, monomer V. Treatment of V with pyridine gave 2-[p-carbophenoxyphenyl]-5,6-diaminobenzimidazole, monomer VI.



Previous work in this laboratory (Reference 5) has shown that aminotosylates could successfully be used in place of amino monomers if the polymerization were carried out in PPA. The tosylates are rather easily purified and are quantitatively hydrolized to the amines in PPA. We prepared two AB-monomers having tosylate groups instead of amino groups. 1,2-Diamino-4,5-bis(p-toluenesulfonamido)-benzene was allowed to react with both the phenyl and methyl monacid chloride teresters to give monomer VII directly and monomer VIII after basic hydrolysis.



VII

VIII

Polymerizations of the AB-monomers as tosylates or hydrochloride salts were carried out in PPA. The monomers were normally maintained (3-4 hours) at 80°-90°C for detosylation or dehydrochlorination to the free amines prior to heating to 180°-200°C for the propagation reaction. Temperatures beyond 200°C in PPA resulted in the formation of insolubles (Table I). The best results were obtained from monomer III. High molecular weight polymer was also obtained by using monomer VI in diphenylsulfone, a solvent recently shown to give high molecular weight m-phenylene PBI (Reference 7).

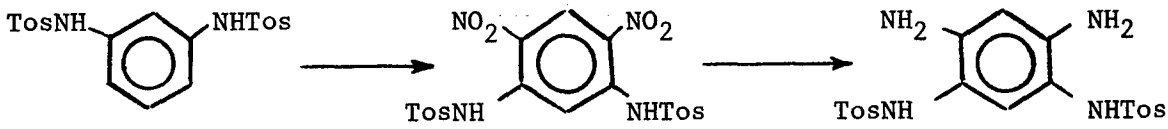
The polymer was completely soluble in methanesulfonic acid and 98% formic acid. Polymer with low intrinsic viscosity ([N] = 0.02-0.2) was soluble in 96% sulfuric acid; however, the polymer was insoluble in all aprotic solvents tested. X-Ray diffraction patterns (Figure 1) of the acid insoluble polymer, formed from the high temperature (225°C) PPA reaction, was compared to a completely soluble polymer (Figure 2). The results showed that the soluble portion had a high degree of order, with Bragg spacing of 5.41, 4.15, and 3.75A, and the insoluble sample was polycrystalline with spacings of 9.81, 6.10, 4.67, 3.66, 3.15, and 2.63A. It can therefore be assumed that the problem associated in the synthesis of high-molecular-weight all-"para" PBI is not one of crosslinking but of induced crystallization during synthesis. Many factors may affect the crystallization of the polymer, such as, concentration, molecular weight, shear, as well as temperature.

TABLE I

Polymerization of AB-Monomers

Monomer	Polymerization Solvent	Temp.	Solubility	[N]
III	PPA	200°C	$MeSO_3H$ Formic	1.3
III	PPA	195°C	$MeSO_3H$ Formic	1.2
III	PPA	225°C	Insoluble	
V	PPA	180°C	$MeSO_3H$ Formic	0.4
VI	$\phi SO_2\phi$	250°C	$MeSO_3H$	1.1
VII	PPA	200°C	$MeSO_3H$ H_2SO_4 Formic	0.2
VIII	PPA	180°C	$MeSO_3H$ H_2SO_4 Formic	0.02

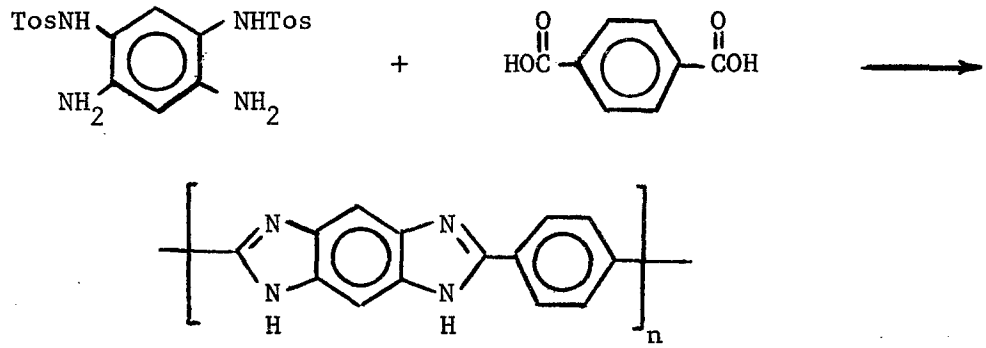
Another method used successfully to obtain a high-molecular-weight all-"para" PBI was the use of a bis-, ortho-aminotosylate in place of TAB. The monomer, 1,3-diamino-4,6-(p-toluenesulfamido)benzene IX, was prepared from the nitration of 1,3-toluenesulfamidobenzene followed by catalytic reduction in N,N-dimethylacetamide:



IX

Due to the hydrogen bonding of the amino groups with the sulfone oxygens, the monomer is very stable to air oxidation and could be recrystallized to within a half-degree-melting-point range from anhydrous methanol. The monomer is a white crystalline solid which can be quantitatively hydrolized in an acid medium to give the free TAB.

Stoichiometric quantities of IX with terephthalic acid were slowly heated to 95°C, whereupon the ditosylate was hydrolized to the free amine. Heating the reaction mixture to 195°C for 6 hours produced very high molecular weight PBI $[\eta] = 5.0$; i.e., the use of 1,3-diamino-4,6-(p-toluenesulfamido)benzene as a monomer replacement for TAB, and the process by which the polymer is prepared, represents a sixfold increase in molecular weight over that reported in the literature (Reference 4).



SECTION III

CONCLUSIONS

A series of new phenyl-substituted benzimidazo compounds have been prepared where the phenyl group is attached to the two position of the imidazo ring and contains a carboxylic acid group or acid derivatives, para to the point of imidazo attachment. The benzimidazo is substituted in the 5,6 positions with amino groups or amino derivatives, which enables the compounds to be used as AB-monomers in the preparation of poly-[1,7-dihydrobenzo[1,2-d:4,5-d]diimidazole-2,2-diyl)-1,4-phenylene]. Polymerization of the various AB-monomers in both acidic and aprotic solvents resulted in polymers with intrinsic viscosities of 1.1 to 1.3, as determined in methanesulfonic acid.

A new aromatic amino monomer 1,3-diamino-4,6(p-toluenesulfamido)benzene has been prepared and used as a replacement for 1,2,4,5-tetraaminobenzene in the PPA polymerization with terephthalic acid. The monomer has excellent shelf life, can be purified to within a half-degree-melting-point range, and can be stored for extended periods of time without light and air oxidation. Since the monomer can be extensively purified, very high molecular weight polymer, $[N] = 5.0$, was obtained, which represents a sixfold increase in molecular weight over that reported in the literature.

Concentrated solution properties (analogous to those for all-"para" polybenzamides, Reference 1) of the polymer will be carried out in an effort to evaluate its potential as a high-modulus super-strength material.

SECTION IV

EXPERIMENTAL

1. MONOMERS

2-[p-Carboxyphenyl]-5,6-diaminobenzimidazole Hydrochloride III

A. 2-[p-Carbomethoxyphenyl]-5,6-dinitrobenzimidazole II

To a solution containing 10 g (45.8 mmole) of chlorocarbonyl-methyl-benzoate dissolved in 100 ml of dichlorobenzene was added 3.0 g (15.3 mmole) of 1,2-diamino-4,5-dinitrobenzene. The resulting mixture was carefully heated to reflux under nitrogen (frothing), and was maintained at that temperature for two hours. The solution was then allowed to cool in ice for one hour, and precipitate that formed was filtered by suction, washed with benzene, and air-dried. The crude product was then allowed to cool in ice for one hour, and the precipitate that formed was filtered by suction, washed with benzene, and air-dried. The crude product was then purified in a manner completely analogous to that previously described for the synthesis of 2-[p-carbophenoxyphenyl]-5,6-dinitrobenzimidazole. Recrystallization from THF/n-propanol by distillation to a small volume <u>in vacuo</u> yielded 3.2 g (62%) of 2-[p-carbomethoxyphenyl]-5,6-dinitrobenzimidazole as light yellow needles, m.p., 239°-240°. Calcd for $C_{15}H_{10}N_4O_6$: C, 52.65; H, 2.92; N, 16.37; and M.W. = 342.19. Found: C, 51.78; H, 3.13; N, 15.66; and M.W. = 342 (mass spectrum). The infrared spectrum (KBr pellet) exhibited absorptions at: 1725 (C=O) (vs), 1695 (s), 1665 (sh), 1600 (m), 1545 and 1335 (s) [NO_2], 1290 (vs), and 1120 cm^{-1}.

B. 2-[p-Carboxyphenyl]-5,6-dinitrobenzimidazole

To a solution containing 4.8 g (87.6 mmole) of KOH dissolved in 200 ml of water was added 10 g (29.2 mmole) of 2-[p-carbomethoxyphenyl]-5,6-dinitrobenzimidazole. The resulting mixture was heated at 90° under nitrogen for 8 hours, after which it was allowed to cool to room temperature. The solution was then slowly acidified with 50% HCl, liberating the dinitro-acid as a light tan precipitate. The product was collected by filtration, washed with several portions of distilled water, then air-dried. Recrystallization from THF/heptane afforded golden platelets, m.p.-dec. above 350°C. The infrared spectrum (KBr pellet) exhibited absorptions at: 3200-2800 (broad absorption), 2680 (w), 2560 (w_2), 1700-1670 (vs-broad absorption), 1535 (s), 1420 (s), 1335 (s), 1275 (broad), 1100 (m), and 810 cm^{-1}. Calcd for $C_{14}H_8N_4O_6$: C, 51.12; H, 2.46; N, 17.07. Found: C, 51.01; H, 2.59; N, 17.15.

C. 2-[p-Carboxyphenyl]-5,6-diaminobenzimidazole Hydrochloride III

A solution of 5 g (16.7 mmole) of 2-[p-carboxyphenyl]-5,6-dinitrobenzimidazole in 200 ml of methanol at 0° was thoroughly purged with nitrogen. To this was carefully added 500 mg of 10% palladium on charcoal, and 30 ml of concentrated HCl. The hydrogenation flask was then pressurized with 55 lbs/in^2 of hydrogen and the flask was shaken at room temperature for 8 hours. After the reaction period had elapsed, the solution was filtered by suction, and the filtrate evaporated to dryness <u>in vacuo</u>. The residual yellow solid was re-dissolved in a minimum of boiling methanol (which contained a trace of HCl), and the filtered solution added to 50 ml of concentrated HCl. Removal of the methanol from the solution <u>in vacuo</u> and subsequent cooling in ice yielded 4.2 g

(82%) of 2-[p-carboxyphenyl]-5,6-diaminobenzimidazole hydrochloride as fluffy yellow needles. The infrared absorption: C, 55.18; H, 4.30; N, 18.39; Cl, 11.63. Found: C, 54.82; H, 4.33; N, 18.77; Cl, 12.01.

2(p-Carbophenoxyphenyl)-5,6-diaminobenzimidazole Dihydrochloride IV

A. 2-[p-Carbophenoxyphenyl]-5,6-dinitrobenzimidazole

To a solution containing 10 g (38.4 mmole) of p-chlorocarbonylphenylzoate dissolved in 100 ml of dichlorobenzene was added 2.53 g (12.8 mmole) of 1,2-diamino-4,5-dinitrobenzene. The resulting mixture was carefully heated under nitrogen to reflux (frothing) and was maintained at that temperature for two hours. The solution was then allowed to cool in ice for one hour, and the precipitate that formed was filtered by suction, washed with benzene, and air-dried. The crude product was chromatographed on a 2 inch x 18 inch dry column of silica gel. Elution with methylene chloride removed traces of impurities, while further elution of the column with 20/1 methylene chloride/THF slowly removed a broad band of the desired product, leaving a third band of side product on the column. After all of the second band had been removed from the column, the solvent was removed <u>in vacuo</u>, leaving a pale yellow residue. Recrystallization from THF/n-propanol yielded 3.0 g (58%) of 2-[p-carbophenoxyphenyl]-5,6-dinitrobenzimidazole as pale yellow needles, m.p., 239°-240°. The infrared spectrum (KBr pellet) exhibited absorptions at 1720 (s) [ester C=O], 3300 (w) [imidazole N-H], 1690 (sh), 1660 (m), 1535 (vs) [nitro], 1335 (s) [nitro], 1290 (vs), and 1120 cm^{-1}. Calcd for $C_{20}H_{12}N_4O_6$: C, 59.41; H, 2.99; N, 13.85. Found: C, 60.01; H, 3.14; N, 12.73.

B. 2-[p-Carbophenoxyphenyl]-5,6-diaminobenzimidazole Dihydrochloride IV

A solution containing 5 g (12.4 mmole) of 2-[p-carbophenoxyphenyl]-5,6-dinitrobenzimidazole dissolved in 100 ml of methanol was thoroughly purged with nitrogen at 0°. To this was carefully added 200 mg of 10% palladium on charcoal, and 20 ml of concentrated HCl. The flask was pressurized with 55 lbs/in^2 of hydrogen, and was shaken at room temperature for 8 hours. At that time, the contents of the flask were filtered, and the filtrate, which was evaporated to dryness in vacuo, yielded 5.5 g (95%) of 2-[p-carbophenoxyphenyl]-5,6-diaminobenzimidazole dihydrochloride as a yellow powder. The infrared spectrum (KBr pellet) exhibited absorptions at 1725 (vs), 1650 (m), 1525 (m), 1435 (m), 1290 (vs), and 1115(s). Calcd for $C_{20}H_{16}N_4O_2$ 2HCl: C, 57.57; H, 4.35; N, 13.43; Cl, 16.99. Found: C, 57.13; H, 4.27; N, 12.95; Cl, 16.44.

2-[p-Carbophenoxyphenyl]-5,6-diaminobenzbenzimidazole VI

A. 2-[p-Carbophenoxyphenyl]-5,6-diaminobenzimidazole

To 25 ml of pyridine was added under nitrogen 2.5 g (5.2 mmole) of 2-[p-carbophenoxyphenyl]-5,6-diaminobenzimidazole dihydrochloride, prepared by the above procedure. The dark solution was stirred at room temperature for 1/2 hour and then poured into one liter of ice water, liberating the bright yellow free amine. The yellow diamine thus formed was immediately filtered by suction, air-dried, and then recrystallized from methanol/water, yielding 1.2 g (68%) of 2-[p-carbophenoxyphenyl]-5,6-diaminobenzimidazole as a yellow powder, m.p., 237°. The infrared spectrum (KBr pellet) exhibited absorptions at 3400 (broad), 1720 (s),

1640 (broad), 1525 (m), 1430 (m), 1280 (vs), and 1110 (m). Calcd for $C_{20}H_{16}N_4O_2$: C, 69.76; H, 4.68; N, 16.27; and M.W. = 344.38. Found: C, 69.13; H, 4.52; N, 15.88; and M.W. = 344.

2-[p-Carbophenoxyphenyl]-5,6-bis(p-toluenesulfonamide) Benzimidazole VII

A. 2-[p-Carbophenoxyphenyl]-5,6-bis(p-toluenesulfonamide) Benzimidazole

To a solution containing 8.7 g (33.6 mmole) of p-chlorocarbonylphenylbenzoate dissolved in 50 ml of dichlorobenzene was added 5 g (11.2 mmole) of 1,2-diamino-4,5-bis(p-toluenesulfonamido) benzene. The resulting mixture was carefully heated to reflux under nitrogen (frothing), and was maintained at that temperature for two hours. The solution was then distilled to half the original volume, and heptane was added to precipitate the yellow product. The crude product was filtered, washed with several portions of hexane, and air-dried. The material thus obtained was reprecipitated three times from THF solution using hexane. Recrystallization from methanol afforded 5.6 g (77%) of 2-[p-carbophenoxyphenyl]-5,6-bis(p-toluenesulfonamido) benzimidazole as an amorphous yellow powder. The infrared spectrum (KBr pellet) exhibited absorptions at 3340-3200 (broad), 1715 (vs), 1650 (m), 1590 (m), 1520 (s), 1330 (m), 1160 (vs), 1110 (vs), and 1015 (m) cm^{-1}. Calcd for $C_{34}H_{28}N_4O_6S_2$: C, 62.56; H, 4.32; N, 8.58. Found: C, 62.34; H, 4.82; N, 8.25.

2-[p-Carboxyphenyl]-5,6-bis(p-toluenesulfonamido)benzimidazole VIII

A. 2-[p-Carbomethoxyphenyl]-5,6-bis(p-toluenesulfonamido)benzimidazole

To a solution containing 6.8 g (33.6 mmole) of p-chlorocarbonylmethylbenzoate dissolved in 50 ml of dichlorobenzene was added 5 g (11.2 mmole) of 1,2-diamino-4,5-bis(p-toluenesulfonamido)benzene. The resulting mixture was carefully heated to reflux under nitrogen (frothing), and was maintained at that temperature for two hours. The solution was then distilled to half of the original volume, and heptane was added to precipitate the yellow product. The crude product was filtered, washed with several portions of hexane, and air-dried. The material thus obtained was reprecipitated three times from THF solution using hexane. Recrystallization from methanol afforded 4.8 g (72%) of 2-[p-carbomethoxyphenyl]-5,6-bis(p-toluenesulfonamido)benzimidazole as an amorphous yellow powder. The infrared spectrum (KBr pellet) exhibited absorptions at 3200-3300 (broad), 2950 (w), 1720 (vs), 1660 (sh), 1600 (m), 1520 (s), 1480 (sh), 1435 (m), 1400 (m), 1330 (sh), 1285 (s), 1160 (fs), 1115 (s), 1091 (m), cm^{-1}. Calcd for $C_{29}H_{26}N_4O_6S_2$: C, 58.97; H, 4.44; N, 9.49. Found: C, 58.46; H, 4.21; N, 9.20.

B. 2-[p-Carboxyphenyl]-5,6-bis(p-toluenesulfonamido)benzimidazole

To an aqueous solution containing 1.3 g (23 mmole) of KOH dissolved in 50 ml of water was added 5.0 g (8.5 mmole) of 2-[p-carbomethoxyphenyl]-5,6-bis(p-toluenesulfonamido)benzimidazole. The resulting mixture was heated at 90° for 8 hours, at which time it was filtered by suction, and

the filtrate acidified with 50% HCl. The crude acid which precipitated was chromatographed on silica gel (elution with ethyl acetate), affording an amorphous yellow powder, m.p.-dec. 240°. The infrared spectrum exhibited absorptions at 1680 (s) cm^{-1} (COOH), 1420 (m), 1285 (s), 1155 (vs), and 1085 (s). Calcd for $C_{28}H_{24}N_4O_6S_2$: C, 58.32; H, 4.20; N, 9.72. Found: C, 57.92; H, 40.5; N, 9.36.

1,3-Diamino-4,6-(p-toluenesulfamido)benzene IX

A. 1,3-Dinitro-4,6-(p-toluenesulfamido)benzene

To 100 ml of acetic anhydride was added dropwise 15 ml of 70% nitric acid at a rate to maintain the temperature below 5°C. After the addition was complete, 17 g (0.0445 mole) of 1,3(p-toluenesulfamido)benzene was added at a rate to maintain the temperature below 15°C. The solution was stirred at room temperature for 12 hours. The yellow precipitate was collected, washed with water, and recrystallized from acetone to yield 18 g (80%) of the product, m.p., 213°-215°C. Anal. calcd for $C_{20}H_{18}N_4S_2O_8$: C, 47.42; H, 3.58; N, 11.05. Found: C, 47.46; H, 3.37; and N, 10.80.

B. 1,3-Diamino-4,6-(p-toluenesulfamido)benzene IX

A "Parr" hydrogen pressure bomb was charged with 10 g (0.0197 mole) of 1,3-dinitro-4,6(p-toluenesulfamido)benzene, 150 ml of N,N-dimethylacetamide and 1 g of catalyst (10% palladium on powdered charcoal). The bomb was pressurized with 50 psi of hydrogen and allowed to shake for 12 hours. The reaction mixture was suction filtered through celite into one liter of stirred diethyl ether. The resulting white precipitate was

collected and air-dried. Recrystallization from anhydrous methanol gave 7 g, 80% yield of product, m.p., 221-221.5°C. Anal. calcd for $C_{20}H_{22}N_4S_2O_4$: C, 53.79; H, 4.96; N, 12.54. Found: C, 53.68; H, 4.95; and N, 12.29.

2. POLYMERS

Polymerization of 2-[p-Carboxyphenyl]-5,6-diaminobenzimidazole Hydrochloride III

A polymerization flask equipped with nitrogen inlet and outlet tubes and mechanical stirrer was thoroughly flamed and purged with nitrogen. To this was added 50 g of polyphosphoric acid, and the viscous material stirred at 150° under nitrogen for 3 hours. The flask was then cooled in ice, opened, and 2 g (6.56 mole) of 2-[p-carboxyphenyl]-5,6-diamino-benzimidazole hydrochloride carefully added. The flask was closed, and the resulting suspension stirred at 90° for 8 hours under nitrogen to decompose the hydrochloride salt. At that point, a clear, brown solution remained. The temperature of the heating bath was slowly raised over a period of three hours to a maximum of 200°, and was maintained at that level for 8 hours. During that time, a blue opalescence became evident in the reaction solution, which is characteristic of solutions of this polymer in acidic solvents. The polymer solution was precipitated into a large volume of methanol, and then washed with several portions of methanol. The precipitated polymer was stirred with one liter of 10% ammonium hydroxide solution, then rinsed with several portions of distilled water, and finally freeze-dried. The fluffy yellow polymer thus obtained was soluble in methane sulfonic acid, exhibiting an intrinsic

viscosity in that solvent of 1.3. Calcd for $C_{14}H_8N_4$: C, 72.40; H, 3.47; N, 24.12. Found: C, 70.56; H, 3.28; and N, 22.66.

Polymerization of 2-[Carbophenoxyphenyl]-5,6-diaminobenzimidazole VI in Phenyl Sulfone

A polymerization flask equipped with nitrogen inlet and outlet tubes and mechanical stirrer was thoroughly flamed and purged with nitrogen. To this was added a mixture containing 5.0 g (14.5 mmole) of monomer VI and 25 g of diphenyl sulfone. The reaction flask was then slowly heated to 250°, and maintained at that temperature for 6 hours. During this time, phenol sublimed from the reaction mixture, and a precipitate formed. The flask was cooled to 125°, and the polymer suspension poured into 500 ml of methanol. The polymer thus precipitated was collected on a filter frit, washed several times with small portions of methanol, and dried. Reprecipitation from methane sulfonic acid into methanol, followed by successive washings with 5% ammonium hydroxide, methanol, and benzene yielded 2.9 g of polymer as a dark tan powder, exhibiting an inherent viscosity of 1.1 dl/g. Calcd for $C_{14}H_8N_4$: C, 72.40; H, 3.47; N, 24.12. Found: C, 70.93; H, 3.40; and N, 22.44.

Polymerization of 2-[Carbophenyl]-5,6-diaminobenzidazole Dihydrochloride V in PPA

A polymerization flask equipped with nitrogen inlet and outlet tubes and mechanical stirrer was thoroughly flamed and purged with nitrogen. To this was added 50 g of polyphosphoric acid, and the viscous material stirred at 150° under nitrogen for 3 hours. The flask was then cooled in ice, opened, and 2.0 g (4.8 mmole) of monomer V was carefully added. The

flask was closed, and the resulting suspension stirred at 90° for 8 hours under nitrogen to decompose the hydrochloride salt. At that point, a clear, brown solution remained. The temperature of the heating bath was then slowly raised over a period of three hours to a maximum of 200°, and was maintained at that level for 8 hours. During that time, a blue opalescence became evident in the reaction solution, which is characteristic of solutions of the polymer in acidic solvents. The polymer solution was precipitated into a large volume of methanol, and then washed with several portions of methanol. The precipitated polymer was stirred with one liter of 10% ammonium hydroxide solution, then rinsed with several portions of distilled water, and finally freeze-dried in vacuo. The fluffy yellow polymer thus obtained was soluble in methane sulfonic acid, exhibiting an inherent viscosity in that solvent of 0.4 dl/g (0.35 g/dl). Calcd for $C_{14}H_8N_4$: C, 72.40; H, 3.47; N, 24.12. Found: C, 71.05; H, 3.13; and N, 22.81.

Polymerization of 2-[p-Carbophenoxyphenyl]-5,6-diaminobenzimidazole VI in Phenyl Sulfone

A polymerization flask equipped with nitrogen inlet and outlet tubes and mechanical stirrer was thoroughly flamed and purged with nitrogen. To this was was added a mixture containing 5.0 g (14.5 mmole) of monomer VI and 25 g of diphenyl sulfone. The reaction flask was then slowly heated to 250%, and maintained at that temperature for 6 hours. During this time, phenol sublimed from the reaction mixture, and a precipitate formed. The flask was cooled to 125°, and the polymer suspension poured into 500 ml of methanol. The polymer thus precipitated was collected on a filter frit, washed several times with small portions of methanol, and

dried. Reprecipitation from methane sulfonic acid into methanol, followed by successive washings with 5% ammonium hydroxide, methanol, and benzene yielded 2.9 g of polymer as a dark tan powder, exhibiting an inherent viscosity of 1.1 dl/g in methane sulfonic acid (0.35 g/dl). Calcd for $C_{14}H_8N_4$: C, 72.47; H, 3.47; N, 24.12. Found: C, 70.93; N, 3.40; and N, 22.44.

Polymerization of 2-[p-Carbophenoxyphenyl]-5,6-bis(p-toluenesulfonamido)benzimidazole VII

A polymerization flask equipped with nitrogen inlet and outlet tubes and mechanical stirrer was thoroughly flamed and purged with nitrogen. To this was added 50 g of polyphosphoric acid, and the viscous material stirred at 150° under nitrogen for 3 hours. The flask was then cooled in ice, opened, and 2.0 g (3.06 mmole) of monomer VII was carefully added. The flask was closed, and the resulting suspension stirred at 90° for 8 hours under nitrogen to hydrolyze the tosylate and ester groups, liberating the diamino-acid monomer. At that point, a clear, brown solution remained. The temperature of the heating bath was then slowly raised over a period of three hours to a maximum of 200°, and was maintained at that level for 8 hours. The dark brown polymer solution was precipitated into a large volume of methanol. Workup in the usual manner afforded a brownish-yellow polymer which exhibited an inherent viscosity of 0.2 dl/g in methanesulfonic acid (0.35 g/dl).

Polymerization of 2-[p-Carboxyphenyl]-5,6-bis(p-toluenesulfonamido)benzimidazole

A polymerization flask equipped with nitrogen inlet and outlet tubes

and mechanical stirrer was thoroughly flamed and purged with nitrogen. To this was added 50 g of polyphosphoric acid, and the viscous material stirred at 150° under nitrogen for 3 hours. The flask was then cooled in ice, opened, and 2.00 g (34.7 mmole) of monomer was carefully added. The flask was closed, and the resulting suspension stirred at 90° for 8 hours under nitrogen to hydrolyze the tosylate groups, liberating the diamino-acid monomer. At that point, a cloudy brown suspension remained. The temperature of the heating bath was then slowly raised over a period of three hours to a maximum of 200°, and was maintained at that level for 8 hours. The dark brown polymer solution was precipitated into a large volume of methanol. Workup in the usual manner afforded a brownish-yellow polymer which exhibited an inherent viscosity of 0.02 dl/g in methanesulfonic acid (0.35 g/dl).

Polymerization of 1,3-Diamino-4,6-(p-toluenesulfamido)benzene IX with Terephthalic Acid in PPA

To 100 g of deoxygenated polyphosphoric acid were added 1.15 g (0.00256 mole) of 1,3-diamino-4,6-(p-toluenesulfamido)benzene and 0.4279 g (0.00256 mole) of terephthalic acid. The mixture was slowly heated (4°/min) to 90°C and maintained at that temperature for six hours. The temperature was then increased at the same rate, 190°C, and maintained at that temperature for sixteen hours. The resulting viscous solution was poured out of the flask at 190°C into a beaker and allowed to cool to room temperature. The polymer was precipitated in methanol, using a blender to facilitate mixing. The fibrous yellow material was washed twice with 1-liter portions of anhydrous methanol methanesulfonic acid and drying in the above manner gave 0.8 g (93%). An intrinsic viscosity

of 4.9 dl/g in 100% methanesulfonic acid was determined. Anal. calcd for $C_{14}H_8N_4$: C, 72.41; H, 3.45; N, 24.14. Found: C, 72.23; H, 3.56; and N, 23.48.

SECTION V

REFERENCES

1. B. K. Daniels, J. Preston, and D. A. Zaubelies (Monsanto Co.), U.S. Patent 3,600,269 (1971).
2. S. L. Kwolek (E. I. duPont deNemours & Co., Inc.), U.S. Patent 3,671,542 (1972).
3. D. C. Raia, Plastic World, Dec. 17, (1973).
4. H. Vogel and C. S. Marvel, J. Polymer Sci., 50, 511 (1961).
5. Y. Iwakura, K. Uno, and Y. Iami, J. Polymer Sci., A 2, 2605 (1964).
6. F. E. Arnold, J. Polymer Sci., A 1, 2079 (1970).
7. F. L. Hedberg, AFML-TR-72-267 (1973).

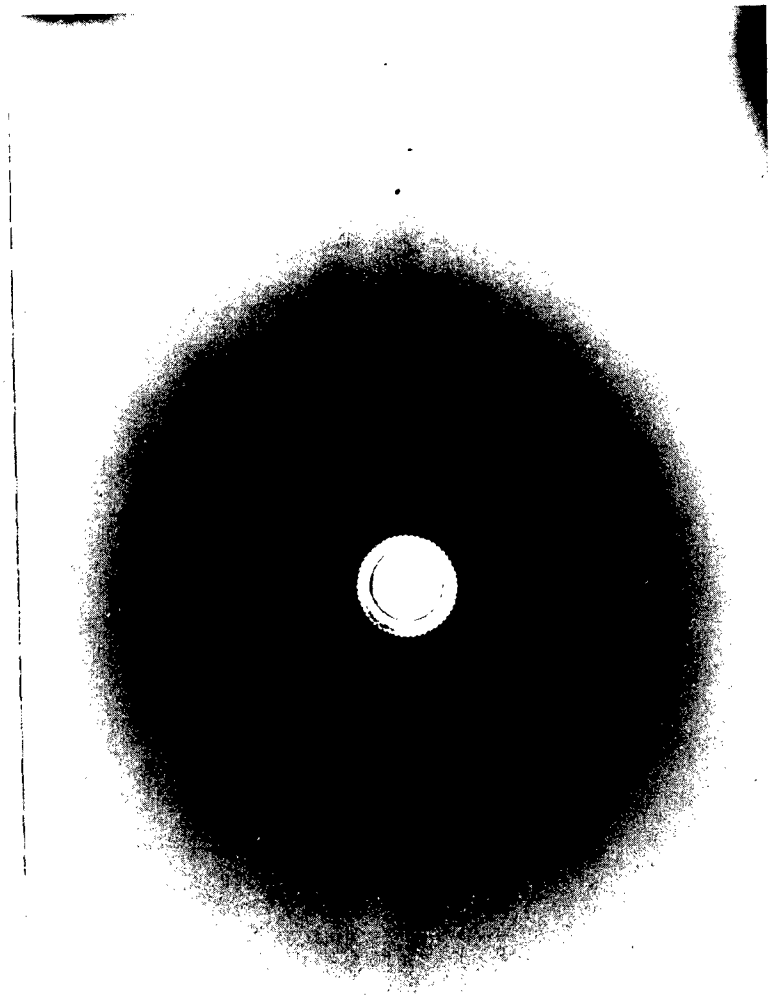


FIGURE 1. X-RAY DIFFRACTION PATTERN OF ACID INSOLUBLE POLYMER

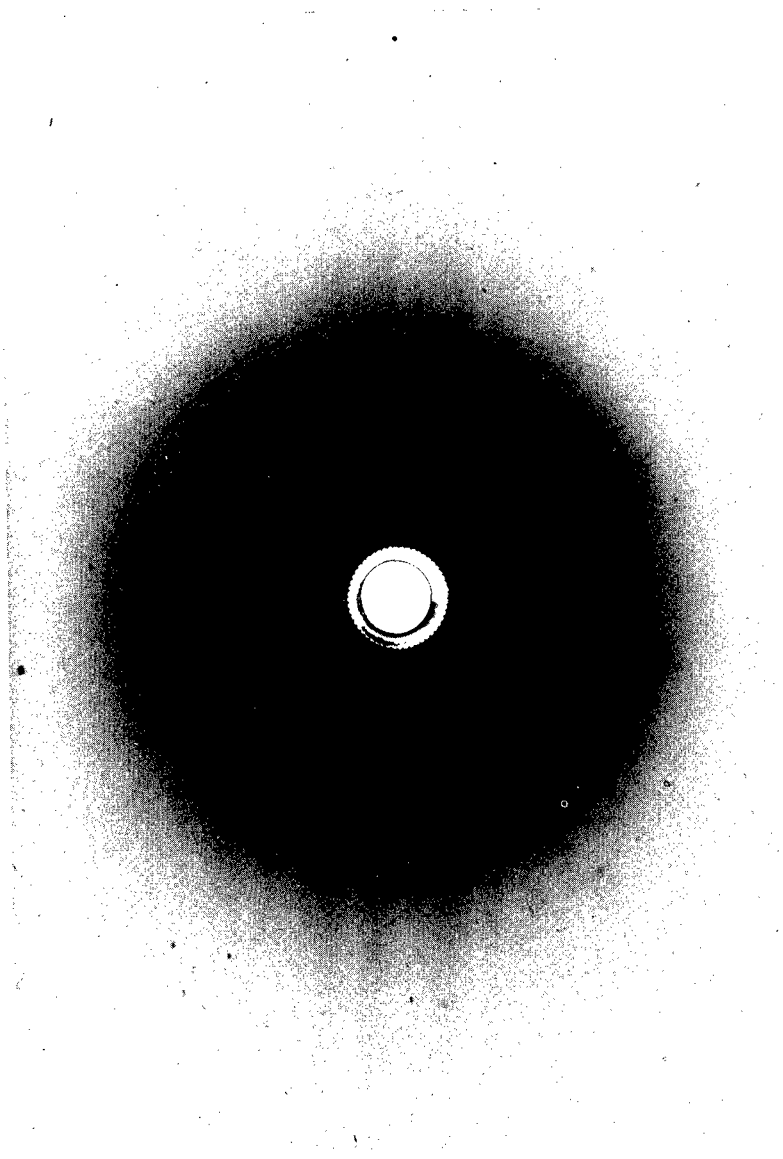


FIGURE 2. X-RAY DIFFRACTION PATTERN OF ACID SOLUBLE POLYMER

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