JOURNAL OF POLYMER SCIENCE: PART A VOL. 2, PP. 5005-5016 (1964)

2,7-Disubstituted 1,3,6,8-Tetraazopyrene and Related Polymers

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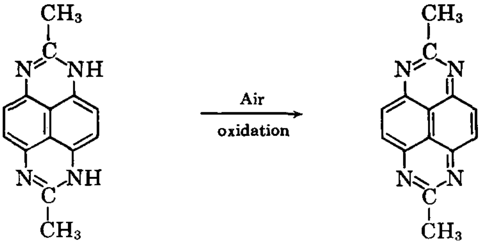
Synopsis

2,7-Disubstituted derivatives of 1,3,6,8-tetraazopyrene were synthesized as model compounds for some polymers of similar structure. Conjugated and high molecular weight polymers were obtained by polycondensation of 1,4,5,8-tetraaminonaphthalene with various diphenyl esters of bifunctional aromatic acids. The inherent viscosities of a number of polymers ranged from approximately 0.15 to 0.70. Most of the polymers are infusible and some of them are insoluble in the usual organic solvents. The thermal stability properties of the polymers were very good.

Many years ago, Dimroth and Roos[1] observed the formation of a tetraazopyrene compound by the reduction of tetranitronaphthalene in formic acid solution by the use of stannous chloride followed by oxidation with ferric chloride.

By catalytic reduction of 1,4,5,8-tetranitronaphthalene in a mixture of acetic acid and acetic anhydride, we obtained a product which presumably has structure (I) which on isolation in air was oxidized to the interesting condensed heterocyclic compound (II).



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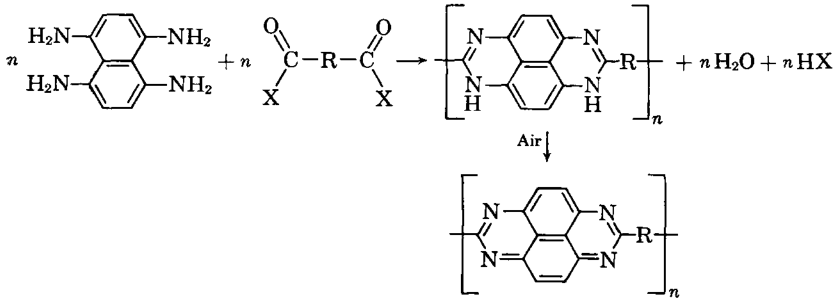
We were able to synthesize the dimethyl- and diphenyl-tetraazopyrene by interaction of the reduction product of 1,4,5,8-tetranitronaphthalene with the phenyl esters of acetic and benzoic acids.

In order to prepare a conjugated and thermally stable polymer, we investigated this condensation reaction with some bifunctional aromatic reagents:



(2)

where X is Cl or OC_6H_5 and R is the aromatic nucleus.

DISCUSSION

2,7-Dimethyl-1,3,6,8-Tetraazopyrene

Catalytic reduction of 1,4,5,8-tetranitronaphthalene in a mixture of acetic acid and acetic anhydride yielded a brownish compound (I), melting at 260°C. with decomposition. This product oxidized spontaneously when recrystallized from alcohol in the air to yield 2,7-dimethyl-1,3,6,8-tetraazopyrene (II).

The same reaction products were obtained by interaction of a solution of 1,4,5,8-tetraaminonaphthalene with phenyl acetate, but all attempts to employ acetyl chloride in this condensation reaction failed because of some side reactions of the amino groups with the acid chloride functions.

The 2,7-dimethyl-1,3,6,8-tetraazopyrene was obtained as yellow needles subliming without decomposition at a temperature above 280°C. The compound is very slightly soluble in diethyl ether and cold ethanol; it is slightly soluble in acetone, chloroform, carbon tetrachloride, sulfuric acid, boiling ethanol and dimethylsulfoxide; it can be recrystallized from the latter solvents. It is soluble to the extent of 6% by weight in cold formic acid.

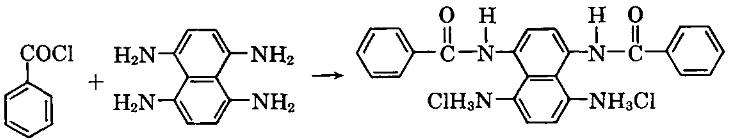
The infrared spectrum showed aromatic C—H stretching vibration at 3050 cm.$^{-1}$, bands associated with aromatic C═C and C═N at 1570, 1550, 1500, and 1490 cm.$^{-1}$, methyl group hydrogen atoms at 1355 and 1345 cm.$^{-1}$, and C—H out-of-plane deformation vibration associated with two adjacent free hydrogen atoms in an aromatic system at 855 cm.$^{-1}$.

In concentrated sulfuric acid solution the ultraviolet absorption was as follows: 400 mμ (ϵ = 9,360), 335 mμ (ϵ = 9,360), 330 mμ (ϵ = 5,610), 320 mμ (ϵ = 4,910), and 227 mμ (ϵ = 25,100).

Without success, we tried to show by nuclear magnetic resonance spectrometry the presence of the quinone cycle due presumably to the oxidation of the compound in air as the solubility of 2,7-dimethyl-1,3,6,8-tetraazopyrene in carbon tetrachloride or in deuterated dimethylsulfoxide is too low.

2,7-Diphenyl-1,3,6,8-Tetraazopyrene

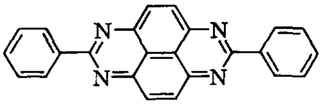
When the reaction is carried out with benzoyl chloride, only a partial condensation seems to occur, probably due to salt formation on the adjacent amino groups.



III (3)

Indeed, the elementary analysis of the reaction product agrees with the structure (III); further, the infrared spectra show an absorption band at 1755 cm.$^{-1}$, frequency characteristic of carbonyl groups.

By condensation of 1,4,5,8-tetraaminonaphthalene with phenyl benzoate, we were able to synthesize the model compound, 2,7-diphenyl-1,3,6,8-tetraazopyrene (IV):



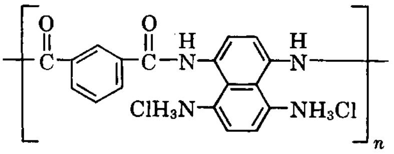
IV

This compound is a brown powder not melting below 300°C. and having about the same solubility characteristics as the dimethyl derivative; however, its purification was more difficult because the diphenyl derivative does not sublime. The infrared spectra showed absorption at 3050 cm.$^{-1}$ (aromatic C-H), 1570, 1550, 1500, and 1490 cm.$^{-1}$ (aromatic C=C and C=N), 855 cm.$^{-1}$ (aromatic C—H; 2 adjacent free H) and 765 and 635 cm.$^{-1}$ (aromatic C—H; 5 adajcent free H).

In concentrated sulfuric acid, the ultraviolet absorption was as follows: 400 mμ (ϵ = 7,160), 337 mμ (ϵ = 15,400), 315 mμ (ϵ = 16,700), 263 mμ (ϵ = 31,100), 235 mμ (ϵ = 30,000), and 220 mμ (ϵ = 50,800).

Polytetraazopyrenes with Mixed Aromatic Units

Several attempts to synthesize polymers from tetraaminonaphthalene and isophthaloyl chloride, in solution or in melt, failed to yield the expected polymers; indeed, as previously reported for the reaction with benzoyl chloride, only a partial polycondensation with the tetraamino compound occurred to yield a low molecular weight (intrinsic viscosity 0.020–0.025) polymer which appeared to be the amide hydrochloride (V).

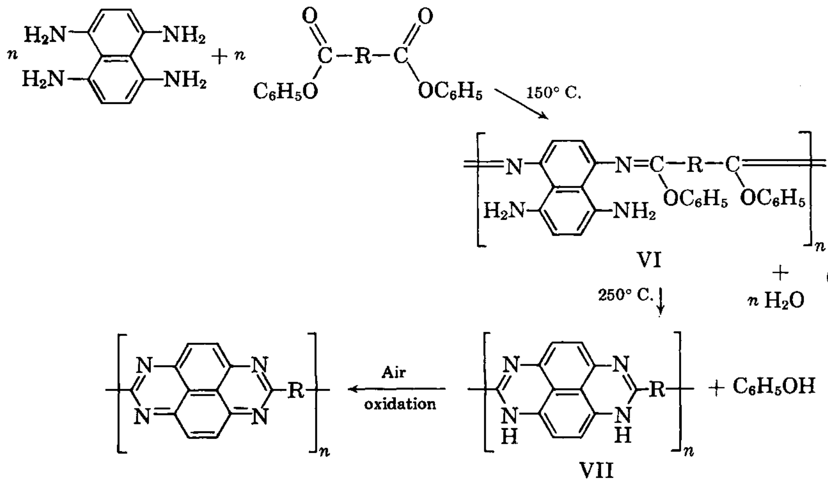


V

The ring closure did not take place, however. Further, we observed a great deficiency in nitrogen in most of the products, due probably to some oxidation reactions of the amine or amine hydrochloride groups with loss of nitrogen.

High molecular weight materials were obtained by heating together the 1,4,5,8-tetraaminonaphthalene and various diphenyl esters of aromatic dibasic acids, at high temperatures in an inert atmosphere.

According to the proposed reaction mechanism for the polybenzimidazoles,[2,3] the polycondensations of 1,4,5,8-tetraminonaphthalene with diphenyl esters are as shown in eq. (4):



(4)

where R is isophthalic, terephthalic, 2,6-naphthalenic, or oxybisbenzoic nucleus.

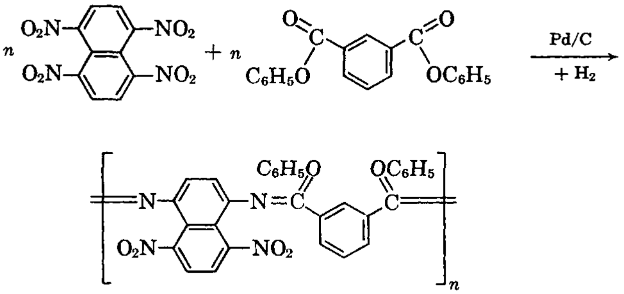
These polymers are brown or black powders, not melting below 400°C., with inherent viscosities ranging from 0.15 to 0.70; their infrared spectra showed the same absorptions as 2,7-diphenyl-1,3,6,8-tetraazopyrene, the only differences observed being at the frequencies characteristic of the aromatic nucleus R. The soluble polymer fractions in concentrated sulfuric acid showed wide ultraviolet absorptions with maxima located around 355, 290, and 276 mμ for the polymers synthesized from diphenyl isophthalate, and at 350, 285, 261, and 235 mμ for those synthesized from diphenyl terephthalate.

The condensations were initiated at temperatures around 150°C. to yield a polymer having presumably the structure VI, but the intramolecular cyclization reaction occurred only at higher temperatures; for example, the reaction carried out at a temperature below 200°C. yielded a polymer containing a great amount of oxygen and the infrared spectrometry showed the presence of some primary NH_2 groups (absorption at 3450 and 3300 $cm.^{-1}$).

However, the oxygen content of the polymers was much lower and the inherent viscosity was higher when the condensation reaction was carried out at a temperature over 250°C. or when the polymer synthesized at low temperature was reheated over 300°C. under vacuum.

The decrease of oxygen content due to the intramolecular condensation involves a diminution of solubility of the polymers. We observed that the polymers containing more than 6% oxygen are slightly soluble in diglyme, benzene, and chloroform and completely soluble in dimethylformamide, acetamide, and sulfoxide; also it is possible to get some brittle films by evaporation of the solutions. When the oxygen content is lower than 6%, the polymers are insoluble in the usual organic solvents, but soluble in concentrated sulfuric acid. Sometimes only a partial solubility of these polymers in concentrated sulfuric acid was observed, probably due to the formation of some crosslinks by intermolecular elimination of phenol.

Further, it was observed that it is better to carry out the reaction in two parts: first, the reduction of 1,4,5,8-tetranitronaphthalene; and second, the polycondensation of the unstable tetraamino compound with the diester. When the reduction of the tetranitro compound is carried out in the presence of the ester, we obtained primarily a polymer having a higher oxygen content than that of the samples prepared in two steps at the same reaction temperature. Presumably, when the reduction is carried out in the presence of the diester component there is some partial condensation of the ester with the amino groups before the reduction of the tetranitro compound, and then the steric hindrance of the preformed chain prevents the completion of the reduction and condensation.



(5)

In some samples, infrared absorptions at 1550 and 1350 $cm.^{-1}$, frequencies due to the valence vibration of $R_3C—NO_2$ bonds, were observed.

We have also noted that whatever the experimental conditions, a polymer sample free of oxygen was never obtained; the oxygen content is too high to be ascribed to the presence of ester groups only at the end of the chain.

From the viscosity data we can estimate a molecular weight of 10,000 as a minimum, and in this case the oxygen percentage due to the presence of two terminal ester groups should be equal only to 0.64%, whereas the found average content of oxygen is 2.5%. There seem to be some failures in the ring closure along the chain due to small amounts of trinitro compound in the starting material or of a tetranitro isomer other than the 1,4,5,8.

The thermal stability of the polymers has been studied by thermogravimetric analysis (TGA).

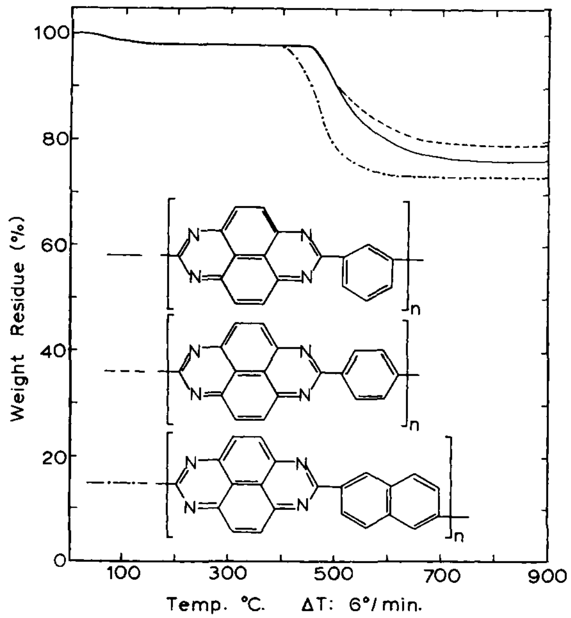


Fig. 1. TGA in nitrogen.

TGA was performed in a commercial Stanton thermobalance; a flowing nitrogen or air atmosphere was used. As it appears from the TGA curves presented in Figure 1 and 2, the polymers synthesized from diphenyl isophthalate or terephthalate have almost identical TGA curves; they showed a similar initial loss of about 2% in weight up to 410°C., followed by 22% loss up to 840°C. in a nitrogen atmosphere. TGA in air showed an initial loss of 1% from room temperature up to 340°C. and a rapid loss of 98% between 340°C. and 710°C. The polymer synthesized from diphenyl-2,6-naphthalenedicarboxylate showed an initial weight loss of less than 1% from room temperature up to 170°C. It lost 26% between 390° and 850° C. in nitrogen and 99.5% between 360 and 780°C. in air.

Seemingly, these new polymers are slightly less thermally stable than aromatic polybenzimidazoles in either nitrogen or air,[2] when we consider the starting temperatures of decomposition.

Electron spins resonance studies of the solid polymers or solutions in dimethylacetamide of the soluble fractions have shown that these high conjugated polymers contained from 1.9 to 9.7 × 10^{19} spins/g. The radicals are not trapped in the solid but are present on the polymer chains as is shown by the fact that a signal was observed in the polymer solutions. However, it was not possible to get information about the location of the free electrons on the carbon or nitrogen atoms from the structure of the observed ESR signals because of the low resolution of these signals due to some interactions through the polymer chains.

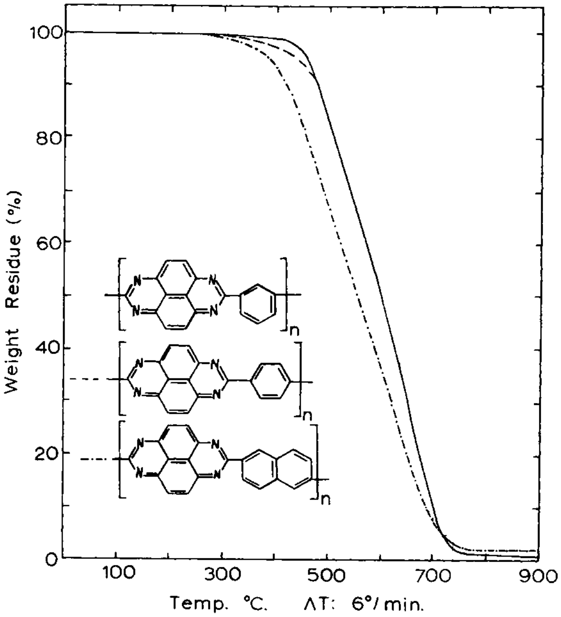


Fig. 2. TGA in air.

An ESR signal was also observed in dimethylacetamide solutions of the model compound, the 2,7-diphenyl-1,3,6,8-tetraazopyrene.

Room temperature resistivities and dielectric constants were determined on the polymers prepared from isophthalic, terephthalic, and 2,6-naphthalene dicarboxylic acids. The results (Table I) are typical of insulating organic polymers.

TABLE I

Polymer	Resistivity, ohm-cm.	Dielectric constant
Isophthalic derivative (flake)	1×10^{15}	3 (100 Mcycles)
Terephthalic derivative (flake)	5×10^{13}	4 (100 Mcycles)
2,6-Naphthalene nucleus (flake)	2×10^{14}	3 (100 Mcycles)

EXPERIMENTAL

Monomers

1,4,5,8-Tetranitronaphthalene. The tetranitronaphthalene was synthesized by nitration of 1-nitronaphthalene[4] in 52% yield. The 1,4,5,8-isomer was isolated from the mixture by extraction with boiling acetone (16 ml./g.) in a total yield of 18.4%. The product does not melt below 350°C. but partially decomposes at about 315–320°C.

ANAL. Calcd. for $C_{10}H_4N_4O_8$: C, 39.00%; H, 1.30%; N, 18.10%; O, 41.60% Found: C, 39.24%; H, 1.35%; N, 17.05%.

Phenyl Acetate, Phenyl Benzoate, Diphenyl Isophthalate and Terephthalate. The commercial esters (Eastman Kodak Company) were recrystallized twice from methanol with application of decolorizing Darco.

Diphenyl Naphthalene-2,6-dicarboxylate. 2,6-Naphthalenedicarboxylic acid chloride was synthesized by heating 2,6-naphthalenedicarboxylic acid with a mixture of phosphorus pentachloride and phosphorus oxychloride, and recrystallized from benzene (70% yield).

The diphenyl ester was obtained by heating the acid chloride with phenol; the reaction product was recrystallized twice from methanol with application of decolorizing Darco. The overall yield of diphenyl naphthalene 2,6-dicarboxylate was 35%; m.p. 215–216°C.

ANAL. Calcd. for $C_{24}H_{18}O_4$: C, 78.33%; H, 4.38%; O, 7.09%. Found: C, 78.18%; H, 4.51%.

Diphenyl Oxybisbenzoate. The diphenyl oxybisbenzoate was synthesized by Burdick and Jackson Laboratories by oxidation of the dimethyl derivative, followed by esterification of the diacid. The compound (m.p. 185–187°C.) was used without further purification.

Model Compounds

2,7-Dimethyl-1,3,6,8-tetraazopyrene. To a suspension of 800 mg. of 1,4,5,8-tetranitronaphthalene in 100 ml. of a mixture of equal parts of glacial acetic acid and acetic anhydride were added 200 mg. of palladium catalyst on charcoal and this mixture was shaken in a pressure flask for about 40 hr. at 50°C. with hydrogen under a pressure of 50 psi. The mixture was filtered and the solution was evaporated to dryness under reduced pressure. The brown residue was sublimed twice under reduced pressure and then recrystallized several times from ethanol. After recrystallization, the product was again sublimed at 280°C. without melting or decomposition. The yield of yellow needles was 40% of the theoretical amount.

ANAL. Calcd. for $C_{14}H_{10}N_4$: C, 71.78%; H, 4.30%; N, 23.92%. Found: C, 72.03%; H, 4.33%; N, 23.66%.

The same tetraazopyrene derivative was also synthesized from phenyl acetate.

A suspension of 616 mg. of 1,4,5,8-tetranitronaphthalene and 100 mg. of palladium catalyst on charcoal in 20 ml. of diglyme (bis-2-methoxy ethyl ether, purified by distillation on lithium aluminum hydride, b.p. 160–163° C.) was shaken for 45 hr. at 50°C. with hydrogen under a pressure of 50 psi. The reaction mixture was then filtered through a sintered glass, avoiding any contact with the atmosphere, and the filtrate was added, under nitrogen, to a solution of 544 mg. of phenyl acetate in 10 ml. of diglyme (molar ratio ester/nitro = 2). This mixture was heated at about 110°C. under an inert atmosphere for 2 hr. and then the diglyme was removed by distillation. The residue was heated at 200°C., under reduced pressure, for 1 hr., and then recrystallized from ethanol and purified as previously reported.

The yield of yellow needles was 36% of the theoretical amount.

ANAL. Found: C, 71.50%; H, 4.29%; N, 23.55%.

2,7-Diphenyl-1,3,6,8-tetraazopyrene. A suspension of 616 mg. of 1,4,5,8-tetranitronaphthalene and 100 mg. of palladium catalyst on charcoal in 20 ml. of diglyme was shaken for 45 hr. at 50°C. with hydrogen under a pressure of 50 psi. The reaction mixture was then filtered under inert atmosphere and the filtrate added to a solution of 793 mg. of phenyl benzoate in 10 ml. of diglyme (molar ratio ester/nitro = 2). This mixture was heated at about 110°C., under nitrogen for 2 hr., the solvent was removed by distillation and the brown residue heated at 300°C. under reduced pressure for 1 hr. The reaction product was purified by dissolution in dimethyl sulfoxide and precipitation in ice cold methanol. It was then washed several times with diethyl ether and dried at 0.1 mm. Hg to a constant weight to give a 40% yield. The product did not melt below 350°C.

ANAL. Calcd. for $C_{24}H_{14}N_4$: C, 80.44%; H, 3.91; N, 15.50%. Found: C, 79.14%; H, 5.14%; N, 13.77%.

Polycondensations

Polymers from Diphenyl Isophthalate. (*a*) In a pressure flask 616 mg. of 1,4,5,8-tetranitronaphthalene and 100 mg. of palladium catalyst on charcoal in 30 ml. of diglyme were shaken with 632 mg. of diphenyl isophthalate (molar ratio ester/nitro = 1) under 50 psi of hydrogen.

The polymer was isolated by distillation of the solvent, dissolution of the residue in dimethylacetamide or dimethyl sulfoxide, filtration to separate the reduction catalyst and precipitation of the filtrate in a alcohol–water mixture or in benzene. The polymer was then washed several times with methanol and diethyl ether and dried at 0.1 mm. Hg to a constant weight.

The reaction carried out at 130°C. for 65 hr. yields a polymer fractionated in two parts: (*1*) a fraction soluble in diglyme (71% yield; inherent viscosity in dimethylacetamide = 0.15. Anal: C, 65.38%; H, 4.83%; N, 11.68%; O, 13.53%); and (*2*) a fraction insoluble in diglyme but soluble in dimethylacetamide (11% yield; inherent viscosity in dimethylacetamide = 0.28. Anal.: C, 59.09%; H, 4.26%; N, 16.40%).

When the reduction was carried out at 130°C. for 28 hr., and the reaction mixture was heated under reduced pressure at 280°C. for 3 hr., there was obtained a 60% yield of a polymer soluble in dimethylsulfoxide (inherent viscosity in DMSO = 0.47; Anal.: C, 71.66%; H, 3.25%; N, 16.40%) and a 21% yield of insoluble material.

Finally, at the same reduction temperature for 50 hr. and an additional heating of the reaction mixture under nitrogen at about 350°C. for 5 hr., the yield was 32% of polymer soluble in DMSO (inherent viscosity in DMSO = 0.70. Anal.: C, 73.20%; H, 4.07%; N, 15.33%; O, 8.78%) and 48% of insoluble polymer (Anal.: C, 73.26%; H, 3.84%; N, 18.00%; O, 7.57%).

ANAL. Calcd. for $(C_{18}H_{10}N_4)_n$: C, 77.14%; H, 2.86%; N, 20.00%.

The yields were calculated on the basis of the theoretical structure $(C_{18}H_{10}N_4)_n$, and several values are probably too high on account of the presence of some residual oxygen in the polymers as it was shown by the elementary analysis.

(*b*) A suspension of 1.232 g. of 1,4,5,8-tetranitronaphthalene and 200 mg. of palladium catalyst on charcoal in 20 ml. of diglyme was shaken with hydrogen under a pressure of 50 psi at 50°C. for 46 hr. The reaction mixture was then filtered under an inert atmosphere and the filtrate was added to a solution of 1.264 g. of diphenyl isophthalate in 10 ml. of diglyme (molar ratio ester/nitro = 1). This solution was heated at 180°C. under nitrogen for 3 hr.; then, the diglyme was distilled. The black residue was then heated at 300°C. under reduced pressure for an additional 2 hr. Under such experimental conditions there was obtained 12% of polymer soluble in DMSO (inherent viscosity in DMSO = 0.52 and in concentrated sulfuric acid 0.50. Anal.: C, 73.00%; H, 3.84%; N, 16.71%; O, 5.40%) and 60% of polymer insoluble in DMSO (inherent viscosity in concentrated H_2SO_4 = 0.66. Anal.: C, 75.22%; H, 3.10%; N, 18.63%; O, 2.40%).

Polymers from Diphenyl Terephthalate. (*a*) 1,4,5,8-Tetranitronaphthalene (616 mg.) and 100 mg. of palladium catalyst on charcoal in 40 ml. of diglyme were shaken with 632 mg. of diphenyl terephthalate at 60°C. for 48 hr. under 50 psi hydrogen pressure. The diglyme was then distilled off under nitrogen and the residue heated at 200°C. for 1 hr. under reduced pressure. This experimental procedure yields 73% of polymer soluble in DMSO with an inherent viscosity in DMSO of 0.24.

(*b*) A suspension of 1.232 g. of 1,4,5,8-tetranitronaphthalene and 200 mg. of palladium catalyst on charcoal in 30 ml. of diglyme was shaken at 50°C. for 40 hr. with hydrogen under a pressure of 50 psi. The reaction mixture was then filtered under an inert atmosphere and the filtrate added to a solution of 1.264 g. of diphenyl terephthalate in 10 ml. of diglyme and heated at 170°C. under nitrogen for 3 hr. The diglyme was distilled off and the residue was heated at 300°C. under reduced pressure for 2 hr.

to yield 31% of soluble polymer (inherent viscosity in DMSO = 0.46. Anal.: C, 72.63%; H, 3.96%; N, 11.12%; O, 9.72%) and 62% polymer insoluble in DMSO, but soluble in concentrated sulfuric acid (inherent viscosity in concentrated H_2SO_4 = 0.60. Anal.: C, 75.33%; H, 3.94%; N, 18.20%; O, 2.55%).

ANAL. Calcd. for $(C_{18}H_{10}N_4)_n$: C, 77.14%; H, 2.86%; N, 20.00%.

(*c*) An attempt to promote the intramolecular cyclization at a lower temperature by carrying out the polycondensation in the presence of an organic base was unsuccessful. For example, the reduction product of 1,4,5,8-tetranitronaphthalene in diglyme solution was heated at 120°C. for 25 hr. with diphenyl terephthalate in the presence of pyridine, but almost all of the starting material was recovered.

Polymers from Diphenyl 2,6-Naphthalenedicarboxylate. A solution of 1.432 g. of diphenyl 2,6-naphthalenedicarboxylate in 20 ml. of diglyme was added to a solution of the reduction product of 1.232 g. of 1,4,5,8-tetranitronaphthalene in 40 ml. of diglyme (molar ratio ester/nitro = 1). The mixture was heated at 250°C. under nitrogen for 3 hr. and the solvent removed by distillation. The residue was then heated at 300°C. under reduced pressure for 2 hr. to give a yield of insoluble, black polymer of 73%.

ANAL. Calcd. for $(C_{22}H_{12}N_4)_n$: C, 79.50%; H, 3.70%; N, 16.80%. Found: C, 77.04%; H, 4.63%; N, 15.56%.

Polymers from Diphenyl 4,4-Oxybisbenzoate. A solution of 820 mg. of diphenyl oxybisbenzoate in 10 ml. of diglyme was added to a solution of the reduction product of 616 mg. of 1,4,5,8-tetranitronaphthalene in 25 ml. of diglyme (molar ratio ester/nitro = 1). The mixture was heated at 250°C. under nitrogen for 3 hr. and the solvent was distilled off. The residue was then heated at 300°C. under reduced pressure for 2 hr. A low melting (186°C.) and easily soluble polymer was obtained in a 13% yield (inherent viscosity in DMSO = 0.13. Anal.: C, 73.42%; H, 4.75%; N, 10.08%; O, 9.24%).

The yield of polymer not melting below 350°C. and insoluble in usual solvents, but slightly soluble in concentrated sulfuric acid was 50%. The inherent viscosity of this polymer in concentrated H_2SO_4 was 0.34.

ANAL. Calcd. for $(C_{24}H_{14}O)_n$: C, 77.00%; H, 3.70%; N, 15.00%; O, 4.30% Found: C, 76.14%; H, 4.26%; N, 11.98%; O, 6.77%.

The authors wish to express their thanks to Dr. Gordon Tollin, University of Arizona, for help in obtaining and interpreting the electron spins resonance diagram.

For the TGA curves, we wish to thank Dr. W. F. Gresham, Plastics Department, E. I. du Pont de Nemours and Company, Inc.

We are grateful to Mr. J. L. Gillson, Central Research Department, E. I. du Pont de Nemours and Company for determining the resistivities and dielectric constants of our polymers.

One of us (F. Dawans) is indebted for a travel grant from the French Petroleum Institute (Rueil-Malmaison, France).

The financial support of the Plastics and Textile Fibers Departments of E. I. du Pont de Nemours and Company, Inc., is gratefully acknowledged.

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Résumé

Des dérivés 2,7-disubstitués du tétraazopyréne 1,3,6,8 ont été synthétisés comme composés modèles pour des polymères de structure similaire. Des polymères entièrement conjugués et de poids moléculaires élévés ont été obtenus par polycondensation du naphthalène 1,4,5,8-tetraaminé avec divers esters phényliques d'acides aromatiques bifonctionnels. Les viscosités inhérentes de ces polymères sont de l'ordre de 0.15 à 0.70. La plupart de ces polymères sont infusibles et certains d'entre eux sont insolubles dans les solvants classiques. La stabilité thermique de ces polymères s'est révélée être bonne.

Zusammenfassung

2,7-Disubstituierte Derivate von 1,3,6,8-Tetraazopyren wurde als Modellverbindung für einige Polymere mit ähnlicher Struktur synthetisiert. Konjugierte Polymere mit hohem Molekulargewicht wurden durch Polykondensation von 1,4,5,8-Tetraaminonaphthalin mit verschienen Diphenylestern von bifunktionellen aromatischen Säuren erhalten. Die Viskositätszahl einer Reihe von Polymeren bewegte sich etwa zwischen 0,15 bis 0,70. Die meisten Polymeren sind nicht schmelzbar, und einige sind in den gebräuchlichen organischen Lösungsmitteln unlöslich. Die thermische Stabilität der Polymeren ist sehr gut.

Received February 16, 1964
Revised March 9, 1964