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HIGH-TEMPERATURE POLYAMIDES FROM NEW HEXAHYDROBENZODIPYRROLE MONOMERS

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HIGH-TEMPERATURE POLYAMIDES FROM NEW HEXAHYDROBENZODIPYRROLE MONOMERS

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I. INTRODUCTION

The Army has a high priority program to provide protective clothing to air and tank crewmen who are subject to possible exposure to intense heat and flame as a result of accident or enemy action. Presently available clothing materials derived from synthetic polymeric fibers have been evaluated in laboratory tests and also on full scale mannequins. The mannequins were exposed to fuel fires simulating real situations. These materials are capable of only partially fulfilling the requirements established for these items in regard to time of exposure and thermal protection.

Among several lines of attack on the problem, a notable effort has been an intensive search for new high temperature linear polyamide polymers as the basis for obtaining fibrous textile materials. This paper reports on the synthesis of a new class of heterocyclic polyamides made possible by the successful synthesis and isolation of two new hexahydrobenzodipyrrole monomers, the realization of which has eluded the efforts of other researchers since 1947. These newly prepared monomers reacted readily with diacid chlorides to form polyamides. A number of such polymers has been achieved with a selected group of diacid chlorides and a limited characterization by standard techniques provides data indicating that outstanding thermal properties are possible.

It is proposed to describe other potential uses of these two monomers as the basis for the synthesis of compounds useful in a variety of other military applications.

II. BACKGROUND OF HEXAHYDROBENZODIPYRROLE POLYMERS

There is a rather extensive literature on hexahydrobenzo-

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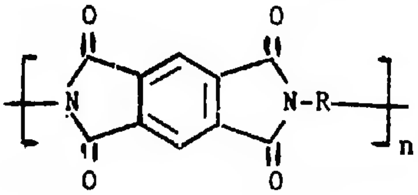
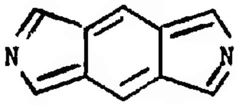
dipyrrole polymers. Two types predominate, the first being the pyromellitimide polymers of the 1,3,5,7-tetroxo- species illustrated below; these are polyamide-imides rather than pure polyamides. The nomenclature of these compounds is based on benzodipyrrole and has been thoroughly discussed by H. Lee (1).

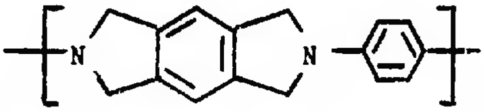


Typical Pyromellitimide Polymer



Benzodipyrrole

The second type of hexahydrobenzodipyrrole polymer was apparently first prepared by Shono et al (2) who condensed 1,2,4,5-tetrakis (chloromethyl)benzene with various aliphatic and aromatic diamines to form linear hexahydrobenzodipyrrole polymers of the diphenylene-dipyrrolino-benzene type shown below. These, however, are polyamines, not polyamides.

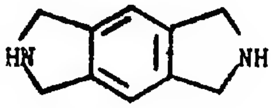


Poly(N,N'-di-phenylene-di-pyrrolino-benzene)

Our search of the literature has failed to reveal products of the type we are describing here, and on this basis we feel that the hexahydrobenzodipyrrole polyamides are the first such to be reported.

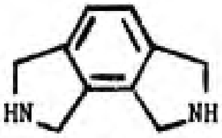
III. RESULTS AND DISCUSSION

The monomers upon which our study is based are isomers having the structures:



I

1,2,3,5,6,7-Hexahydrobenzo(-)
[1,2-c:4,5-c']dipyrrole



II

1,2,3,4,5,6-Hexahydrobenzo(-)
[1,2-c:3,4-c']dipyrrole

The preparation of these monomers and a list of the polymers made therefrom are indicated in Figures 1A, 1B and 2.

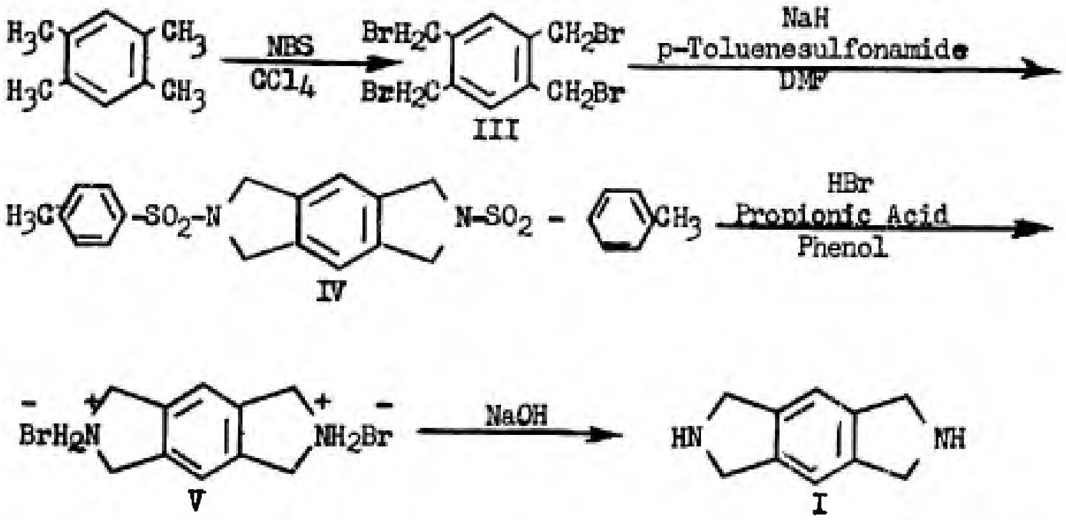


Figure 1A. Synthesis of Monomer I

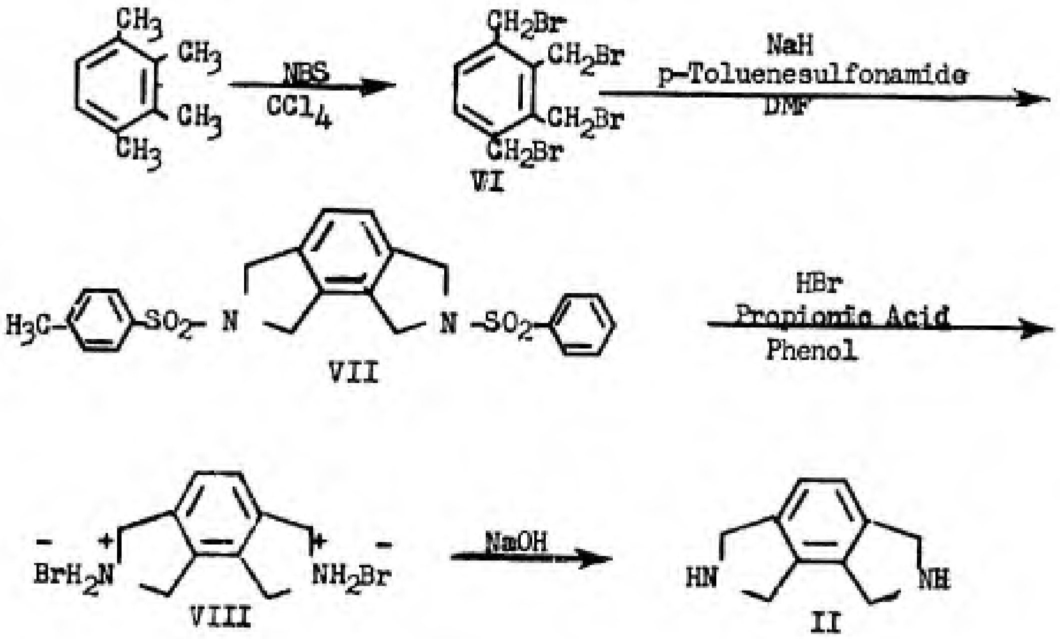
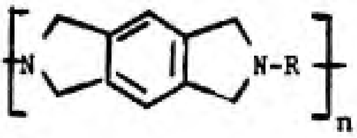
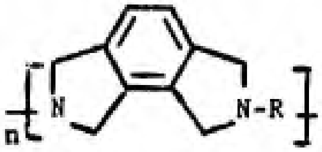


Figure 1B. Synthesis of Monomer II

The initial effort directed to the synthesis of I was made by Ruggli and Geiger (3), but they were unable to isolate the product from their reaction mixture. Our successful synthetic route to this monomer (I) is shown in Figure 1A. A similar procedure was used for the preparation of II. The structures of compounds I and II have been proven by mass, nmr and ir spectroscopy, elemental analysis and by conversion to a number of derivatives characteristic of secondary amines.

Polyamides are prepared from these two monomers by solution condensation with 5 selected acid chlorides as shown in Figure 2 to provide products ranging in structure from partially aromatic to fully aromatic. The less aromatic polymers may be compared to nylon whereas the wholly aromatic type falls within the category of a superpolyamide of which Nomex* presently used in uniforms is





Polymer I	Where R =	Poly(bis-isoindolyl	Polymer II
I-A	$-CO-(CH_2)_4-CO-$	Adipamide	II-A
I-S	$-CO-(CH_2)_8-CO-$	Sebacamide	II-S
I-T	 -CO- CO-	Terephthalamide	II-T
I-I	 -CO CO-	Isophthalamide	II-I
I-P	 CO- CO-	Phthalamide	II-P

Figure 2. Polyamides of I and II

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* Trademark E. I. duPont de Nemours and Company

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representative. This latter product is, in fact, a point of reference in the data which follows.

The reactions for producing these 10 selected polymers were carried out in the temperature range 0 to 3°C. with a molecular ratio of 1:1 of reagents.

Complete characterization of each polymer would prove too costly in both time and effort since the work being reported is directed primarily to the preparation of materials with outstanding thermal and fire protective capabilities. It was decided therefore, to examine those properties which would permit continuing studies of only those materials that afforded the best thermal protection.

1. Solvents

All polyamides in this series were soluble in strong solvents such as 95% sulfuric acid, hexafluoroisopropanol and m-cresol. No other common solvents were found for polymer I-T. For other polymers, viscous spinning dopes were possible from hot dimethyl formamide, dimethyl acetamide, N-methyl pyrrolidone and hexamethylphosphoramide. In solvents such as ethylene diamine and ethylene triamine, gel-formations were common indicating some form of cross-linking.

2. Thermogravimetric Analyses (TGA)

Thermogravimetric analyses were accomplished on all polymers in the temperature range of 0-760°C under nitrogen and at atmospheric pressure. All possess good thermal stability under these conditions as indicated by the data below(Nomex wt. loss, 50%).

Polymer	Wt. Loss (%)	Polymer	Wt. Loss (%)
I-A	76	II-A	76
I-S	65	II-S	75
I-T	62	II-T	49
I-I	63	II-I	49
I-P	57	II-P	60

Thermograms showing temperature versus percent weight loss for both I- and II-type polyamides revealed some interesting details as shown by Figures 3 and 4 respectively. A thermogram of Nomex was run under the same conditions and is included for comparison. Early weight losses are due to release of tightly-bonded water. Generally the onset of decomposition is in the range of 300°C. or higher. Polymer I-I decomposes at a very uniform rate and stands

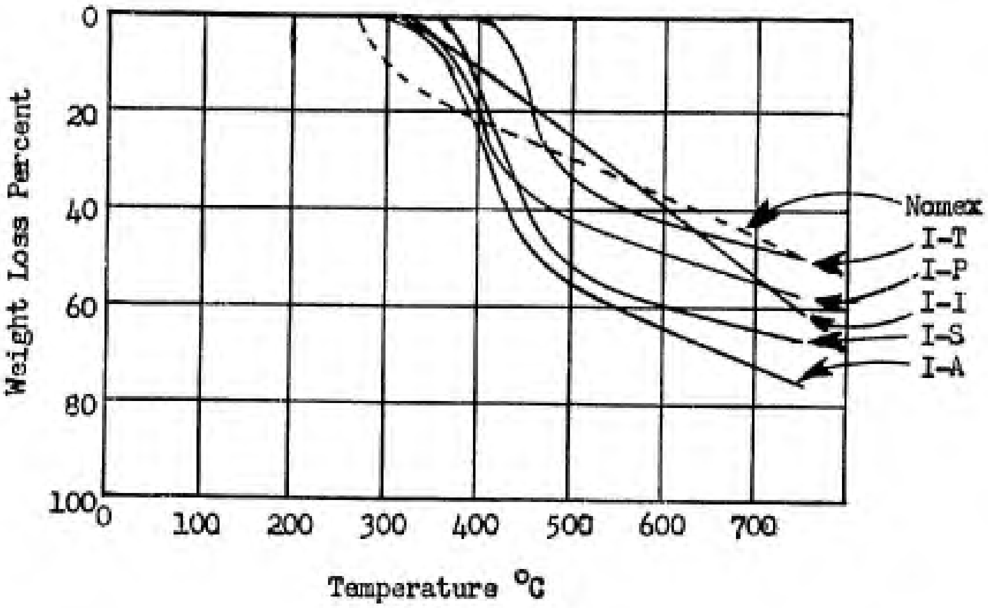


Figure 3 Thermograms of I Polyamides and Nomex

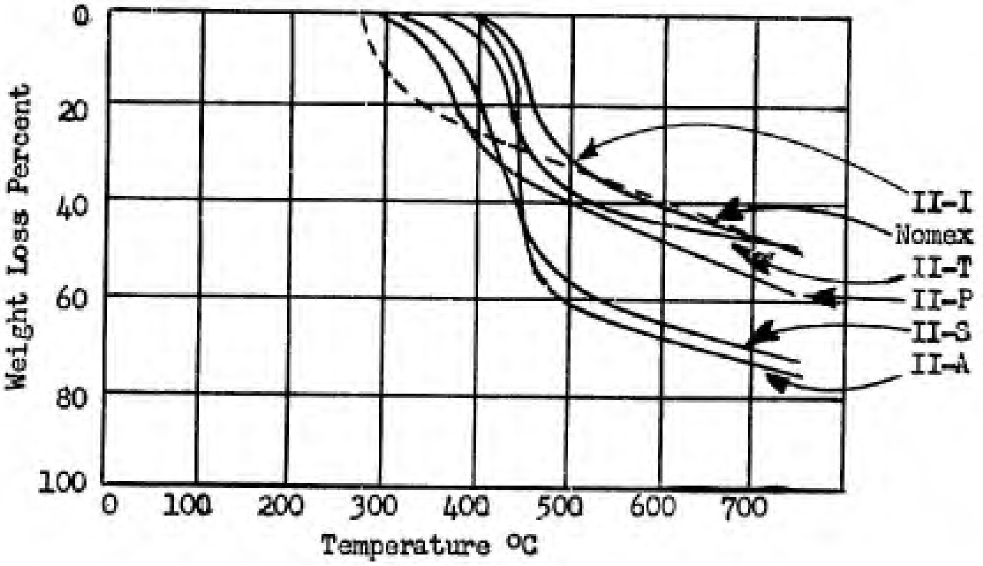


Figure 4 Thermograms of II Polyamides and Nomex

alone in this category. All of the new polymers have thermal properties quite similar to those of Nomex.

3. Differential Thermal Analyses (DTA)

Featureless curves were obtained on untreated I- and II-type polyamides from -50°C to the onset of decomposition points determined by TGA. Thus the absence of crystalline melting points (T_m) and glass transition temperatures (T_g) imply that these types of polymers are amorphous.

4. Melting Points (mp) and Polymer-Melt Temperatures (PMT)

With one exception, I- and II-type polyamides do not have melting points as determined in the usual manner. Generally they undergo decomposition at the high temperatures and swell or intumesce without the display of fluidity. As a result, PMT's were not possible. Polymer I-I does, however, have a melting point coincident with decomposition (306-310°C) and a PMT (300-310°C).

5. Intrinsic Viscosities

Intrinsic viscosities were measured on all polymers of I and II in 95% sulfuric acid at 25°C. The results, which ranged from 0.09 to 0.27 indicate that molecular weights of the polymers prepared thus far are low.

6. Fibers and Films

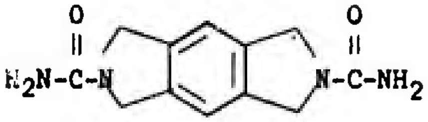
In preliminary experiments, fibers and films were successfully prepared from viscous dopes of these hexahydrobenzodipyrrole polyamides.

Experiments are currently in progress to determine conditions which will provide fibers and films of maximum utility.

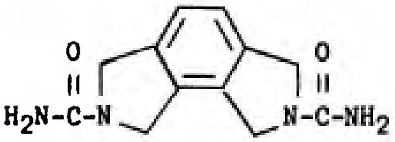
IV. OTHER APPLICATIONS OF MONOMERS I AND II

A. Syntheses of Additional Monomers.

Both monomers I and II have been used to prepare other monomers (5) such as 1,2,3,5,6,7-hexahydrobenzo[1,2-*c*:3,4-*c*'](-)dipyrrole-2,6-dicarboxamide (IX) and 1,2,3,4,5,6-hexahydrobenzo(-)[1,2-*c*:3,4-*c*']dipyrrole-2,5-dicarboxamide (X) shown below. Both should form thermally-stable polyureas.



IX



X

B. Miscellaneous Applications

Structures and chemical reactions of I and II indicate their reactivities to be equivalent to that of piperazine (XI), derivatives of which have innumerable uses. On this basis the synthesis of analogous compounds with military applications is easily visualized. Some examples of the uses of piperazine derivatives which illustrate the potential for derivatives of I and II are impact-resistant nylon (6), wool shrinkproofing agents (7), jet-fuel antistatic additive (8), anthelmintics (9), antispasmodics and anticonvulsants (10), antituberculars (11), cockroach insecticides (12), treatment for hemorrhagic shock (13), antitussives (14) and hypertension control (15).

XI

V. CONCLUSIONS

All polyamides prepared during this study from monomers I and II show good thermal stability as indicated by TGA. Initial properties of the bulk polymers compare favorably with those of Nomex. Variations of the preparation show promise of furnishing products with improved properties.

VI. EXPERIMENTAL DETAILS

Percentages are by weight unless otherwise indicated. Melting points are uncorrected. For infrared spectra, only essential absorption bands are given representing group frequencies. Nuclear magnetic resonance spectra (nmr) are measured in parts per million (σ) downfield from tetramethylsilane as internal standard. Mass spectra are determined at 70 eV. Values for intrinsic viscosity are determined in 95% sulfuric acid at 25°C. TGA are programmed at 20°C per minute in nitrogen flow rate of 9 cc per minute at atmospheric pressure. The preparation of monomer I, including intermediates, is detailed in a Technical Report (see Reference 4) while the synthesis of II has not been previously reported.

1,2,4,5-Tetrakis(bromomethyl)benzene (III) (4)

1,2,3,5,6,7-Hexahydro-2,6-di-(p-tolylsulfonyl)benzo(-)[1,2-*c*:4,5-*c*']dipyrrole (IV) (4)

1,2,3,4,5,7-Hexahydrobenzo[1,2-*c*:4,5-*c*']dipyrrole Dihydrobromide (V) (4)

1,2,3,5,6,7-Hexahydrobenzo[1,2-*c*:4,5-*c*']dipyrrole (I) (4)

1,2,3,4-Tetrakis(bromomethyl)benzene (VI)

A slurry of prehnitene (1,2,3,4-tetramethylbenzene) (67.1 g, 0.50 mol), N-bromosuccinimide (NBS) (356 g, 2.00 mol) and benzoyl peroxide (3 g) in one liter of carbon tetrachloride was refluxed for 2 hr after which insoluble succinimide was filtered from the hot solution. Chilling the solution overnight yielded, after filtering and air-drying, 106.5 g (47.9% of yellow, crude product, mp 104-114°C. For elemental analysis, a sample was recrystallized from 95% ethanol (6 g per 100 ml solvent) and dried overnight (61°C, 10 mm) to yield colorless crystals, mp 120-122°C.

Anal. Calcd for $C_{10}H_{10}Br_4$: C, 26.70; H, 2.24; Br, 71.06. Found: C, 27.13; H, 2.37; Br, 70.03

1,2,3,4,5,6-Hexahydro-2,5-di-(p-tolylsulfonyl)benzo(-) 1,2-*c*:3,4-*c*' dipyrrole (VII)

To a stirring mixture of an excess of sodium hydride (54% of dispersed in mineral oil, 5.55 g, 0.125 mol) in 30 ml of purified DMF, at room temperature and under dry nitrogen, was added dropwise a solution of an excess of p-toluenesulfonamide (21.4 g, 0.125 mol) in 75 ml DMF during 1-1/4 hr. The resulting suspension was stirred an additional 1 hr at room temperature and subsequently 1 hr on a water bath at 65-70°C. A solution of VI (11,3 g, 0.025 mol) in 100 ml DMF was then added dropwise to the mixture over a 1 hr

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period with continued vigorous stirring and the bath temperature maintained at 65-70°C. Near the end of the addition, all particles had dissolved. Removing the bath, stirring continued until the solution reached room temperature. The solution was then filtered and poured on 750 ml of ice water and the resulting precipitate filtered off and washed five times with cold water. The crude product, VII, was recrystallized from a 75:25 mixture of n-butanol and 95% ethanol and dried overnight (120°C, 10 mm) to afford a fine, white crystalline material (8.89 g, 76.5%), mp 228-240°C dec; ir (KBr) 1160 and 1345 (C-SO_2-N); nmr (DMSO) σ 1.35 (s,6,CH_3), 3.59 (s,8, CH_2) 6.09 (s,2,ø-H), 6.78-6.34 (m,8,ø-H).

1,2,3,4,5,6-Hexahydrobenzo[1,2-*c*:3,4-*c*']dipyrrole dihydrobromide (VII)

A stirring mixture of VII (4.68 g, 0.01 mol), phenol (6.4 g), 48% hydrobromic acid (77 ml) and propionic acid (33 ml) was refluxed for 55 hr. After evaporation of solvents, the dry residue was dissolved in a minimum of water. Five washings with ether to remove phenols also removed the color. Following concentration of the solution to about 1/3 its original volume and refrigeration overnight, a brown precipitate was filtered, taken up in hot absolute methanol, decolorized, acidified with 2 ml hydrobromic acid and chilled overnight to produce, after drying (61°C, 10 mm), 1.23 g (33%) of VII as a fine white powder, mp 268-274°C dec.

Anal. Calcd for $C_{10}H_{14}Br_2N_2$: C, 37.30; H, 4.38; Br, 49.63; N, 8.69. Found: C, 36.99; H, 4.28; Br, 49.62; N, 8.74.

1,2,3,4,5,6-Hexahydrobenzo[1,2-*c*:3,4-*c*']dipyrrole (II)

A solution of VII (0.717 g, 0.002 mol) was prepared by adding 4-5 drops of carbon dioxide-free water with stirring, followed by addition of 12 drops of 33% sodium hydroxide solution to partly precipitate II. Solution and extraction was accomplished with ten 100-ml portions of ethyl ether followed by drying over anhydrous sodium carbonate overnight. A slightly yellow solid obtained after evaporation of the ether was sublimed (98°C, 8 mm) to give II, (0.204 g, 57%), mp 102-103°C dec; ir 3155 (NH); nmr ($DCCl_3$) σ 2.20 (s,2,NH), 4.22-4.15 (d,8,CH_2), 7.10 (s,2,ø-H);

Poly(N,N'-di-1,2,3,5,6,7-hexahydrobenzo[1,2-*c*:4,5-*c*'](-)dipyrrole adipamide) (I-A)

In a reaction vessel fitted with a jacketed high-speed stirrer and a "T" tube for maintaining a nitrogen atmosphere, a solution of purified I (5 g, 0.031 mol) in 100 ml dry methylene chloride and triethylamine (6.3 g, 0.062 mol) was added. After stirring for two minutes water and dry-ice chunks were placed in the jacket. Stirring continued for 10 minutes or until the solution temperature ranged from 0-3°C. Adipyl chloride (5.6 g, 0.031 mol) in 100 ml methylene chloride was added all at once. After stirring for an additional five minutes the polymer was precipitated by pouring the mixture into 500 ml n-hexane followed by washing successively four times with 200 ml portions of cold water, hot water, acetone and methanol and dried to give I-A (6.4 g, 76%); solvents: DMF, hexafluoroacetone, hexafluoroisopropanol, N-methyl-2-pyrrol-idone, 95% sulfuric acid and m-cresol; TGA 0-760°C, 76% weight loss.

Poly(N,N'-di-1,2,3,5,6,7-hexahydrobenzo[1,2-*c*:4,5-*c*'](-)dipyrrole sebacamide) (I-S)

Following the procedure for I-A above, I (3.87 g, 0.024 mol) and triethylamine (6.3 g, 0.048 mol) in 80 ml methylene chloride were reacted with sebacoyl chloride (5.7 g, 0.02 mol) in 80 ml methylene chloride to give I-S (6.4 g, 82%); solvents: same as in I-A; TGA 0-760°C, 65% weight loss.

Poly(N,N'-di-1,2,3,5,6,7-hexahydrobenzo[1,2-*c*:4,5-*c*'](-)dipyrrole terephthalate) (I-T)

In the apparatus described for I-A, the dihydrobromide salt V (2.17 g, 0.006 mol) was placed and the nitrogen atmosphere system resumed. By a dropper funnel triethylamine (2.68 g, 0.027 mol) in 50 ml methylene chloride was added and the mixture stirred at least five minutes to insure complete solution of the free base I formed by the reaction. After adding water and carbon dioxide pellets to the jacket, the procedure for I-A was followed. Terephthaloyl chloride (1.37 g, 0.006 mol) in 50 ml methylene chloride was added all at once. After washing I-T was obtained (1.06 g, 36.6%); solvents: 95% sulfuric acid, hexafluoroisopropanol and m-cresol; TGA 0-760°C, 62% weight loss; intrinsic viscosity: 0.27

Poly(N,N'-di-1,2,3,5,6,7-hexahydrobenzo[1,2-*c*:4,5-*c*'](-)dipyrrole isophthalamide) (I-I)

Following the procedure of I-T, dry hydrobromide salt V (0.9 g, 0.0028 mol) was reacted with triethylamine (1.13 g, 0.0111 mol) in 22.5 ml methylene chloride and isophthaloyl chloride (0.566 g, 0.0028 g) in 22.5 ml methylene chloride to give I-I (0.82 g, 100%); MP 306-310°C; solvents: same as I-A; TGA 0-760°C, 63% weight loss; PMT 300-310°C; intrinsic viscosity 0.12.

Poly(N,N'-di-1,2,3,5,6,7-hexahydrobenzo[1,2-*c*:4,5-*c*'](-)dipyrrole phthalamide) (I-P)

Following the procedure of I-T, the dry dihydrobromide salt V 0.9 g, 0.0028 mol) was reacted with triethylamine (1.13 g, 0.011 mol) in 22.5 ml methylene chloride and phthaloyl chloride (0.566 g, 0.0028 mol) in 22.5 ml methylene chloride to obtain I-P (0.275 g, 33.9%); solvents: same as for I-A; TGA 0-760°C, 57% weight loss.

Poly(N,N'-di-1,2,3,4,5,6-hexahydrobenzo[1,2-*c*:3,4-*c*'](-)dipyrrole adipamide) (II-A)

Following the procedure of I-T, the dry dihydrobromide salt VI (0.7 g, 0.022 mol) was reacted with triethylamine (0.88 g, 0.0087 mol) in 17.5 ml methylene chloride and adipyl chloride (0.39 g, 0.0022 mol) in 17.5 ml methylene chloride to give II-A (0.49 g, 83%); solvents: same as for I-A; TGA 0-760°C, 76% weight loss.

Poly(N,N'-di-1,2,3,4,5,6-hexahydrobenzo[1,2-*c*:3,4-*c*'](-)dipyrrole sebacamide) (II-S)

Following the procedure of I-T, the dry dihydrobromide salt VI (0.50 g, 0.0016 mol) was reacted with triethylamine (0.65 g, 0.0048 mol) in 17.5 ml methylene chloride and sebacoyl chloride (0.38 g, 0.0016 mol) in 17.5 ml methylene chloride to give II-S (0.23 g, 43%; solvents: same as for I-A; TGA 0-760°C, 75% weight loss.

Poly(N,N'-di-1,2,3,4,5,6-hexahydrobenzo[1,2-*c*:3,4-*c*'](-)dipyrrole terephthalamide) (II-T)

Following the procedure of I-T, the dry dihydrobromide salt VI (1.94 g, 0.006 mol) was reacted with triethylamine (2.49 g, 0.024 mol) in 45 ml methylene chloride and terephthaloyl chloride (1.25 g, 0.006 mol) in 45 ml methylene chloride to obtain II-T (1.79 g, 97.3%); solvents: same as for I-A; TGA 0-760°C, 49% weight loss.

Poly(N,N'-di-1,2,3,4,5,6-hexahydrobenzo[1,2-*c*:3,4-*c*'](-)dipyrrole isophthalamide) (II-I)

Following the procedure of I-T the dry dihydrobromide salt VI (2.99 g, 0.124 mol) was reacted with triethylamine (4.04 g, 0.049 mol) in 100 ml methylene chloride and isophthaloyl chloride (2.03 g, 0.0124 mol) in 100 ml methylene chloride to obtain II-I (3.53 g, 98%); solvents: same as for I-A; TGA 0-760°C, 49% weight loss.

Poly(N,N'-di-1,2,3,4,5,6-hexahydrobenzo[1,2-*c*:3,4-*c*'](-)dipyrrole phthalamide) (II-P)

Following the procedure of I-T the dry dihydrobromide salt VI was reacted with triethylamine (0.99 g, 0.0087 mol) in 17.5 ml methylene chloride and phthaloyl chloride (0.426 g, 0.0022 mol) in 17.5 ml methylene chloride to obtain II-P (0.4 g, 66.4%); solvents: same as for I-A; TGA 0-760°C, 60% weight loss.

VII. ACKNOWLEDGEMENTS

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