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Georgios P. Karayannidis[a]; Irini Sideridou-karayannidou[a]
[a] Laboratory of Organic Chemical Technology, Aristotelian University of Thessaloniki, Thessaloniki, Greece

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Synthesis and Properties of Pyrrones Containing p-Benzoquinone Units

GEORGIOS P. KARAYANNIDIS and IRINI SIDERIDOU-KARAYANNIDOU

Laboratory of Organic Chemical Technology
Aristotelian University of Thessaloniki
Thessaloniki, Greece

ABSTRACT

Novel pyrrones were synthesized by one-stage polycondensation in polyphosphoric acid of 2,3,5,6-tetraamino-1,4-benzoquinone with pyromellitic anhydride, 3,3',4,4'-benzophenonetetracarboxylic dianhydride, 1,4,5,8-naphthalenetetracarboxylic dianhydride, or 3,4,9,10-perylenetetracarboxylic dianhydride. The prepared polymers showed a considerable percentage of imide linkages, so they were heated at 350°C under high vacuum to increase the ring closure to the pyrrone structure. The polymers were insoluble in all common polar aprotic solvents, even in dimethylacetamide-water mixture, after reduction with sodium dithionite, but were slightly soluble in concentrated sulfuric and methanesulfonic acid. The thermal decomposition of the polymers (weight loss 5%) started above 400°C both under nitrogen and in air.

INTRODUCTION

Pyrrones [1] with excellent thermal stability derived from aromatic tetraamines and dianhydrides of aromatic tetracarboxylic acids are insoluble in common organic solvents and are infusible. Partial, or occasionally complete, solubilization can be brought about in concentrated

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sulfuric acid and methanesulfonic acid. The incorporation of anthraquinone recurring units into the polymer chain, by use of 1,2,5,6-tetraaminoanthraquinone [2-5], caused a slight solubility of the polymers in aqueous dimethylacetamide after reduction with alkaline sodium dithionite. However, it was found that these polymers undergo degradation during reduction, resulting in a considerable fall in molecular weight, which is attributed to the significant concentration of imide linkages remaining in the macromolecule as a result of incomplete cyclization [3].

An attempt to prepare a pyrrone containing p-benzoquinone units in the polymer chain by use of 2,3,5,6-tetraamino-1,4-benzoquinone (TABQ) or 2,3,5,6-tetraamino-1,4-hydroquinone tetrahydrochloride (TAHQ·4HCl) and pyromellitic dianhydride (PMDA) or 2,5-dicarbomethoxyterephthaloyl dichloride, as monomers, in a low-temperature (25°C) polycondensation in N,N-dimethylacetamide (DMAc) and thermal treatment (300°C) in a second step, was unsuccessful, yielding the corresponding poly(amino imide) [6].

The present paper is concerned with high-temperature solution polymerization in polyphosphoric acid (PPA) of TABQ with dianhydrides of aromatic tetracarboxylic acids Ia-d (Scheme 1) for preparation of the corresponding pyrrones IIa-d.

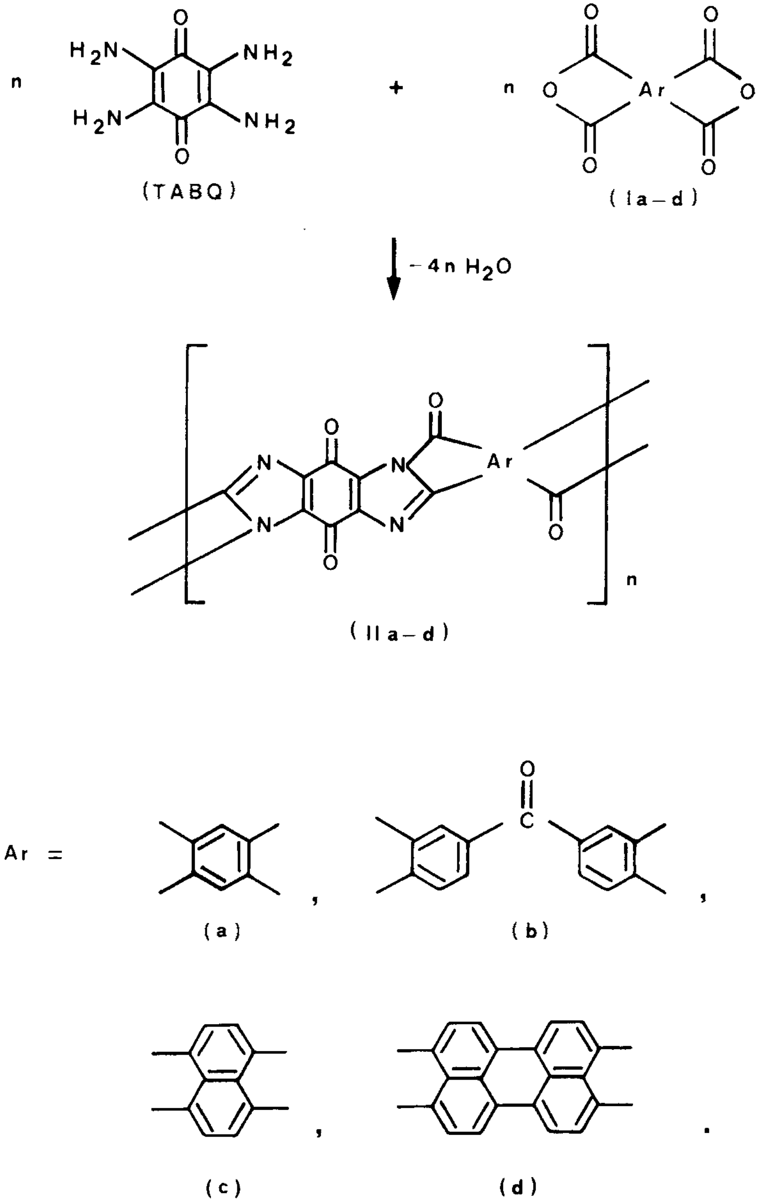
The following dianhydrides were used: PMDA, 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA), and 3,4,9,10-perylenetetracarboxylic dianhydride (PTDA). After polycondensation the polymers were heated at 350°C under vacuum for several hours to complete ring closure of macromolecules.

The preparation of the above polymers was aimed at investigating the possibility of reductive solubilization and also evaluating their thermal stability in nitrogen and air.

EXPERIMENTAL

Measurements

Elemental analysis was carried out with a Perkin-Elmer Model No. 240 instrument. The combustion time was 4 min and precautions were taken to avoid water absorption by the samples. IR spectra were recorded with a Perkin-Elmer spectrophotometer Model No. 281-B in KBr pellets, after mulling of the samples in a freezer mill. The UV spectra were measured on concentrated sulfuric acid solutions with a Pye-Unicam SP-8000 spectrophotometer. Inherent viscosities were measured at 25°C with Ubbelohde viscometers. The solutions of polymers for viscosity measurements were prepared by addition of 20.0 mL of concentrated sulfuric acid to 0.1 g of accurately weighed polymer. These solutions were warmed for 3 h at 50°C,


n
O
H2N
NH2
H2N
NH2
O
(TABQ)
+
n
O
O
O
Ar
O
O
O
(Ia–d)
–4n H2O
O
O
N
N
N
N
Ar
O
O
n
(IIa–d)
Ar =
(a)
(b)
C
O
(c)
(d)

SCHEME 1.

shaken mechanically (with glass balls in the flask) for 2 days at room temperature, and filtered through clean, dry, and weighed sintered-glass funnels. The filtrate was immediately used for determination of the relative viscosity. The collected solids were thoroughly washed with distilled water and methanol, and the funnel and solids were weighed after drying at 100°C and cooling to room temperature to determine the amount of insoluble polymer. The percent solubility and inherent viscosities were then calculated.

TG analysis of the polymers was carried out using a Perkin-Elmer thermobalance TGS-2 in nitrogen and in air ($\Delta T = 5°C/min$). Samples of approximately 5 mg were dried in the instrument at 150°C for 0.5 h before carrying out the runs.

Materials

Polyphosphoric acid (PPA) ("zur Synthese" from Merck) contained 84% P_2O_5.

Antimony trichloride (reagent from BDH, purity 99.5%) was dried by keeping it molten at 130°C for 3 h under a stream of dry nitrogen before use [7].

2,3,5,6-Tetraamino-p-benzoquinone (TABQ) was prepared according to the literature [8].

Pyromellitic dianhydride (PMDA) (Ia) (from Fluka) was recrystallized from acetic anhydride and sublimated under vacuum. Mp 286-287°C.

3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA) (Ib) (from K&K) was recrystallized from acetone. Mp 225-226°C.

1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTDA) (Ic) from K&K) was recrystallized from acetic acid and sublimated in vacuum. Mp >360°C.

3,4,9,10-Perylenetetracarboxylic dianhydride (PTDA) (Id) ("zur Synthese" from Merck) was used without further purification. Mp >360°C.

Polymers

General Procedure

In a three-necked flask equipped with nitrogen inlet-outlet and a stirrer, PPA was heated at 200°C for 2 h and then cooled under nitrogen. With the temperature maintained at 50°C, the tetramine (10 mmol) and the dianhydride (10 mmol) were added under a thin stream of nitrogen, and the reaction solution was heated under nitrogen at 50°C for 1 h. Then the flask was progressively heated (about 2°C/min) in a fluidized bath to 200°C, and heating was continued at 200°C for 3 h. The concentration of starting materials in PPA was 2% by weight. The polymer was isolated by pouring the cooled reaction solution into dilute ammonium carbonate solution and keeping it overnight. The mixture was centrifuged, and the precipitate was washed thoroughly with water and methanol and dried at 150°C/0.1 torr for 6 h.

Poly{(4,12-dihydro-6H-4,6,12-trioxoisoindolo-[1,2-a]-benzo-[2,3-d:5,6-d']-diimidazole-1,2,8,9-tetrayl)-9-carbonyl} (IIa). Yield 2.07 g (66%); black powder; η_{inh} = 0.60 dL/g (c = 0.2%).

Analysis: Calculated for $(C_{16}H_2N_4O_4)_n$: C, 61.15%; H, 0.64%; N, 17.83%. Found: C, 56.59%; H, 1.27%; N, 16.20%.

The presence of imide linkages in this compound is obvious, so it was heated for 5 h at 350°C/0.1 torr. After heating, the polymer was insoluble in sulfuric acid, and the η_{inh} could not be determined. IR (KBr): 3420, 3160 (broad, ν_{NH}), 1765, 1710, 1650, 1610, 1520, 1450, 1400, and 1350 cm^{-1}. UV-Vis (H_2SO_4): 226, 315, 535 nm.

Analysis: Found: C, 58.26%; H, 1.15%; N, 17.25%.

Second Procedure

Polymer IIa was also prepared by solution polycondensation of TABQ with PMDA in molten antimony trichloride according to a literature method [5]. Equimolecular amounts of tetraamine and dianhydride with a total concentration of monomers of 5% were used, and the reaction was carried out for 1 h at 80°C and 5 h at 170°C. Yield 65%; black powder; η_{inh} = 0.12 dL/g (c = 0.15%).

Analysis: Found: C, 56.14%; H, 1.71%; N, 16.13%.

After heating for 5 h at 350°C/0.1 torr, the polymer showed an η_{inh} = 0.18 dL/g (c = 0.08%). IR (KBr): 3440, 3160 (broad ν_{NH}), 1765, 1715, 1650, 1610, 1520, 1450, 1400, and 1350 cm^{-1}. UV-Vis (H_2SO_4): 227, 315, and 537 nm.

Analysis: Found: C, 58.49%; H, 1.38%; N, 17.14%.

Poly{(4,12-dihydro-6H-4,6,12-trioxoisoindolo[1,2-a]benzo-[2,3-d:5,6-d']diimidazole-1,2,8-triyl)-8-carbonyl-(4-carbonyl-1,3-phenylene)} (IIb). Yield 70%; black powder; η_{inh} = 0.75 dL/g (c = 0.14%).

Analysis: Calculated for $(C_{23}H_6N_4O_5)_n$: C, 66.03%; H, 1.45%; N, 13.39%. Found: C, 62.43%, H, 2.08%; N, 12.14%.

After heating for 5 h at 350°C, the polymer was insoluble in sulfuric acid. IR (KBr): 3440 (broad ν_{NH}), 1770, 1710, 1660, 1610, 1500, 1400, 1350, 1290, and 1240 cm^{-1}. UV-Vis (H_2SO_4): 229, 315, and 533 nm.

Analysis: Found: C, 63.44%; H, 1.94%; N, 12.95%.

Poly{(4,14-dihydro-6H-4,6,14-trioxobenzo-[1,2,3-e,d]-isoquinolo-[1,2-a]-benzo-[2,3-d:5,6-d']-diimidazole-1,2,9,20-tetrayl)-10-carbonyl} (IIc). Yield 90%; black powder; η_{inh} = 0.11 dL/g (c = 0.24%).

Analysis: Calculated for $(C_{20}H_4N_4O_4)_n$: C, 65.94%; H, 1.11%; N, 15.38%. Found: C, 61.73%, H, 1.78%; N, 14.54%.

After heating for 5 h at 350°C, the polymer showed $\eta_{inh} = 0.15$ dL/g (c = 0.16%). IR (KBr): 3400 (broad ν_{NH}), 1780, 1650, 1610, 1570, 1440, 1340, and 1260 cm^{-1}.

Analysis: Found: C, 63.87%; H, 1.46%; N, 15.06%.

Poly{(4,17-dihydro-6H-4,6,14-trioxoperyleno-[4,3-c,d]-pyrido-[2,1-a]-benzo-[2,3-d:5,6-d']-diimidazole-1,2,11,12-tetrayl)-12-carbonyl} (IId). Yield 96%; red powder; $\eta_{inh} = 0.08$ dL/g (c = 0.30%).

Analysis: Calculated for $(C_{30}H_8N_4O_4)_n$: C, 73.77%; H, 1.65%; N, 11.47%. Found: C, 68.70%; H, 2.14%; N, 9.5%.

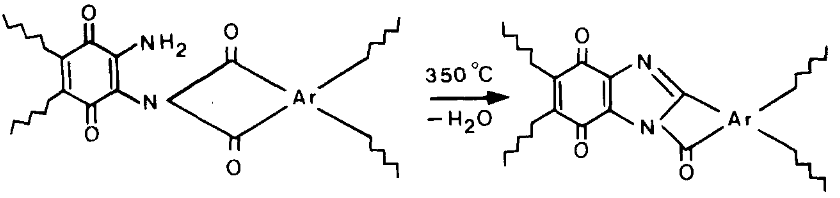
After heating, the brown-red polymer showed an $\eta_{inh} = 0.12$ dL/g (c = 0.18%). IR (KBr): 3440, 3120 (broad ν_{NH}), 1770, 1730, 1650, 1610, 1590, 1500, 1400, 1300, and 1230 cm^{-1}. UV-Vis (H_2SO_4): 220, 240, 380, and 540 cm^{-1}.

Analysis: Found: C, 71.73%; H, 2.02%; N, 11.18%.

RESULTS AND DISCUSSION

Pyrrones (IIa-d) were prepared by a one-stage reaction of the corresponding monomers (high-temperature polycondensation in PPA), while the two-stage reaction via the corresponding prepolymers (low-temperature polymerization in polar aprotic solvents and thermal cyclodehydration) is not effective because of the very low solubility (< 5%) of TABQ in the polar aprotic solvents and the low nucleophilicity of the amino groups of TABQ [9]. For the polycondensation, the monomers were added to PPA at 50°C because it was observed that TABQ is self-condensed during heating in PPA above 60°C. To avoid side reactions of the monomers [10], they were used in equimolecular amounts and heated slowly (about 2°C/min) to polycondensation temperature (200°C). The elemental analysis data of the polymers thus obtained and their IR spectra (bands at 3400 and 3120 due to free amino groups and at 1770-1765, 1715-1710, and 1350 cm^{-1} characteristic of imide bonds) revealed the presence of a considerable amount of "defective" uncyclized imide linkages. To increase this low cyclization degree, the polymers were heated at 350°C under vacuum (Scheme 2).

The ring closure in the structure of the prepared pyrrones was increased by this heating (cyclization degree was about 50-65%), but it was not completed as revealed by elemental analysis and IR spectra of the polymers, which showed only a reduction of the absorbance of bands due to free amino groups and imide bonds with respect to the absorbance of the quinone carbonyl band at 1650 cm^{-1} [11]. Also, the



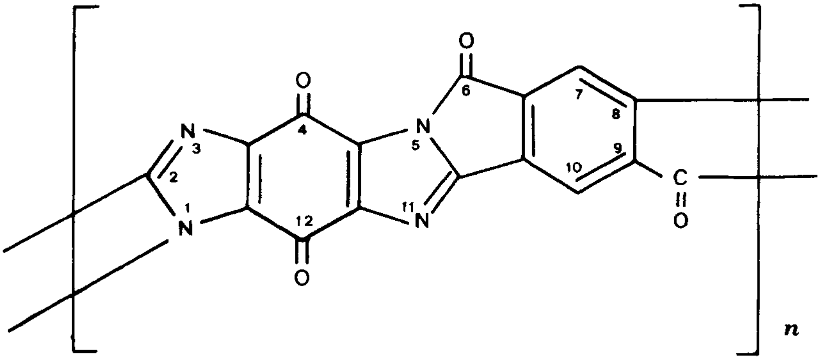
(III) (II)

SCHEME 2.

absorption bands at 533-540 nm of the prepared pyrrones are probably due to the presence of free amino groups. The higher cyclization degree of pyrrones IIc and IId (derived respectively from NTDA and PTDA) than that of pyrrones IIa and IIb (from PMDA and BTDA) (Scheme 3) could be ascribed to the higher efficiency of cyclization afforded by the configuration of reactive groups in NTDA and PTDA. Pyrrones IIc and IId were also obtained in higher yields than the pyrrones IIa and IIb, but they exhibited much lower inherent viscosities than the latter. The lower cyclization degree of the pyrrone IIa than the corresponding one prepared from 1,2,4,5-tetraaminobenzene (TAB) [10] by the same procedure is due to the lower reactivity of the free amino groups of the corresponding prepolymers (Structure III) because of the presence of the electroniophilic quinone carbonyl groups.

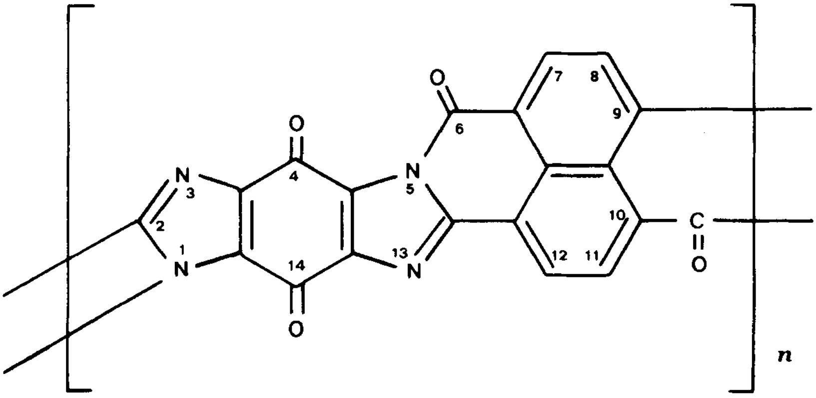
All pyrrones were obtained as fine powders, not melting below 400°C, insoluble in all polar aprotic solvents, and slightly soluble only in concentrated sulfuric acid and methanesulfonic acid (before the final heating at 350°C for pyrrones IIa and IIb). Brittle films were obtained from such solutions of pyrrones IIa and IIb in methanesulfonic acid, probably because of the low concentration (0.2%) of the solutions. Attempts to solubilize the pyrrones by reduction with sodium dithionite in alkaline aqueous dimethylacetamide were unsuccessful because all of them were practically insoluble even after 3 days' stirring with simultaneous heating at 50°C in this strong basic medium. This insolubility must be attributed to crosslinked material and probably to the hindrance to formation of the leuco form of the polymers, because the conformation of the macromolecules results in poor accessibility of the functional groups. The presence of the absorption band at 1650 cm^{-1} in the IR spectra of the pyrrones, which is due to the quinone carbonyl group, must be considered as an indication that this group did not take part in side reactions during the polycondensation and the final heating.

Polymer IIa was also prepared by polycondensation of TABQ with PMDA in molten antimony trichloride, which is referred to [5] as an exceptionally good solvent for pyrrone-type polymers. The IR spec-



(IIa)

(5/5-pyrrone)



(IIc)

(5/6-pyrrone)

SCHEME 3.

trum of the polymer thus prepared was identical to that of polymer IIa obtained through the PPA polycondensation technique, but the η_{inh} of the former was much lower than that of the latter.

The thermal stability in nitrogen and air of the prepared polymers was evaluated by dynamic TG analysis (Figs. 1 and 2).

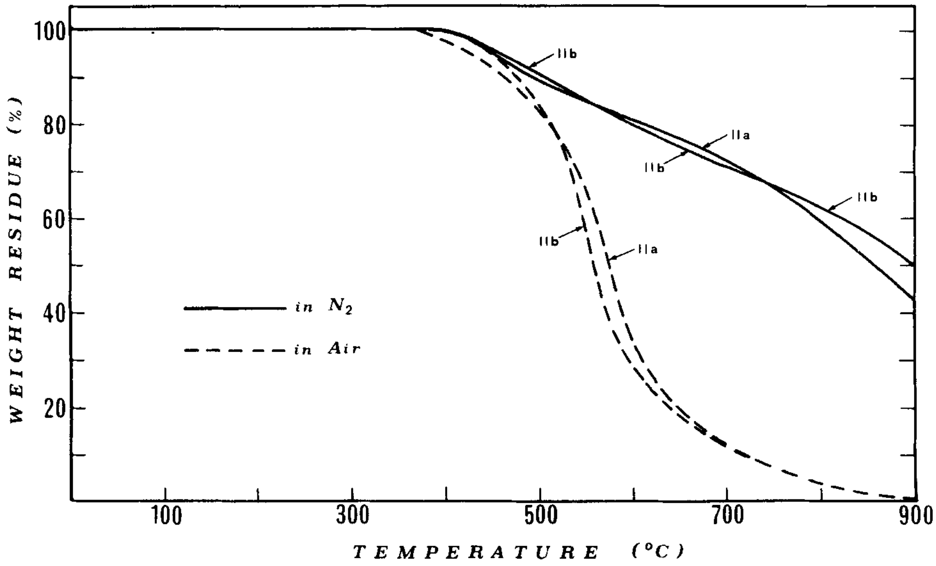


FIG. 1. TG curves for pyrrone IIa and IIb in air and nitrogen atmosphere.

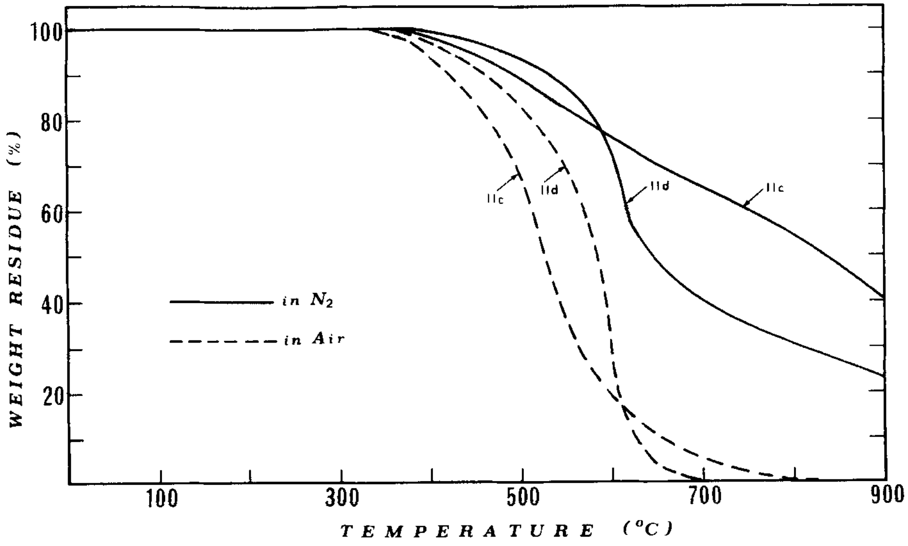


FIG. 2. TG curves for pyrrone IIc and IId in air and nitrogen atmosphere.

TABLE 1. Thermal Stability of Pyrrones IIa-d

Polymer	Temperature of 5% weight loss: In air, °C	Temperature of 5% weight loss: In nitrogen, °C	Half-volatilization point,[a] °C	Percent of total weight loss at 900°C in nitrogen, °C	Temperature of maximum rate of weight loss[b]: In air, °C	Temperature of maximum rate of weight loss[b]: In nitrogen, °C
IIa	425	450	682	57	570	490 800
IIb	448	452	650	50	545	540 850
IIc	390	425	650	58	530	580 815
IId	410	480	610	77	600	590 720

[a] The temperature at which half of the ultimate weight loss occurred in nitrogen.
[b] As recorded by DTG analysis.

Polymers IIa and IIb showed practically the same thermal stability in nitrogen and air, which was higher than the corresponding one of polymer IIc in spite of the higher cyclization degree of the latter (probably because of its lower molecular weight than that of IIa and IIb). Comparison of the curves of Figs. 1 and 2 shows that polymer IId generally exhibited better thermal and thermooxidative stabilities in the region up to 600°C, but lower ones at temperatures above this, than the other pyrrones.

All pyrrones showed two breaks in their TG curves in nitrogen and one break in TG curves in air (Table 1). The lower temperature break in the TG curve in nitrogen can probably be ascribed to the temperature at which the tetraamine component started to decompose, and the high-temperature break to breakdown of the other, more stable components of the macromolecules.

Pyrrone IIa showed a lower temperature of 5% weight loss but a higher half-volatilization point and lower percent total weight loss at 900°C than the corresponding pyrrone [10] prepared from TAB (480°C, 665°C, and 70%) by the same procedure, in spite of its higher amount of uncyclized imide linkages.

The preferred orientation (Scheme 3) and the name (Experimental part) of the polymers prepared are based on proposed nomenclature rules developed by the Nomenclature Committee of the Division of Polymer Chemistry, American Chemical Society.

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