Spontaneous Cyclodehydration of *N*-(*o*-Aminophenyl) Amic Acids

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ABSTRACT: The model reaction between phthalic anhydride and 1,2-diaminobenzene was studied under conditions analogous to those of the low-temperature polycondensation of aromatic dianhydrides with bis(o-diamines) in amide solvents followed by thermal cyclodehydration in condensed state to form ladder polyimidazopyrrolones (polypyrrones). The intermediate *N*-(*o*-aminophenyl)phthalamic acid was found to undergo spontaneous cyclodehydration to give *N*-(*o*-aminophenyl)phthalimide and 2-(*o*-carboxy-phenyl)benzimidazole. The reaction occurred at ambient temperature in the presence of water or alcohol without using a dehydration agent. The yield of imide-amine and/or carboxy-benzimidazole depended on the temperature of the condensation reaction. Temperatures below 0°C appeared to favor the formation of the carboxy-benzimidazole. Thermal cyclization of *N*-(*o*-aminophenyl)phthalamic acid passed through the same intermediates: imide-amine and carboxy-benzimidazole. The former converted to corresponding pyrrone above 200°C, while the secondary cyclization of the latter started above 250°C. Spontaneous cyclodehydration was also observed for polyamide acid-amine precursors obtained by low-temperature polycondensation of pyromellitic dianhydride with 3,3′-diaminobenzidine. The prepolymer solutions in DMF diluted with water at room temperature turned to a gel after 48–72 h. A spectroscopic study of the resulting polymers indicated the presence of significant amounts of imide cycles. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 609–619, 1998

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INTRODUCTION

Polyimidazopyrrolones, commonly referred to as polypyrrones, represents one of the most studied classes of heteroarylene ladder polymers.[1] They attracted attention in the mid-sixties because theoretical calculations[2,3] indicated that these polymers could significantly exceed their single-chain counterparts in terms of the resistance to thermal, oxidative, photochemical, radiative, and other kinds of degradation. Experimental verification of this theory showed that despite the fact that polypyrrones undergo only negligible weight loss up to 600°C, their stability is controlled by the weaker residual precursor units resulting from incomplete cyclodehydration.[1,4]

The cyclodehydration is difficult to be completed, and perfect defectless pyrrone structure cannot be reached for various reasons, including kinetic interruption effect,[5] decarboxylation,[6]
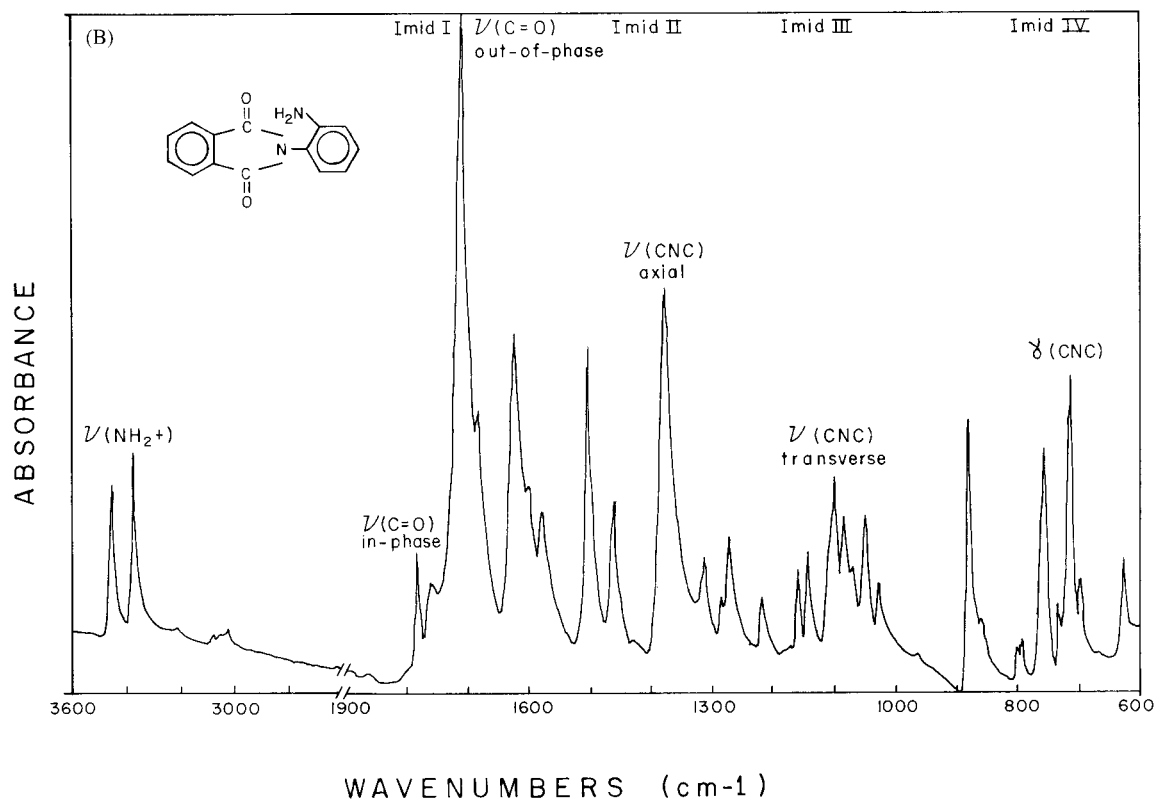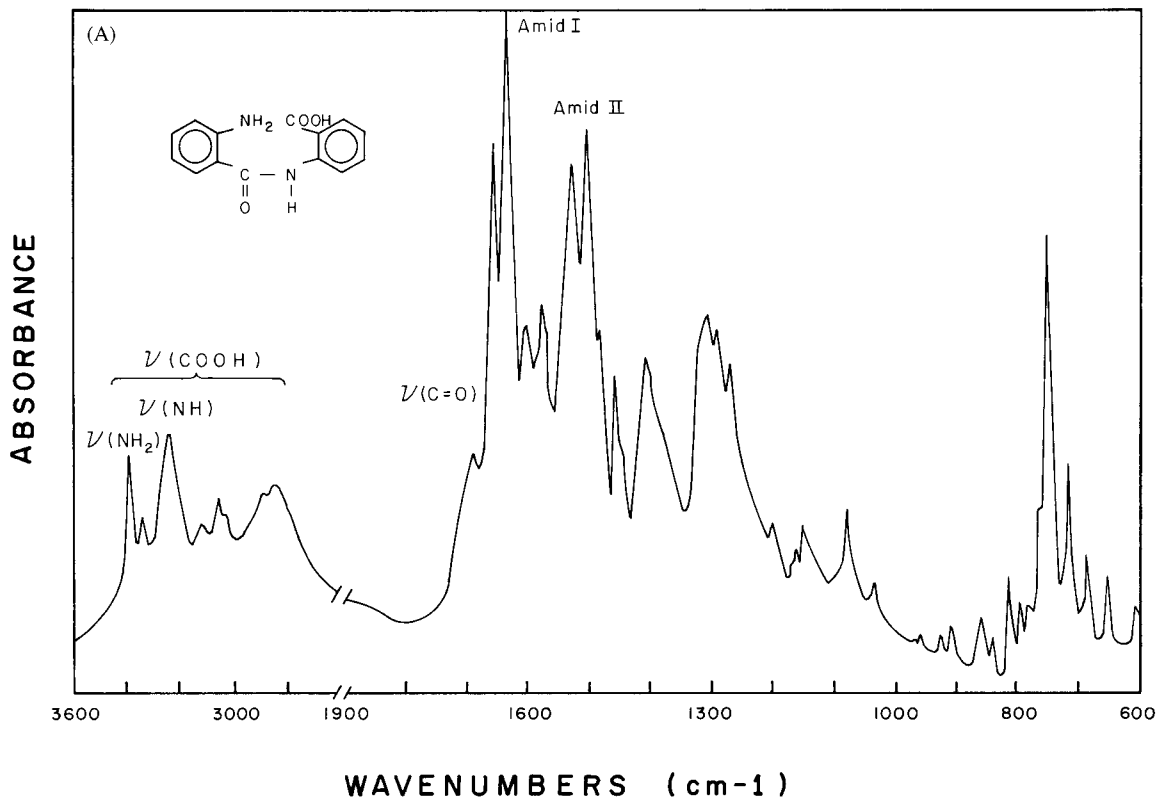
Figure 1 FTIR spectra of N-(o-aminophenyl)phthalamic acid (I) (A); N-(o-amino-phenyl)phthalimide (II) (B); and 1,2-benzoylenebenzimidazole (pyrrone, IV) (C).
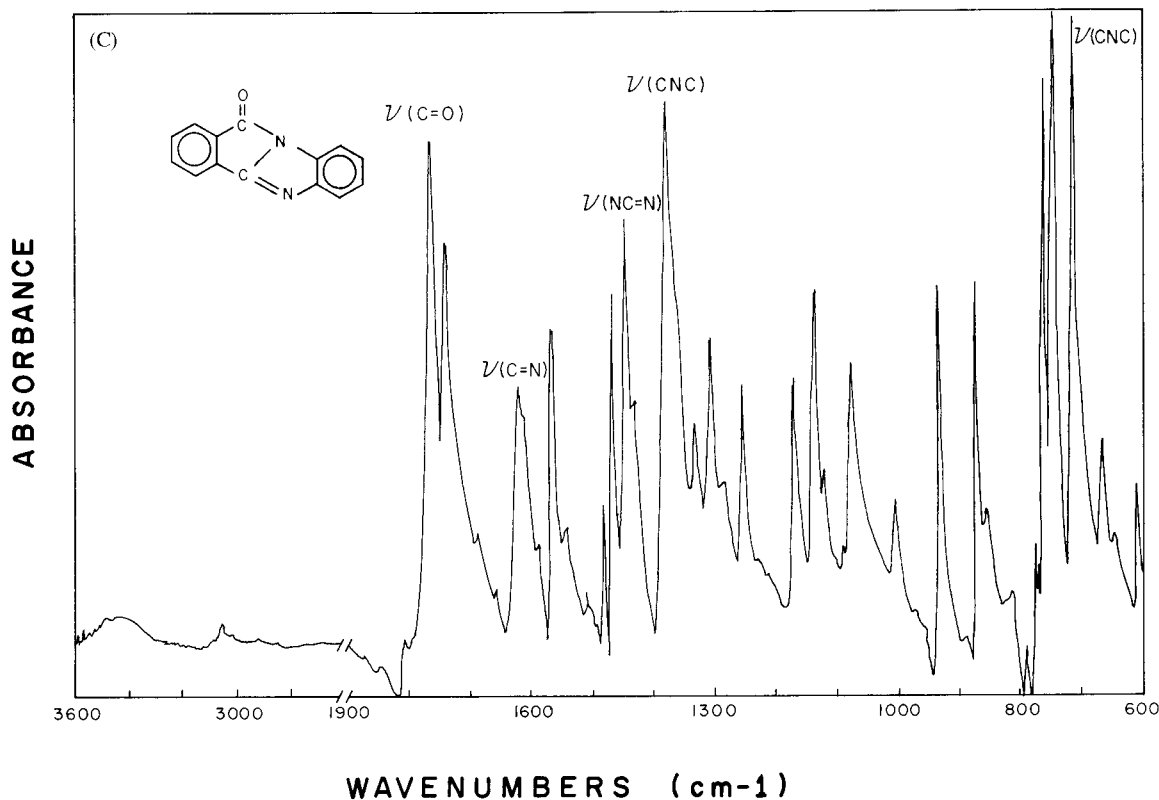
Figure 1 (*Continued from the previous page*)

and other chemical decomposition reactions[7] very possible under the severe conditions of high temperature curing. Nevertheless, the interest to pyrrones seems to have been renewed nowadays after nonlinear optical effects and interesting electro-optic properties were demonstrated for some of these highly conjugated structures.[8–10]

In a recent article,[11] Zhou and Lu reported the synthesis of polybenzimidazobenzophenanthrolines via thermal treatment of a prefabricated polymer precursor obtained by low-temperature polycondensation of a naphthalenetetracarboxylic dianhydride with tetraamines in *N,N'*-dimethylacetamide. The method is similar to the well-known two-step procedure widely used for the preparation of intractable polyheteroarylenes such as polyimides, polybenzimidazoles, polybenzoxazoles, etc. It was reported to be preferable for the polypyrrones because of the relatively mild reaction conditions and convenient separation of the polymers from the solvents.[11]

In fact, the stepwise route to polypyrrones was described in detail in an early patent[12] and its mechanism was extensively studied in numerous investigations.[5,6,13–16] It was found that despite apparent simplicity all steps of this method—low-

temperature condensation of dianhydrides with tetraamines and following thermal cyclodehydration of the resulting precursor to the desired polypyrrone—were accompanied by various side reactions. No final agreement has yet been reached over the principal pathway of this complicated process, its main intermediates, and the mode of their transformation to the final products.

In the present work these questions have been analyzed by using a model reaction between phthalic anhydride and 1,2-diaminobenzene. The obtained data were compared with the results of the stepwise polycondensation of pyromellitic dianhydride and 3,3'-diaminobenzidine.

EXPERIMENTAL

Materials

All reagents were supplied by Aldrich Chemical Co. Phthalic anhydride and 1,2,4,5-benzenetetracarboxylic dianhydride (pyromellitic dianhydride) were recrystallized from acetic anhydride and sublimated under vacuum. The 1,2-diaminobenzene and 3,3'-diaminobenzidine were recris-
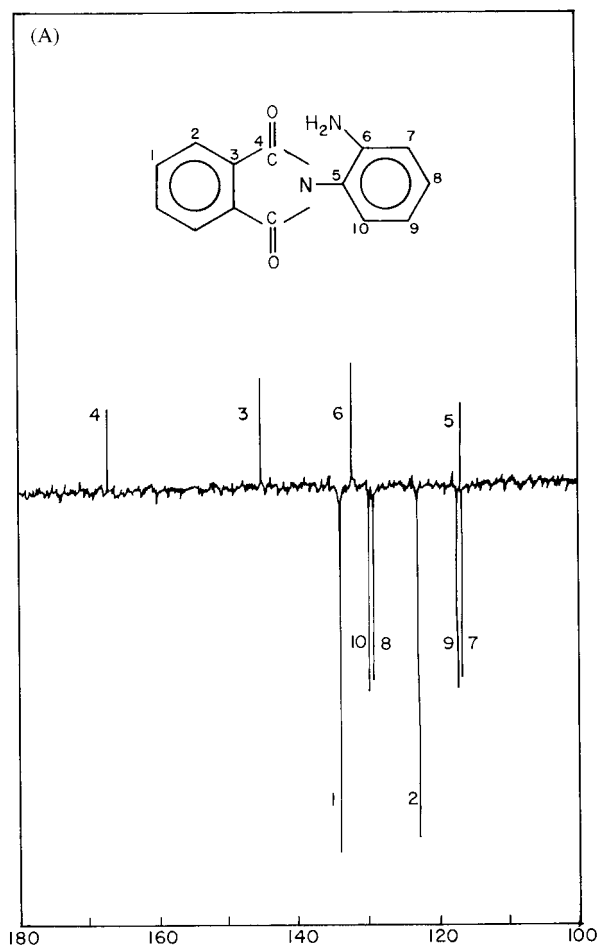
Figure 2 ATP-NMR spectra of *N*-(*o*-aminophenyl)phthalimide (II) (A); and 2-(*o*-carboxyphenyl)benzimidazole (III) (B).

tallized repetitively from ethanol before use. The *N,N'*-dimethylformamide (DMF) and *N*-methyl-2-pyrolidone (NMP) were dried and distilled over barium oxide under vacuum. The solvents were stored over 4 Å molecular sieves. The rest of reagents and solvent were used as received.

Model Compounds

The general reaction scheme applied in this work for the synthesis of the model compounds is shown in the Results and Discussion section.

N-(o-aminophenyl)phthalamic Acid (I)

A solution of 14.8 g (0.10 mol) of phthalic anhydride in 70 mL of DMF were added dropwise to a stirred solution of 10.8 g (0.10 mol) of 1,2-diaminobenzene in 100 mL of DMF. The solution was stirred at 20°C for 90 min and then precipitated

in toluene. Recovered white crystals (about 75–85% of the theoretical yield) were carefully washed with acetone and dried under vacuum at room temperature, m.p. 154°C (lit.[13,15] m.p. 147–152°C). The FTIR spectrum is shown in Figure 1(A).

N-(o-aminophenyl)phthalimide (II)

The reaction solution of the above amino acid-amine I was diluted with water (100% by volume). Precipitation of yellow needle-shaped crystals (25–35% of theoretical amount) was observed within 48–72 h after the dilution. The crystals were filtered out and purified either by recrystallization from chloroform or by sublimation at 190°C and 10^{-4} mmHg, m.p. 196°C (lit.[13,15] m.p. 194–195°C). The FTIR spectrum can be seen in Figure 1(B). The assigment of the ^{13}C carbon signals was achived by APT-NMR [Fig. 2(A)].
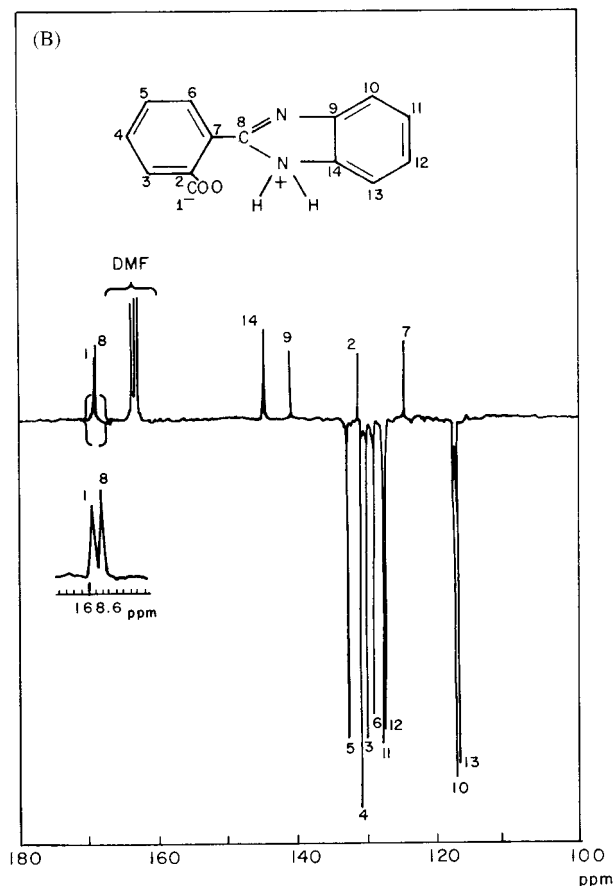
Figure 2 (*Continued from the previous page*)

2-(o-carboxyphenyl)benzimidazole (III)

The synthesis of *N*-(*o*-aminophenyl)phthalamic acid (I) was repeated at −10°C. The rest of conditions were similar to those mentioned above. Dilution of the reaction solution with icy water resulted in the precipitation of white spherical crystals (25% of theoretical amount) within 45–60 min. The precipitate was filtered out, washed with water, and dried under vacuum at room temperature, m.p. 248°C (lit.[13,15] m.p. 245°C). The APT-NMR spectra is presented in Figure 2(B).

1,2-Benzoylenebenzimidazole (Pyrrone, IV)

The *N*-(*o*-aminophenyl)phthalimide was sealed in a glass ampoule under argon atmosphere and heated at 200°C for 1 h. The FTIR spectrum of the resulting pyrrone, m.p. 214°C (lit.[13,15] m.p. 215°C) is shown in Figure 1(C). A product with identical FTIR signature and m.p. was also produced by heating 2-(*o*-carboxyphenyl)benzimidazole (III) at 255°C under similar conditions. The conversion was close to 100% in both cases.

Polymer Synthesis

The polyimidazopyrrolone (polypyrrone) was obtained by the conventional stepwise polycondensation[5,6,11–14] of pyromellitic dianhydride (PMDA) and 3,3′-diaminobenzidine (DAB). The general reaction route of this process is presented in Scheme I.

Tetraamine, DAB, was dissolved in DMF and the solution was cooled to 0°C. The exact stoichiometric amount of the dianhydride PMDA was gradually added as a solid. The final concentration of solids was about 10 wt %. The reaction solution was stirred at 0°C for 5 h. Then it was cast on glass plates and dried at room temperature under vacuum to produce the precursor PA-AA films. These films were converted to the final polypyrrone PM-DAB by heated at 350°C for 1 h under argon atmosphere.

Measurements

Inherent viscosity of the precursor PA-AA (η_{inh}) was determined in 0.5 g/dL *N,N*-dimethylform-
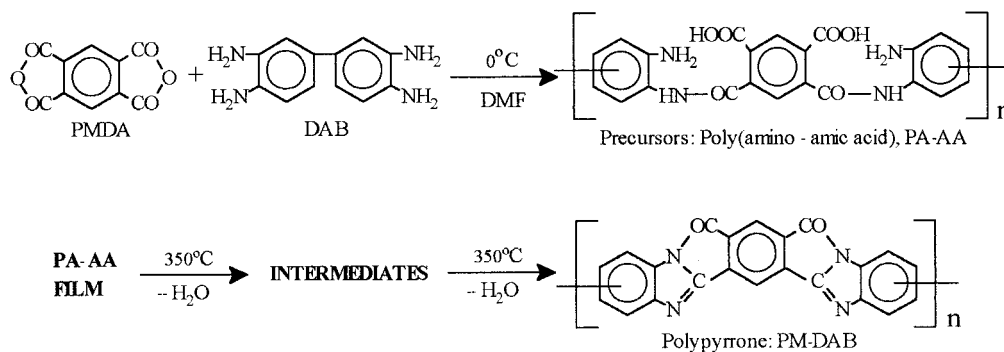
Scheme 1

amide (DMF) solutions in a Ubbelohde viscometer at 25°C. It ranged from 0.8 to 1.5 dL/g. The FTIR and NMR (^{1}H: 300 MHz and ^{13}C: 75 MHZ) spectra were recorded by using a NICOLET 510P and a VARIAN UNITY 300 spectrometers, respectivelly. Mass spectra were obtained on a Jeol JMS-AX505HA spectrometer using a 70 eV electron impact ion source. A Du Pont, high-resolution Thermogravimetric Analyzer, TGA 2950, was used for the thermal analysis at a heating rate of 5°C/min.

RESULTS AND DISCUSSION

The low-temperature polycondensation of aromatic dianhydrides and tetraamines is known to be very sensitive to the stoichiometry of the reagents. Intensive gelation has been observed in the final stage of this reaction in most previous articles [13,14] if a slight excess of the dianhydride was used in an attempt to increase the molecular weight of the resulting precursor PA-AA. It may be naturally explained by the possibility of intermolecular crosslinking caused by the acylation of "free" amino groups of PA-AA by the excessive anhydride units. However, it is difficult to collect direct evidences in favor of this proposal via studying the resulting polymers, while model compounds could offer more opportunities for solving this problem.

In this work the ratio of phthalic anhydride and 1,2-diaminobenzene used for the model reaction was varied from exact stoichiometry to 50 mol % excess of each monomer. The products of the low-temperature condensation of these reagents in DMF were subjected to thermogravimetric analysis. The usefulness of this method for quantitative study of the thermal transformations was found to be very limited in this case because inter-

mediate *N*-(*o*-aminophenyl)phthalimide **II** (see Scheme 2) and final pyrrone **IV** sublimated intensely during the test. However, TGA made it possible to separate and further analyze the products with lower vapor's pressure.

Figure 3 illustrates that the yield of such compounds may be very high if one of the reagents is added in excess. It almost reached 50% when the molar ratio phthalic anhydride/1,2-diaminobenzene was 1/1.5, in contrast to only 8% observed for the products of the reaction of exact stoichiometric amounts of the same reagents.

This highly thermally stable product was identified by mass spectra as *o*-phenylenebisbenze-imidazole (**VI** in Scheme 2)—EI-MS m/z (rel. int. %): 310 (100, M$^+$), 309 (79.6, M$^+$-1), 221 (13.7, M$^+$-C$_6$H$_3$N), 155 (12, M^+-C$_{10}$H$_7$N$_2$). The mass spectrum data were in agreement with the results of FTIR analysis, exhibiting characteristic bands of benzimidazole [15] at 1620 and 1441 cm^{-1}.

Similar thermograms were also obtained when the anhydride was added in excess. The resulting product in this case was identified as *N,N'*-diphthaloyl-*o*-phenylenediamine **V** (see the FTIR spectra in Fig. 4). Thus, it can be concluded that the use of excessive amounts of either the anhydride or the diamine leaded to the formation of the comparable quantities of the trinuclear byproducts: bis-imide **V** or bis-benzimidazole **VI,** respectively. The yield of both of them increased proportionally to the excess of the corresponding reagent.

The formation of the trinuclear compounds V or VI should be considered as a model of intermolecular reactions in the polymer precursor PA-AA resulting in branching and crosslinking. It was possible to minimize it to less then 10% (see Fig. 3) by setting the exactly equimolar amounts of the reagents. Lower temperatures and optimization of dosification technique supposedly might be
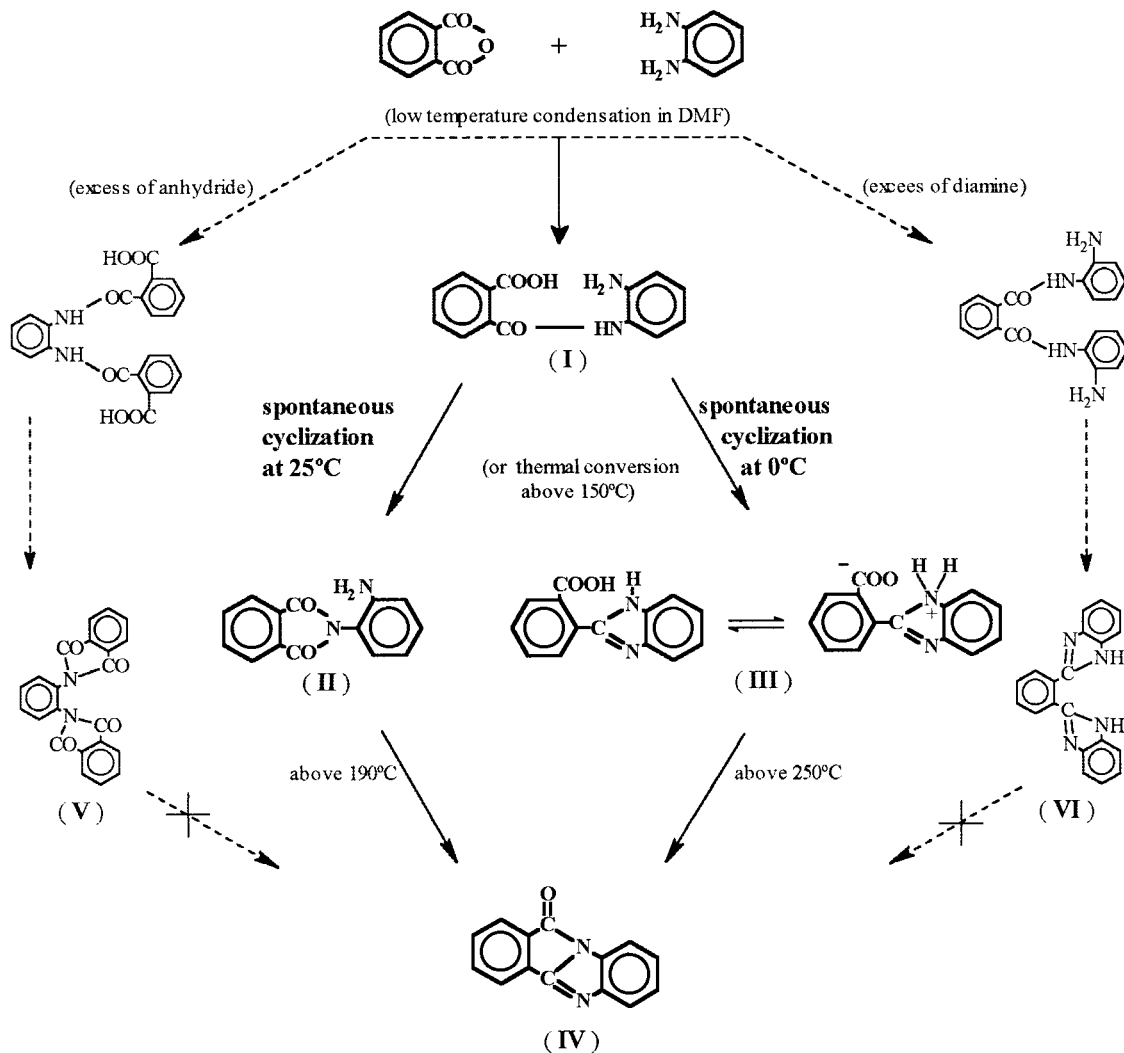
Scheme 2

helpful for further suppressing of these undesirable side reactions.

No final agreement has yet been reached in the literature over the principal pathway of *N*-(*o*-aminophenyl)phthalamic acid **I** cyclodehydration to the pyrrone. The opinions about main intermediates of this process split in favor of 2-(*o*-carboxyphenyl)benzimidazole **III**,[16,17] *N*-(*o*-aminophenyl)phthalimide **II**,[13] or both of them.[15,18] In addition, Dawans and Marvel[18] proposed that primary cyclodehydration of **I** may also include the formation of the eight-membered cyclic diamide **VII** (see Scheme 3) that could exist in an equilibrium with the amino-imide **II,** and Paudler and Zeiler[19] pointed out that this reaction might also lead to a lacton structure **VIII.**

It was shown in a recent molecular simulation study using semiempirical quantum mechanics methods included into the CERIUS software package,[20] that the primary cyclodehydration of *N*-(*o*-aminophenyl)phthalamic acid **I** to any one of the intermediates mentioned above: II, III, VII, or VIII, would result in a sufficient decrease of the system's free energy, ΔG. Thus, all these pathways could be permitted thermodynamically. The maximum decrease of ΔG were obtained for 2-(*o*-carboxyphenyl)benzimidazole **III** and *N*-(*o*-aminophenyl)phthalimide **II** that might be considered as the most probable precursors to pyrrone. Their thermodynamic prevalence became more prominent at temperatures higher than 100°C.

On the stage of secondary cyclodehydration *N*-(*o*-aminophenyl)phthalimide **II** appears to be the most preferable precursor to yield pyrrone. However, the advance over 2-(*o*-carboxyphenyl)benz-
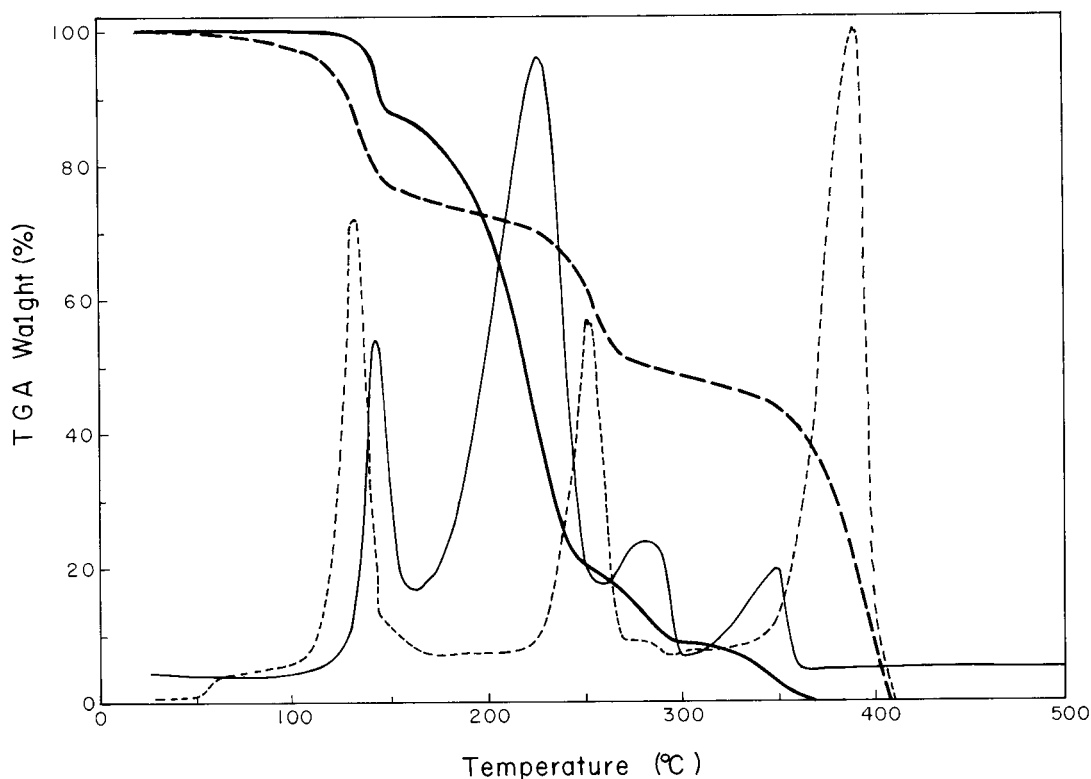
Figure 3 Thermograms of the precipitates obtained by the reaction of phthalic anhydride and 1,2-diaminobenzene: solid line—stoichioimetric amounts of the reagents; dotted line—50% molar excess of 1,2-diaminobenzene.

imidazole **III** is very small, thus both **II** and **III** could be taken into account as possible intermediates with a little superiority of the former.[20]

Such a conclusion appears to be in agreement with previously reported experimental data[15,18] as well as with the results of this study. The FTIR analysis of the products resulting from the prolonged heating of solventless N-(o-aminophenyl)phthalamic acid **I** at 175°C indicated the presence of significant amounts of intermediates **II** and **III**. Despite the interference of sublimation process the conversion of both of these precursors to pyrrone could be observed on the TGA curve shown in Figure 3 (solid line) above 190 and 250°C, respectively. These values correspond well with the temperatures of secondary cyclodehydration of the pure forms of these compounds.[13-19]

A more detailed investigation of N-(o-aminophenyl)phthalamic acid **I** transformations disclosed its ability for spontaneous cylodehydration to the corresponding amino-imide **II** or carboxybenzimidazole **III**. It is known that imides and imidazoles are generally formed from thermodynamically stable precursors: amic acids or amino

amides, respectively, at elevated temperatures. These cyclodehydration reactions (thermal cyclization) normally occur quantitatively above 100°C, and temperatures as high as 300°C are required for kinetic reasons to complete the conversion of the corresponding polymers.[21] The alternative chemical cyclization frequently used in the polyimide chemistry can be accomplished at room temperature by treating the precursor poly-(amic acids) with a dehydration agent (usually acetic anhydride) in the presence of a tertiary amine as a catalyst.[22]

In contrast to these basic options, N-(o-aminophenyl)phthalamic acid **I** was found to undergo primary cyclodehydration to the heterocyclic structures **II** or **III** at temperatures from 0° to 25°C with no use of any dehydration agent or catalyst. The cyclization took place in the reaction DMF solutions when it were diluted with water or ethanol (50/50 by volume). Temperatures around 0°C favored to the formation of 2-(o-carboxyphenyl)-benzimidazole **III**: white spherical crystals precipitated 30 min after dilution of the DMF solutions with water at 0°C were identified by NMR
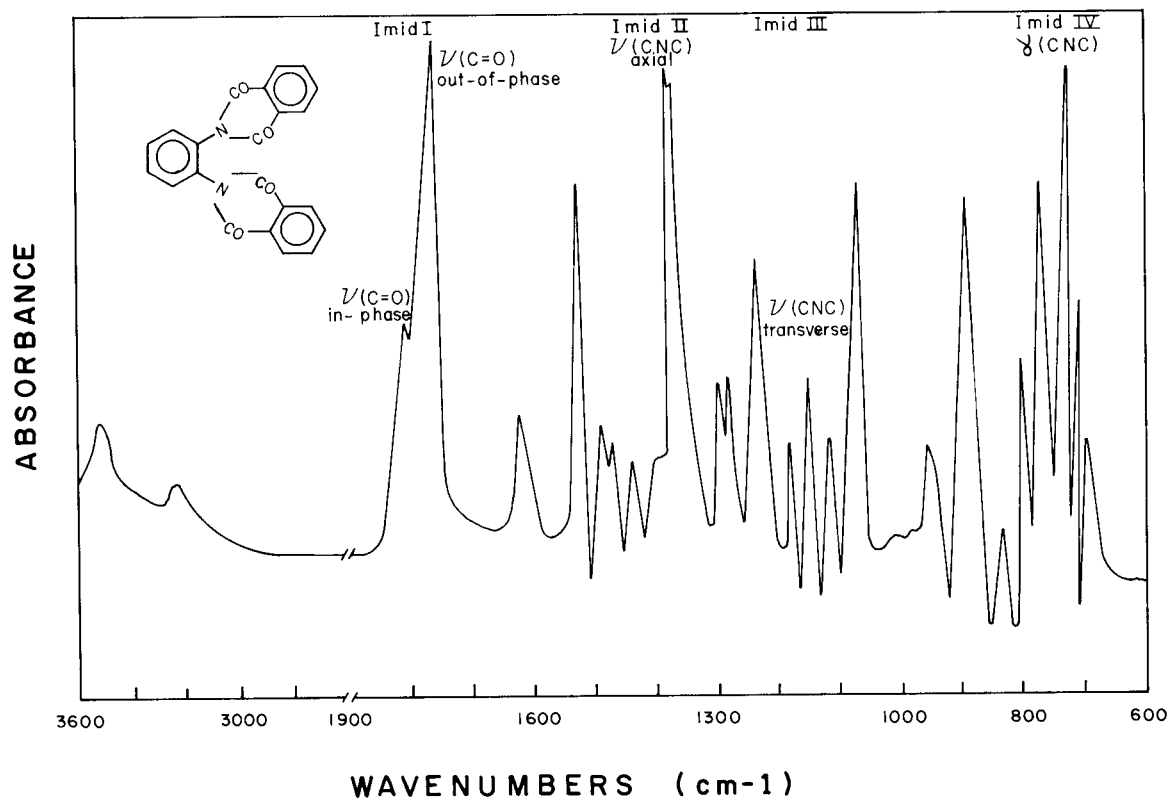
Figure 4   FTIR spectrum of *N,N'*-diphthaloyl-*o*-phenylenediamine V.

analysis and m.p. The spectral data indicated that under these conditions the compound **III** may exist as a zwitterion.[15] The highest carbon signal found in the ATP-NMR spectrum [Fig. 2(B)] is located at 168.522 ppm that rather corresponds to carboxy anion. The presence of more than one proton bonded to protonated nitrogen atom of the imidazole cycle was also well distinguished at 9.642 ppm in the integral PMR spectrum. Meanwhile, the acidic hydrogen can still be observed as a week diffused halo under the aromatic peaks in the range from 8.5 to 6.5 ppm. This could mean that ionization was not completed and the two forms coexisted in equilibrium.

The yellow needle shaped crystals of *N*-(*o*-aminophenyl)phthalimide **II** precipitated within 48–72 h after the reaction solutions obtained and stored at 25°C was diluted with water or ethanol.
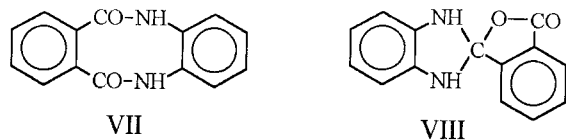
Scheme 3

The FTIR spectrum in Figure 1(B) shows the presence of NH_2 peaks at 3500 and 3450 cm^{-1} and characteristic bands of the imide cycle at 1780–1720, 1381, 1108, and 720 cm^{-1}. The imide carbonyl absorption looks complicated because both components of the typical duplet ($\nu_{C=O}$ in- and out-of-phase) are split by Fermi resonance in the same way as it was reported for various substituted *N*-phenylphthalimides.[23] The obtained data were in good agreement with the results of the APT-NMR study [Fig. 2(A)] indicating appropriate number and positions of the carbonyl and aromatic carbons of *N*-(*o*-aminophenyl)phthalimide **II**.

The maximum conversion of the spontaneous cyclodehydration of *N*-(*o*-aminophenyl)phthalamic acid **I** to yield either **II** or **III** was below 30%. It could be explained by a possible equilibrium between different isomeric products **II, III,** and **VII** that might be established at low temperatures.[20] The variation in the reaction medium, time, and temperature is supposed to be helpful for increasing the yield of the particular isomer **II** or **III**. Any resolution of this problem may lead to the creation of a novel low temperature route to functional polyheteroarylenes (amino-polyimides
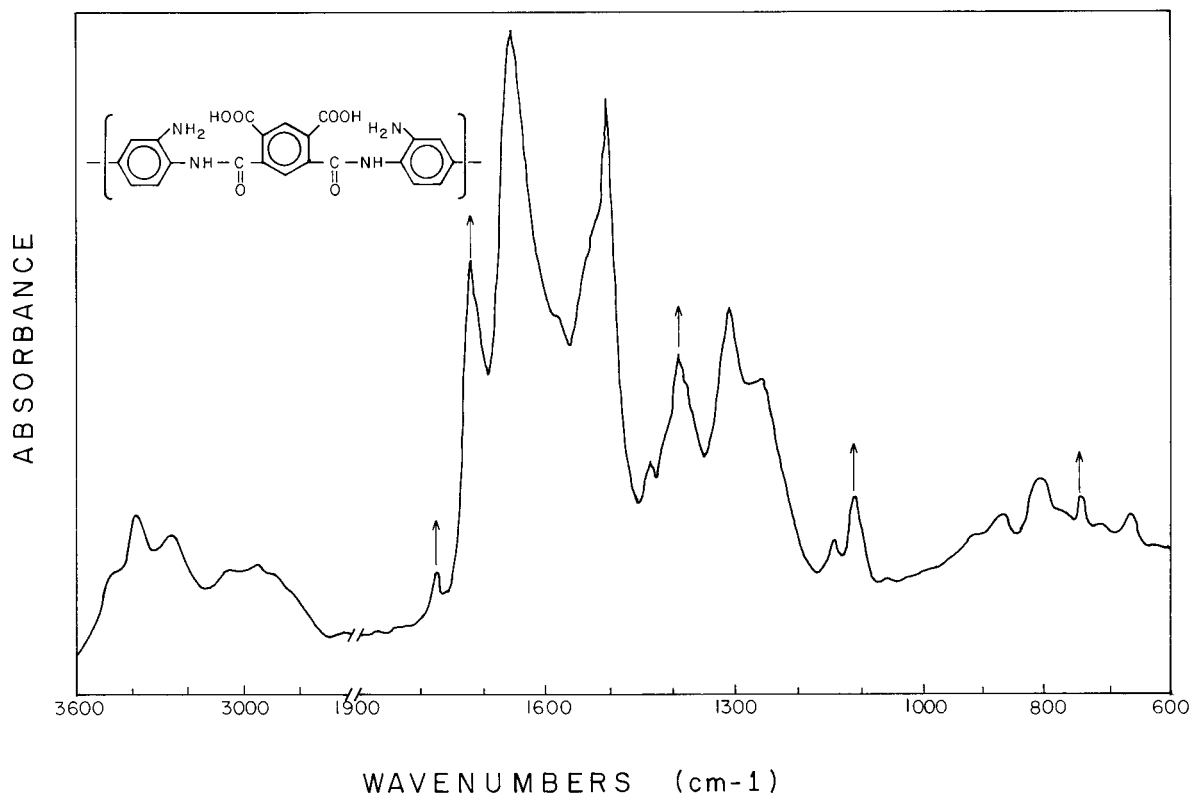
Figure 5 FTIR spectrum of poly(amino-amic acid) PA-AA film treated with water for 48 h at 25°C.

or carboxy-polybenzimidazoles, in particular) that have been attracting an increasing attention in recent years.[24]

The spontaneous cyclodehydration observed for the model compounds was reproduced for the polymer PA-AA precursor obtained by the low temperature polycondesation of PMDA and DAB (see Scheme 2). The dilution of the reaction solution in DMF with water or ethanol (75/25 by volume) caused irreversible gelation within 48 h. The resulting gel was dried to form a thin film and analyzed by FTIR. The spectra in Figure 5 shows the presence of notable amounts of imide cycles: characteristic bands at 1776 ($\nu_{C=O}$ in-phase around 1716 cm^{-1} is mixed with the carboxyl peak of PA-AA), 1387; 1113, and 723 cm^{-1}. Partial imidization (approximate conversion about 10–15%) was also registered when the PA-AA films were dried to constant weight and then immersed into water or ethanol for 48–72 h while no structural change or a decrease in solubility were noticed for the precursor in dry DMF solutions or in the condensed state in the absence of aqueous media.

CONCLUSIONS

The study of the model reaction between phthalic anhydride and 1,2-diaminobenzidine demonstrated that the use of an excess of any of this monomers over the stoichiometric quantity led to the intensive formation of trinuclear o-phenylenebisbenze-imidazole **VI** or N,N'-diphthaloyl-o-phenylenediamine **V.** Both these compounds could be considered as prototypes of crosslinked or branched structures complicating the conversion of PA-AA precursors to polypyrrones.

The N-(o-aminophenyl)phthalimide **II** and 2-(o-carboxyphenyl)benzimidazole **III** was found to be the main products of the primary thermal cyclization of N-(o-aminophenyl)phthalamic acid **I** in the condensed state. They could be then converted to the final pyrrone **IV** above 190 and 250°C, respectively.

The same intermediates **II** and **III** were also obtained by the spontaneous cyclodehydration of N-(o-aminophenyl)phthalamic acid **I.** The reaction occurred at ambient temperatures in the

presence of water or alcohol without using a dehydration agent.

The spontaneous cyclization was also observed for the polyamide-acid-amine precursor resulted from low temperature polycondensation of pyromellitic dianhydride and 3,3′-diaminobenzidine. The formations of notable amounts of imide cycles were registered after the prepolymer were treated at room temperature with water or ethanol in solution or the condensed state.

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