A Low-Temperature Route to Polyimides

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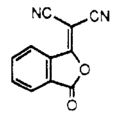
ABSTRACT: 3-Dicyanomethylidene phthalide, a new phthalic anhydride analog, was synthesized by condensation of phthalic anhydride with malononitrile followed by treatment with phosphorus oxychloride. Several model reactions with aromatic amines and phenylhydrazine disclosed unexpected chemistry producing the corresponding imide in tetrahydrofuran or *N*-methylpyrrolidone solvent at *room temperature.* A difunctional pyromellitic dianhydride analog, 3,7-bis(2,2-dicyanomethylidene)pyromellitide, was also synthesized using similar reaction conditions. The polymerization reaction of this new monomer with oxydianiline and the subsequent curing reaction to polyimide are discussed.

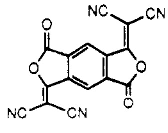
Introduction

Recently we have been studying synthetic routes for the introduction of dicyanomethylidine groups in place of carbonyl oxygen atoms into thermally stable polymers as a means of modifying reactivity as well as enhancing the solubility of such materials.[1,2] (Chlorodicyanovinyl)benzene, as an analog of the corresponding acid chloride, has been prepared and reacted with aromatic amines to form enaminonitrile linkages via a vinylic nucleophilic substitution reaction.[3] We have synthesized difunctional monomers, such as bis(chlorodicyanovinyl)benzenes, which have been used for polymerization with various diamines to give high molecular weight polymers containing the dicyanomethylidene group in the polymer backbone. These new polymers exhibited excellent thermal stability, ready solubility in simple solvents, and many other interesting properties attributable to the presence of the polarizable dicyanomethylidene groups.[1,4]

We have used the same synthetic methodology to prepare, for the first time, a phthalic anhydride derivative (I) which exemplifies this approach. Several model reactions with aromatic amines and phenylhydrazine disclosed unexpected chemistry producing the corresponding imide in tetrahydrofuran or *N*-methylpyrrolidone solvent at *room temperature.*[5] In contrast, it is known, generally, that imides are formed from stable amic acid precursors, the reaction product of an anhydride and an amine, only at elevated temperatures. A difunctional monomer, a new pyrometallitic diahydride analog (II), was also synthesized, and the polymerization reaction with oxydianiline (ODA) was carried out.



(I)

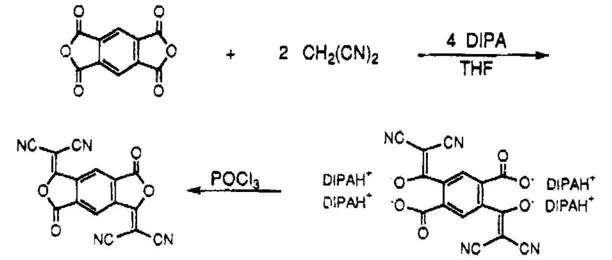


(II)

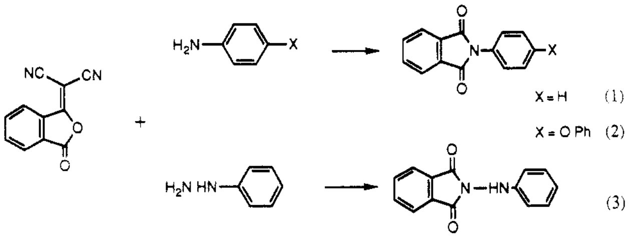
Experimental Section

A. Synthesis of Compound II. 3,7-Bis(2,2-dicyanomethylidene)pyromellitide (II) was prepared from pyromellitic dianhydride and malononitrile in two steps as shown in Scheme I.

Scheme I



Scheme II



3,6-Bis(2,2-dicyano-1-hydroxyvinyl)-1,4-benzenedicarboxylic Acid, Diisopropylamine Salt. Pyromellitic dianhydride (5.35 g, 24.5 mmol) and malononitrile (3.24 g, 49.0 mmol) were dissolved in 300 mL of THF. Diisopropylamine (DIPA, 14 mL, 99.9 mmol) was added dropwise, over 1 h. A yellow precipitate formed as the reaction mixture was stirred for 20 h at room temperature. The light yellow, solid product was easily filtered and washed with pure THF and then dried in vacuo at 100 °C for 2 days. Crude product (17.5 g, 95% yield) consisted of both para- and meta-like products. The mixture was recrystallized from methanol/water to obtain 8.5 g of predominantly para-like product from the first crop of crystals. The product decomposes above 170 °C. IR (KBr): 3442, 3034, 2986, 2852, 2736, 2506, [2200, 2184] (CN), 1734, 1624, 1558, 139.8, 1362 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 7.39 (s, 2H, aromatic H), 3.23 (hep, 8H, CH), 1.15 (d, 24H, CH$_3$). ^{13}C NMR (DMSO-d_6): δ 188.5 (vinyl C–O), 167.5 (C=O), [141.9 (2C), 128.15] (aromatic C), [122.3, 121.0] (CN), 47.7 (*C*–CN), 46.1 (CH), 18.8 (CH$_3$). Anal. Calcd for $C_{40}H_{66}N_8O_6$: C, 63.63; H, 8.81; N, 14.84. Found: C, 62.99; H, 8.7; N, 14.70.

3,7-Bis(2,2-dicyanomethylidene)pyromellitide. 3,6-Bis(2,2-dicyano-1-hydroxyvinyl)-1,4-benzenedicarboxylic acid, tetra-DIPA salt (2.54 g, 3.36 mmol) was reacted with 1.2 mL of POCl$_3$ in 50 mL of methylene chloride. The reaction mixture was stirred for 20 h at room temperature under nitrogen. The solution turned dark brown and a solid product precipitated as the reaction proceeded. The light brown solid was filtered and washed with dry methylene chloride to remove phosphorus oxychloride and then dried to obtain 0.8 g (77%) of crude product. The product was recrystallized from acetic anhydride to give 0.55 g (53%) of light yellow, crystalline solid. (The work-up procedures must be done under a dry atmosphere as quickly as possible, because

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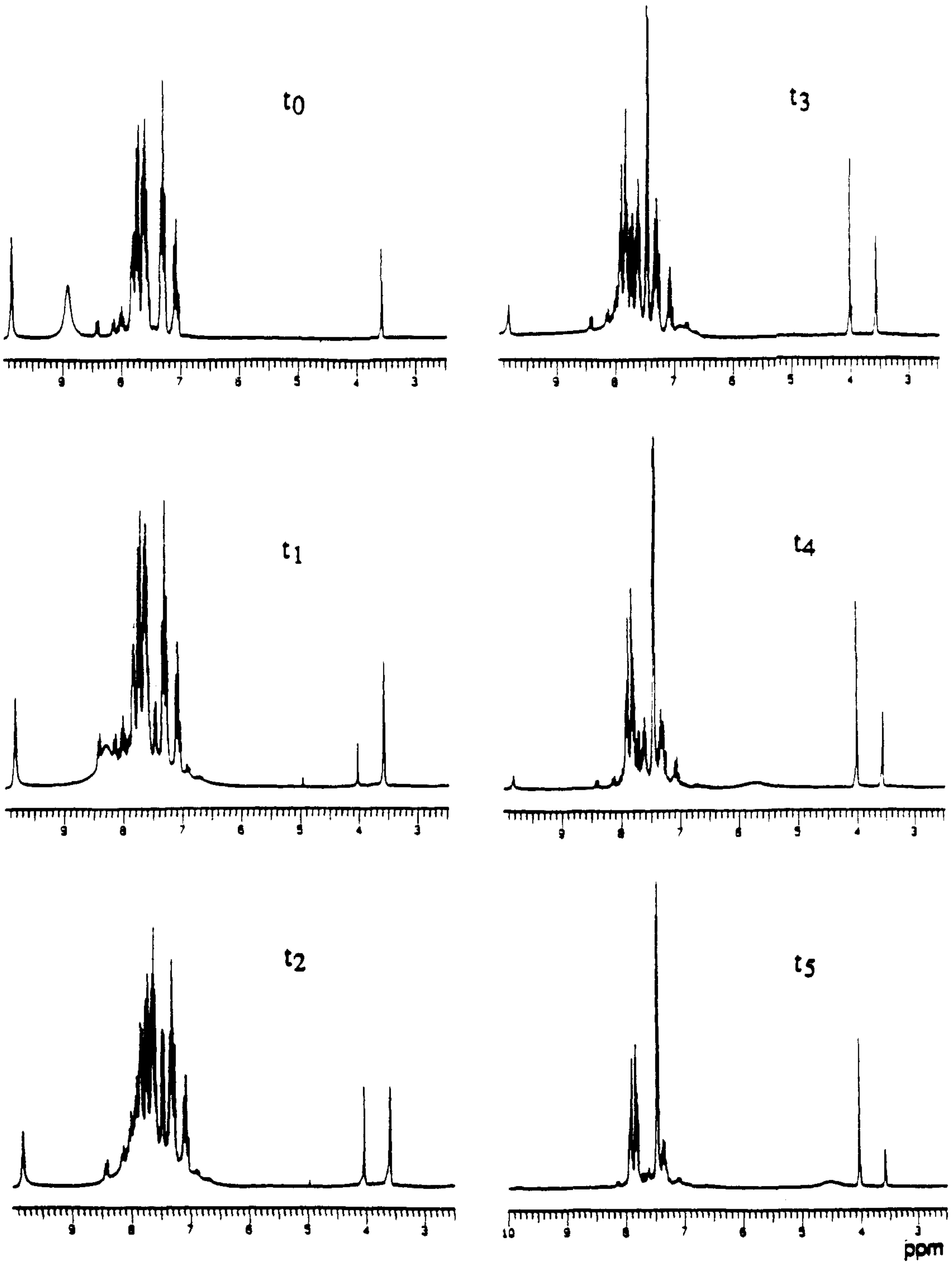
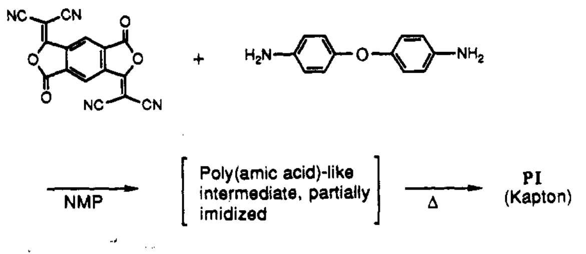


Figure 1. NMR spectral changes as a function of reaction time for the model reaction, pseudoanhydride (I), and aniline.

the product is susceptible to hydrolysis.) Mp: 396 °C (DSC). IR (KBr): 2241 (CN), 1835 (anhydride C=O), 1629, 1285, 1193, 1116, 1000, 874, 692 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 8.98 (s, 2H, aromatic H). ^{13}C NMR (acetone-d_6): δ 160.54 (C=O), [139.7, 133.3] (aromatic C without hydrogen), 123.7 (aromatic C with hydrogen), [111.5, 109.7] (CN), 64.9 (C–CN). Anal. Calcd for $C_{16}H_2N_4O_4$: C, 61.16; N, 17.83. Found: C, 61.09; N, 17.92.

B. Polymerization. To a stirred solution of 4,4′-diaminodiphenyl ether (0.271 g, 1.354 mmol) in 15 mL of dry NMP was added pseudodianhydride (0.425 g, 1.354 mmol) directly as a crystalline solid under argon. A brick-red color appeared instantly, but as the solid monomer dissolved and reacted, the solution turned orange-yellow and gradually became viscous. The reaction mixture, after stirring for 24 h at room temperature, remained homogeneous. The viscous solution was pipetted into an aluminum dish and was allowed to dry. Free-standing films were obtained after drying in a vacuum oven (~1 Torr) at 60 °C for 1 h and were used for further characterization and curing studies by thermogravimetric analysis. Also thin films were cast on NaCl plates for IR analysis.



Results and Discussion

Model Reactions. Two aromatic amines and phenylhydrazine were used for model reactions with the pseudoanhydride (I). Typically, to a pseudoanhydride

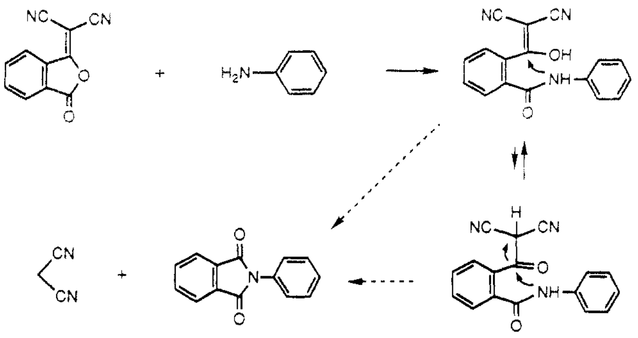


Figure 2. Proposed reaction mechanism of the model reaction.

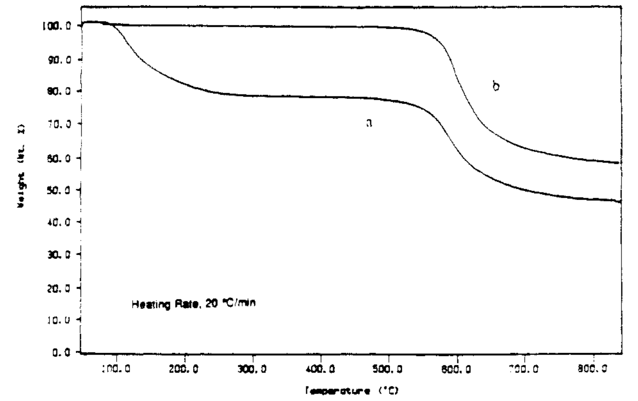


Figure 3. TGA thermograms of prepolymer (a) and a Kapton film (b).

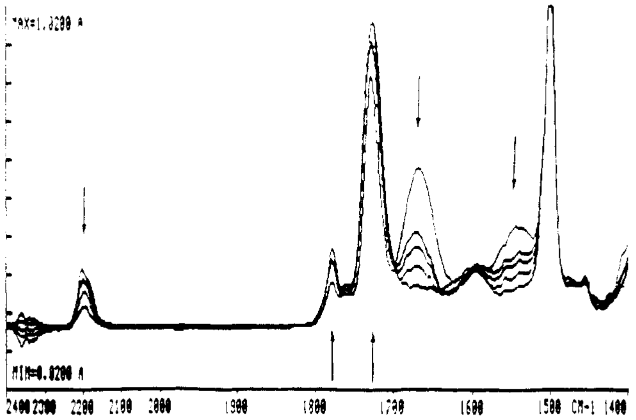


Figure 4. Changes in IR absorptions as a function of curing time.

solution in THF or *N*-methylpyrrolidone was added slowly, an amine solution in the same solvent, and the resulting amber solution was stirred for 24 h or more at room temperature. The solution was then precipitated into water to give the corresponding imides **1**–**3** (Scheme II) as off-white powders in 75–90% yield.[5] The reaction with phenylhydrazine forms exclusively *N*-anilinophthalimide (**3**).[5]

The model reaction of the pseudodianhydride (II) with 2 equiv of aniline was done in NMP. The product, *N,N'*-diphenylpyromellitimide, slowly precipitated from the solution as the reaction proceeded. The melting points and spectroscopic data (MS, IR, and ^{1}H and ^{13}C NMR) of these model compounds matched well with those of the known compounds.[6]

From model reactions of the pseudoanhydride (I) with several amines, the corresponding imides were obtained in high yield as shown in Scheme II. The same reaction was also conducted in an NMR tube using THF-d_8 as the solvent. It was observed that the characteristic peaks of each component immediately disappeared when mixed, and a pattern representative of an amic acid with amide N*H* at 9.8 ppm and a broad O*H* proton at 8.8 ppm (variable depending on concentration) appeared. The intensity of the N*H* proton peak from the amic acid intermediate at 9.8 ppm decreased and the broad O*H* peak moved upfield with decreasing intensity, and a new peak at 4.0 ppm, assigned as the CH_2 protons of malononitrile, increased as the reaction proceeded. Figure 1 shows NMR spectral changes of this model reaction.

The reaction probably proceeds by fast nucleophilic attack of the amine at the carbonyl carbon atom to produce the amic acid analog intermediate, and then this intermediate slowly decomposes to form imide either by direct addition to the enol aided by the neighboring group effect or via a small amount of reactive ketodinitrile existing in rapid equilibrium with the enol followed by elimination of malononitrile. This proposed reaction mechanism is shown in Figure 2. The difference in the chemistry of the pseudoanhydride compared to that of phthalic anhydride obviously rests on the dicyanomethylidene functionality. Attack at the carbonyl group yields a more stable enolate anion, and the elimination of the malononitrile anion rather than the hydroxide ion is favored by the enhanced stability granted by the presence of two conjugated nitrile groups (pK_a of malononitrile = 11; pK_a of H_2O = 15.74).[7]

Polymerization. A solution polymerization of the pseudodianhydride monomer with ODA was carried out in NMP at room temperature. Thin films can be cast from polymer solutions which were obtained after stirring for 24 h. (It was observed that the clear solution became cloudy upon extended stirring because of the precipitation of polymer from the solution as the imidization reaction proceeded.) A thin film, in its partially imidized form, obtained by drying in vacuum (~1 Torr) at 60 °C for 1 h was used for further curing studies using thermogravimetric analysis (TGA) and FT-IR spectroscopy. Figure 3a shows the thermogram of the original film with constant heating. From around 100 °C, weight loss is observed and the slope decreases and levels at higher temperatures. No weight loss was observed beyond 300 °C, indicating that the curing reaction was almost completed. After about 23 wt % initial weight loss, the resulting material was stable to around 500 °C and then decomposed beyond that temperature. The onset of the second weight loss matched with that of a commercial Kapton film (Figure 3b). The initial weight loss upon heating probably includes both residual solvent in the original film and malononitrile released from the cyclization reaction.

Figure 4 shows the changes of IR absorption bands in the region between 1400 and 2400 cm^{-1} as a function of curing time at 120 °C in vacuum. It is apparent that the CN stretching band at 2204 cm^{-1}, the strong band at 1668 cm^{-1}, namely, amide I, and the broad band at around 1550 cm^{-1}, mixed mode of substituted vinyl group and amide II, decrease gradually as the curing time increases. On the other hand, the increase in the intensity of the characteristic imide band at 1778 and 1728 cm^{-1} is obvious as a function of time. Figure 5 shows the IR spectrum of a sample after curing for 20 h at 120 °C in vacuum, which matches the spectrum of a Kapton polyimide film except for a residual small CN absorption band at around 2200 cm^{-1}. If we assume that the preparation (60 °C, in vacuo, 1 h) of the film used in this study did not change the extent of imidation from that attained in solution and that the final intensity of the band at 1728 cm^{-1} represents complete cure, we can estimate that the extent of imidization attained in homogeneous solution is on the order of 75%. The detailed kinetic analysis of this complicated process is currently under investigation.

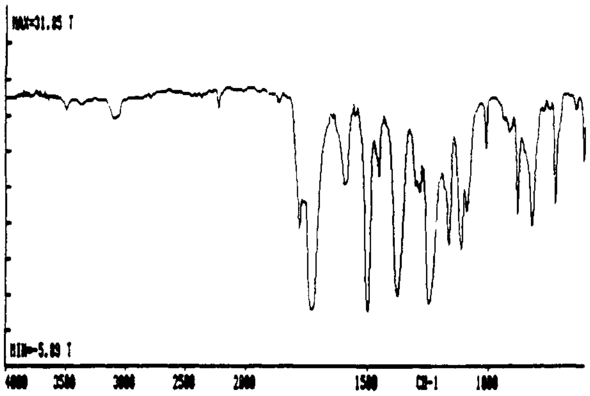


Figure 5. IR spectrum of a cured sample.

Even though the room-temperature imidization was demonstrated from the model reactions and polymerization, the reaction in the solid state of the cast film seems to exhibit the same typical features of solid-phase thermal cyclization processes of common polyimides.[8] As the reaction proceeds and imide rings are formed, molecular chain rigidity increases and the glass transition temperature of the reacting polymer shifts toward higher temperature. As a result, polymer molecular motion is frozen and the imidization reaction becomes inactive.

Conclusions. We have demonstrated that the enhanced reactivity of a novel anhydride functionality can be used to produce a PMDA–ODA polyamic acid analog which undergoes partial (~75% over 24 h) spontaneous conversion to polyimide at room temperature in homogeneous solution. Beyond 24 h the solution becomes turbid as polyimide begins to precipitate and ultimately becomes a gel. The implications of these results for the development of a low-temperature process for the production of polyimides are currently under investigation.

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References and Notes

(1) Moore, J. A.; Robello, D. R. *Macromolecules* **1989**, *22*, 1084.
(2) Wallenfels, K.; Friedrich, K.; Rieser, J.; Ertel, W.; Thieme, K. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 261.
(3) Rappoport, Z. *Acc. Chem. Res.* **1981**, *14*, 7.
(4) Moore, J. A.; Kim, J.-H. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1990**, *31* (2), 696.
(5) Moore, J. A.; Kim, J.-H. *Tetrahedron Lett.* **1991**, *32* (29), 3449.
(6) 2-Phenyl-1*H*-isoindole-1,3(2*H*)-dione [520-03-6], (2) 2-(4-phenoxyphenyl)-1*H*-isoindole-1,3(2*H*)-dione [19357-24-5], (3) 2-(phenylamino)-1*H*-isoindole-1,3(2*H*)-dione [4870-16-0].
(7) March, J. *Advanced Organic Chemistry*: *Reactions, Mechanism and Structure*, 3rd ed.; John Wiley and Sons: New York, 1985; p 221.
(8) Mittal, K. L. *Polyimides*; Plenum Press: New York, 1984; Vol. 1, p 259.