REEVALUATION OF TETRAHYDROPHTHALIC ANHYDRIDE AS AN END CAP FOR IMPROVED OXIDATION RESISTANCE IN ADDITION POLYIMIDES

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TITLE RUNNING HEAD. Tetrahydrophthalic anhydrides as end caps.

ABSTRACT. Several substituted 1,2,3,6-tetrahydrophthalic anhydride end caps—including the 3-phenyl, 3-methoxy, 3-trimethylsilyloxy, and 3,6-diphenyl analogs—were synthesized via the Diels-Alder condensation of the corresponding butadienes and maleic anhydride. These anhydrides, as well as the commercially available 3-hydro and 4-methyl analogs, were each ground together with methylenedianiline in a 2:1 ratio and heated gradually from 204 °C to 371 °C, with the thermolysis followed by NMR. Generally speaking, a transformation via monoimide to bisimide was observed in the lower temperature range, followed by competition between crosslinking and aromatization. We believe that this competition produces a substantial percentage of aromatic product, with the concomitant lowering of the relative amount of crosslinking and is responsible for improving both thermal oxidative stability of tetrahydrophthalic end capped polyimides and their substantial frangibility. The thermolysis of the tetrahydrophthalimides under inert atmosphere dramatically lowers the amount of aromatization hence, the mechanism for aromatization is an oxidative one.

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INTRODUCTION. Fiber-reinforced high-temperature polyimide matrix composites offer significant advantages in structural applications over other materials, because of their low density and high specific strength. These composites are attractive for use in aerospace systems, e.g. aircraft engines, airframe, missiles, and rockets, where weight is critical. This weight reduction has substantial benefits in terms of fuel savings, increased passenger or cargo load, or increased speed and maneuverability. The durability and reliability of materials used in aerospace components is a critical concern. Among the materials requirements for these applications are a high glass-transition temperature, T_g, (at least 25 °C higher than the intended use temperature), good high-temperature stability in a variety of environments, and good mechanical properties over a wide range of temperatures. In general, the stability and/or T_g of most organic polymers limit their use, at best, to applications in which temperatures are not higher than 300 °C.

Addition-curing polyimides were investigated to improve the processibility of condensation polyimides without adversely affecting their stability and high-temperature performance. The most noteworthy development is the Polymerization of Monomer Reactant (PMR) family of polyimides, in particular PMR-15[1]. Figure 1 is the typical reaction scheme for the formation of these end capped addition polyimides (PMR-15). For PMR-15, reinforcement fibers are impregnated with a solution of the dialkyl ester of 3,3',4,4'-benzophenonetetracarboxylic diacid diester (BTDE), methylenedianiline (MDA), and the monomethyl ester of 5-norbornene-2,3-dicarboxylic acid (nadic acid ester, NE), in a low boiling solvent, typically methanol or ethanol. In the first step of this process, these monomers undergo imidization at temperatures around 200 °C to yield short-chain norbornene end capped polyimide oligomers, (formulated molecular weight = 1500 g/mol for PMR-15). At temperatures above 300 °C, these oligomers undergo a crosslinking reaction involving the norbornene end cap.[2]

- Figure 1 here -

Ironically, however, it is this very end cap, so important to processing, that accounts for much of the weight loss in the polymer on aging in air at elevated temperatures (>315 °C). Thus, the end cap limits the use of PMR polyimides to lower temperature parts of the engine and/or shorter lifetimes. Researchers have tried to improve the stability by a variety of means, but most prominently by utilizing structures with more aromatic character, e.g. Cycap, V-cap, PEPA, acetylene terminated imides (ATI), benzocyclobutenes and biphenylenes.[3] However, each modification resulted in changes in the nature of the crosslinking, undesirable changes in processibility and/or mechanical behavior, lower T_g and, at times, sizable increases in cost (e.g., Cycap).

Over the past decade, we have been exploring various aspects of this thermo-oxidative degradation in the hope of gleaning clues on how to design new end caps which will slow down this degradation, and prolong the use lifetime of polyimide materials. Several years ago, we reported a number of studies on the thermo-oxidative aging of a modification of PMR-15, in which we ^{13}C-labeled the norbornenyl end cap at the methyne carbon α to the carbonyl groups.[4,5,6] Based on this work, we concluded that this oxidation proceeds through two primary pathways (Figure 2).

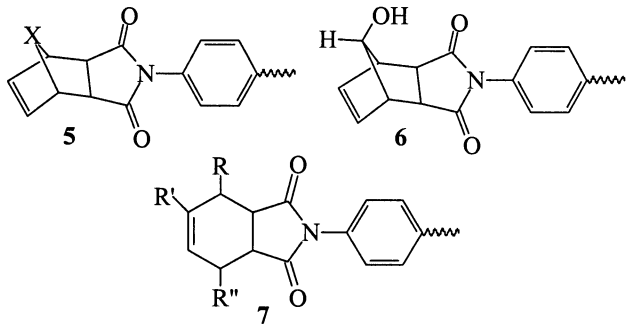
- Figure 2 here -

Path A degradation proceeds through initial opening of the norbornyl ring to form a biradical which undergoes attack of oxygen to form a 2-hydroxy substituted maleimide **2.** Path B degradation proceeds through oxidation of the bridging methylene of the norbornene moieties followed by carbon monoxide extrusion. Aromatization of the intermediate biradical leads to substituted quinone **3** or phthalimide **4,** and related secondary degradation products.

Path A oxidation products like **2** are cleavage products that are most likely formed concomitant with large amounts of weight loss in the polymer system. In contrast, structures like **3** and **4** from path B are formed with very little weight loss. Therefore, new end cap structures that more strongly favor path B

degradation should lead to lower weight loss in addition polyimides, and result in less shrinkage and cracking in the oxidation layer.[4]

Recently, we reported on our design of new end caps that might favor path B degradation.[7,8] We proposed to utilize structures like **5** below where X is more labile than the C-7 methylene of the nadic end cap or is easily oxidized to a more labile group under aging conditions. In particular, we studied the 7-hydroxy analog **6** (i.e., **5**, X=CHOH). We provided evidence that, in the air-aging polymer, the hydroxy-bearing carbon oxidizes to carbonyl and should, therefore, more highly favor path B degradation. Indeed, the solid NMR spectral changes observed are all consistent with rapid conversion of the aliphatic crosslink to an aromatic one via Path B or bridge degradation.



We now report our studies on 1,2,3,6-tetrahydrophthalimide **7** (R=R′=R″=H), an end cap that contains no X group at all. This structure was investigated by TRW and NASA in the 1980's and found to yield composites with TOS values *better* than PMR-15, but which were quite frangible.[9] St. Clair and St. Clair[10] tried **7** as an end cap for polyimide adhesives. However, they reported that no crosslinking occurred in this system until 415 °C, as evidenced by differential scanning calorimetry (DSC). If the crosslinking temperature could be lowered - either by substitution on the ring or by catalysis - this might be a viable replacement for the norbornene end cap. Indeed, onset of decomposition for polymers made with this end cap was shown to be at a higher temperature than for the norbornenyl-analog.

EXPERIMENTAL. Solution NMR spectra were obtained on a Varian 400, and Bruker 300 and 200 MHz Fourier transform spectrometers, using TMS as the internal standard. Assignments were

facilitated by double resonance, APT, Hetcor, COSY and NOESY experiments. The carbon numbering of the various compounds used in the spectral assignments is shown in equations 1 and 2. Infrared absorptions were determined with a Nicolet 510P FTIR. High resolution mass spectra (HRMS) were run on a VG-Fison AutoSpecE High Resolution Spectrometer. The following TA Instruments machines were used for standard thermal analyses: Q 1000 Reversible DSC; 2910 DSC; 2940 TMA; 2950 Hi-Res TGA. The TGA/MS/IR system used was comprised of a TA Instruments 2950 TGA whose effluent gas was split, one arm leading via a heated (ca. 240 °C) transfer-line to a Nicolet Nexus 470 FTIR, while the other arm led via a heated (ca. 240 °C) deactivated capillary to a Finnigan Polaris Q Mass Spectrometer. Analytical thin layer chromatography (TLC) was performed using Merck silica gel microcards. Maleic anhydride (Aldrich), *cis*-1,2,3,6-tetrahydrophthalic anhydride (**10a**, Aldrich), 4-methyl-*cis*-1,2,3,6-tetrahydrophthalic anhydride (**10e**, TCI-EP) are commercially available and were used as supplied. Compounds **10b,**[11] **10c**[12] and **10f**[13] are known in the literature. Nevertheless, the ^{13}C spectral data is unreported, while the ^{1}H NMR data is missing, inaccurate or of relatively low resolution; hence, these are cited below where appropriate.

3-Phenyl-*cis*-1,2,3,6-tetrahydrophthalic Anhydride (10b): The title compound was prepared by refluxing equimolar amounts of *trans*-1-phenyl-1,3-butadiene[14] (**8b**, 10.9 g, 84 mmol) and maleic anhydride (8.2 g, 84 mmol) in toluene (225 mL) for 16h under nitrogen. The orange solution was placed in the freezer overnight to give a yellow-brown precipitate. The latter was filtered and air dried to give **10b** as a light yellow powder (14.8 g, 65 mmol, 77% yield); mp 119.2-120.8 °C. The mother liquor was evaporated and residue was recrystallized from ether to give an additional 2 g (total yield 87%); mp 116.8-117.8. The product was purified by treating it with charcoal and recrystallizing from boiling ethyl acetate/hexane. Colorless product (13 g, 57 mmol; 68% overall yield) was obtained; mp 121.5-122.5 ^{0}C (lit.[11] 120-121 ^{0}C).

10b: ^{1}H NMR ($CDCl_3$) δ 7.37-7.24 (m, 3H, H_p and H_m), 7.21-7.17 (m, 2H, H_o), 6.222 (m, 1H, H_4), 6.149 (m, 1H, H_5), 3.803 (m, 1H, H_3), 3.545 (dd, J=10 and 7 Hz, 1H, H_2), 3.453 (td, J=10 and 2 Hz, 1H, H_1), 2.896 (dm, J=18 Hz, 1H, H_6-*cis* to Ph), 2.426 (m, 1H, H_6-*trans* to Ph); ^{13}C NMR ($CDCl_3$) δ

173.766 (C_7), 170.699 (C_8), 137.321 (C_{ipso}), 129.729 (C_4), 128.742 (C_m), 128.659 (C_o), 127.907 (C_5), 127.596 (C_p), 45.822 (C_2), 40.144 (C_3), 39.051 (C_1) 22.335 (C_6); IR (KBr) 1845, 1778 and 1708 (anhydride), 1658 (C=C) cm^{-1}; HRMS (DCI, CH_4) calcd ($C_{14}H_{12}O_3$, M^+) 228.0786, obsd 228.0780.

3-Methoxy-*cis*-1,2,3,6-tetrahydrophthalic Anhydride (10c):[12] The title compound was prepared by dissolving equimolar amounts of *trans*-1-methoxy-1,3-butadiene (**8c**, Aldrich, 5.0 g, 59 mmol) and maleic anhydride (5.8 g, 59 mmol) in acetonitrile (100 mL). The reaction mixture was stirred at room temperature for 24 h under nitrogen. The solvent was rotary evaporated and the resulting light yellow liquid (10.6 g; 58 mmol; 98% yield) solidified upon standing. The latter was gradually dissolved in 10 portions of hot ether (50-75 mL each), and the resulting solution concentrated down to 150 mL, at which time crystallization began to give the desired product (9.0 g, 48 mmol, 83% yield); mp 96.0-97.5 °C (lit.[12] 94-96 °C).

10c: ^{1}H NMR ($CDCl_3$) δ 6.14 (second order "inverted triplet", 2H, H_4 and H_5), 7 4.23 (m, 1H, H_3), 3.335 (td, J=10 and 4 Hz, 1H, H_1), 3.225 (dd, J=10 and 6 Hz, 1H, H_2), 3.26 (s, 3H, MeO), 2.71 (dd, J=16 and 6 Hz, 1H, H_6), 2.67-2.46 (m, 1H, $H_{6'}$); ^{13}C NMR ($CDCl_3$) δ 174.14 (C_7), 171.15 (C_8), 131.86 (C_4), 126.58 (C_5), 70.12 (C_3), 56.58 (OCH_3), 45.77 (C_1), 36.48 (C_2), 21.54 (C_6).

3-Trimethylsilyloxy-*cis*-1,2,3,6-tetrahydrophthalic Anhydride (10d): The title compound was prepared by dissolving equimolar amounts of 1-trimethylsilyloxy-1,3-butadiene (**8d**, mixture of *cis* and *trans* isomers, Aldrich, 8.54 g, 60 mmol) and maleic anhydride (5.88 g, 60 mmol) in acetonitrile (100 mL). The reaction mixture was stirred at room temperature for 24 h under nitrogen. The solvent was rotary evaporated to give a light yellow liquid (14 g; 58 mmol; 97% yield). The product was identified based on its spectral data, which compared favorably with those of the known 3-(*t*-butyldimethylsilyloxy)-6-methyl analog.[15] Only one set of absorptions were observed in the ^{1}H NMR, though two sets could be detected in the ^{13}C NMR spectral data. Based on peak heights, the two components, presumably **10d** (*cis*) and **10d'** (*trans*), are present in an approximate ratio of 95:5, respectively.

10d: ^{1}H NMR ($CDCl_3$) δ 6.012 (ddd, J=10, 5 and 2 Hz, 1H, H_4), 5.925 (ddd, J=10, 6 and 3 Hz, 1H, H_5), 4.534 (dd, J=5 and 4 Hz, 1H, H_3), 3.295 (td, J=10 and 5 Hz, 1H, H_1), 3.065 (dd, J=10 and 4 Hz, 1H, H_2), 2.638 (ddt, J=18, 5 and 2.5 Hz, 1H, H_6), 2.442 (ddd, J= 18, 10 and 5 Hz, 1H, $H_{6'}$), -0.019 (s, 9, Me_3Si); ^{13}C NMR ($CDCl_3$) δ 174.45 (C_7), 171.61 (C_8), 130.19 (C_4), 128.27 (C_5), 62.59 (C_3), 47.22 (C_1), 35.98 (C_2), 20.74 (C_6), -0.22 (Me_3Si; IR (KBr) 1867, 1779 and 1711 (anhydride), 1658 (C=C), 1252 (Si-C), 1056 and 846 (Si-O-C) cm^{-1}; HRMS (EI) calcd ($C_{10}H_{13}O_4Si$, M^+-CH_3) 225.0583, obsd 225.0563.

10d': ^{13}C NMR ($CDCl_3$) δ 174.14 (C_7), 172.10 (C_8), 130.96 (C_4), 129.08 (C_5), 62.81 (C_3), 45.95 (C_1), 36.88 (C_2), 21.69 (C_6), 1.91 (Me_3Si).

3,6-Diphenyl-*cis*-1,2,3,6-tetrahydrophthalic Anhydride (10f): Although the literature[13] suggests preparing **10f** in a Parr bomb, we found that this is unnecessary. The title compound was prepared instead by refluxing equimolar amounts of *trans, trans*-1,4-diphenyl-1,3-butadiene (**8f**, Aldrich, 8.25 g, 40 mmol) and maleic anhydride (4 g, 40 mmol) in *p*-xylene (100 mL) for 48h under nitrogen. On cooling a white solid formed, which was filtered, washed with ether and air dried to give **10f** (10 g, 33 mmol, 82% yield); mp 205-209 °C. Further recrystallization from chloroform yielded purified product (8.2 g, 27 mmol, 67% overall yield); mp 215-217 °C (lit[13] 208-209 ^{0}C).

10f:[13] ^{1}H NMR ($CDCl_3$) δ 7.47-7.33 (m, 10H, aryl), 6.558 (s, 2H, H_4 and H_5), 3.846 (bd, J=4.8 Hz, 2H, H_3 and H_6 – double resonance studies reveal that the broadening stems from small couplings with the vinyl and aromatic hydrogens), 3.740 (dd, J=4.8 and 2.4 Hz, 2H, H_1 and H_2); ^{13}C NMR ($CDCl_3$) δ 169.69 (C_7 and C_8), 137.85 (C_{ipso}), 132.05 (C_4 and C_5), 128.72 (C_m), 128.63 (C_o), 127.67 (C_p), 47.46 (C_3 and C_6), 41.18 (C_1 and C_2); IR (KBr) 1849, 1812 and 1773 (anhydride), 1656 (C=C) cm^{-1}; HRMS (DCI) calcd ($C_{20}H_{16}O_3$, M^+) 304.1099, obsd 304.1070.

Preparation of Bisimides 12, 15, 17 and 21: Anhydride (**10,** phthalic anhydride or succinic anhydride **22**) and diamine (**16a** or **b**) in a 2:1 molar ratio were ground together and heated at 204 °C (400 °F) for 1 h. As determined by NMR, in nearly each case, the primary product at this stage was the desired bisimide. However, cyclohexene bisimide **12** was accompanied by a small amount (generally

<2%) of the intermediate monoimide **11** (see eq. 1). (The spectrum of the latter is quite distinctive because of its AA'XX' pattern of the H-10' and H-11' aromatic protons at ca. 6.6 and 7.0 ppm, respectively.) However, in the case of **10b** and **10f**, the ratio of monoimide:bisimide (**11**:**12**) was 2:1 and 3:1, respectively; bisimide **12** was the primary product when the reaction mixture was heated further at 315 °C for 0.5 h. In the case of **10d**, the anhydride and MDA were dissolved in THF and the solvent evaporated; NMR analysis revealed the presence of bisimide **12d**. Heating to 204 °C resulted in a 34% weight loss, accompanied by the disappearance of the distinctive trimethylsilyloxy peak in the NMR of the residual solid. The NMR and HRMS data strongly suggest that the product obtained is the 3-hydroxy bisimide **12g**.

11a: ^{1}H NMR ($CDCl_3$) 6.96 (d, J=9 Hz, 2H, $H_{11'}$), 6.62 (d, J=9 Hz, 2H, $H_{10'}$), 3.88 (s, 2H, H_{13}); HRMS (DCI, CH_4) calcd ($C_{21}H_{20}N_2O_2$, M^+) 332.1525, obsd 332.1527.

12a: TMA: T_m=206.19 ^{0}C (confirmed by DSC); ^{1}H NMR ($CDCl_3$) δ 7.255 and 7.155 (AA'BB'm, 8H, H_{10} and H_{11}), 5.97 (m, 4H, H_4 and H_5), 4.01 (s, 2H, H_{13}), 3.20 (m, 4H, H_1 and H_2), 2.70 (dm, 4H, H_3 and H_6); 2.30 (dm, 4H, $H_{3'}$ and $H_{6'}$); ^{13}C NMR ($CDCl_3$) δ 179.33 (C_7 and C_8), 140.93 (C_9), 130.28 (C_{12}), 129.76 (C_{11}), 127.91 (C_4 and C_5), 126.65 (C_{10}), 41.20 (C_{13}), 39.32 (C_1 and C_2), 23.89 (C_3 and C_6); IR (KBr) 1780 and 1709 (imide C=O), 1625 (C=C), 1512 (Ar) cm^{-1}; HRMS (DCI, CH_4) calcd ($C_{29}H_{26}N_2O_4$, M^+) 466.1893, obsd 466.1901.

11b: TMA T_m=90.79 °C (confirmed by DSC); ^{1}H NMR ($CDCl_3$) δ 7.36-7.14 (m, 9H, aryl), 7.03 (d, J=8 Hz, 2H, $H_{11'}$), 6.46 (d, J=8 Hz, 2H, $H_{10'}$), 6.14 (m, 2H, H_4 and H_5), 3.94 (m, 1H, H_3), 3.85 (s, 2H, H_{13}), 3.46 (dd, J=9 and 6 Hz, 1H, H_2), 3.345 (td, J=9 and 2 Hz, 1H, H_1), 2.99 (dm, J=14 Hz, 1H, H_6), 2.565 (ddm, J=14 and 9 Hz, 1H, $H_{6'}$); ^{13}C NMR ($CDCl_3$) δ 178.83 (C_7), 176.80 (C_8), 141.76 (C_{ipso}), 140.71 ($C_{9'}$), 140.50 (C_9), 138.31 (($C_{12'}$ and C_{12}), 129.60 ($C_{11'}$), 129.45 (C_{11}), 128.98 (C_o), 128.68 (C_m), 127.69 (C_4), 127.63 (C_p), 127.04 (C_5), 126.48 (C_{10}), 126.42 ($C_{10'}$), 44.72 (C_2), 41.14 (C_{13}), 40.92 (C_3), 37.90 (C_1) 21.69 (C_6); IR (KBr) 3471 and 3358 (NH_2), 1779 and 1711 (imide C=O), 1600 (C=C), 1513 (Ar) cm^{-1}; HRMS (DCI, CH_4) calcd ($C_{27}H_{24}N_2O_2$, M^+) 408.1838, obsd 408.1827.

12b: DSC: T_m=87.1 °C; ^{1}H NMR ($CDCl_3$) δ 7.39-7.17 (m, 18H, aryl), 6.125 (m, 4H, H_4 and H_5), 4.13 (bs, 2H, H_{13}), 4.03 (s, 2H, H_3), 3.42 (dd, J=8 and 3 Hz, 2H, H_2), 3.245 (ddd, J=10, 8 and 2 Hz, 2H, H_1), 2.55 (m, 4H, H_6 and $H_{6'}$); ^{13}C NMR ($CDCl_3$) δ 179.17 (C_7), 178.31 (C_8), 141.76 (C_{ipso}), 140.09 (C_9), 130.54 (C_4), 130.25 (C_{12}), 129.82 (C_o), 128.95 (C_{11}), 127.63 (C_5), 127.53 (C_m), 126.95 (C_p), 126.52 (C_{10}), 46.79 (C_2), 41.23 (C_{13}), 40.06 (C_3), 38.67 (C_1) 23.79 (C_6); IR (KBr) 1779 and 1711 (imide C=O), 1600, 1513 (Ar) cm^{-1}; (DCI, CH_4) calcd ($C_{41}H_{34}N_2O_4$, M^+) 618.2519, 618.2538.

11c: ^{1}H NMR ($CDCl_3$) 6.98 (d, J=9 Hz, 2H, $H_{11'}$), 6.62 (d, J=9 Hz, 2H, $H_{10'}$); HRMS (DCI, CH_4) calcd ($C_{22}H_{22}N_2O_3$, M^+) 362.1630, obsd 362.1611.

12c: TMA: T_m=75.1 °C; ^{1}H NMR ($CDCl_3$) δ 7.27 (AA'BB'm, 4H, H_{11}), 7.19 (AA'BB'm, 4H, H_{10}), 6.17 (m, 4H, H_4 and H_5), 4.31 (m, 2H, H_3), 4.03 (s, 2H, H_{13}), 3.28 (s, 6H, OMe), 3.165 (dd, J=14 and 8 Hz, 2H, H_2), 3.15 (m, 2H, H_1), 2.665 (m, 4H, H_6 and $H_{6'}$); ^{13}C NMR ($CDCl_3$) δ 179.33 (C_7), 176.40 (C_8), 140.93 (C_9), 132.23 (C_4), 130.47 (C_{12}), 129.82 (C_{11}), 127.84 (C_5), 126.76 (C_{10}), 71.73 (C_3), 56.70 (OMe), 45.31 (C_2), 41.29 (C_{13}), 36.76 (C_1) 22.28 (C_6); IR (KBr) 1779 and 1711 (imide C=O), 1611 (C=C), 1513 (Ar) cm^{-1}; HRMS(DCI, CH_4) calcd ($C_{29}H_{18}N_2O_4$, M^+–$2CH_3OH$–$2H_2$) 458.1267, obsd 458.1260.

12d: ^{1}H NMR ($CDCl_3$) δ 7.19 (m, 4H, H_{11}), 6.90 (m, 4H, H_{10}), 5.90 (m, 4H, H_4 and H_5), 4.56 (m, 2H, H_3), 3.71 (s, 2H, H_{13}), 3.185 (td, J=10 and 5 Hz, 1H, H_1), 2.955 (dd, J=10 and 4 Hz, 1H, H_2), 2.59 (m, 1H, H_6), 2.44 (m, 1H, $H_{6'}$), -0.09 (s, 9, Me_3Si).

11e: ^{1}H NMR ($CDCl_3$) 6.96 (d, J=8 Hz, 2H, $H_{11'}$), 6.62 (d, J=8 Hz, 2H, $H_{10'}$), 3.88 (s, 2H, H_{13}); HRMS (DCI, CH_4) calcd ($C_{22}H_{22}N_2O_2$, M^+) 346.1681, obsd 346.1679.

12e: ^{1}H NMR ($CDCl_3$) δ 7.25 (AA'BB'm, 4H, H_{11}), and 7.14 (AA'BB'm, 4H, H_{10}), 5.61 (m, 2H, H_5), 4.01 (s, 2H, H_{13}), 3.22 (m, 4H, H_2 and H_1), 2.62 (m, 2H, H_6 or $H_{6'}$), 2.28 (m, 4H, H_3 and $H_{6'}$ or H_6), 1.76 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 179.45 (C_7), 179.20 (C_8), 140.83 (C_9), 136.57 (C_4), 130.21 (C_{11}), 129.66 (C_{10}), 126.42 (C_{12}), 120.15 (C_5), 41.13 (C_{13}), 39.68 (C_2), 39.25 (C_1), 28.91 (C_3), 24.53 (C_6),

23.51 (CH_3); IR (KBr) 1779 and 1708 (imide C=O), 1611 (C=C), 1512 (Ar) cm^{-1}; HRMS (DCI, CH_4) calcd ($C_{31}H_{30}N_2O_4$, M^+) 494.2206, obsd 494.2182.

11f:[16] TMA T_m=131.09 °C (confirmed by DSC); ^1H NMR ($CDCl_3$) δ 7.48-7.20 (m, 14H, aryl), 7.044 (d, J=8.4 Hz, 2H, $H_{11'}$), 6.860 (d, J=8.4 Hz, 2H, $H_{10'}$), 6.496 (s, 2H, H_4 and H_5), 3.882 (bd, J= 4.9 Hz, 2H, H_3 and H_6), 3.849 (s, 2H, H_{13}), 3.612 (dd, J= 4.9 and 2.2 Hz, 2H, H_1 and H_2); ^{13}C NMR ($CDCl_3$) δ 174.89 (C_7 and C_8), 143.49 (C_{ipso}), 140.50 ($C_{9'}$), 139.10 ($C_{12'}$ and C_{12}), 137.42 (C_9), 131.27 (C_4 and C_5), 129.38 ($C_{11'}$), 128. 89 (C_o), 128.81 (C_{11}), 128.32 (C_m), 127.99 (C_p), 127.13 (C_{10}), 126.20 ($C_{10'}$), 46.41 (C_1 and C_2), 41.60 (C_3 and C_6), 40.87 (C_{13}); IR (KBr) 3414 and 3379 (NH_2), 1782 and 1714 (imide C=O), 1682 (C=C), 1597, 1513 (Ar) cm^{-1}; HRMS (DCI, CH_4) calcd ($C_{33}H_{28}N_2O_2$, M^+) 484.2151, obsd 484.2160.

12f: TMA T_m=117.87 °C (confirmed by DSC); ^1H NMR ($CDCl_3$) δ 7.48-7.10 (m, 28H, aryl), 6.029 (s, 4H, H_4 and H_5), 4.012 (s, 2H, H_{13}), 3.882 (bd, J= 4.0 Hz, 4H, H_3 and H_6), 3.202 (dd, J= 4.0 and 1.6 Hz, 4H, H_1 and H_2); ^{13}C NMR ($CDCl_3$) δ 176.77 (C_7 and C_8), 143.42 (C_{ipso}), 140.68 (C_9), 129.98 (C_{12}), 129.85 (C_4 and C_5), 129.62 (C_{11}), 128. 80 (C_o), 127.98 (C_m), 127.09 (C_p), 126.16 (C_{10}), 45.98 (C_1 and C_2), 41.02 (C_{13}), 39.75 (C_3 and C_6); IR (KBr) 3414 and 3379 (NH_2), 1782 and 1714 (imide C=O), 1682 (C=C), 1597, 1513 (Ar) cm^{-1}; HRMS (DCI, CH_4) calcd ($C_{53}H_{42}N_2O_4$, M^+) 770.3145, obsd 770.3135

12g: ^1H NMR ($CDCl_3$) δ 7.3-7.1 (m, 8H, H_{10} and H_{11}), 6.12 (m, 2H, H_4), 5.94 (m, 2H, H_5), 4.53 (m, 2H, H_3), 4.01 (s, 2H, H_{13}), 3.92 (bs, 1H, OH), 3.45 (dd, J=10 and 6 Hz, 2H, H_2), 3.30 (m, 2H, H_1), 2.60 (m, 4H, H_6 and $H_{6'}$); ^{13}C NMR ($CDCl_3$) δ 178.90 (C_7 and C_8), 141.30 (C_9), 134.60 (C_4), 131.11 (C_{12}), 129.91 (C_{11}), 126.89 (C_5), 126.61 (C_{10}), 66.36 (C_3), 44.53 (C_2), 41.29 (C_{13}), 38.24 (C_1) 23.88 (C_6); IR (KBr) 3467 (OH), 1774 and 1708 (imide C=O), 1612 (C=C), 1512 (Ar) cm^{-1}; HRMS (DCI, CH_4) calcd ($C_{29}H_{26}N_2O_6$, M^+) 498.1791, obsd 498.1758

15a: ^1H NMR ($CDCl_3$) δ 7.96 (AA'BB'm, 4H, H_3 and H_6) and 7.79 (AA'BB'm 4H, H_4 and H_5), 7.37 (s, 8H, H_{10} and H_{11}), 4.10 (s, 2H, H_{13}); ^{13}C NMR ($CDCl_3$) δ 167.28 (C_7 and C_8), 140.46 (C_9), 134.32 (C_4 and C_5), 131.79 (C_{12}), 129.87 (C_1 and C_2), 129.72 (C_{11}), 126.60 (C_{10}), 123.70 (C_3 and C_6), 41.20 (C_{13});

IR (KBr) 1777 and 1718 (imide C=O), 1511 (Ar) cm^{-1}; HRMS (DCI, CH_4) calcd ($C_{29}H_{18}N_2O_4$, M^+) 458.1267, obsd 458.1264.

17a: ^1H NMR ($CDCl_3$) δ 8.005 (AA'BB'm, 4H, H_3 and H_6), 8.003 (d with hyperfine AA'XX' splitting, J=8 Hz, 4H, H_{11}), 7.837 (AA'BB'm, 4H, H_4 and H_5), 7.673 (d with hyperfine AA'XX' splitting, J=8 Hz, 4H, H_{10}); ^{13}C NMR ($CDCl_3$) δ 194.70 (C_{13}), 166.95 (C_7 and C_8), 136.62 (C_9), 135.71 (C_{12}), 134.85 (C_4 and C_5), 131.73 (C_1 and C_2), 130.99 (C_{11}), 126.11 (C_{10}), 124.11 (C_3 and C_6); IR (KBr) 1783 and 1712 (imide C=O), 1733 (C=O), 1513 (Ar) cm^{-1}; HRMS (DCI, CH_4) calcd ($C_{29}H_{16}N_2O_5$, M^+) 472.1059, obsd 472.1074.

21: TMA: T_m=90.19 ^0C (confirmed by DSC); ^1H NMR ($CDCl_3$) δ 7.285 and 7.199 (ABq with additional hyperfine AA'BB' splitting, J=8.4 Hz, 4H each, H_6 and H_5 respectively), 4.024 (s, 2H, H_8), 2.859 (s, 8H, H_3); ^{13}C NMR ($CDCl_3$) δ 176.24 (C_2), 140.90 (C_7), 130.02 (C_4), 129.76 (C_6), 126.48 (C_5), 40.07 (C_8), 28.34 (C_3); IR (KBr) 1776 and 1706 (imide C=O), 1512 (Ar) cm^{-1}; HRMS (DCI, CH_4) calcd ($C_{21}H_{18}N_2O_4$, M^+) 362.1267, obsd 362.1300.

Thermolysis of Bisimides 12: A 2:1 mixture of anhydride **10** and MDA were heated for 1 hr at 204 ^0C (400 ^0F; generally yielding cyclohexene bisimides **12**, as described above), then at 315 ^0C (600 ^0F) for 30 min, at 340 ^0C (650 ^0F) for 50 min, and finally at 371 ^0C (700 ^0F) for 30 min. After each step, the reaction product was cooled, weighed, ground to a powder and a sample removed for spectroscopic analysis. Product yields and weight losses are summarized in Tables 1 and 2, respectively. Both the crosslinking of **12** to **13**, and its aromatization to **15**, were observed. The crosslinking can be readily detected by the appearance of aliphatic multiplets in region of 1.5-2.5 ppm. On the other hand, the phthalimides formed on aromatization have a pair of distinctive AA'BB' multiplets located downfield in the region 7.6-8.0 ppm and separated by ca 0.2 ppm. The HRMS data confirms the formation of half (**14**) and fully (**15**) aromatized imides. In the case of the thermolysis of **12c**, only **13a**, **14a** and **15a** were observed. For **12d**, **12g** was also detected, in addition to **13a**, **14a** and **15a** (see Table 1). In the case of the analogs **12e**, **13e**, and **15e**, the respective vinyl, alkyl and aromatic methyls are easily discernible at

1.76, ca. 0.95 (*vide infra*) and 2.54 ppm. What's more, as expected, there are three methyl groups observed for the crosslinked **13e**, each corresponding to one of the following isomers: head-to-head, head-to-tail, and tail-to-tail.

13a: ^{1}H NMR ($CDCl_3$) δ 4.02 (s, 2H, H_{13}).

14a: ^{1}H NMR ($CDCl_3$) δ 4.05 (s, 2H, H_{13}); HRMS (DCI, CH_4) calcd ($C_{29}H_{22}N_2O_4$, M^+) 462.1580, obsd 462.1557.

15a: as above.

13b: ^{1}H NMR ($CDCl_3$) δ 3.89 (s, 2H, H_{13}).

14b: ^{1}H NMR ($CDCl_3$) δ 4.00 (s, 2H, H_{13}); parent peak not observed in HRMS.

15b[17]: ^{1}H NMR ($CDCl_3$) δ 7.95 (dd, J= 4 and 1 Hz, 2H, H_6), 7.80 (t, J= 4 Hz, 2H, H_5), 7.70 (dd, J= 4 and 1 Hz, 2H, H_4), 7.62-7.52 (m, 4H, pendant Ar), 7.52-7.38 (m, 6H, pendant Ar), 7.38-7.10 (m, 8H, Ar), 4.03 (s, 2H, H_{13}); ^{13}C NMR ($CDCl_3$) δ 166.91 (C_7), 166.81 (C_8), 141.42 (C_3), 140.37 (*ipso*), 140.14 (C_2), 136.35 (C_4), 135.97 (C_{12}), 134.08 (C_5), 132.84 (C_9), 129.53 (C_{11}), 129.39 (C_o), 128.76 (C_p), 128.02 (C_m), 126.98 (C_1), 126.62 (C_{10}), 122.79 (C_6), 41.03 (C_{13}); HRMS (DCI, CH_4) calcd ($C_{41}H_{26}N_2O_4$, M^+) 610.1893, obsd 610.1840.

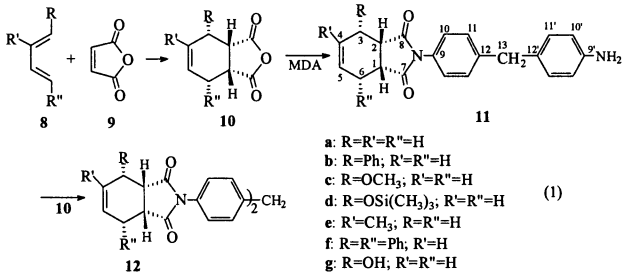
13e: ^{1}H NMR ($CDCl_3$) δ 0.99, 0.96 and 0.93 (each s, CH_3), 4.02 (s, 2H, H_{13}).

14e: ^{1}H NMR ($CDCl_3$) δ 4.08 (s, 2H, H_{13}); HRMS (DCI, CH_4) calcd ($C_{31}H_{26}N_2O_4$, M^+) 490.1893, obsd 490.1888.

15e: ^{1}H NMR ($CDCl_3$) δ 7.82 (d, J= 4 Hz, 2H, H_6), 7.74 (s, 2H, H_3), 7.70 (d, J= 4 Hz, 2H, H_5), 4.05 (s, 2H, H_{13}), 2.54 (s, 6H, CH_3); HRMS (DCI, CH_4) calcd ($C_{31}H_{22}N_2O_4$, M^+) 486.1580, obsd 486.1521.

15f: ^{1}H NMR ($CDCl_3$) δ 7.712 (s, 4H, H_6), 7.63-7.55 (m, 8H, pendant Ar), 7.50-7.40 (m, 12H, pendant Ar), 7.40-7.00 (m, 8H, Ar), 4.02 (s, 2H, H_{13}); ^{13}C NMR ($CDCl_3$) δ 166.91 (C_7 and C_8), 141.42 (C_3 and C_6), 140.34 (*ipso*), 140.31 (C_1 and C_2), 140.01 (C_9), 136.33 (C_4 and C_5), 136.18 (C_{12}), 129.46 (C_o), 128.71 (C_p), 128.71 (C_{11}), 128.02 (C_m), 126.72 (C_{10}), 41.03 (C_{13}); HRMS (DCI, CH_4) calcd ($C_{53}H_{34}N_2O_4$, M^+) 762.2519, obsd 762.2534.

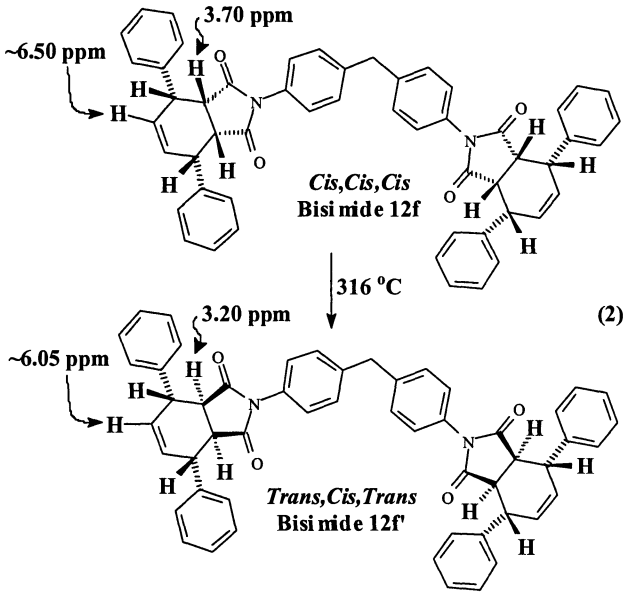
RESULTS AND DISCUSSION. We have synthesized several substituted tetrahydrophthalic anhydrides for possible use as end caps[18] - including the 3-phenyl (**10b**), 3-methoxy (**10c**), 3-trimethylsilyloxy (**10d**), and 3,6-diphenyl (**10f**) analogs - via the Diels-Alder addition of the corresponding butadienes **8** and maleic anhydride **9** (eq. 1). The butadienes are commercially available, with the exception of *trans*-1-phenylbutadiene, which was prepared according to the procedure of Grummit and Becker.[14] As shown in eq. 1, when substituents R and R" lie *trans* to the diene moiety in **8**, they end up in **10** (and the corresponding imides **11** and **12**) aligned predominantly, if not exclusively, *cis* to the anhydride (or imide) moiety. The hydrogens at C_3, C_2, C_1 and C_6 are aligned *cis*, *cis*, *cis* to each other. This is a result of the preferred *endo* addition in Diels-Alder reactions.[13,19] Two additional tetrahydrophthalic anhydrides, the 3-hydro (**10a**, Aldrich) and 4-methyl (**10e**, TCP-EP) analogs are commercially available.



(1)

Anhydrides **10** and methylenedianiline in a 2:1 ratio were then ground up together and heated at 204 °C (400 °F) for 1 h. As a rule and as determined by NMR, the primary product at this stage was bisimide **12**, which was accompanied by a small amount (<2%) of the intermediate monoimide **11** (eq. 1). The spectrum of the latter is quite distinctive because of the AA'XX' pattern of the H-10' and H-11' aromatic protons at ca. 6.6 and 7.0 ppm, respectively. Three notable exceptions to the above rule were the 3-phenyl (**10b**), 3,6-diphenyl (**10f**) and 3-silyloxy (**10d**) derivatives. In the case of **10b** and **10f**, the ratio of monoimide:bisimide (**11**:**12**) was 2:1 and 3:1, respectively, with bisimidization presumably slowed by steric hindrance. The bisimides **12b** and **12f** were the primary product when the reaction

mixture was heated further to 315 °C (see Table 1). Noteworthy, is the fact that while the vinyl and bridgehead hydrogens in 3,3-diphenyl anhydride (**10f**) and monoimide (**11f**) resonate at ca. 6.5 and 3.7 ppm, respectively, they are observed ca. 0.5 ppm upfield at 6.05 and 3.20 ppm in the corresponding bisimide **12f**. We believe that this corresponds to a conversion of the highly congested *cis, cis, cis* **12f** (with the phenyls and anhydride rings on the same face) to the less hindered *trans, cis, trans* isomer **12f'** (eq. 2); this isomerization will, in turn, affect the diamagnetic anisotropy felt by the aforementioned hydrogens.[20] Facile high temperature (315 °C) enolization presumably mediates this isomerization.

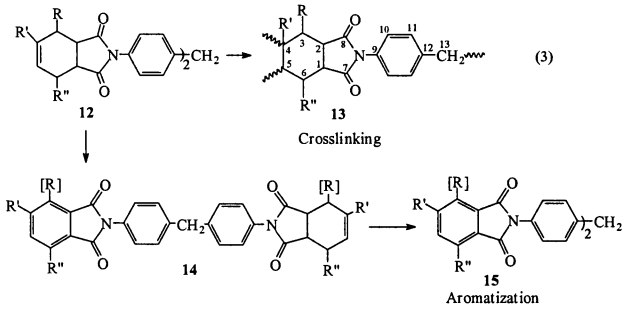


(2)

In the case of the 3-silyloxy derivative **10d**, heating at 204 °C resulted in a 34% weight loss (see Figure 3), accompanied by the disappearance of the distinctive trimethylsilyloxy peak in the NMR of the residual solid. The NMR and HRMS data strongly indicate that the product obtained is the 3-hydroxy bisimide **12g**. DSC and TGA/MS/IR studies suggest that imidization and hydrolysis occur in tandem at ca. 155 °C, accompanied by the formation and loss of hexamethyldisiloxane (commercially available from Aldrich). Theoretical weight loss for both water due to imidization and hexamethyldisiloxane is 28%. Additional weight loss is due to aromatization of some 35% of the 3-hydroxy bisimide **12g** to half-aromatized product **14.**.

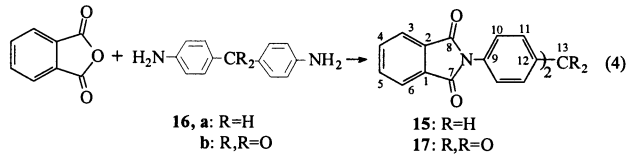
The polyimide model compounds (n = 0) were heated gradually to 370 °C and the thermal-oxidative transformations followed by NMR. Product yields are summarized in Table 1. Figure 3 presents the weight loss data. Particularly noteworthy is the observation that *the tetrahydrophthalic end caps not only experience the expected crosslinking yielding **13**, but aromatize as well to the phthalic analog **15*** (eq. 3).

- Table 1 and Figure 3 here -



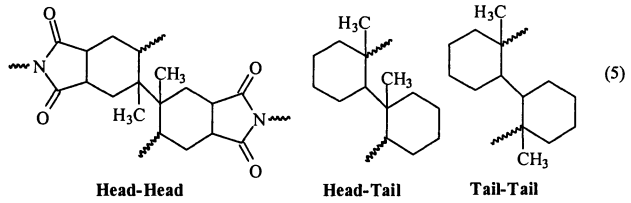
(3)

The crosslinking can be readily detected by the appearance of multiplets in the region of 1.5-2.2 ppm. (Interestingly, Table 1 reveals that crosslinking begins at temperatures substantially lower than the 415 °C indicated by St. Clair and St. Clair.[10]) On the other hand, the phthalimides formed on aromatization have a pair of distinctive AA'BB' multiplets located downfield in the region 7.6-8.0 ppm and separated by ca 0.2 ppm. An authentic sample of **15a** was prepared, as above, by grinding together a 2:1 ratio of phthalic anhydride and methylenedianiline (**16a**) and then heating the mixture at 204 °C for 1 h (eq. 4). (For the purpose of comparison, the phthalic bisimide of diaminobenzophenone (**17**) was similarly prepared and found to be absent from the product mixture.)



(4)

In the case of the 4-methyl analogs **12e**, **13e**, and **15e**, the respective vinyl, alkyl and aromatic methyls are easily discernible at 1.76, ca. 0.96 (*vide infra*) and 2.54 ppm. What's more, for the crosslinked **13e**, there are ***three*** methyl groups observed (at 0.99, 0.96 and 0.93 ppm in a ratio of 3:6:2), presumably[21] corresponding to head-to-head, head-to-tail, and tail-to-tail isomers (eq. 5).



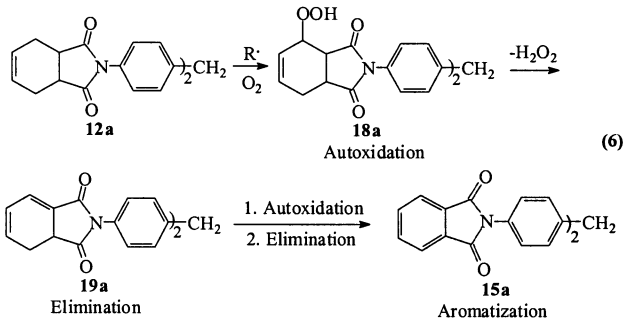
(5)

It is known that the central C-13 methylene group of MDA is amazingly sensitive to the nature of the substituents attached to the amines on either side.[22] Thus, the chemical shift of the methylene in tetrahydrophthalimide **12** (4.01 ppm for **12a**) is different from bisphthalimide **15** (4.10 ppm for **15a**). However, we were surprised to see on heating not <u>two</u> methylene absorptions at ca. 4 ppm but <u>three</u>! Since, this third peak increases initially and then decreases, we believe it corresponds to the initially formed non-symmetrical half-aromatized bisimide **14** (appearing at 4.05 ppm for **14a**; eq. 2). Indeed, HRMS data confirms the presence of **14** in the thermolysis product mixtures (see experimental section). We additionally believe that the methylene for the crosslinked product **13** appears very close (ca 0.01 ppm downfield at 4.02 ppm for **13a**) to the chemical shift of **12**. Indeed, during the thermal treatment, the methylene peak of **12** broadens and shifts ca 0.01 ppm downfield with the concomitant decrease in the olefinic hydrogens at ca 6 ppm.

Integration of the various peaks at ca. 4 ppm was used to calculate the product distribution appearing in Table 1. These calculations were confirmed by use of the other distinctive resonances (olefinic, phthalic, etc.) mentioned above. It must be noted, however, that there may well be some small amount of aromatic product formed at elevated temperatures arising from already crosslinked structures which are expected to appear under the broad aromatic multiplet appearing between 7.4—7.2 ppm . As noted in the Introduction, this is actually the desired scenario, where crosslinking occurs through the double

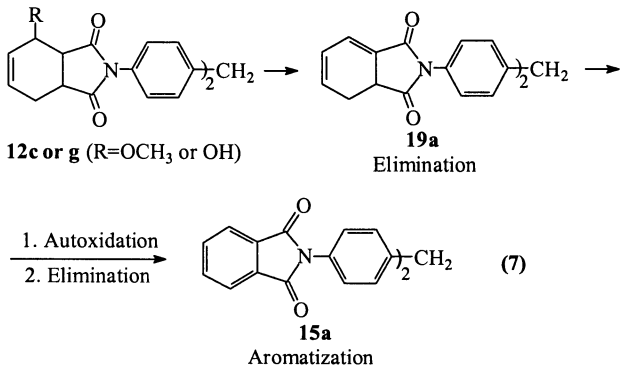
bond of the end cap, followed by preferentially Path B degradation on further aging. We simply cannot distinguish in the peaks at ca. 4 ppm between crosslinked aromatic structures and **15**.

Such oxidative aromatizations are precedented.[23] In the case of **12a**, **12b** and **12e**, this presumably involves the free radical hydroperoxidation of the cylohexene ring at the allylic positions followed by elimination of H_2O_2 (eq. 6).



(6)

When R is an oxy linkage, as in the 3-methoxy analog **12c** and the 3-hydroxy analog **12g** (obtained from trimethylsiloxy **10d)**, aromatization is accompanied and presumably initiated by elimination of the ether substituent ultimately yielding **15a** (eq. 7). Theoretical weight loss for loss of the methoxy groups is approximately 12%. [As noted previously, the silyl ether **12d** is first hydrolyzed at ca. 155 °C to the hydroxy group (i.e., to **12g**) which upon further heating is converted to **13a** and **15a**.]



(7)

Consistent with the difference in the mechanism is the observation that aromatization is not observed until 315 °C in the case of **12a**, **12b**, **12e** and **12f**, but aromatic products are observed even at 204 °C for

12c and **12g**. The elimination of the methoxy group in heating the **12c** to 315 °C is reflected in the relatively large weight loss (12%; see Figure 3) observed at this stage.

In the thermolysis of the phenylated bisimides **12b** and **12f,** aromatization at 343 °C is accompanied by substantial weight loss and the formation of bissuccinimide **21** (Table 1 and Figure 3, and eq. 8). An authentic sample of **21** was prepared, as above, by grinding together a 2:1 ratio of succinic anhydride and methylenedianiline (**16a**) and then heating the mixture at 204 °C for 1 h. The bissuccinimide **21** is readily identified in the reaction mixture by the succinic ring C_3 methylene which appears as a singlet at 2.86 ppm (^{1}H NMR) and at 28.34 ppm (^{13}C NMR). In addition, the non-conjugated imide carbonyl at C_2 appears at 176.24 ppm (^{13}C). We attribute the formation of **21** to a retro Diels-Alder reaction in which the resulting butadienes **8b** or **8f** are volatilized at the elevated temperature.[24] The concomitantly formed bismaleimide **20** is presumably reduced by bisimide **12** which is undergoing aromatization at the same time to **15**.

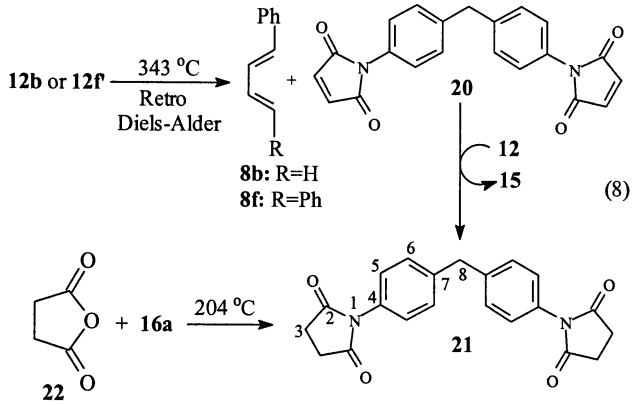


Figure 4 graphs the effect of temperature on the amount of crosslinking and the degree of aromatization (defined as the percent of fully aromatized product plus half the percent of half-aromatized product) in the air thermolysis of the various derivatives of **12**. This figure highlights several interesting observations.

- Figure 4 here -

Outstanding is the rapid rate of aromatization and crosslinking observed for the trimethylsilyloxy case **10d**; indeed, by 315 °C, no unreacted bisimide **12** remains. As discussed above, by 200 °C in this system, the bisimide **12d** has been converted to the hydroxy analog **12g** – and it is in fact the high reactivity of the latter that is noteworthy.

Comparing the parent tetrahydrophthalic bisimide **12a** with that of the 4-methyl analog **12e,** we find that substitution on the double bond in the latter case slows crosslinking slightly, and somewhat favors aromatization, beginning even as low as 315 °C. We note as well that higher temperatures favor aromatization.. The data in Table 1 reveals that in the case of **12a** at 343 °C, the ratio of crosslinking to degree of aromatization [**13a:(14**/2+**15**)] is ca. 2:1; however at 371 °C this drops to 4:3. In the case of **12e**, this ratio drops from 1:1 to 1:2.

Turning now to the phenylated analogs, we observe that crosslinking is partially inhibited in the case of the 3-phenylated **12b** and totally inhibited in the 3,6-diphenyl analog **12f**. Presumably, the cause is steric in nature. In the case of **12b**, we again see a rise in the rate of aromatization as we go from 343 to 371 °C. For **12f**, with crosslinking inhibited, aromatization is essentially complete by 343 °C.

We believe that it is this substantial percentage of aromatic product, with the concomitant lowering of the relative amount of crosslinking, which is responsible for both the improved TOS of tetrahydrophthalic end capped polyimides and their substantial frangibility.[9,10]

If the mechanism for aromatization is an oxidative one, then thermolysis of the tetrahydrophthalimides **12** under inert atmosphere should lower the amount of aromatization dramatically. This is indeed the case, as shown in Table 2. Two samples (0.5 g) of powdered **12a** were thermolyzed at 343 °C for 3 h: prior to thermolysis, one of the samples was sealed under vacuum in a sealed tube after deoxygenating the powder via five vacuum/argon cycles; the second sample was left open to air. In the case of the sample in inert atmosphere, aromatization was substantially inhibited; thus, the degree of aromatization dropped from 38% in air down to 8%. At the same time, the ratio crosslinking to the degree of aromatization rose from ca. 1:1 in air down to almost 10:1. It should be noted that despite the exclusion

of oxygen, some residual aromatization is, nevertheless observed; it presumably results from radical induced disproportionation.

- Table 2 here -

We are currently investigating the thermal-oxidative stability of tetrahydrophthalic end capped polyimides either processed under inert atmosphere or those in which aromatization is inhibited by the substitution pattern on the end cap.

ACKNOWLEDGMENT. We thank Daniel Scheiman of QSS, Inc. for performing thermal analysis and FT-IR, and Linda Ingraham of the Ohio Aerospace Institute for assistance with thermolysis runs. We also thank the High Operating Temperature Propulsion Components (HOT_PC) Program at NASA Glenn for their kind support.

Table 1: Product distribution in the air thermolysis of a 2:1 mixture of anhydrides **10a-e** and methylenedianiline (**11**: monoimide; **12**: bisimide; **13**: crosslinked structure; **14**: half-aromatized product; **15**: fully aromatized product.)

Anhydride **10**	204 °C (1 h)	315 °C (30 min)	343 °C (50 min)	371 °C (30 min)
a (3-H)	**11a** (2%) **12a** (98%)	**11a** (0.5%) **12a** (98%) **13a** (1%) **14a** (-----) **15a** (0.5%)	**11a** (-----) **12a** (35%) **13a** (35%) **14a** (29%) **15a** (1%)	**11a** (-----) **12a** (11%) **13a** (40%) **14a** (37%) **15a** (12%)
b (3-Ph)	**11b** (67%) **12b** (33%)	**11b** (16%) **12b** (38%) **13b** (-----) **14b** (14%) **15b** (32%)	**11b** (7%) **12b** (12%) **13b** (6%) **14b** (35%) **15b** (32%) **21** (8%)	**11b** (-----) **12b** (-----) **13b** (11%) **14b** (21%) **15b** (56%) **21** (12%)
c (3-OMe)	**11c** (< 1%) **12c** (>95%) **15a** (5%)	**12a** (12%) **13a** (17%) **14a** (47%) **15a** (24%)	**12a** (-----) **13a** (19%) **14a** (47%) **15a** (34%)	**12a** (-----) **13a** (19%) **14a** (33%) **15a** (49%)
d (3-$OSiMe_3$)	**12g** (61%) **13a** (4%) **14a** (35%)	**12g** (-----) **13a** (35%) **14a** (13%) **15a** (52%)	---[a]	---[a]
e (4-Me)	**11e** (7%) **12e** (93%)	**11e** (6%) **12e** (85%) **13e** (-----) **14e** (-----) **15e** (9%)	**11e** (-----) **12e** (34%) **13e** (28%) **14e** (15%) **15e** (23%)	**11e** (-----) **12e** (4%) **13e** (31%) **14e** (14%) **15e** (51%)
f (3,6-diPh)	**11f** (75%) **12f'** (25%)	**11f** (2%) **12f'** (88%) **13f** (-----) **15f** (10%)	**11f** (-----) **12f'** (2%) **13f** (-----) **15f** (86%) **21** (12%)	**11f** (-----) **12f'** (-----) **13f** (-----) **15f** (85%) **21** (15%)

a. This stage was skipped because all bisimide **12** had already reacted.

Table 2: Product distribution in the thermolysis of **12a** in air and inert atmosphere at 343 °C for 3 h.

Conditions	**12a** **Cyclohexene Bisimide**	**13a** **Crosslinked**	**14a** **Half-Aromatized**	**15a** **Fully Aromatized**
Under Air	0%	42%	40%	18%
In Inert Atmosphere	7%	77%	16%	---

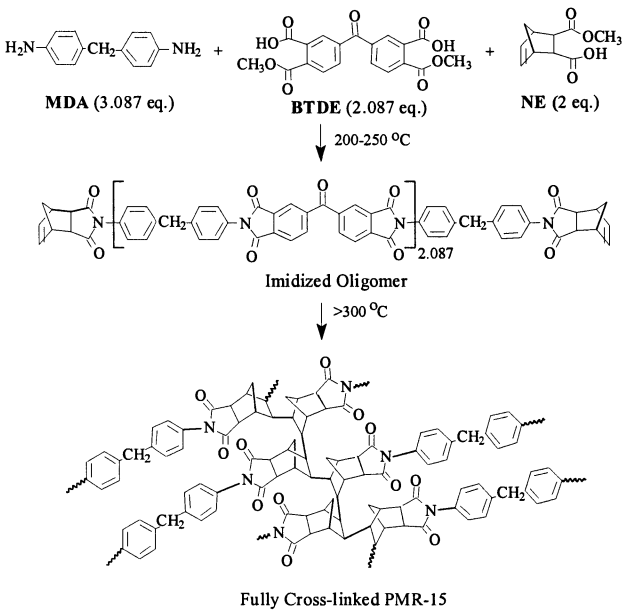


Figure 1. Reaction scheme for the preparation of fully crosslinked PMR-15.

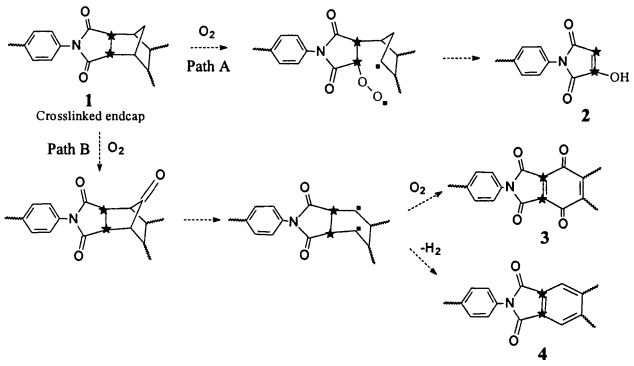


Figure 2. End cap degradation pathways (★=labeled carbons).

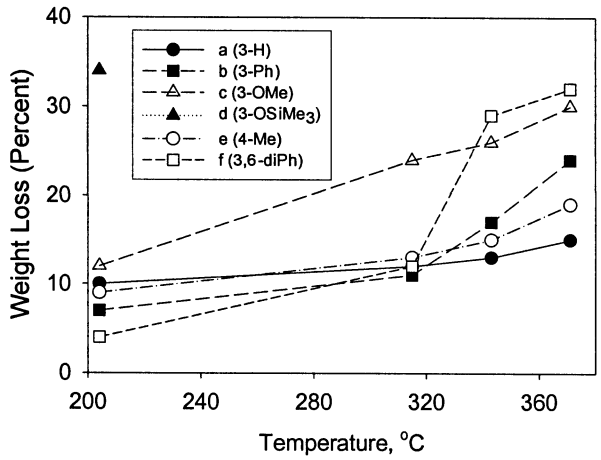


Figure 3. Weight loss on cure and thermolysis of bisimides **12** formed from 1:2 mixtures of MDA and anhydrides **10**. Imidization only accounts for between 4 and 7% of the weight loss observed.

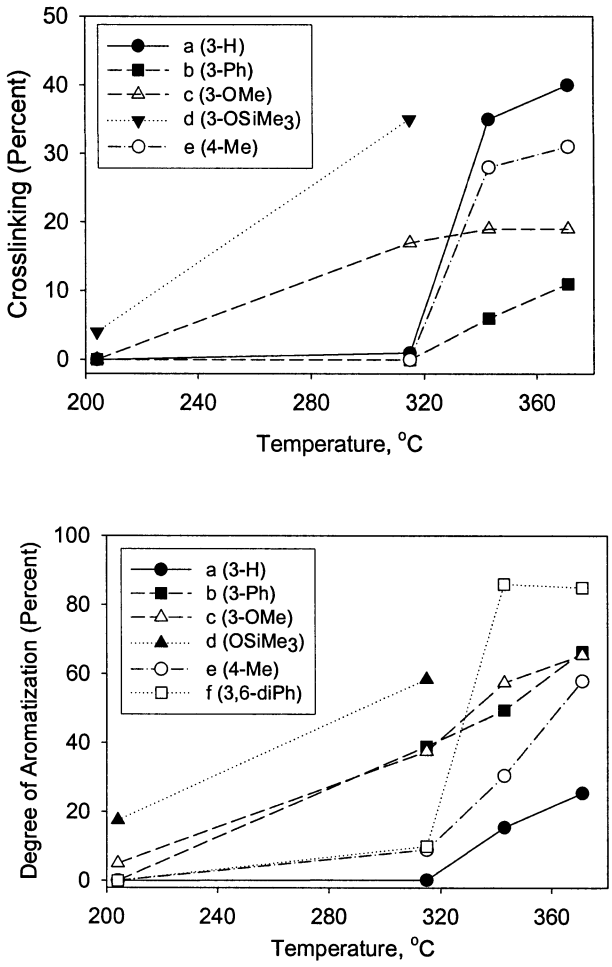


Figure 4. Percent crosslinking (above) and degree of aromatization (below) in the air thermolysis of substituted bisimides **12** formed from 1:2 Mixtures of MDA and 1,2,3,6-tetrahydrophthalic anhydrides **10a-f**.

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suggestion.

21. Based on Bio-Rad ChemWindow 6.5 ^{1}H NMR calculations.
22. Cf. Milhourat-Hammadi, A.; Chayrigues, H.; C. Merienne; Gaudemer, A. *J. Polym. Sci., Part A: Polym. Chem.*, **1994**, *32* 203-217.
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24. The boiling point of *trans*-1-phenyl-1,3-butadiene (**8b**) is reported[14] to be 80 °C at 8 mm. This corresponds (nomograph) to a boiling point of ca. 220 °C at 760 mm. The boiling point of commercial (Aldrich) *trans,trans*-1,4-phenyl-1,3-butadiene (**8f**) is 350 °C. The TGA of the 2:1 mixture of **8f** and MDA heated to 204 °C shows a T_d at 239 °C (corresponding to imidization) and 352 (corresponding to retro Diels Alder), with onset in both cases ca. 20 °C earlier. DSC confirms these transitions.