

Thermal characteristics of precursors to a difunctional imide monomer

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NATAS2010 Conference Special Issue
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Abstract A difunctional imide monomer may be produced from 4-nitrophthalic anhydride and *m*-phenylenediamine. The requisite anhydride may be generated by nitration of phthalimide followed by hydrolysis to the corresponding acid and dehydration. All intermediate compounds have been fully characterized using spectroscopic and thermal methods.

Keywords Thermal fragmentation · 1,3-Di(4-nitrophthalimido)benzene · Fuel cell membranes · 4-Nitrophthalimide

Introduction

Over the past century, the consumption of fossil fuels has powered a transformation of human society and has formed the basis for a standard of living unmatched in history. However, the depletion of fossil fuel reserves and the degradation of the earth's environment as a consequence of the large scale use of these materials has generated substantial interest in alternate forms of energy and methods of utilization. One of these is the development of proton exchange (or polymer electrolyte) fuel cells (PEMFCs) [1–3]. Potentially, PEMFCs offer great advantages over current technologies, particularly as electrical power sources for vehicles. These devices are more efficient in the conversion of chemical energy to electrical energy than present technologies. They utilize hydrogen as fuel and

produce water as the only by-product. Thus, fuel cells represent “clean” technology, and all the major automakers have fuel cell projects underway. However, many problems remain to be overcome before PEMFCs become standard power units for automobiles. One of these is the development of a durable, efficient proton exchange membrane [1–3]. Currently, perfluorinated ionomers, such as Nafion, represent the most commonly used membrane materials. Although these materials display excellent chemical and mechanical properties, high cost and relatively low operational temperatures represent significant limitations. These limitations have stimulated attempts to develop new materials for membrane construction. These are often highly aromatic polymeric structures, poly(arylene ether)s, poly(arylene ether sulfone)s, poly(ether ether ketone)s and the like [1]. Most usually, sulfonate groups are introduced either in a monomer or the finished polymer to provide proton exchange sites. Polymers containing phosphonic acid groups offer some advantages over those with sulfonic acid groups [4]. These materials provide high thermal and oxidative stability, high proton conductivity at elevated temperatures, low hydration conditions and reduced water uptake which reduces membrane swelling [3]. In this case, a monomer required for the generation of thermally stable polymers with high phosphonic acid content has been generated from phthalimide and fully characterized by spectroscopic and thermal methods.

Experimental

General

In general, reactions were carried out in a dry (all glassware was dried in an oven overnight at 120 °C and allowed to cool

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under a stream of dry nitrogen prior to use) three-necked, round-bottomed flask fitted with Liebig condenser bearing a gas-inlet tube, a magnetic stirring bar (or Trubore stirrer), and a pressure-equalizing dropping funnel (or syringe port). Chromatography was accomplished using SilaFlash P60 (230–400 mesh silica; Silicycle) in a column of appropriate size and hexane/ethyl acetate as eluant. Silica-coated Mylar plates (ThermoFisher Scientific) were used for thin layer chromatography (TLC). Melting points were determined by differential scanning calorimetry (DSC) using a Perkin Elmer Pyris Diamond instrument. All samples were analyzed at a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$ in a constant nitrogen purge of 50 mL min^{-1} . Thermal decomposition temperatures were obtained using a TA Instruments 2950 Hi-Res TG instrument interfaced with the Thermal Analyst 2100 control unit. Most generally, a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$ was used. TA Thermal Advantage software was used for data analysis. Samples (5–10 mg) were contained in a platinum pan. The sample compartment was purged with dry nitrogen at 50 mL/min during analysis. Nuclear magnetic resonance (NMR) spectra were obtained using a 10–25% solution in deuteriochloroform or dimethyl sulfoxide- d_6 and a Varian Mercury 300 MHz spectrometer. Proton and carbon chemical shifts are reported in parts-per-million (δ) with respect to tetramethylsilane (TMS) as internal reference ($\delta = 0.00$). Phosphorus chemical shifts are in δ with respect to triphenyl phosphate as internal reference ($\delta = -18.0$). Infrared (IR) spectra were obtained using thin films between sodium chloride plates or solid solutions (1%) in anhydrous potassium bromide (as discs) and a Nicolet MAGNA-IR 560 spectrometer. Absorptions were recorded in wave numbers (cm^{-1}), and absorption intensities were classified in the usual fashion as very weak (vw), weak (w), and medium (m), strong (s), and very strong (vs) relative to the strongest band in the spectrum. Mass spectra were obtained using a Hewlett-Packard 5890A gas chromatograph/mass spectrometer (MSD) with an ionizing potential of 70 electron volts and temperature programmed elution into the spectrometer inlet (90–200 $^{\circ}\text{C}$).

Materials

Common solvents and reagents were obtained from ThermoFischer Scientific or the Aldrich Chemical Company. Phthalimide, acetic anhydride, *m*-phenylenediamine, and 1,4-diazabicyclo[2.2.2]octane (DABCO) were obtained from the Aldrich Chemical Company.

Synthesis

4-Nitrophthalimide

To a stirred, cold (10 $^{\circ}\text{C}$) solution of 250 mL of fuming aqueous nitric acid in 1600 mL of concentrated aqueous

sulfuric acid was added, portionwise, 210.1 g (1.43 mol) of phthalimide at a rate such that the temperature of the mixture was maintained between 10 and 15 $^{\circ}\text{C}$ [5]. The mixture was allowed to warm to room temperature and to stir overnight. The yellow solution was slowly poured, with stirring, onto 2 kg of ice. The crude product which precipitated was collected by filtration at reduced pressure. The crude product was suspended in 2 L of ice-water, and the mixture was stirred vigorously for several minutes. The solid was collected by filtration at reduced pressure. The wash, collection procedure was repeated four times. The crude product was recrystallized from ethanol to afford 190.30 g (69.3% yield) of 4-nitrophthalimide as yellow crystals, mp 203 $^{\circ}\text{C}$ (DSC). ([6], 198 $^{\circ}\text{C}$), decomposition onset 203 $^{\circ}\text{C}$ (TG): FTIR (ATR, cm^{-1}) 3329 (m), N–H, 3104 (w), 3058 (w), C_{sp^2} –H, 1734 (m), 1699 (vs), C=O, 1622 (w), aromatic nucleus, 1545 (s), 1348 (s), $-\text{NO}_2$; $^1\text{H-NMR}$ (δ , CDCl_3) 8.03 (A portion of an ABX pattern, $J_{\text{AB}} = 8.1\text{ Hz}$, $J_{\text{AX}} = 0.6\text{ Hz}$, 1H, aromatic proton), 8.38 (X pattern of an ABX pattern $J_{\text{BX}} = 2.1\text{ Hz}$, $J_{\text{AX}} = 0.6\text{ Hz}$, 1H, aromatic proton), 8.57 (B pattern of an ABX pattern $J_{\text{AB}} = 8.1\text{ Hz}$, $J_{\text{BX}} = 2.1\text{ Hz}$, 1H, aromatic proton), 11.8 (broad s, 1H, imide proton); $^{13}\text{C-NMR}$ (δ , CDCl_3) 117.8 (aromatic carbon atom *ortho* to carbonyl), 124.5 (aromatic carbon atom *ortho* to a nitro group), 129.5 (aromatic carbon atom *ortho* to both a nitro and carbonyl group), 134.0 (aromatic carbon attached to a carboxyl group), 137.3 (aromatic carbon atom attached to a carbonyl group *meta* to a nitro group), 151.4 (aromatic carbon atom attached to a nitro group), 167.3 (carbonyl carbon atom *meta* to a nitro group), 167.6 (carbonyl atom *para* to a nitro group); MS (*m/z*, % of base) 192 (M^+ , 100), 103 ($\text{C}_7\text{H}_3\text{O}^+$, 82), 75 (C_6H_3^+ , 69).

4-Nitrophthalic acid

A mixture of 80.0 g (0.42 mol) of 4-nitrophthalimide in a solution of 26.8 g (0.66 mol) of sodium hydroxide in 240 mL of water was heated at solvent reflux for 10 min [6]. The solution was made barely acidic to litmus by addition of concentrated nitric acid solution. After the neutralization point was reached, an additional 70 ml of the nitric acid solution was added. The resulting solution was brought to solvent reflux for 3 min, allowed to cool to room temperature, and extracted with two 300-mL portions of diethyl ether. The ether layers were combined and dried over anhydrous sodium sulfate. The ether solution was poured into a pre-weighed crystallizing dish, and the solvent was allowed to slowly evaporate to provide the crude product. Recrystallization of the crude product from ethyl acetate/hexane (1:3) afforded 83.67 g (89.3% yield) of 4-nitrophthalic acid as yellow crystals, mp 172 $^{\circ}\text{C}$ (DSC), ([6], 163–164 $^{\circ}\text{C}$), onset of decomposition 180 $^{\circ}\text{C}$ (TG):

FTIR (ATR, cm^{-1}) 3091 (v. broad, m) carboxyl group, 1732 (s), 1709 (vs) (carbonyl group), 1612 (m), aromatic nucleus, 1534 (s), 1350 (s) (nitro group); $^1\text{H-NMR}$ (δ , DMSO-d_6) 7.88 (A portion of an ABX pattern, $J_{\text{AB}} = 9.0$ Hz, 1H), 8.38 (B portion of an ABX pattern, $J_{\text{AB}} = 9.0$ Hz, $J_{\text{BX}} = 2.3$ Hz), 8.43 (X portion of an ABX pattern, $J_{\text{BX}} = 2.3$ Hz); $^{13}\text{C-NMR}$ (δ , DMSO-d_6) 123.7, 126.2, 129.8, 133.0, 139.4, 148.2 (aromatic carbon atoms), 166.4, 167.8 (carbonyl carbon atoms); MS (m/z , % base) 193 ($[\text{M}-18]^+$, 4), 149 ($\text{C}_7\text{H}_3\text{NO}_3^+$, 100), 103 ($\text{C}_7\text{H}_3\text{O}^+$, 51), 75 (C_6H_3^+ , 52).

4-Nitrophthalic anhydride

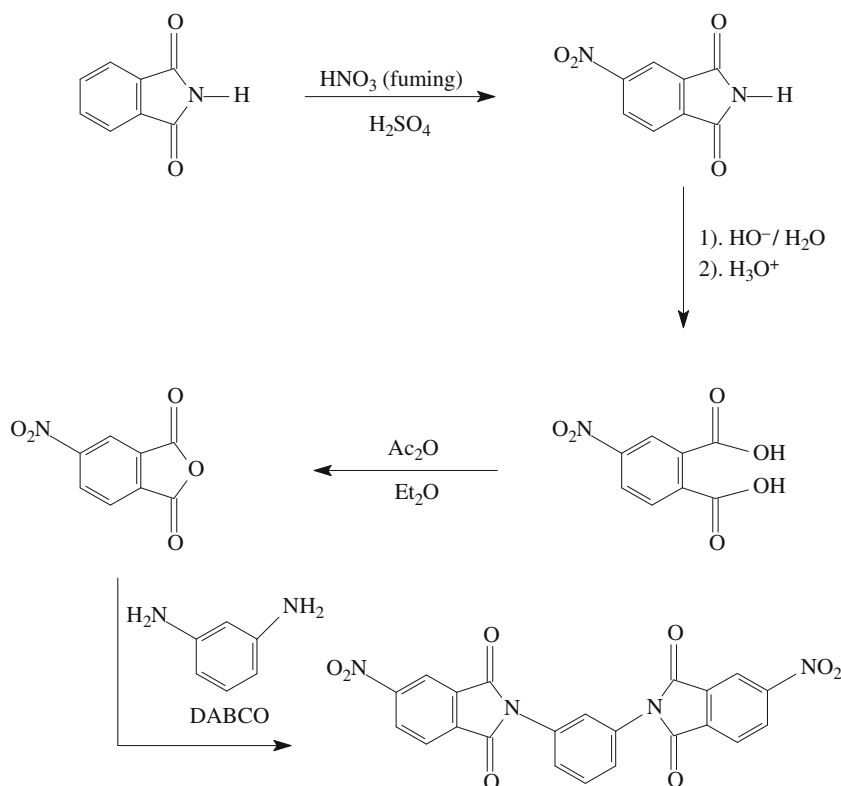
A solution of 40.3 g (0.19 mol) of 4-nitrophthalic acid and 50 mL (54.0 g, 0.53 mol) of acetic anhydride in 100 mL of anhydrous diethyl ether was stirred overnight at room temperature. Solvent and acetic acid were removed by rotary evaporation at reduced pressure to afford the crude product as a residual solid. The crude material was suspended and stirred in cold diethyl ether and then collected by filtration at reduced pressure. This process was repeated. The collected material was allowed to dry to provide 32.17 g (88.0% yield) of 4-nitrophthalic anhydride, mp 121 °C (DSC) ([7], 120–121 °C), decomposition onset 190 °C (TG): FTIR (ATR, cm^{-1}) 3013 (w), $\text{C}_{\text{sp}2}\text{-H}$, 1782 (vs), C=O, 1613 (w), aromatic nucleus, 1545 (s), 1347 (s),

nitro group; $^1\text{H-NMR}$ (δ , DMSO-d_6) 7.86 (A portion of an ABX pattern, $J_{\text{AB}} = 8.2$ Hz, 1H), 8.38 (B portion of an ABX pattern, $J_{\text{AB}} = 8.2$ Hz, $J_{\text{BX}} = 2.3$ Hz), 8.43 (X portion of an ABX pattern, $J_{\text{BX}} = 2.3$ Hz, 1H); $^{13}\text{C-NMR}$ (δ , DMSO-d_6) 123.8, 126.2, 129.9, 133.0, 139.4, (aromatic carbon atoms), 148.2 (aromatic carbon atom attached to a nitro group), 166.4, 167.8 (carbonyl carbon atoms); MS (m/z , % base) 193 (M^+ , 5.5), 149 ($\text{C}_7\text{H}_3\text{NO}_3^+$, 100), 103 ($\text{C}_7\text{H}_3\text{O}^+$, 59), 75 (C_6H_3^+ , 76).

1,3-Di(4-nitrophthalimido)benzene

A mixture of phthalic anhydride (1.0 g, 5.18 mmol), *m*-phenylenediamine (0.28 g, 2.59 mmol) and DABCO (0.06 g, 0.50 mmol) was crushed in a mortar and pestle for 2 min [8]. The crushed solid was suspended in water (5.0 mL). The solid was collected by filtration at reduced pressure and recrystallized from ethanol to provide 0.52 g (23.4% yield) of 1,3-(4-nitrophthalimido)benzene as yellow crystals, mp 198 °C (DSC), decomposition onset 184 °C (TG): FTIR (ATR, cm^{-1}) 3078 (w), $\text{C}_{\text{sp}2}\text{-H}$, 1708 (m), 1674 (s), carbonyl, 1613 (s), aromatic nucleus, 1528 (s), 1347 (s), nitro group; $^1\text{H-NMR}$ (δ , DMSO-d_6) 6.15 (d, $J = 2.0$ Hz, 1H), 6.18 (overlapping s and d, 2H), 6.87 (t, $J = 7.8$ Hz, 1H), 8.16 (A portion of an ABX pattern, $J_{\text{AB}} = 8.5$ Hz, 1H), 8.35 (B portion of an ABX pattern, $J_{\text{AB}} = 8.5$ Hz, $J_{\text{BX}} = 2.6$ Hz, 1H), 8.70 (X portion of an ABX pattern,

Scheme 1 Synthesis of 1,3-di(4-nitrophthalimido)benzene



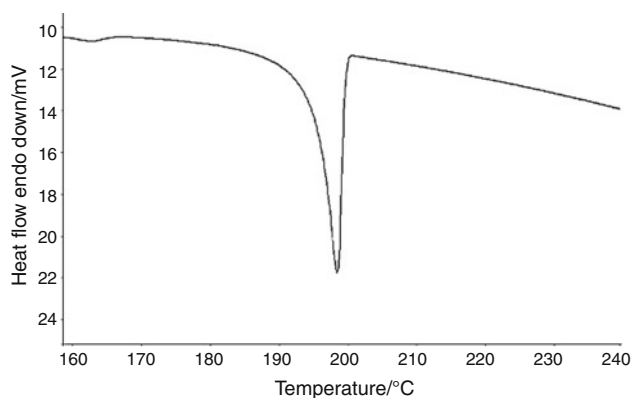


Fig. 1 DSC thermogram for 4-nitrophthalimide

$J_{\text{BX}} = 2.6$ Hz, 1H); ^{13}C -NMR (δ , DMSO- d_6) 104.3, 107.8, 125.3, 125.7, 129.8, 132.5, 134.9, 139.9, 144.7, 148.2, 166.1 (C=O), 166.9 (C=O).

Results and discussion

To construct a polymer that might serve as a useful membrane material for proton exchange fuel cells, a difunctional imido monomer is required. This compound may be prepared from phthalimide as outlined below (Scheme 1). Nitration of phthalimide provided the 4-nitro derivative as a pale yellow solid mp 203 °C (DSC) (Fig. 1).

It undergoes smooth single-step decomposition with an onset temperature for degradation of 203 °C (Fig. 2).

The infrared spectrum of this compound (Fig. 3) contains bands for N–H absorption (3329 cm^{-1}), aromatic C–H absorption ($3104, 3058\text{ cm}^{-1}$), absorption for an aromatic nucleus (1622 cm^{-1}), and absorption for a nitro group ($1545, 1348\text{ cm}^{-1}$).

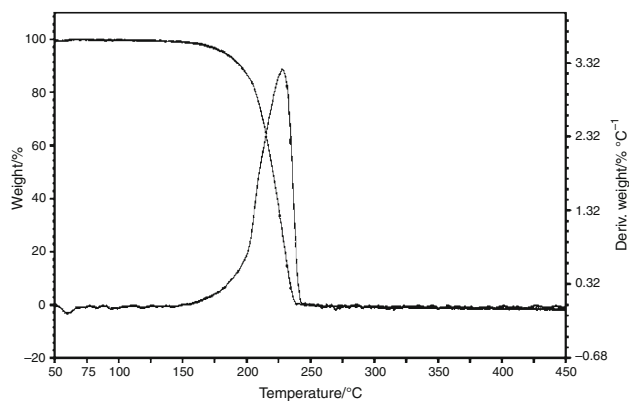


Fig. 2 Thermal decomposition of 4-nitrophthalimide

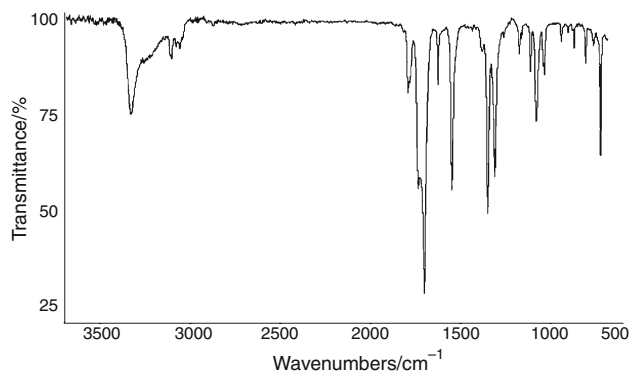


Fig. 3 Infrared spectrum of 4-nitrophthalimide

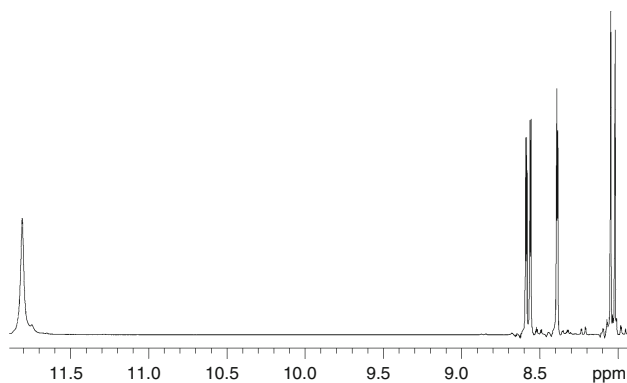


Fig. 4 Proton NMR spectrum of 4-nitrophthalimide

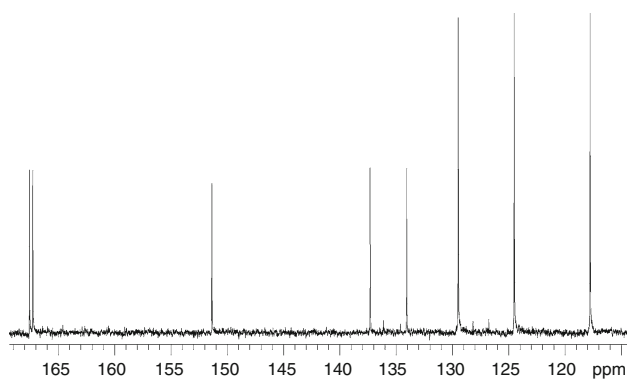
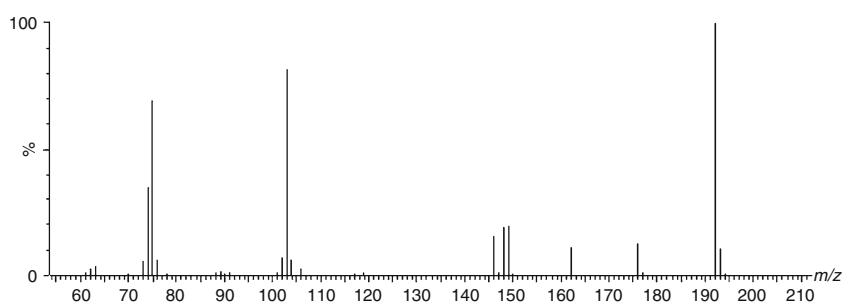
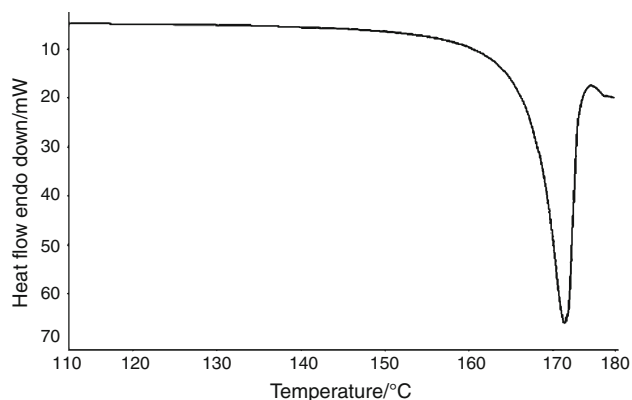
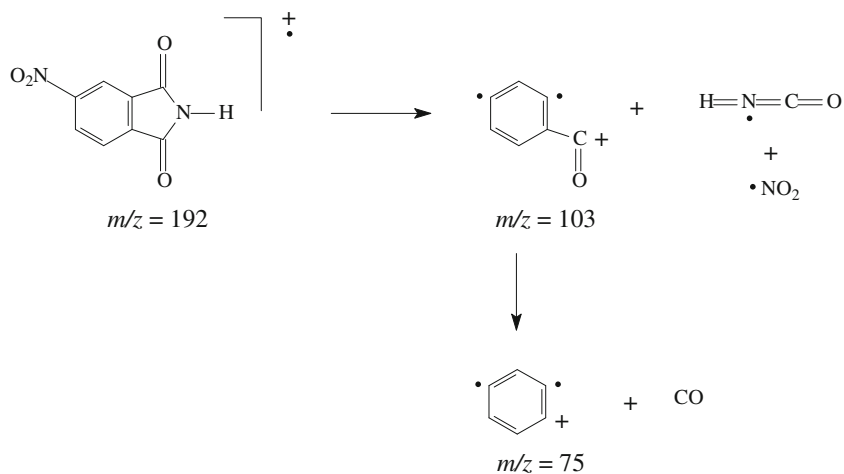
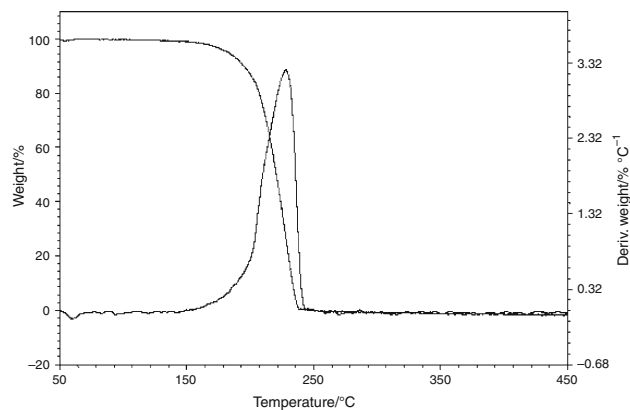


Fig. 5 Carbon-13 NMR spectrum of 4-nitrophthalimide

The proton NMR spectrum is displayed in Fig. 4. It contains an ABX pattern, δ 8.03–8.58, for the aromatic protons and a broad singlet at δ 11.8 for the imide proton. The carbon-13 NMR spectrum (Fig. 5) of this compound contains absorption for aromatic carbon atoms at δ 117.8, 124.5, 129.5, 134.0, 137.3, and 151.4 and absorption for the carbon atoms of the carbonyl groups at δ 167.3 and 167.6.

The mass spectrum of this compound (Fig. 6) contains a base peak at m/z 192 (molecular ion) and prominent peaks

Fig. 6 Mass spectrum of 4-nitrophthalimide**Scheme 2** Mass spectral fragmentation pattern for 4-nitrophthalimide**Fig. 7** DSC thermogram for 4-nitrophthalic acid**Fig. 8** Thermal decomposition of 4-nitrophthalic acid

at m/z 103 and 75. The fragmentation pattern is outlined in Scheme 2.

Base-catalyzed hydrolysis of 4-nitrophthalimide generates the corresponding dicarboxylic acid. This material was obtained as a yellow solid, mp 172 °C (DSC) (Fig. 7).

This material undergoes smooth thermal decomposition in a single step with an onset for degradation at 180 °C (Fig. 8).

The infrared spectrum of this material (Fig. 9) contains broad carboxyl absorption at 3500–2500 cm^{-1} , carbonyl absorption at 1732 and 1709 cm^{-1} , absorption for an aromatic nucleus at 1612 cm^{-1} , and absorption for a nitro group at 1534 and 1350 cm^{-1} .

The proton NMR spectrum (Fig. 10) of this compound consists of an ABX pattern, δ 7.88–8.43, and a singlet for the carboxyl proton at δ 11.7.

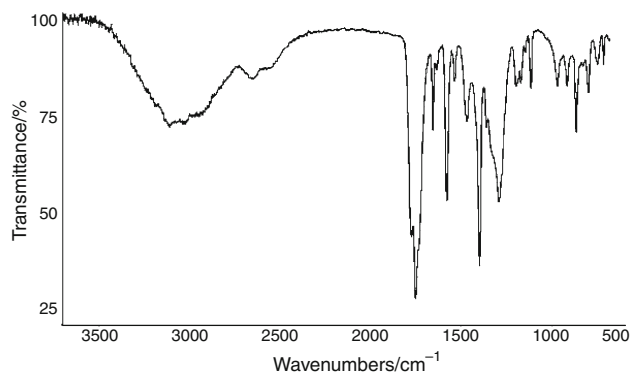


Fig. 9 Infrared spectrum of 4-nitrophthalic acid

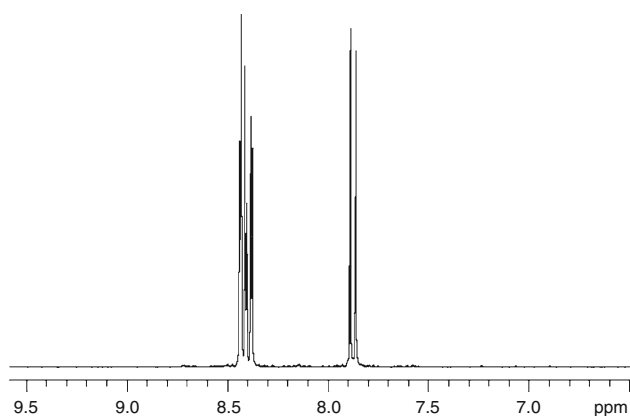


Fig. 10 Proton NMR spectrum of 4-nitrophthalic acid

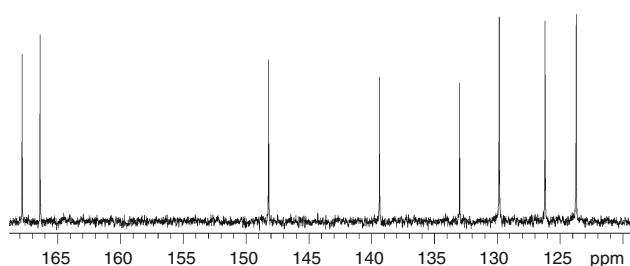
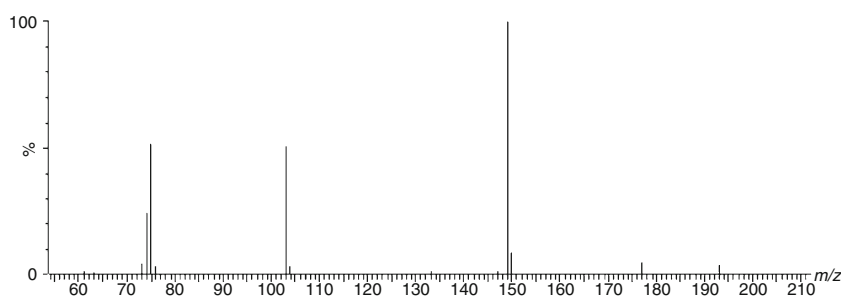


Fig. 11 Carbon-13 NMR spectrum of 4-nitrophthalic acid

Fig. 12 Mass spectrum of 4-nitrophthalic acid



The carbon-13 NMR spectrum (Fig. 11) contains absorptions for aromatic carbon atoms at δ 123.7, 126.2, 129.8, 133.0, 139.4, and 148.2 as well as carbonyl carbon atom absorptions at δ 166.4 and 167.8

The mass spectrum of this compound (Fig. 12) contains a base peak at m/z 149 and major fragment peaks at m/z 193 ($[M-18]^+$), 103, and 75. The fragmentation pattern is presented in Scheme 3.

The dicarboxylic acid may be converted to the corresponding anhydride by dehydration with acetic anhydride. 4-Nitrophthalic anhydride was obtained as pale yellow crystals, mp 121 °C (DSC) (Fig. 13).

The material undergoes smooth decomposition with an onset for degradation at 190 °C (Fig. 14).

The infrared spectrum of this compound contains aromatic C–H absorption at 3013 cm^{-1} , carbonyl absorption at 1782 cm^{-1} , absorption for an aromatic nucleus at 1613 cm^{-1} , and absorptions for a nitro group at 1545 and 1347 cm^{-1} . The spectrum is displayed in Fig. 15.

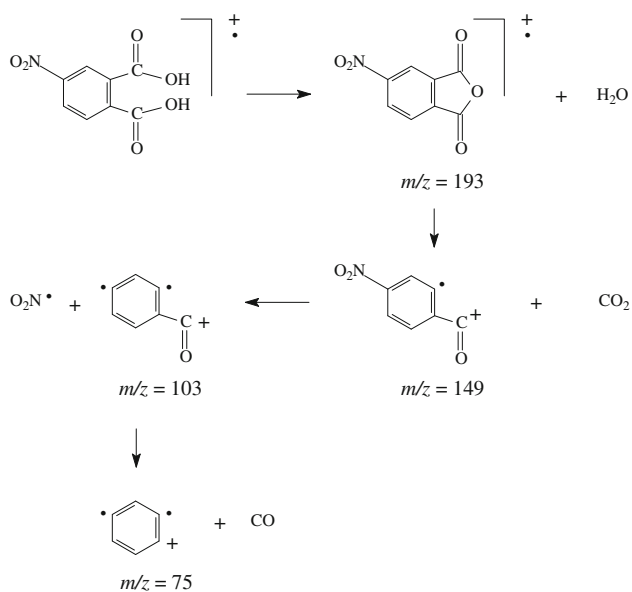
The corresponding proton NMR spectrum shown in Fig. 16 consists of an ABX pattern, δ 7.86–8.43.

The carbon-13 NMR spectrum (Fig. 17) contains absorptions for aromatic carbon atoms at δ 123.8, 126.2, 129.9, 133.0, 139.4, and 148.2 and absorption for carbonyl carbon atoms at δ 166.4 and 167.8. The mass spectrum of this compound (Fig. 18) contains a molecular ion peak at m/z 193, a base peak at m/z 149 and major fragmentation peaks at 103 and 75. The fragmentation pattern is outlined in Scheme 4.

Condensation of 4-nitrophthalic anhydride with *m*-phenylenediamine in the presence of the nucleophilic catalyst, DABCO, afforded 1,3-di(4-nitrophthalimido)benzene as yellow crystals, mp 198 °C (DSC).

The infrared spectrum of this compound (Fig. 19) contains aromatic C–H absorptions at 3078 cm^{-1} , carbonyl absorptions at 1708 and 1674 cm^{-1} , aromatic absorption at 1607 cm^{-1} , and nitro group absorption at 1528 and 1347 cm^{-1} .

The corresponding proton NMR spectrum (Fig. 20) contains absorptions for protons of the central aromatic



Scheme 3 Mass spectral fragmentation pattern for 4-nitrophthalic acid

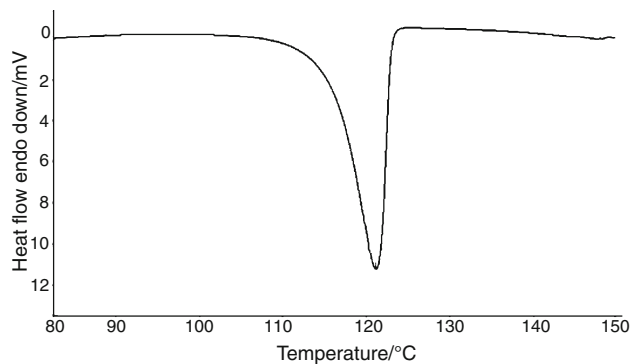


Fig. 13 DSC thermogram for 4-nitrophthalic anhydride

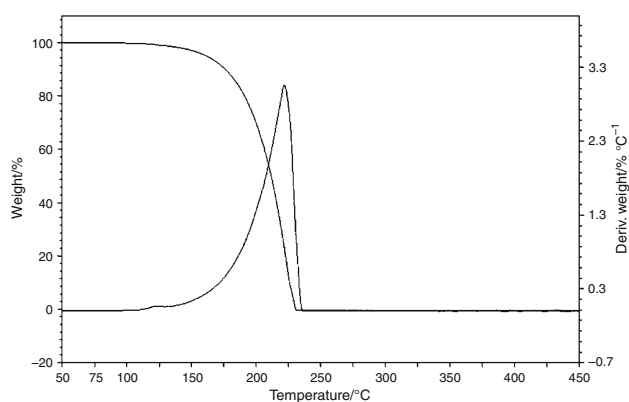


Fig. 14 Thermal decomposition of 4-nitrophthalic anhydride

unit at δ 6.15, 6.18, and 6.87 as well as an ABX pattern (δ 8.16–8.70) for the protons of the nitrophthalimido group.

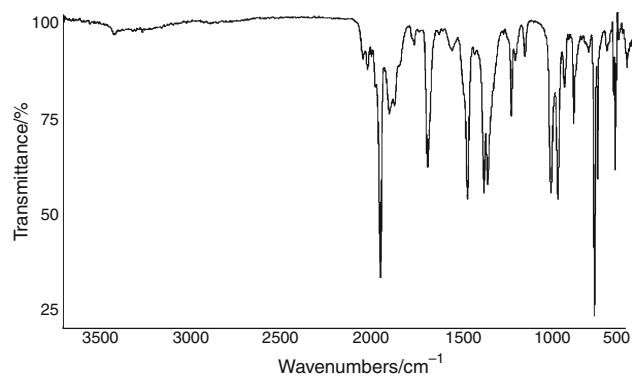


Fig. 15 Infrared spectrum of 4-nitrophthalic anhydride

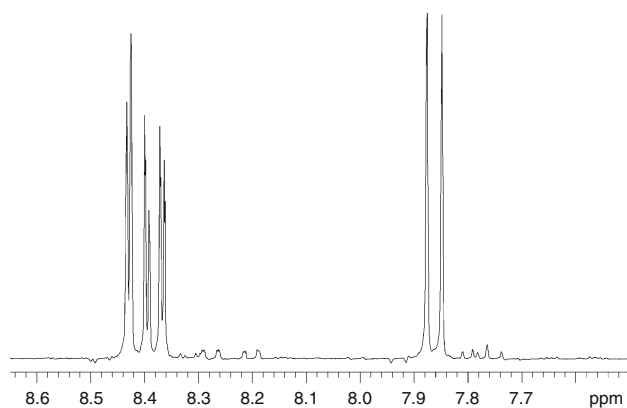


Fig. 16 Proton NMR spectrum of 4-nitrophthalic anhydride

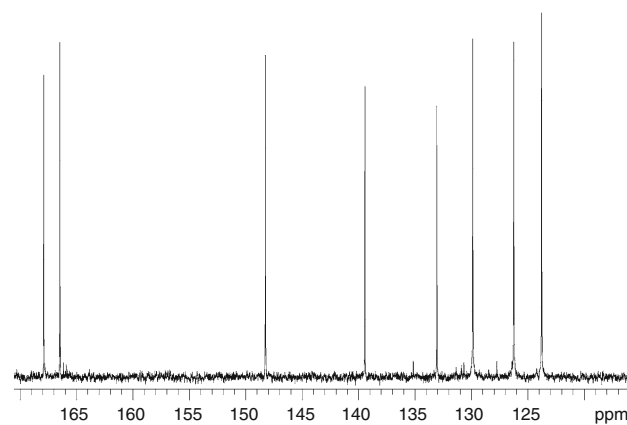
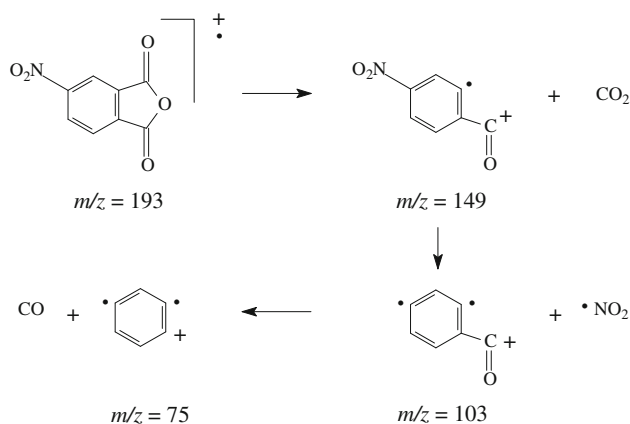
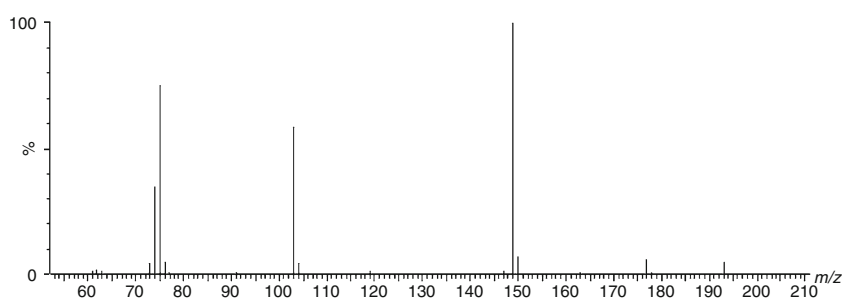


Fig. 17 Carbon-13 NMR spectrum of 4-nitrophthalic anhydride

The carbon-13 NMR spectrum (Fig. 21) contains absorptions for the central aromatic unit at δ 104.3, 107.8, 129.8, and 148.2 and absorptions for the carbon atoms of

Fig. 18 Mass spectrum of 4-nitrophthalic anhydride



Scheme 4 Mass spectral fragmentation pattern for 4-nitrophthalic anhydride

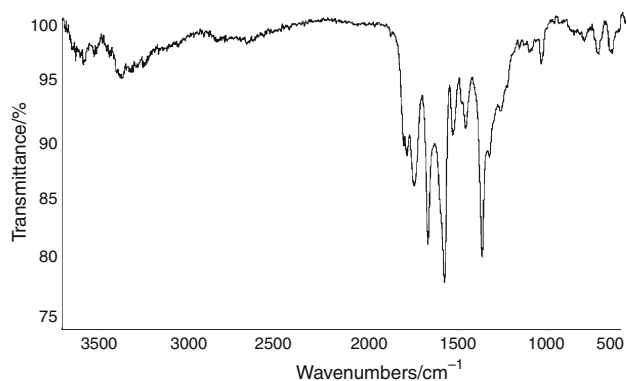


Fig. 19 Infrared spectrum of 1,3-di(4-nitrophthalimido)benzene

nitrophthalimido groups at δ 125.3, 125.7, 132.5, 134.9, 139.9, and 144.7. Absorptions for the carbonyl carbon atoms appear at δ 166.1 and 166.9.

1,3-Di(4-nitrophthalimido)benzene undergoes thermal decomposition in two steps (Fig. 22). The extrapolated onset temperatures for the first step is 184 °C and for the second 312 °C. The first mass loss probably reflects fragmentation of one of the imido units.

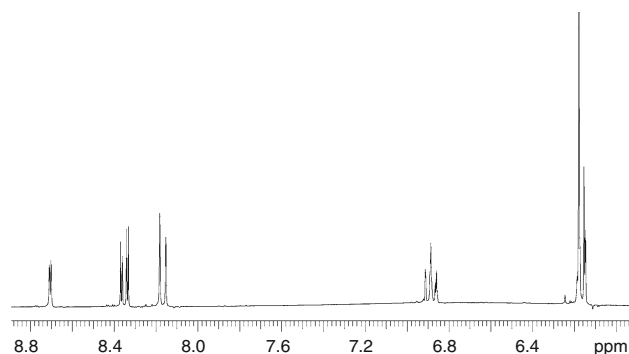


Fig. 20 Proton NMR spectrum of 1,3-di(4-nitrophthalimido)benzene

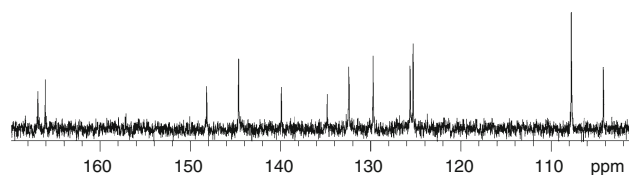


Fig. 21 Carbon-13 NMR spectrum of 1,3-di(4-nitrophthalimido)benzene

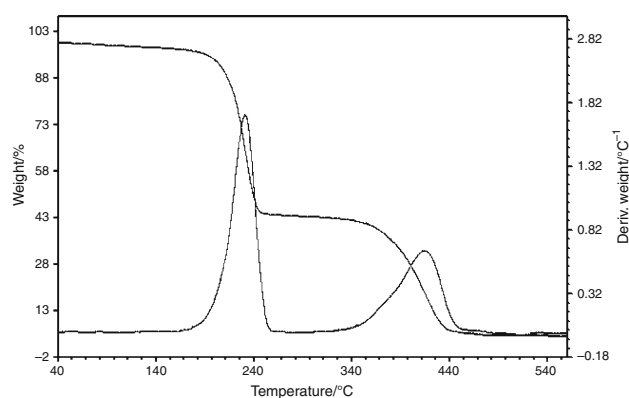


Fig. 22 Thermal decomposition of 1,3-(4-nitrophthalimido)benzene

Conclusions

A difunctional monomer, 1,3-(4-nitrophthalimido)benzene, has been prepared from phthalimide as an inexpensive

starting material. This material is a crystalline solid, mp 198 °C. It undergoes thermal decomposition in two stages, probably by fragmentation of the imido groups. Precursors to this monomer have been fully characterized using thermal and spectroscopic methods. The monomer should be reactive toward a variety of arenediol monomers bearing phosphonic acid functionality to generate durable polymeric materials suitable for the generation of useful fuel cell membranes.

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