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Novel Thermooxidatively Stable Poly(ether-imide-benzoxazole) and Poly(ester-imide-benzoxazole)

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ABSTRACT

4-Hydroxy-5-nitrophthalimides were produced via nucleophilic aromatic substitution (NAS) of 4,5-dichloro phthalimide substituents by potassium nitrite. The use of a N-phenylphthalimide having a protected 4'-hydroxyl group allows concurrent deprotection and nitro reduction to amine to give the 4-hydroxy-5-amino-N-(4'-hydroxyphenyl)phthalimide. This key intermediate is the precursor to a poly(ether-imide-benzoxazole), and is the condensable monomer for a poly(ester-imide-benzoxazole). Benzoxazole monomer formation via condensation with *p*-fluorobenzoyl chloride afforded 2-(4'-fluorophenyl)-5,6,-N-[4'(-hydroxyphenyl)imide]-benzoxazole, which was polymerized under NAS conditions to produce a poly(ether-imide-benzoxazole) having an endothermic transition at 454 °C with weight retention of 90% at 500 °C in both air and nitrogen. Solution polycondensation of the 4-hydroxy-5-amino-N-(4'-hydroxyphenyl)phthalimide monomer with isophthaloyl chloride afforded a poly(ester-amide-imide) which was isolated

and thermally cyclodehydrated in the solid state under vacuum to give a poly(ester-imide-benzoxazole) having 95% weight retention at 500 °C in both air and nitrogen, with no detectable DSC transitions up to 500 °C.

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INTRODUCTION

Wholly aromatic polyimides (PI), polybenzoxazoles (PBO) and polyesters (PES, Scheme 1) all have high thermal stabilities, and find use in high strength, high modulus fibers and engineering resins.[1,2,3,4] Drawbacks of these systems are their insolubility and intractability, which cause difficulties in both synthesis and processing. This problem is circumvented in polyimides, especially in thin film formation, through processing of the soluble poly(amic-acid) intermediates. High Tg resins are often made more tractable through the incorporation of either flexible spacer groups or kinks in the polymer backbone, or by regulating the molecular weight via controlled endcapping.[5,6] PBO's are now synthesized relatively easily in one-step procedures using poly(phosphoric acid) (PPA),[7] phosphorous pentoxide/methanesulphonic acid (PPMA)[8] or trimethylsilyl polyphosphate (PPSE)[9] as the condensing medium. The PPA method has also been shown recently to give high molecular weight soluble polyimides.[10] Isolation and thermal cyclodehydration of soluble poly(*o*-hydroxy amide), derived from the polycondensation of diacid derivatives and bis-(*o*-amino phenols) in polar aprotic solvents, is an alternative method for the production of PBO films and fibers.[11] Insolubility is circumvented in polyesters through polycondensations under melt conditions, employing high temperatures (250-350 °C) and metal (Na, K, Mg) acetates as catalysts. The use of methyl- or phenyl-ester derivatives increases the rates of transesterification and polymer formation with significant lowering of the melt reaction temperatures.[1,2]

The attainment of properties not offered by a single polymeric system can often

be realized through either pre- or post-polymerization modifications. The pre-polymerization modifications involves the chemical reaction between two different monomers (copolymerizations) and is especially useful in anionic, cationic and free radical polymerizations.[12,13] Post-polymerization modifications involve physical blending of two different but miscible systems,[14] or chemical reaction of small molecules or polymers (grafting) onto existing polymeric systems (interpenetrating networks, IPNs).[15,16]

A variation of the copolymerization approach that has received much research attention is the polymerization of monomers containing, or capable of forming, two or more different moieties, with expectation of systems having synergistic interactions and properties. For example, Preston and coworkers reported the synthesis and characterization of imide-benzoxazole fibers having synergistic interactions leading to good mechanical properties and thermal decomposition in the 520 to 625 °C range. The fibers were reported to be very thermooxidatively stable, with high tenacities (ranging up to 9 gpd) and excellent retention of tenacity after weeks of heat aging at 300 °C.[17,18] These imide-benzoxazoles were produced by the reaction of diamines containing preformed benzoxazole moieties with dianhydrides to produce soluble poly(amic acid) intermediates which were isolated, processed and then thermally cyclized to obtain the desired polyimide-benzoxazoles.

Hedrick and coworkers reported imide-aryl ether benzoxazole copolymer films with good dimensional and thermal stabilities (T_g > 300 °C) that were tough and ductile as indicated by high elongations (70-110%) and moduli in the 2 to 2.75 GPa range.[19,20,21,22] These systems were also obtained by the reaction of diamines containing preformed

benzoxazole moieties with various dianhydrides. A novel feature of this work was the co-reaction of varying ratios of this monomer and 4,4'-oxydianiline (ODA) with pyromellitic dianhydride (PMDA). Thermal solution cyclization of the obtained poly(amic-acid)benzoxazoles in N-methylpyrrolidinone (NMP) generated soluble poly(imide-arylether-benzoxazoles). This procedure allowed the tailoring of benzoxazole contents in the range of 10-74 wt-%. Low thermal expansion coefficients (two-thirds that of PMDA/ODA polyimide) were realized for copolymers having benzoxazole contents greater than 50 wt-%, making them promising candidates for use in microelectronics.

Hedrick and coworkers further showed that 2-(4'-fluorophenyl)benzoxazoles could undergo quantitative nucleophilic aromatic substitution (NAS) with various phenoxides and in several solvent systems at temperatures of 160-220 °C.[23] Polymerizations were based on the activation towards NAS of the 4'-fluorophenyl group by the benzoxazole ring. The oxazole is equivalent to an electron-withdrawing group in stabilizing the intermediate adduct involved in NAS through delocalization of the negative charge.

In a similar vein with respect to combining functional groups, Kricheldorf and coworkers reported a series of aromatic poly(ester imides) having first order phase transitions between 340 and 390 °C,[24] and poly(ester-imides) containing -$(CH_2)_n$- spacer groups of n=4-12 displaying T_m values from 297 to 393 °C.[25] In another study, Kurita and colleagues reported poly(ester-imides) with good thermooxidative stability, showing just 2% weight loss at 500 °C by thermogravimetric analysis (TGA) in air.[26,27] More recently, Caruso et al., reported a liquid crystalline poly(ester-benzoxazole) having a T_g of 181 °C, a T_m of 408 °C and a decomposition range of 510 to 620 °C.[28]

Structural variations in repeat units possessing both imide and oxazole moieties on the same benzene nucleus became possible based on a discovery involving substitution by potassium nitrite (KNO_2) on 4,5-dichlorophthalimides to give 4-nitro-5-hydroxyphthalimides.[29,30] The generation of adjacent nitro and hydroxy substituents on the same substrate is attributed to the ambident nature of the nitrite ion. Potassium nitrite can attack via the lone pairs of electrons of either the oxygen or nitrogen atoms, depending on the electronegativity of the substrate and/or the reaction conditions. This ambident nature was demonstrated on dinitrohalo- and trinitrobenzenes by Rosenblatt and coworkers, who further showed that the mode of displacement, "O" or "N" attack, also depends on which halogen is displaced.[31] Oxygen attack increases with increasing electronegativity of the halogen; ie, dinitrofluorobenzene reacts totally by "O" attack, whereas dinitroiodobenzene reacts exclusively by "N" attack. Broxton and coworkers confirmed these results, but noted that because of the reactivity of the *nitro* intermediates to further NAS via "O" attack, phenols are usually the end-product of nitrite reactions with halobenzenes.[32,33] These reactions are thus complicated since the substituting nitrite ion can be displaced from the initial product by the leaving group, by other nucleophiles, or by an oxygen of another nitrite ion to give aromatic nitrite esters which hydrolyze to phenols.

The imide group aids in the NAS displacement of halo or nitro groups on the 4 or 4,5 positions of phthalimide substrates. This is demonstrated in the production of polyetherimides via phenoxide displacements on activated phthalimide substrates.[34,35,36] The reaction is facilitated by the delocalization of the negative charge into the imide ring

during the transformation via an addition-elimination mechanism. The displacement rates are influenced more by the polarity of the carbon-to-halogen bond prior to attack than by the leaving abilities of the nitro or halogen groups. The initial attack is rate determining and reaction rates generally decrease in the order of $F \approx NO_2 > Cl > Br$.

We present here work that is aimed at investigating the properties of the polymer system containing the imide and oxazole moieties on the same benzene nucleus. We report the synthesis of several model compounds based on disubstitution of phthalimide derivatives by KNO_2, the AB-type poly(ether-imide-benzoxazole) obtained via the NAS solution polymerization of a monomer containing a preformed imide-benzoxazole, and an AA-BB'-type poly(ester-imide-benzoxazole) derived via a two-step solution polycondensation reaction with subsequent solid state cyclodehydration. Spectral characterization data of intermediates and model compounds are compared to those of the monomers and polymers formed for structural confirmation. The thermal properties of the polymers are evaluated with DSC and TGA.

EXPERIMENTAL

Materials

All chemicals were purchased from Aldrich Chemical Company except dimethyl formamide (DMF) which was purchased from Baker Scientific. All solvents were stored over 4A sieves before use. Solvents used in monomer and polymer syntheses [N-cyclohexylpyrrolidone (CHP), N,N-dimethyl acetamide (DMAc), N,N-dimethyl formamide

(DMF), dimethyl sulfoxide (DMSO) N-methylpyrrolidone (NMP) and sulfolane] were vacuum distilled from NaH (twice when used for polymerization). Pyridine was vacuum distilled from NaOH and stored over 4A sieves. Isophthaloyl chloride was recrystallized form dry hexanes.

Apparatus

FT-IR spectra were obtained with a Perkin-Elmer 1600 spectrometer. ^{13}C solution NMR spectra were obtained with Bruker AC-200 and AC-300 spectrometers while solid state CP/MAS spectra were acquired on Bruker MSL-200 and MSL-400 spectrometers. For materials that were insoluble in conventional NMR solvents, H_2SO_4 and 2-nitropropane/$AlCl_3$[37] were used with a DMSO-d_6 filled capillary as an external reference. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) thermograms were obtained with a Du Pont 9900 controller and thermal analysis modules with heating rates of 20 °C/min under nitrogen purge. Wide angle X-ray diffraction (WAXD) powder patterns were acquired on a Siemens SPD 700P spectrometer.

4,5-Dichlorophthalic Anhydride (1)

A solution of 4,5-dichlorophthalic acid (90 g, 0.383 mol) in diethyl ether was filtered to remove solid impurities, then rotory evaporated to yield a white solid which was vacuum dried. Refluxing for 12 hours in acetic anhydride (150 mL, 1.57 mol) was followed by removal of residual acetic acid and acetic anhydride via rotory evaporation. Addition of anhydrous toluene (ca 25 ml) in two portions with rotory evaporation to azeotropically

remove the last traces of acid and anhydride gave the product that was dried under vacuum at 60 °C for 4 hours. Recrystallization from ethyl acetate gave white crystals of **1** (60.6 g, 0.321 mol, 84% yd); mp 190 °C; IR (KBr): 1862 (m), 1836 (m), 1782 (s), 1312 (s), 1248 (s), 1093 (m), 906 (s),735 (m), 714 (m), and 607 (m) cm^{-1}; ^{13}C NMR (DMSO-d_6): 161.3, 139.2, 131.2, and 127.1 ppm.

General Procedures:

4,5-Dichlorophthalimides: A stirred solution of the respective aromatic amines in 250 mL of DMAc (10-15wt%) was cooled to 0 °C and **1** (equimolar) was added portionwise, with a final rinse with additional dry DMAc (approx 50 mL) to ensure complete transfer. The reaction mixture was allowed to warm to ambient temperature and then stirred for 12 h. It was then heated at 150-160 °C for 6 h during which toluene was added (30 mL) to aid cyclodehydration-imidization via azeotropic removal of water. The reaction mixture was cooled slowly, its volume reduced by rotory evaporation and the residue added to stirred ice-water (approx 1L) to give a yellow precipitate. The precipitate was filtered, washed with water, filtered, air dried and further dried in a vacuum oven at 85 °C.

4,5-Dichloro-N-phenylphthalimide (2a)

Recrystallization from ethyl acetate gave yellow crystals of **2a** (59.3 g, 68% yd); TLC rf: 0.58 (acetone), 0.22 (ethyl acetate); mp 216 °C; IR (KBr): 1787 (w), 1718 (s), 1397 (sm), 1376 (m), 1141(m), 1125 (m), 740 (sm), and 730 (m) cm^{-1}; ^{13}C NMR (DMSO-d_6): 164.2, 137.2, 131.2, 130.9, 128.1, 127.5, 126.2, and 124.7 ppm.

4,5-Dichloro-N-(4'-methylphenyl)phthalimide (2b)

Recrystallization from ethyl acetate gave yellow crystals of **2b** (36.45 g, 80% yd); mp 193 °C; ^{13}C NMR (DMSO-d_6): 165.3, 137.9, 137.4, 131.6, 129.4, 128.9, 127.1, 125.4 and 23.4 ppm.

4,5-Dichloro-N-(4'-methoxyphenyl)phthalimide (2c)

Recyrstallization from ethyl acetate gave yellow crystals of **2c** (40.62 g, 83% yd); mp 120 °C; IR (KBr): 1778 (w), 1718 (s), 1520 (m), 1403 (m), 1376 (w), 1253 (m), 1141 (m), 1125 (m), 1029 (w), 772 (m) and 735 (m) cm^{-1}; ^{13}C MNR (DMSO-d_6): 165.5, 159.0, 137.4, 131.6, 128.6, 125.4, 124.1, 114.2 and 54.4 ppm.

4,5-Dichloro-N-(4'-benzyloxyphenyl)phthalimide (2d)

1-Methylpyrrolidine was added to complex HCl. Recrystallization from DMSO gave yellow crystals of **2d** (63.5 g, 79% yd); TLC rf 0.80 (acetone), 0.82 (ethyl acetate); mp 232-235 °C; IR (KBr): 1787 (w), 1771 (w), 1718 (s), 1707 (s), 1520 (m), 1403 (m), 1376 (ms), 1248 (m), 1148 (m), 1125 (m), 1104 (mw), 1012 (mw), 772 (m), 735 (m), 698 (mw), 602 (mw), and 532 (mw) cm^{-1}; ^{13}C NMR (DMSO-d_6): 164.2, 157.7, 137.0, 136.3, 130.8, 127.4, 127.3, 126.8, 124.4, 124.2, 114.9 and 69.6 ppm.

4-Hydroxy-5-nitro-phthalimides

A mixture of the respective dichlorophthalimide compounds (**2b-d**), potassium nitrite (4 mole excess), DMF (approx 250 mL) and toluene (40 mL) was heated to toluene/water azeotrope reflux temperature in a reaction vessel equipped with a mechanical stirrer, Dean-Stark apparatus and a reflux condenser. The reaction mixture was then heated at reflux for 24 h, cooled, and dilute HCl or HCl/dioxane (1 equivalent) added dropwise. It was then stirred at ambient temperature for 4 h. The reaction mixture was added to ice-

water, filtered and the yellow precipitate isolated.

4-Hydroxy-5-nitro-N-phenylphthalimide (3a)

Recrystallization from ethyl acetate gave **3a** as a yellow solid (23.68 g, 37% yd); mp 225-227 °C; IR (KBr): 1793 (w), 1718 (s), 1643 (m), 1552 (sm), 1504 (m), 1402 (m), 1333 (m), 1253 (m), 1162 (mw), 1120 (m), 746 (sm), and 692 (m) cm^{-1}; ^{13}C NMR (DMSO-d_6): 165.3, 165.2, 156.9, 141.1, 136.0, 131.7, 128.8, 127.1, 120.8, and 113.4 ppm.

4-Hydroxy-5-nitro-N-(4'-methylphenyl)phthalimide (3b)

The precipitate was washed twice with carbon tetrachloride, then dried under vacuum to give **3b** as a yellow solid (24.63 g, 70% yd); mp 246 °C; TLC rf (ethyl acetate) 0.13; IR(KBr): 1760 (m), 1702 (s), 1633 (s), 1558 (s), 1515 (m), 1376 (s), 1313 (s), 1285 (s), 740 (w) cm^{-1}; ^{13}C NMR (DMSO-d_6): 170.7, 167.3, 166.1, 140.0, 137.0, 135.6, 130.0, 129.2, 126.9, 123.8, 121.9, 105.5, 20.7 ppm.

4-Hydroxy-5-nitro-N-(4'-methoxyphenyl)phthalimide (3c)

Recrystallization from ethyl acetate gave **3c** as a yellow solid (18.05 g, 57% yd); mp 239 °C; IR (KBr): 1772 (w), 1723 (s), 1643 (m), 1552 (m), 1520 (m), 1408 (m), 1333 (m), 1253 (s), 1148 (m), 1125 (m), 1029 (m), 810 (m) and 740 (m) cm^{-1}; ^{13}C NMR (DMSO-d_6): 165.8, 165.7, 158.9, 158.1, 141.1, 136.1, 128.6, 124.3, 121.0, 119.5, 114.1, 114.0 and 55.4 ppm.

4-Hydroxy-5-nitro-N-(4'-benzyoxyphenyl)phthalimide (3d)

The filtered solid residue was triturated with ethyl acetate to give **3d** as a yellow solid (24.3 g; 41% yd); mp 255-257 °C; IR (KBr): 1792 (w), 1723 (s), 1643 (w), 1552 (m), 1520 (m), 1408 (m), 1387 (m), 1339 (w), 1253 (s), 1125 (m), 1104 (m), 1012 (m), 810 (m), 940

(m), and 740 (m) cm^{-1}; ^{13}C NMR (DMSO-d_6): 165.7, 165.6, 158.0, 157.1, 141.1, 136.8, 136.1, 128.6, 128.5, 127.9, 124.5, 120.8, 120.6, 115.0, 113.5, and 69.5 ppm.

4-Hydroxy-5-amino-phthalimide

A mixture containing the respective hydroxy-nitro compounds, ammonium formate (2-5 mole excess), 10% palladium on carbon (0.3-0.5 wt%) and DMAc was deaerated and allowed to stir at ambient temperature under a nitrogen atmosphere for 12 h. The reaction mixture was filtered to remove Pd/C, its volume reduced and the residue added to ice-water, filtered and isolated.

4-Hydroxy-5-amino-N-phenylphthalimide (4a)

The solid residue was dried under vacuum at ambient temperature to give **4a** as a bright yellow solid (6.98 g, 86% yd); mp 325-327 °C; IR (KBr): 3498 (m), 3370 (ms), 1671 (m), 1681 (s), 1622 (ms), 1584 (ms), 1419 (m), 1387 (s), and 751 (m) cm^{-1}; ^{13}C NMR (DMSO-d_6): 167.5, 167.4, 148.7, 143.7, 132.5, 128.6, 127.2, 126.9, 124.5, 118.8, 107.8, and 106.6 ppm.

4-Hydroxy-5-amino-N-(4'-methylphenyl)phthalimide (4b)

The precipitate was washed with methanol and dried under vacuum at ambient temperature (8 h), then at 70 °C (2 h) to give **4b** as a yellow solid (2.55 g, 56% yd); mp 341 °C; TLC rf (ethyl acetate) 0.45; IR (KBr): 3380 (s), 1761 (m), 1680 (s), 1611 (m), 1574 (m), 1515 (m), 1387 (s), 1194 (m) and 740 (w) cm^{-1}; ^{13}C NMR (DMSO-d_6): 167.7, 167.5, 148.2, 143.7, 136.8, 129.9, 129.2, 126.9, 124.8, 118.7, 107.8,106.7 and 20.7 ppm.

4-Hydroxy-5-amino-N-(4'-methoxyphenyl)phthalimide (4c)

The yellow precipitate was filtered, washed with diethyl ether and dried under vacuum

for 18 h to give **4c** as a yellow solid (7.93 g, 93% yd); mp 310 °C; IR (KBr): 3848 (m), 3742 (m), 3378 (m), 1760 (w), 1684 (s), 1514 (s), 1390 (m), 1251 (m) and 802 (w) cm^{-1}; ^{13}C NMR (DMSO-d_6): 167.9, 167.7, 8.4, 148.1, 143.6, 128.5, 125.1, 124.9, 118.7, 114.0, 107.8, 106.7 and 55.3 ppm.

4-Hydroxy-5-amino-N-(4'-hydroxyphenyl)phthalimide (4d)

The filtered residue was dissolved in methanol (1L), the solution dried over sodium sulfate, filtered and condensed to give **4d** as a bright yellow solid (12.11 g; 87% yd); mp 330-335 °C (dec); IR (KBr): 3370 (broad, s), 1761 (m), 1707 (s), 1662 (m), 1545 (m), 1515 (s), 1397 (s), 1344 (w), 1221 (m), 1168 (w), 1114 (w), 1082 (w), 804 (m), and 740 (w) cm^{-1}; ^{13}C NMR (DMSO-d6): 167.9, 167.8, 156.7, 148.0, 143.5, 128.5, 124.8, 123.5, 118.7, 115.2, 107.7, and 106.6 ppm.

2-(4'-Fluorophenyl)-5,6-[N-(4'-methoxyphenyl)imide]-benzoxazole (5a)

4-Fluorobenzoyl chloride (1.25 g, 0.0079 mol) was added dropwise to a stirred solution of **4c** (1.24 g, 0.0044 mol) in 25 mL of dry NMP at 0 °C. The reaction mixture was allowed to warm to ambient temperature, stirred for 12 h, and then heated at 180 °C for 6 h. The reaction mixture was cooled, precipitated into 150 mL of ice-water and filtered. The yellow precipitate was then washed with methanol, filtered and dried under vacuum for 20 h. Recrystallization from DMAc gave yellow crystals of **5a** (1.20 g, 73% yd); mp 328 °C; IR (KBr): 1771 (m), 1718 (s), 1622 (m), 1600 (m), 1515 (s), 1494 (s), 1392 (s), 1307 (m), 1275 (m), 1237 (s), 1125 (m) and 740 (m) cm^{-1}; ^{13}C NMR (DMSO-d_6 @ 137 °C): 166.0, 165.5, 164.4, 162.6, 158.5, 156.5, 153.3, 146.0, 129.9, 129.8, 128.4, 128.3,

127.4, 124.5, 121.7, 115.9, 115.6, 114.9, 114.5, 113.8, 106.1 and 54.9 ppm.

2-(4'-Fluorophenyl)-5,6-[N-(4'-hydroxyphenyl)]imide-benzoxazole (5b)

4-Fluorobenzoyl chloride (6.21 g, 0.039 mol) was added dropwise to a stirred solution of **4d** (9.11 g, 0.0337 mol) and pyridine (2.667 g, 0.338 mol) in 100 mL of NMP at 0 °C. The reaction mixture was stirred at 0 °C for 1 h, allowed to warm to ambient temperature and stirred for 8 h, and then heated at 180 °C for 8 h during which *o*-dichlorobenzene (20 mL) was added to aid oxazole formation via azeotropic removal of water. The reaction mixture was then precipitated into methanol (300 mL), filtered, and the residue washed twice with methanol. It was then recrystallized twice from DMSO, the crystals filtered each time and washed with methanol. Vacuum drying gave **5b** as a pale yellow solid (8.72 g, 69% yd); mp 332-335 °C; IR (KBr): 3188 (broad,m), 1771 (m), 1718 (s), 1616 (m), 1606 (m), 1515 (sm), 1499 (s), 1392 (s), 1269 (m), 1243 (s), 1162 (m), 1120 (m), 842 (mw), 815 (m), and 740 m) cm^{-1}; ^{13}C NMR (DMSO-d_6 @ 135°C): 170.3, 167.5, 166.8, 166.1, 153.7, 151.0, 134.5, 132.8, 132.7, 129.4, 129.2, 126.9, 121.7, 120.7, 118.8, 117.9, 117.6, 112.4, and 110.5 ppm. ^{13}C NMR (2-nitropropane/$AlCl_3$, DMSO-d_6 insert): 171.4, 168.0, 166.9, 166.1, 152.9, 152.1, 134.0, 133.8, 129.5, 129.3, 127.6, 124.8, 123.8, 118.3, 117.8, 115.1, 114.2 and 112.5 ppm.

Poly(ether-imide-benzoxazole) (6)

A mixture of **5b** (1.11 g, 0.003 mol) and sodium hydride (97%, 0.0074 g, 0.003 mol) in 10 mL of CHP was allowed to stir at ambient temperature for 4 h. The temperature was

raised to 110 °C for 4 h and then to 270 °C for 12 h. Polymer precipitation was observed during the latter heating segment. The cooled reaction mixture was added to methanol (200 mL), filtered, the residue washed twice with methanol, then vacuum dried for 48 h to give **6** as an olive-yellow solid (1.01 g, 96% yd); mp 454 °C (dec); IR (KBr): 1771 (m), 1723 (s), 1622 (m), 1600 (m), 1510 (sm), 1488 (s), 1376 (sm), 1248 (s), 1168 (m), 1120 (m), 826 (broad, m), and 740 (m) cm^{-1}; ^{13}C NMR (H_2SO_4, DMSO-d_6 insert): 168.2, 167.7, 166.1, 154.1, 150.9, 134.5, 132.9, 132.7, 129.2, 128.6, 124.9, 121.7, 117.9, 112.0, and 109.8 ppm; ^{13}C NMR (2-nitropropane/$AlCl_3$, DMSO-d_6 insert): 167.9, 166.9, 166.2, 155.1, 152.1, 134.4, 133.5, 129.3, 125.7, 121.9, 118.6, 114.6, 112.5, and 111.6 ppm.

Poly(ester-imide-benzoxazole) (8)

A solution of **4d** (0.542 g, 0.002 mol), pyridine (0.32 g, 0.004 mol) and anhydrous NMP (5 mL) was cooled to -10 °C and a solution of isophthaloyl chloride/N...P (0.4082 g, 0.002 mol/3 mL) was added dropwise over a 0.5 h period with mechanical stirring. A color change from dark brown to yellow was observed over this time period. The mixture was allowed to warm to 0 °C, stirred for 3 h, then allowed to warm to ambient temperature and stirred for 4 h. A catalytic amount of stannous octanoate was added, and the mixture heated at 120 °C for 1 h. It was then cooled, precipitated into 200 mL of methanol, and the pale yellow precipitate filtered and washed with methanol. The precipitate was placed in a sublimator under vacuum and heated slowly (1 h) to 320 °C, held for 2 h (during which another color change from yellow to olive green was observed) and then cooled slowly to give **8** (0.25 g, 34% yield); mp >500 °C (DSC), IR (KBr): 3455, 3071, 1777,

1718, 1616, 1510, 1381, 1291, 1248, 1205, 1168, 1114, 1066, 826, 740 and 714 cm^{-1}.

RESULTS AND DISCUSSION

Model Compounds

The dehydration of 4,5-dichlorophthalic acid with acetic anhydride under reflux conditions gave the hygroscopic **1** in good yields. It was stored in sealed containers or, where possible, used immediately. The generation of the phthalimide model compounds, **2**, involved the portionwise addition of **1** at low temperatures to stirred solutions containing the respective aromatic amine derivatives. This addition sequence was required to generate the ring-opened amic acids which were thermally dehydrated (with the aid of toluene as the azeotropic agent) to the cyclic imides (Scheme 2). Due to the reactivity of the anhydride, reverse addition gave mixtures of cyclic and acyclic imides, amic acids and starting materials. Work-up was relatively facile, involving simple precipitation and drying, to give the phthalimide derivatives with yields in the 80 to 94% range.

Typical FT-IR peaks characteristic of the model compounds (**2**) are the unsymmetrical pair of peaks around 1780 and 1720 cm^{-1} (C=O), and the 730 cm^{-1} (imide ring) absorbance. ^{13}C solution NMR chemical shift values for the imide carbonyls are between 164 and 166 ppm. The aromatic carbon with the ipso chlorine substituent resonates at 137 ppm, while oxygen and nitrogen substituents push the values downfield. Figures 1 and 2 include the FT-IR and ^{13}C NMR spectra of **2a**, respectively; the chemical shift assignments are given in Table 1.

The synthesis of 4-hydroxy-5-nitrophthalimides (3) from 4,5-dichlorophthalimides (2) is based on the ambident nature of the nitrite anion (Scheme 3). Potassium nitrite attacks via the lone pair of electrons on either the nitrogen or oxygen atoms with the preference of "N" or "O" attack being determined by both the electronic nature of the substrate and the reaction conditions. Caswell has pointed that the ratio of KNO_2 to dichlorophthalimide should be 4:1 for optimum product yield; lesser ratios give reaction mixtures containing product, intermediates and starting material.[28] This strongly suggests that three or more moles of KNO_2 per mole of dichlorophthalimide are involved in the mechanism.

We presume that the formation of hydroxy nitro phthalimides, 3, proceeds via the reaction mechanism depicted in Scheme 4. This is suggested by the calculated ^{13}C NMR chemical shift values which were derived from empirical model compound data, (Table 1), published chemical shift values[38] and published spectral results.[30,31,32] The two aromatic carbons with chlorine substituents are electronegative, and are located para to the phthalimide carbonyls in I. The calculated chemical shift value for these carbons is 141.2 ppm, very dissimilar to aromatic carbons with ipso fluorine substituents which resonate around 163 ppm. Thus, "N" attack by the nitrite ion is assumed to be the initial mode of substitution. This reaction is facilitated by the formation of a Meisenheimer intermediate with the carbonyls of the imide ring to give II. By a similar rationale, the second chlorine (chemical shift of ipso carbon ca. 136 ppm) is replaced by a nitro group (second "N" attack by KNO_2) due to the activating effect of the ortho nitro group to give III. The carbons ipso to the dinitro substituents are very electronegative and rapid "O"

attack by KNO_2 results in the formation of the nitroso derivative, IV. This intermediate is very unstable and rapidly decomposes in the presence of more nitrite ion to give N_2O_3 and the potassium phenolate salt of the nitro phthalimide, V. By-products of this reaction may result from the "O" attack at the nitro ipso carbon of the mono substituted 4-nitro-5-chloro phthalimide, II, to give the chloronitroso derivative, VI, which should decompose to give the chloro phenolate salt of the phthalimide, VII. Further substitution of VII is unlikely.

These reactions on the phthalimide substrates appear to be facile when the 4'-positions of the N-phenyl substituents are neutral or donate electrons into the imide ring (ie, **2a-c**). However, when this position has an electron withdrawing substituent (ie, 4,5-dichloro-N-[4'-methylcarboxypheny]phthalimide), the imide group becomes hydrolytically unstable and undergoes ring-opening under the reaction conditions used. This precludes the synthesis of the AB monomer precursor, 4-hydroxy-5-nitro-N-(4'-methylcarboxyphenyl)phthalimide, which we could not obtain via this route.

The nitro-hydroxy-phthalimides, **3a-c**, showed typical IR peaks for phthalimides at 1780-1760, 1720-1700, and 740-730 cm^{-1}. A broad absorbance between 3500-3200 cm^{-1} (OH stretch) and at 1405 cm^{-1} (OH bend), and two absorbances around 1550 and 1340 ($Ar-NO_2$) confirm successful substitution with retention of the imide ring. Further evidence is supplied by ^{13}C NMR chemical shifts. The two imide carbonyls are now unique, showing two peaks between 165 and 167 ppm. The presence of 10 aromatic resonances (instead of 7 observed for the symmetric **2**) confirms unsymmetrical substitution at the 4- and 5- positions. The distinct resonances around 157-158 ppm and 141 ppm correspond

to the aromatic carbons with OH and NO_2 substituents, respectively.

The reduction of 3 to 4 posed a special problem. Neutral reaction conditions were needed to negate the possibility of acid or base catalyzed ring-opening of the imide group. The use of ammonium formate as a catalytic hydrogen transfer agent has been shown to selectively reduce aromatic nitro groups in the presence of amides, imidazoles and ester groups.[39,40] We found similar selectivity in the presence of the imide moiety. This process was effective at ambient temperatures and pressures under neutral conditions in DMF, and allowed high yield reduction of the nitrophenol derivatives, especially in DMAc. Conversion was usually quantitative by TLC and ^{13}C NMR analysis, with isolated yields ranging from 50 to 90 %. (Scheme 3)

FT-IR characterization of the amino-hydroxy-phthalimides, **4a-c**, showed peaks for the imide ring at 1780-1760, 1700-1680, and 740-730 cm^{-1}. The broad, intramolecularly hydrogen bonded peak (OH-NO_2) in the 3400 cm^{-1} region of the nitro compounds was resolved into distinct absorbances corresponding to NH_2 and OH stretches, confirming reduction. The ^{13}C NMR chemical shifts for the two imide carbonyls (different para substituents) were between 167.5-168 ppm. The aromatic carbons ipso to the OH and NH_2 substituents appeared around 148 and 144 ppm, respectively, while the 10 unique aromatic peaks were different than those of 3 (Table 1).

Monomer Synthesis and Characterization.

Monomer synthesis comprised use of the (OH-protected) N-(4'-benzyloxyphenyl)phthalimide produced by condensation of 4-benzyloxyaniline with 1.

Displacement of the two chlorine substituents was successful under NAS conditions. HCl-dioxane was used to protonate the potassium hydroxylate intermediate, **3d**, instead of aqueous HCl due to the succeptability of the imide carbonyls to hydrolytic attack (especially with the electron withdrawing nitro substituent in the para position). During the reduction of the nitro group to the amine, the benzyloxy group was concurrently hydrogenalized to generate the 4'-hydroxyphenyl moiety of **4d**. Imide-benzoxazole monomer formation (**5b**) involved the two-step condensation of the ortho hydroxy-amine with *p*-fluoro benzoyl chloride (Scheme 5). Low temperatures and long reaction times were employed to promote optimum amide formation (in lieu of bis-ester generation via condensation with the two OH groups present). Cyclodehydration at 180 °C gave the AB imide-benzoxazole monomer, **5b**, in good yields. This trifunctional compound, 4-hydroxy-5-amino-N-(4'-hydroxyphenyl)phthalimide, (**4d**) also served as the monomer for polymer **8** in the polycondensation reaction with isophthaloyl chloride.

FT-IR and ^{13}C NMR spectra for monomer intermediates were consistent with those of the model compounds (Figures 1 and 2). The structure of monomer **5b** was confirmed by IR peaks at 1771, 1718 and 740 cm^{-1} (imide), 1616 cm^{-1} (C=N; oxazole), 1392 (O-H bend) and 1243 cm^{-1} (C=O stretch, Figure 5); and by ^{13}C solution NMR (2-nitropropane/$AlCl_3$ solvent) peaks at 170.4 and 166.1 ppm (Ar-F doublet, J coupling of 4.3 ppm,129 Hz) 168.0 ppm (oxazole ring), 166.9 ppm (C=O imide), 152.1 ppm (Ar-OH) and 152.9 ppm (Ar ipso to oxygen of the oxazole ring). A total of 20 peaks (3 split by fluorine) corresponding to 17 unique carbons were observed (Figure 6).

POLYMER SYNTHESIS AND CHARACTERIZATION

Poly(ether-imide-benzoxazole) (6)

The polymerization strategy was based on the displacement of the fluorine attached to the 2-phenylbenzoxazole by a sodium phenolate anion to form an ether group. Similar chemistry has been used previously in the formation of benzoxazoles.[21,22] The inertness of the imide carbonyls to sodium phenoxides during the NAS polymerization was a critical consideration in this polymerization for the maintenance of polymer backbone integrity.[33,34,35] The advantage of the AB monomer's inherent stoichiometry combined with the formation of an ether linkage to impart backbone flexibility makes this an attractive approach to a novel polymer structure. Thermally stable polymers were obtained under polymerization conditions employing a variety of solvents and temperatures (Table 2).

Polymer formation was confirmed by the disappearance of the monomer IR absorbances at 3188 (-OH stretch) and 1392 cm $^{-1}$(-OH bend). The 1243 cm^{-1} monomer peak (C-O stretch) was shifted to 1248 cm^{-1} with significant broadening, suggesting conformational and envoirnmental differences. The imide (1771, 1720 and 740 cm^{-1}) and oxazole (1622 cm^{-1}) moieties were still intact (Figure 3). Comparison of the 2-nitropropane/$AlCl_3$ solution ^{13}C NMR spectra of the monomer and polymer confirmed conversion. Specifically, the complete disappearance of resonances corresponding to end-groups at 171.4 and 166.1 ppm (Aryl C-F) was observed along with apperance of a pair of symmetric resonances at 155 and 152 ppm corresponding to the pair of aromatic ether carbons (Figure 4). The H_2SO_4 solution ^{13}C NMR spectrum of 6 was not as well-

resolved as the 2-nitropropane/$AlCl_3$ spectrum, although qualitative differences between monomer and polymer were evident. The solid state CP/MAS spectra of both the monomer (**5b**) and the marginally soluble polymer (**6**) are shown in Figure 5. Peaks characteristic of the monomer are at 165.8 ppm (Ar-F, C=O imide), 155.6 ppm (oxazole carbon), 153.7 ppm (Ar ipso to the oxygen of the oxazole ring), 152.0 ppm (Ar-OH) and 147.0 ppm (Ar ipso to the nitrogen of the oxazole ring) differ from those of the polymer at 167 ppm (C=O imide), 157.5 ppm (oxazole carbon, O-Ar para to oxazole ring), 153.7 (Ar ipso to the oxygen of the oxazole ring, O-Ar para to imide ring) and 147.2 ppm (Ar ipso to the nitrogen to the oxazole ring). The other aromatic peak assignments were made based on model study values.

Poly(ester-imide-benzoxazole) (8)

The synthesis of the soluble poly(ester-amide-imide), **7**, at low temperatures, followed by thermal cyclo-dehydration to the poly(ester-imide-benzoxazole), **8**, in the solid state under vacuum is illustrated in Scheme 6. To afford **7** with preferential attack by the amine and the lone hydroxyl group giving the chain extended **7**, the reaction was performed at -10 °C. Similar procedures employing low temperatures have been used to produce poly(*o*-hydroxy amides) which were isolated and thermally dehydrated to polybenzoxazoles under vacuum in the solid state.[41] Since exclusive reaction of the amine moiety rather than the adjacent hydroxyl has only been reported using the trimethylsilyl activation protection procedure, some scrambling undoubtly occured during the first step of the reaction.[42] Long reaction times were employed to allow equilibration of any kinetically

obtained poly(*o*-amino-esters) to the poly(*o*-hydroxy-amide). Additionally, stannous octoate was added as catalyst and the reaction mixture heated at 120 °C (well below oxazole cyclization temperatures) for 1 h to facilitate this rearrangement. Rearrangement with benzoxazole formation should occur during the second part of the reaction to give the enthalpically favored heteroaromatic.

The structures of **7** and **8** were confirmed by the presence of peaks in the IR characteristic of the imide group at 1778 cm^{-1}, 1718 cm^{-1} and 740 cm^{-1}. The ester peak at 1775 cm^{-1} (C=O) in **7** shifted to lower wavenumbers and appeared as a shoulder on the broadened 1718 cm^{-1} imide (C=O) peak in **8**. The amide I absorption that usually appears around 1650 cm^{-1} may be hidden under the 1718 cm^{-1} peak in **7**. Disappearance of the N-H and O-H stretch of the poly(*o*-hydroxy amide) is evident by the reduction in the intensity of the 3350 cm^{-1} absorption (Figure 6). The ^{13}C NMR solution resonances (Figure 7) at 166.7 and 166.4 ppm (imide C=O), 164.8 ppm (ester C=O) and 163.0 ppm (amide C=O) confirm the structure of **7**. The ^{13}C NMR spectrum of **8** is only presented for qualitative comparison to **7**, due to its marginal solubility in H_2SO_4 and 2-nitropropane/$AlCl_3$ solvent systems. Viscosity measurements were unobtainable for similar reasons.

Polymer Properties

The DSC thermogram showed a transition at 454 °C for polymer **6**, a 116 °C increase over the melting transition of the monomer at 338 °C. This corresponds roughly to the onset of decomposition, although the TGA trace showed retention of 90 % of initial weight

up to 500 °C. Marked birefringence under the cross polarizing microscope indicated crystallinity or a high degree of amorphous sample orientation which was confirmed by the WAXD data. The d-spacing values are presented in Table 3. The inherent viscosity in H_2SO_4 of this polymer was 0.20 dL/g.

The DSC traces of **7**, cooled and rerun (labelled 7-first run and 7-second run) and **8** under nitrogen showed an endo/exotherm at 300 °C (**7**, run#1) corresponding to benzoxazole formation with concurrent water evolution. This transition was absent in run 2 since **7** had been converted to **8**. This latter DSC trace was virtually identical to that of **8** obtained by heat treating **7** at 320 °C under vacuum (Figure 8). The TGA thermograms of **7** and **8** showed both to be more thermally stable in nitrogen than in air. Consistent with DSC data, water evolution during benzoxazole formation in **7** was observed at 300 °C. Furthermore, **8** exhibited weight retention of 95 % at 501 and 505 °C in air and nitrogen, respectively, and a char yield of greater than 65 % at 700 °C under nitrogen (Figure 9).

CONCLUSION

We have obtained a series of 4-nitro-5-hydroxy-phthalimide derivatives that were derived via the nucleophilic aromatic displacement of chlorines at the 4,5-phthalimide positions by potassium nitrite. The generation of two dissimilar groups on the same substrate is attributed to the ambident nature of KNO_2. During the course of the substitution, the electronic state of the phthalimide substrate changes, directing KNO_2 to attack via the

lone pair of electrons on either the oxygen or nitrogen atoms, "O" or "N" attack, respectively. The solution reduction and concurrent deprotection of the N,4'-hydroxyphenyl (benzyloxy) group using ammonium formate proved to be quantitative and selective, leaving the imide functionality intact.

The solution condensation of *p*-fluorobenzolychloride with the reduced and deprotected phthalimide monomer precursor generated the *o*-hydroxyamide which was thermally cyclodehydrated in solution to give the AB imide-benzoxazole monomer. Polymerization of this monomer via nucleophilic displacement of the fluorine (para to the oxazole ring) by a phenolate anion was successful to give high molecular weight poly(ether-imide-benzoxazole). Polymerization under a variety of conditions proved this to be a viabale approach. Polymer structure was confirmed by FT-IR and ^{13}C NMR analysis. Reproducible thermal analysis data (endotherm at 454 °C, and 90% wt retention at 500 °C) indicated good thermal stability.

The solution polycondensation of isophthaloyl chloride with monomer **4d** to generate the soluble poly(ester-amide-imide), **7**, was successful. The isolated material was cured in the solid state under high temperature (320 °C) and vacuum to give the desired poly(ester-imide-benzoxazole) as confirmed by FT-IR and ^{13}C NMR analysis. Cyclodehydration at 320 °C under vacuum was confirmed by DSC and TGA analysis, both showing water evolution and benzoxazole formation via an endo/exotherm and concurrent weight loss at 300 °C, respectively. TGA also confirmed the thermooxidative stability of **8**, showing weight retentions of 95% at 500 °C and a char yield of greater than 65% at 700 °C under nitrogen. The WAXD data indicated a high degree of crystallinity,

with the d-spacing data being presented in Table 2.

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List of Figures

Figure 1. FT-IR (KBr) spectra of 4,5-dichloro-N-(4'-benzyloxy)phenyl- (**2d**, top), 4-hydroxy-5-nitro-N-(4'-benzyloxy)phenyl- (**3d**, middle) and 4-hydroxy-5-amino-N-(4'-hydroxyphenyl)- (**4d**, bottom) phthalimide monomer precursors.

Figure 2. Solution ^{13}C NMR (DMSO-d_6) spectra of 4,5-dichloro-N-(4'-benzyloxy)phenyl- (**2d**, top), 4-hydroxy-5-nitro-N-(4'-benzyloxy)phenyl- (**3d**, middle) and 4-hydroxy-5-amino-N-(4'-hydroxyphenyl)- (**4d**, bottom) phthalimide monomer precursors.

Figure 3. FT-IR (KBr) spectra of hydroxy-fluoro-imide-benzoxazole monomer (**5b**, top) and poly(ether-imide-benzoxazole) (**6**, bottom).

Figure 4. Solution ^{13}C NMR (16 % $AlCl_3$/2-nitropropane, DMSO-d_6 external reference) of hydroxy-fluoro-imide-benzoxazole monomer (**5b**, top) and poly(ether-imide-benzoxazole) (**6**, bottom).

Figure 5. Solid state CP/MAS spectra of hydroxy-fluoro-imide-benzoxazole monomer (**5b**, top) and poly(ether-imide-

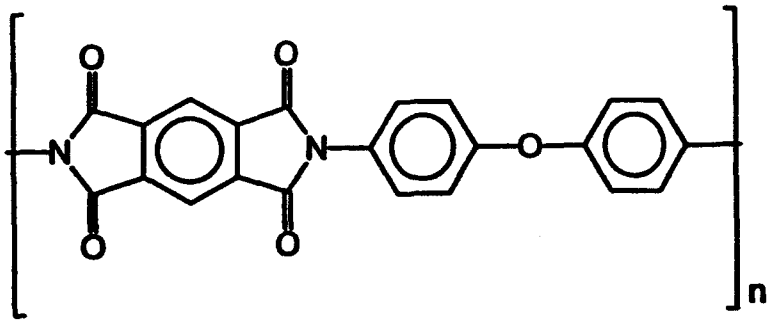
benzoxazole) (6, bottom).

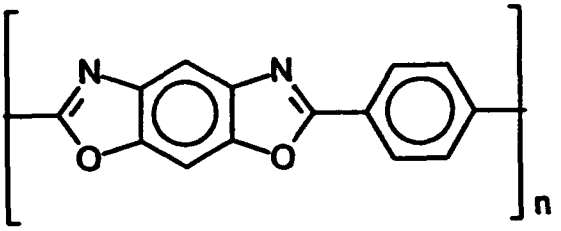
Figure 6. FT-IR spectra of poly(ester-amide-imide) (7, top) and poly(ester-imide-benzoxazole) (8, bottom).

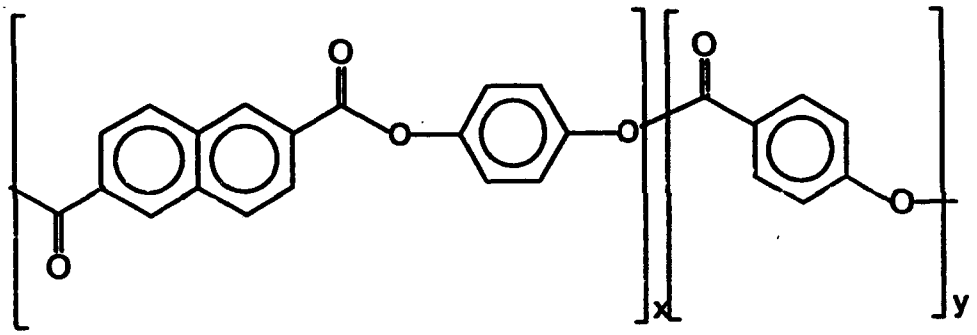
Figure 7. ^{13}C solution NMR spectra of poly(ester-amide-imide) (7, DMSO-d_6, top) and of poly(ester-imide-benzoxazole) (8, H_2SO_4, bottom).

Figure 8. DSC thermograms of poly(ester-amide-imide) (7, run #1, top; run #2, middle) and of poly(ester-imide-benzoxazole) (8, bottom) in nitrogen.

Figure 9. TGA thermogram of isolated poly(ester-amide-imide), 7, and of poly(ester-imide-benzoxazole), 8.







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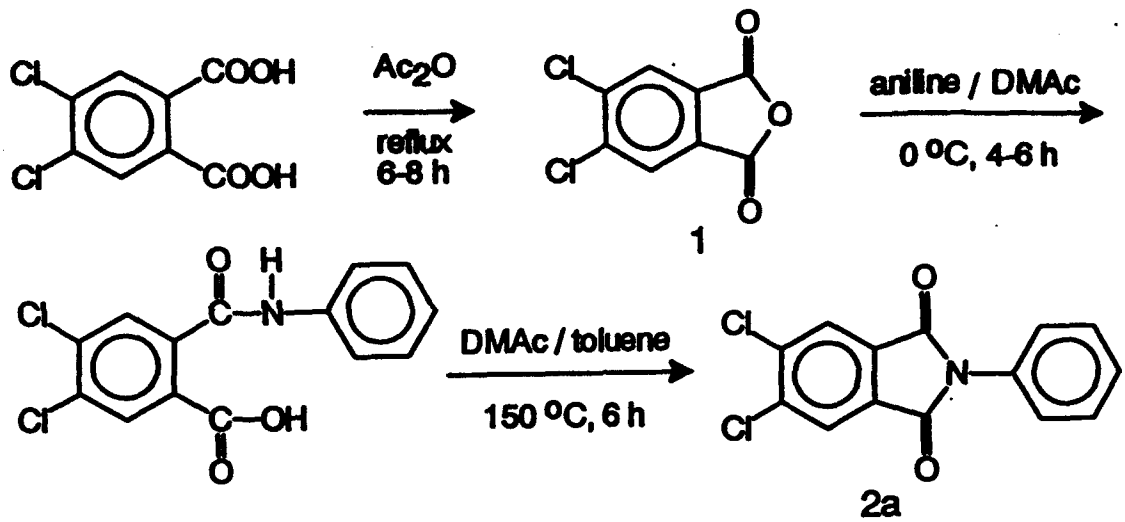
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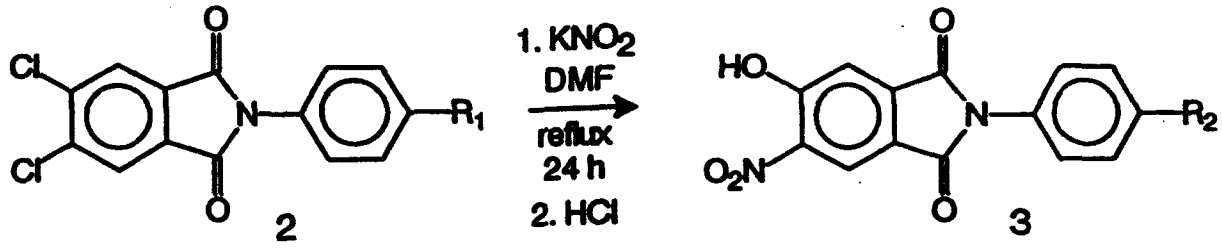
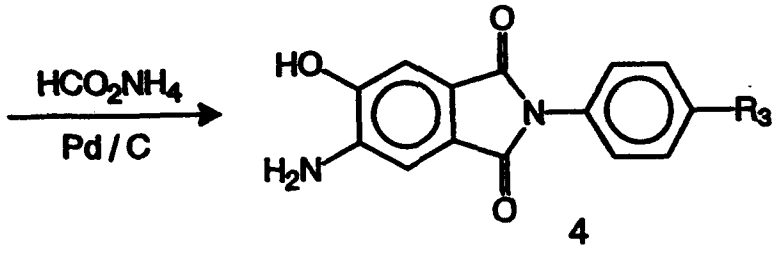
COOH
Cl
COOH
Ac_2O
reflux
6-8 h
Cl
O
Cl
O
O
aniline / DMAc
0 °C, 4-6 h
1
O
H
Cl
C
N
Cl
C
OH
O
DMAc / toluene
150 °C, 6 h
O
Cl
N
Cl
O
2a

Scheme 2





a. R=H

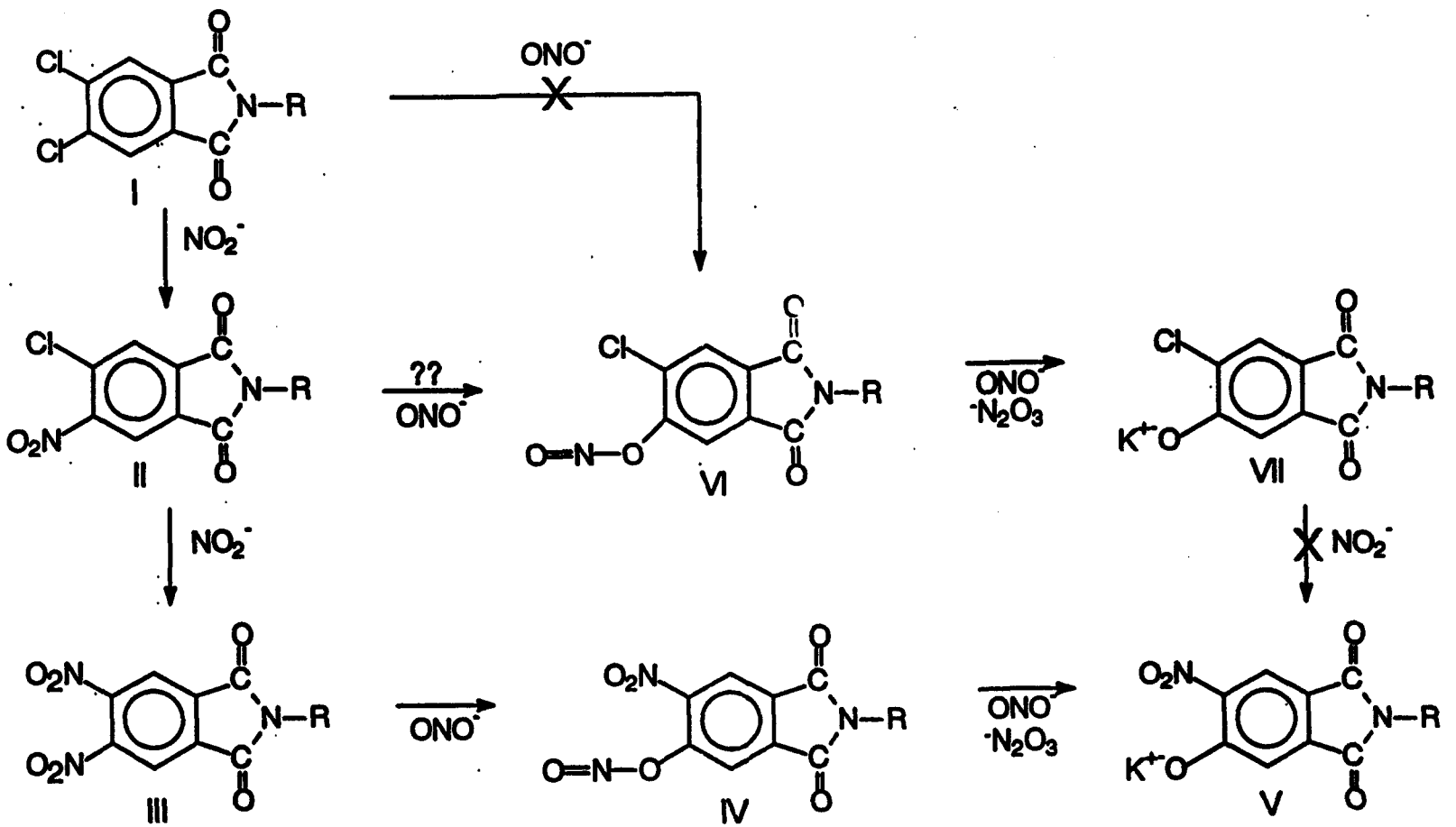
b. R=CH_3

c. R=OCH_3

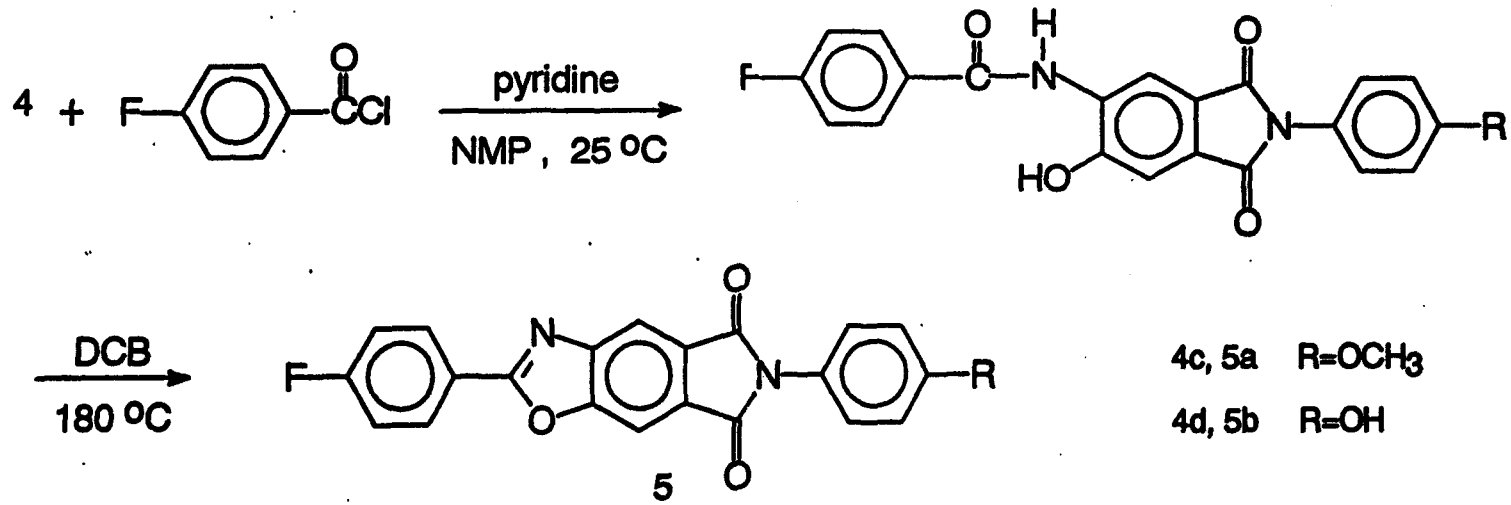
d. R_1R_2=$OCH_2C_6H_5$

R_3=OH

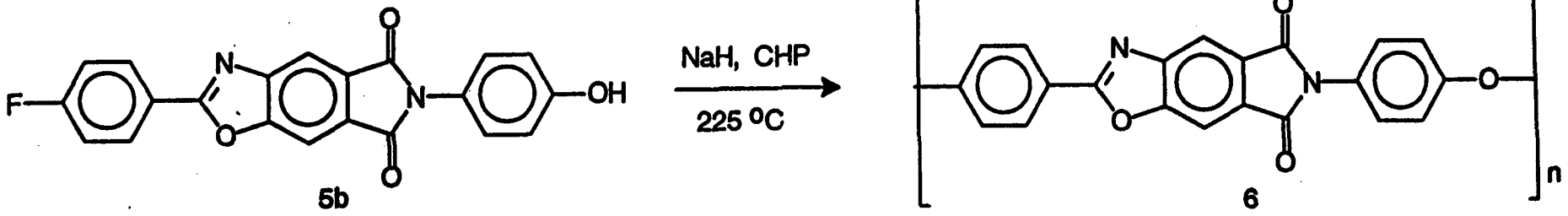
Scheme 3


Cl
Cl
O
C
N–R
C
O
I
ONO⁻
NO₂⁻
O₂N
II
??
ONO⁻
O=N–O
VI
ONO⁻
·N₂O₃
K⁺O
VII
NO₂⁻
O₂N
O₂N
III
ONO⁻
O=N–O
IV
ONO⁻
·N₂O₃
K⁺O
V

Scheme 4


4 +
F
Cl
pyridine
NMP , 25 °C
H
N
HO
R
DCB
180 °C
F
N
O
N
R
5
4c, 5a R=OCH3
4d, 5b R=OH

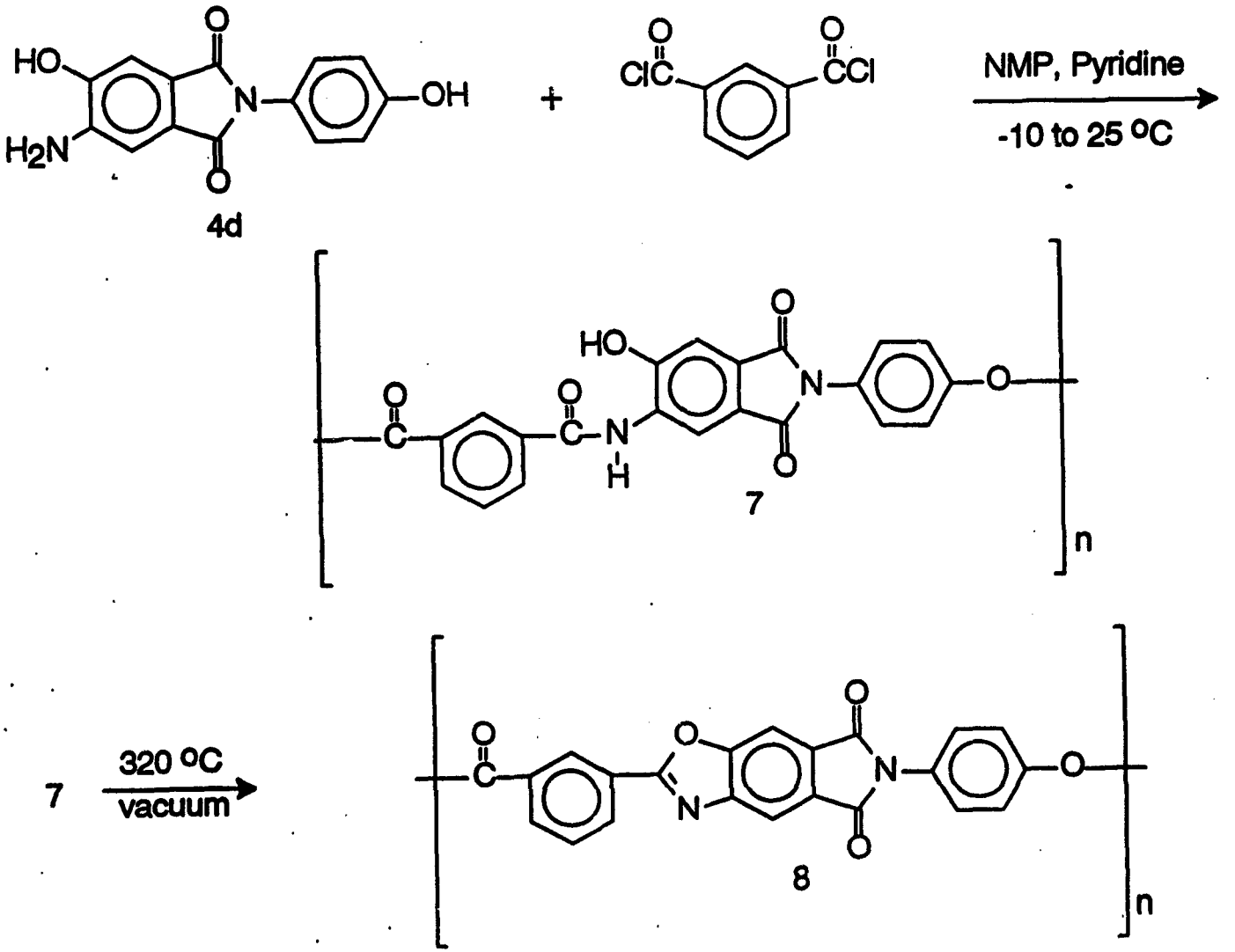
Scheme 5



5b

6

Scheme 6


HO
H2N
OH
4d
+
ClC
CCl
NMP, Pyridine
-10 to 25 °C
HO
N
O
C
N
H
7
n
7
320 °C
vacuum
O
N
8
n

Scheme 7

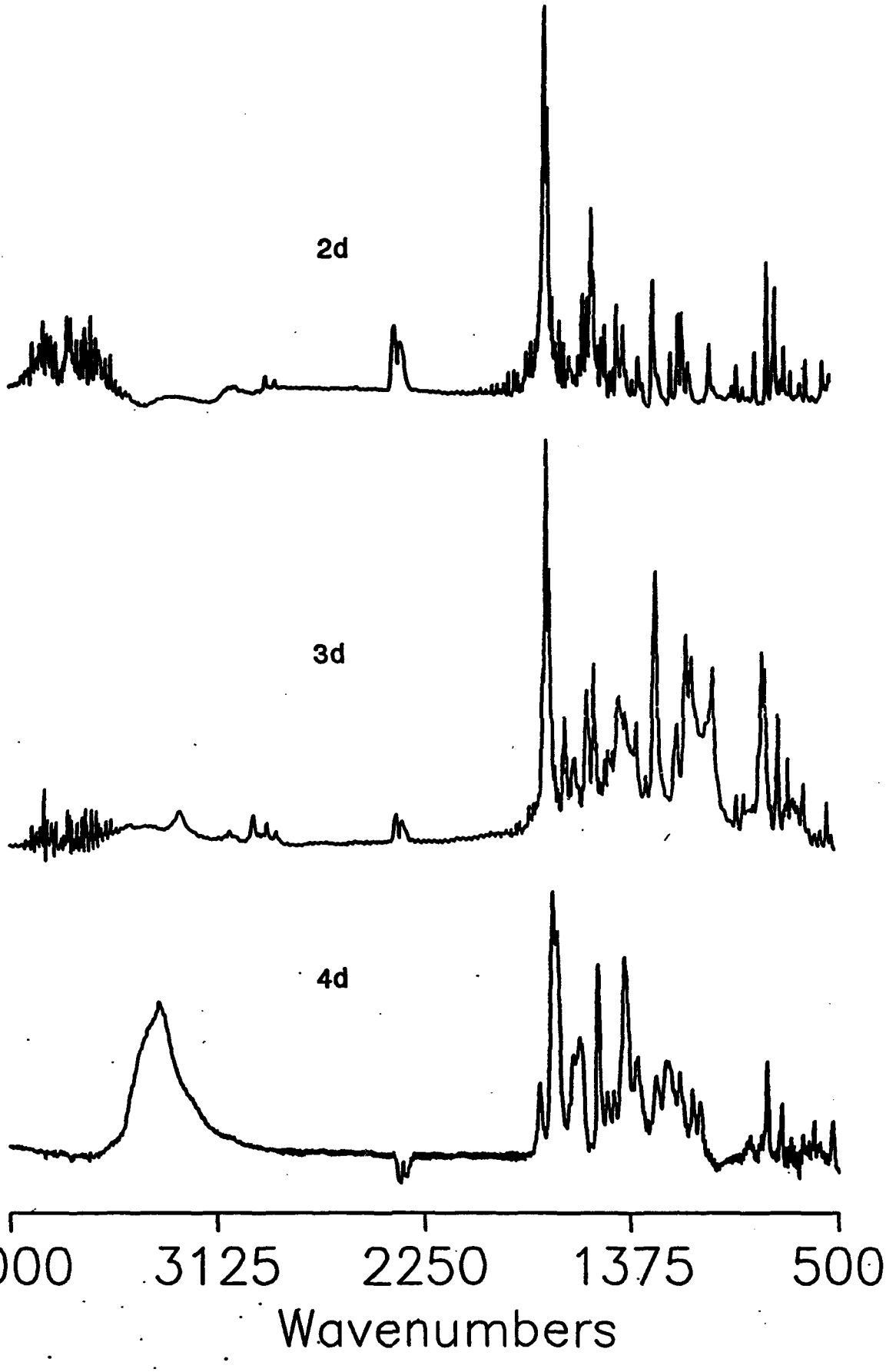


Figure 1

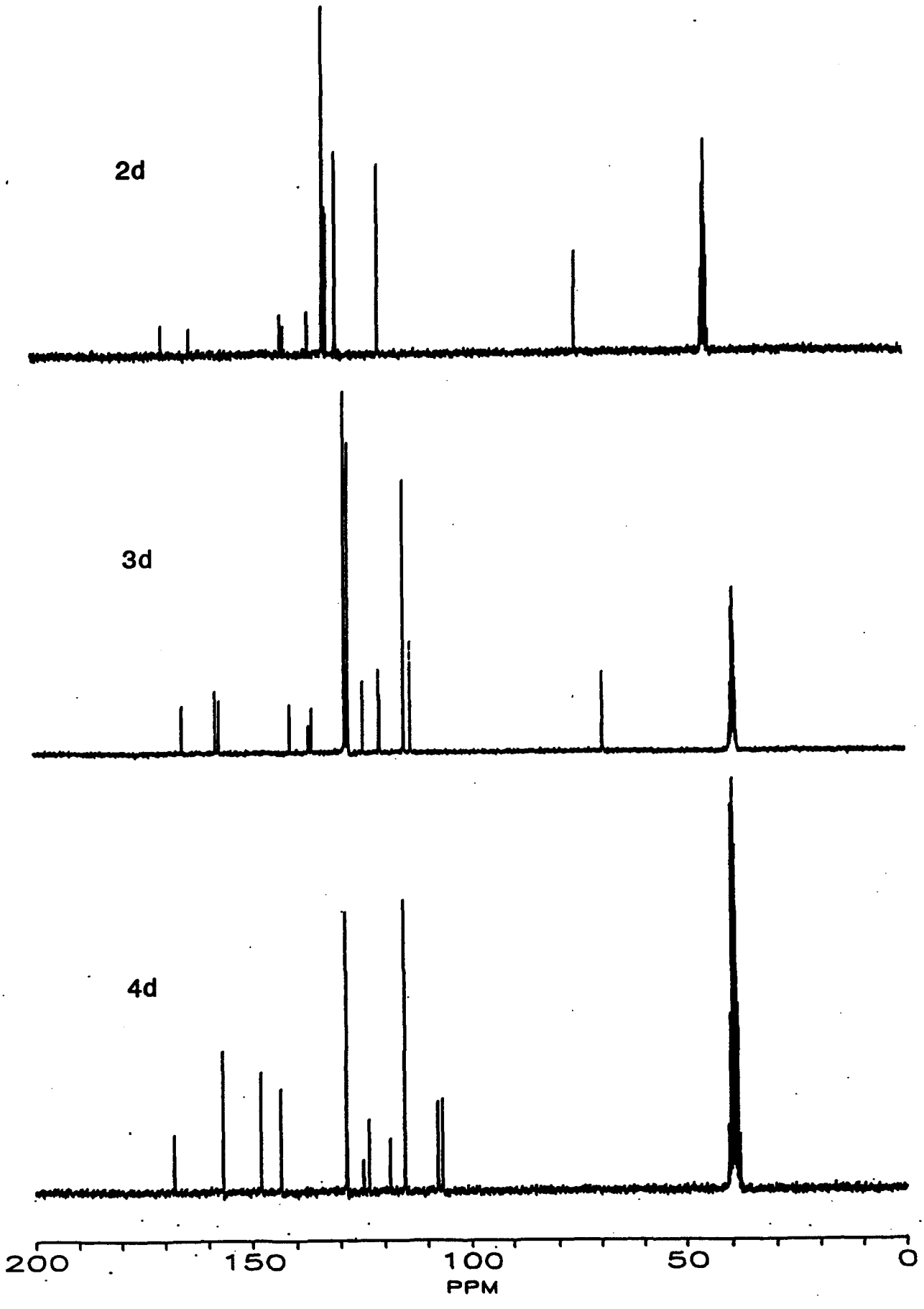


Figure 2

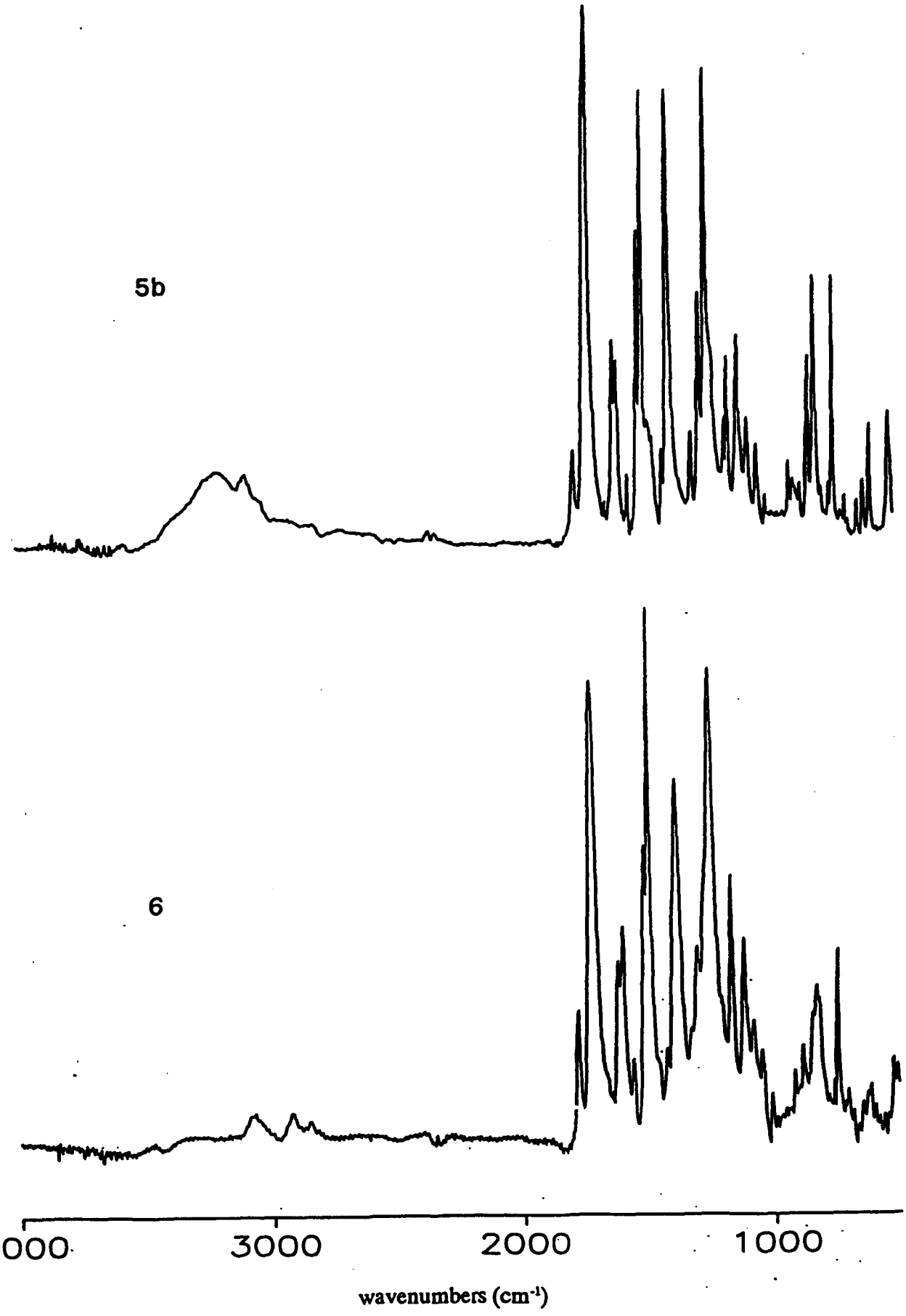


Figure 3

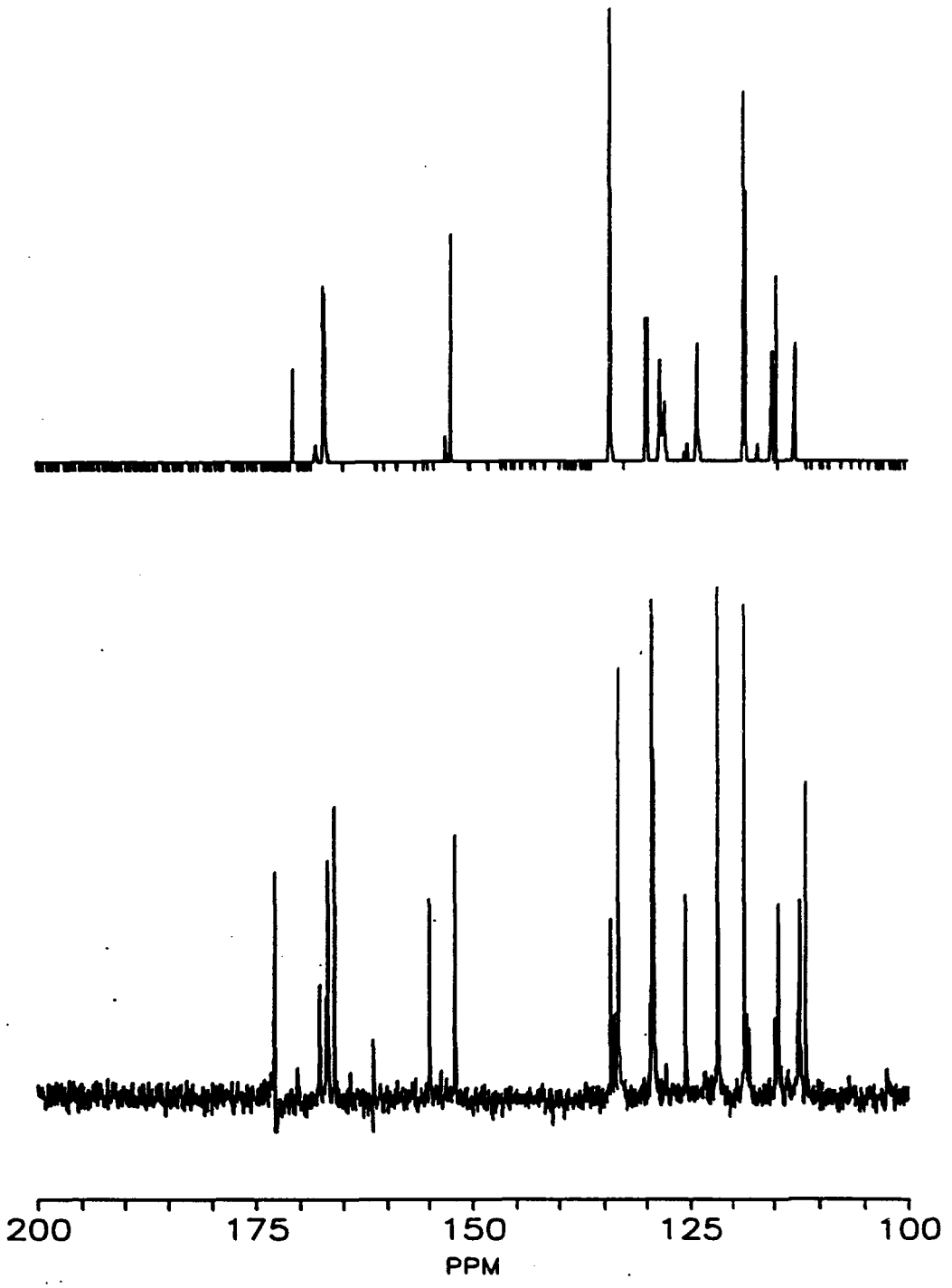


Figure 4

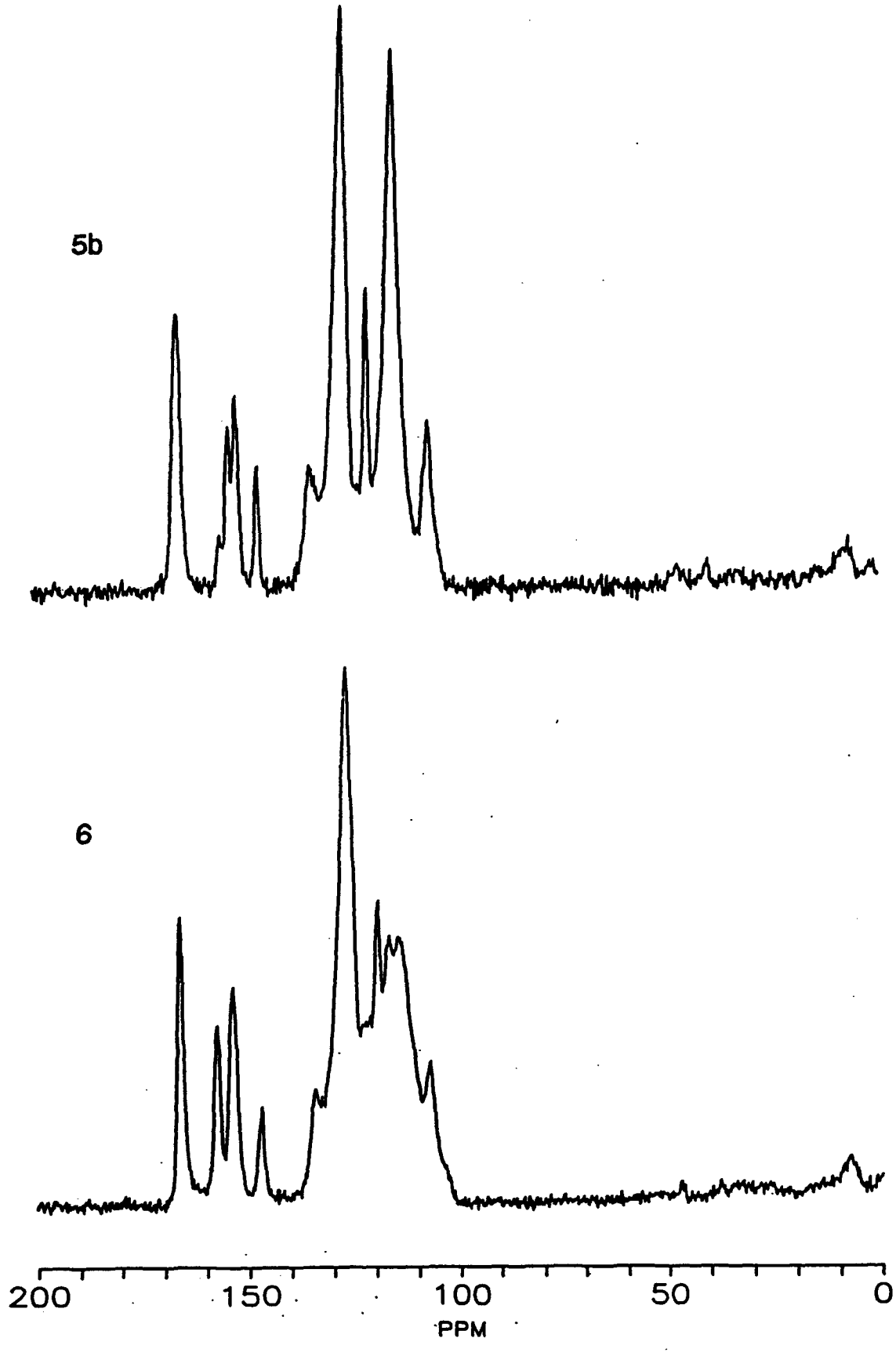


Figure 5

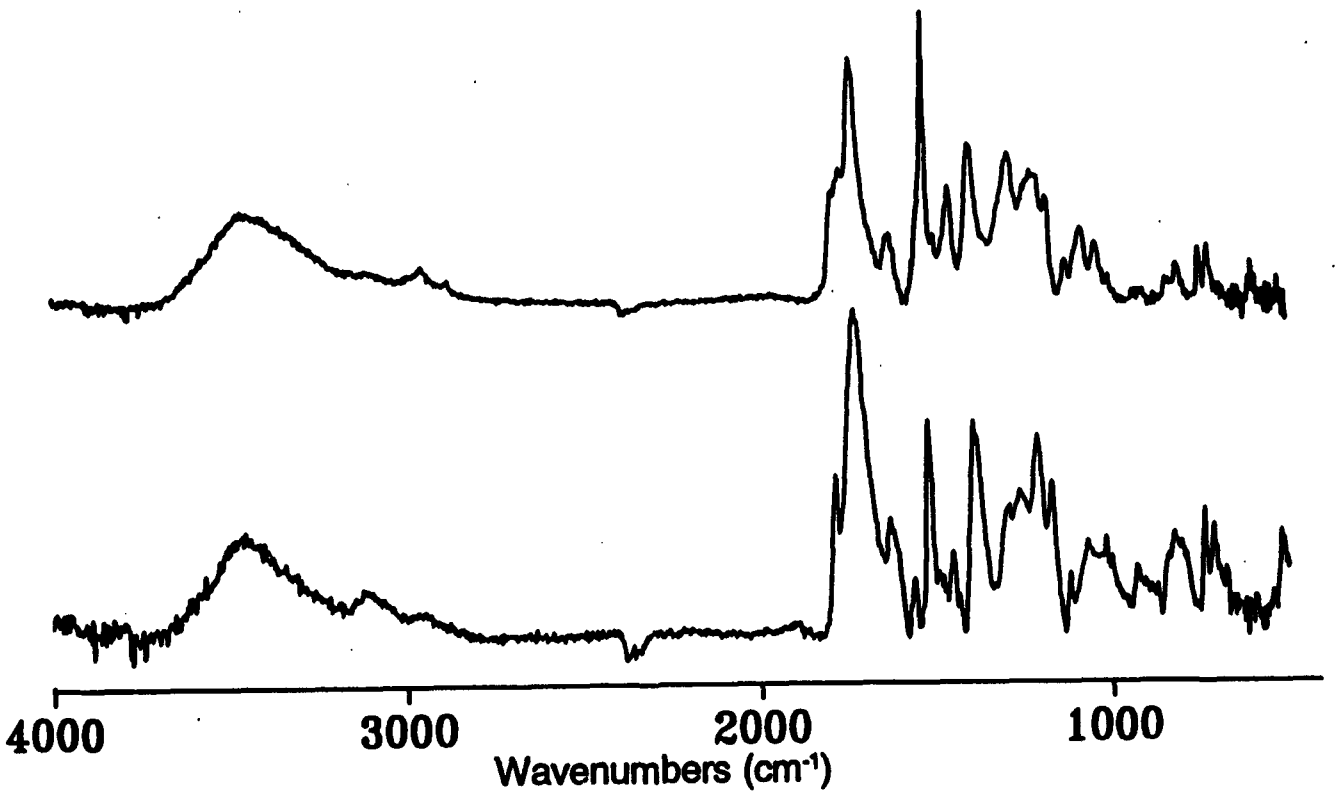


Figure 6

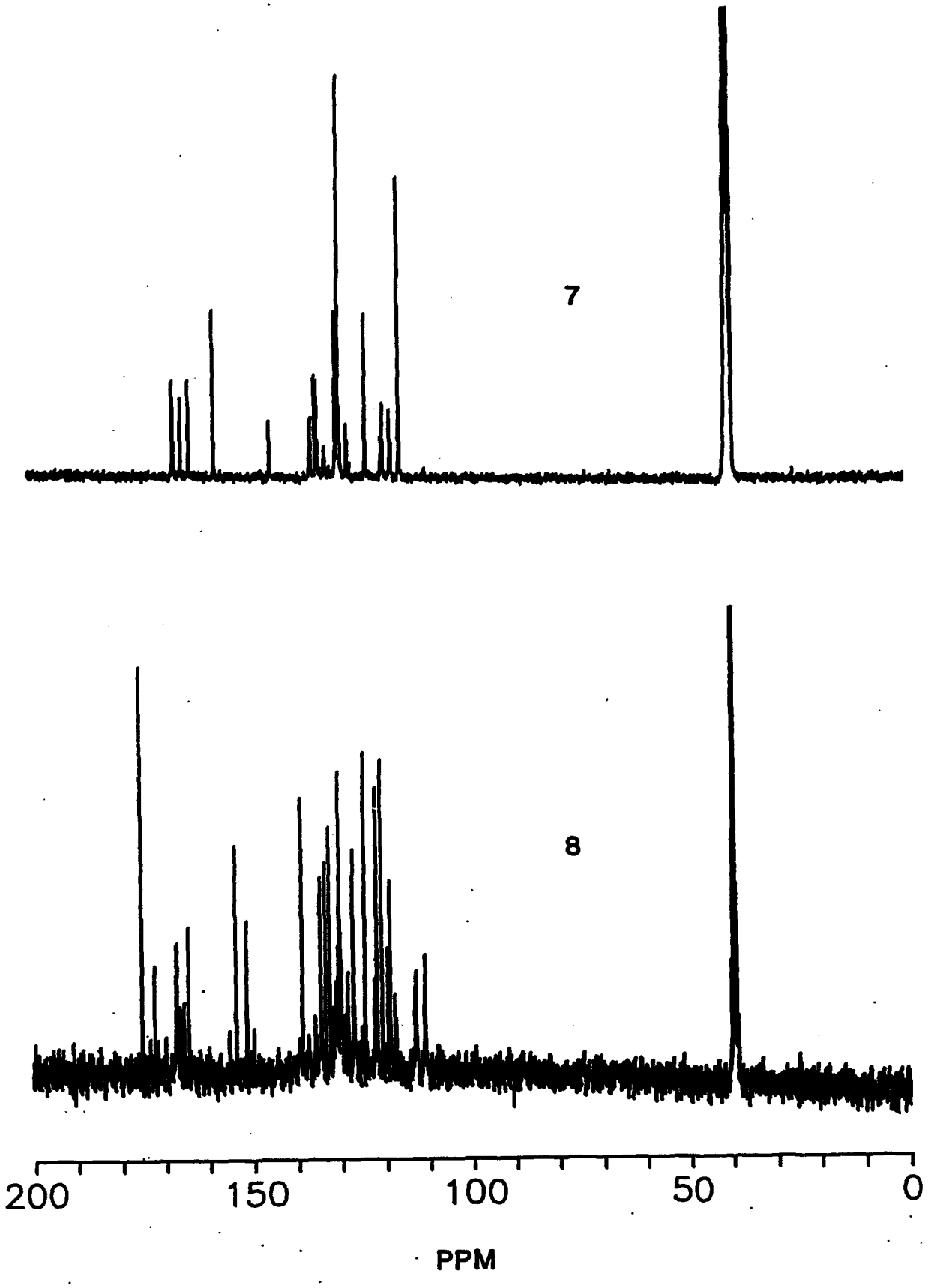


Figure 7

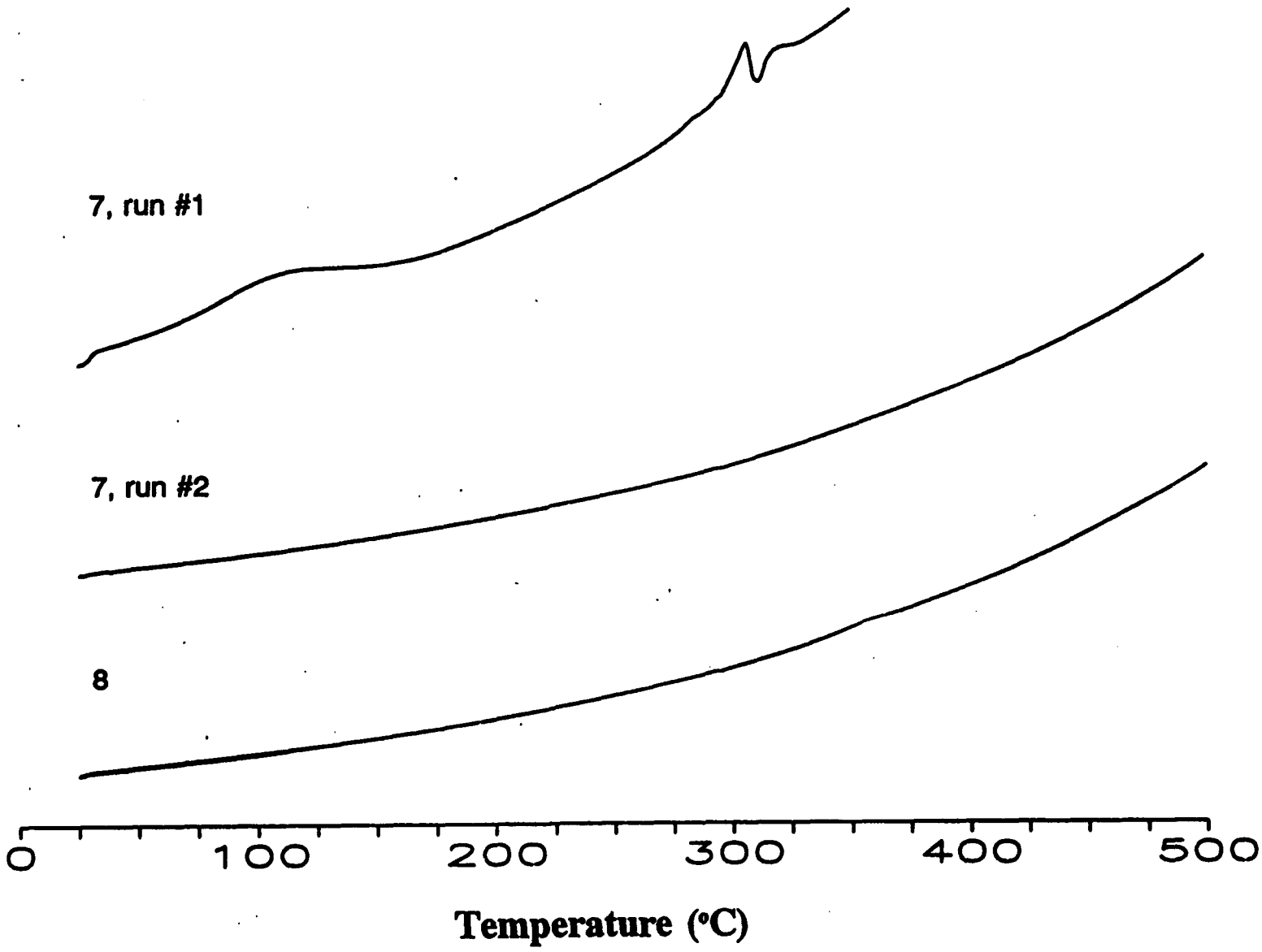


Figure 8

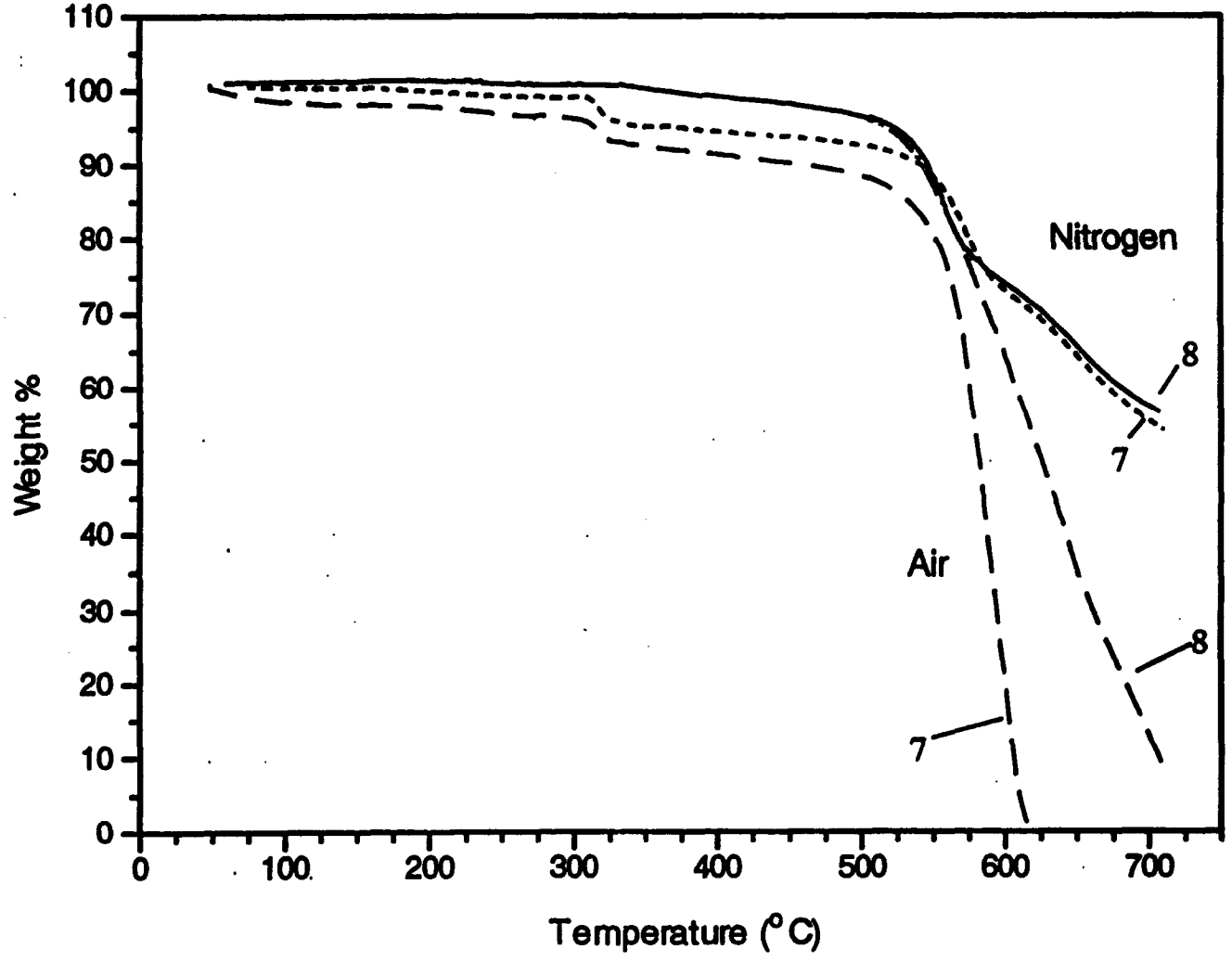

110
100
90
80
70
60
50
40
30
20
10
0
Weight %
0
100
200
300
400
500
600
700
Temperature (°C)
Nitrogen
8
7
Air
8
7

Figure 9

C	1	2a	2b	2c	2d	3a	3b	3c	3d	4a	4b	4c	4d
1						156.9	156.9	158.1	158.0	148.2	148.2	148.1	148.0
2	139.2	137.2	137.4	137.4	140.0	141.1	141.1	141.1	141.1	143.7	143.7	143.6	143.7
3	127.1	124.7	125.4	125.4	126.5	120.8	120.7	121.1	120.8	107.8	107.8	107.8	107.7
4	131.2	131.2	131.6	131.6	130.8	127.1	126.9	119.5	120.6	124.8	124.8	125.1	124.8
5						136.0	136.0	136.1	136.1	118.7	118.7	118.7	118.7
6						113.4	113.3	114.0	113.5	106.7	106.7	106.7	106.6
7	161.3	164.2	165.3	165.5	164.2	165.2	165.3	165.7	165.6	167.7	167.7	167.8	167.8
8						165.3	165.4	165.8	165.7	167.5	167.5	167.9	167.9
A		130.9	129.4	124.1	136.3	131.7	129.0	124.3	124.5	129.9	129.9	124.9	123.5
B		126.2	127.1	128.6	127.3	127.1	126.9	128.6	128.5	126.9	126.9	128.5	128.5
C		128.1	128.9	114.2	114.9	128.8	129.3	114.1	115.0	129.2	129.2	114.0	115.2
D		127.5	137.9	154.0	157.7	128.1	136.0	158.9	157.2	136.8	136.8	158.4	156.7

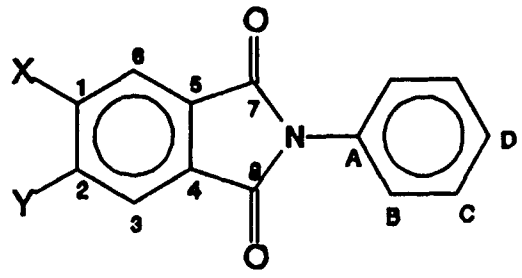
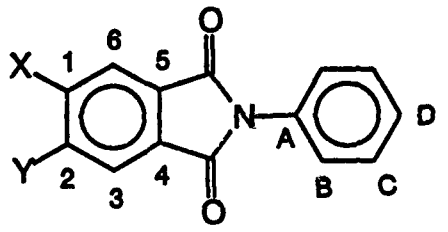


Table 1. Solution ^{13}C NMR Chemical Shifts (DMSO-d_6) of 4,5-disubstituted-N-phenylphthalimide model compounds (**2a-d**, **3a-d** and **4a-d**; X=Cl, OH; Y=Cl, NO_2 and NH_2) and 4,5-dichlorophthalic anhydride (**1**).


X
Y
1
2
3
4
5
6
O
O
N
A
B
C
D

SOLVENT SYSTEM	REACTION TEMP. (°C)	DSC TRANSITION (°C)
NMP/$CaCl_2$/LiCl	200	398
CHP	225	454
CHP/LiCl	200	454
DMSO	180	454
SULFOLANE	275	454

Table 2. Polymerization reaction conditions for poly(ether-imide-benzoxazole) and the DSC transitions of the resulting polymers.

Poly(ether-imide-benzoxazole)			Poly(ester-imide-benzoxazole)		
2θ	θ	d spacing, A	2θ	θ	d spacing, A
2.1	1.05	42.0	5.7	2.85	15.5
5.3	2.65	16.7	14.2	7.1	6.2
15.2	7.6	5.8	15.9	7.95	5.6
23.5	11.75	3.8	23.0	11.5	3.9
26.5	13.25	3.6	26.0	13.0	3.4

Table 3: Wide angle X-ray diffraction data and d spacings of poly(ether-imide-benzoxazole), 6, and poly(ester-imide-benzoxazole), 8.