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SYNTHESIS AND CHARACTERIZATION OF PROCESSABLE POLYIMIDES WITH ENHANCED THERMAL STABILITY

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SYNTHESIS AND CHARACTERIZATION OF PROCESSABLE POLYIMIDES WITH ENHANCED THERMAL STABILITY

INTRODUCTION

Many of the emerging applications of polymers on space vehicles require materials with outstanding thermal stability. These polymers must also be readily processable in order to facilitate their use. Many polymer systems display promising thermal stabilities, but cannot be processed with conventional equipment due to their lack of solubility and/or high transition temperatures. Hence, there has been considerable research carried out to modify the structure of these inherently stable systems in order to affect processability. For example, phenyl groups have been introduced along a polyimide backbone in order to attain solubility [1]. Oxyalkylene linkages have also been incorporated in a polyimide backbone in order to lower transition temperatures [2-4]. One particularly promising approach with polyimide systems has involved the utilization of cardo diamines [5]. The polymers prepared from these diamines display enhanced thermal stability together with excellent solubility. A major objective of this research was to investigate the syntheses and polymerization of a cardo dianhydride. This monomer was to be prepared via the reaction of N-methyl-4-nitrophthalimide with a cardo diol. It was postulated that the polymerization of the dianhydride with aromatic diamines would result in processable polymers with outstanding thermal stability.

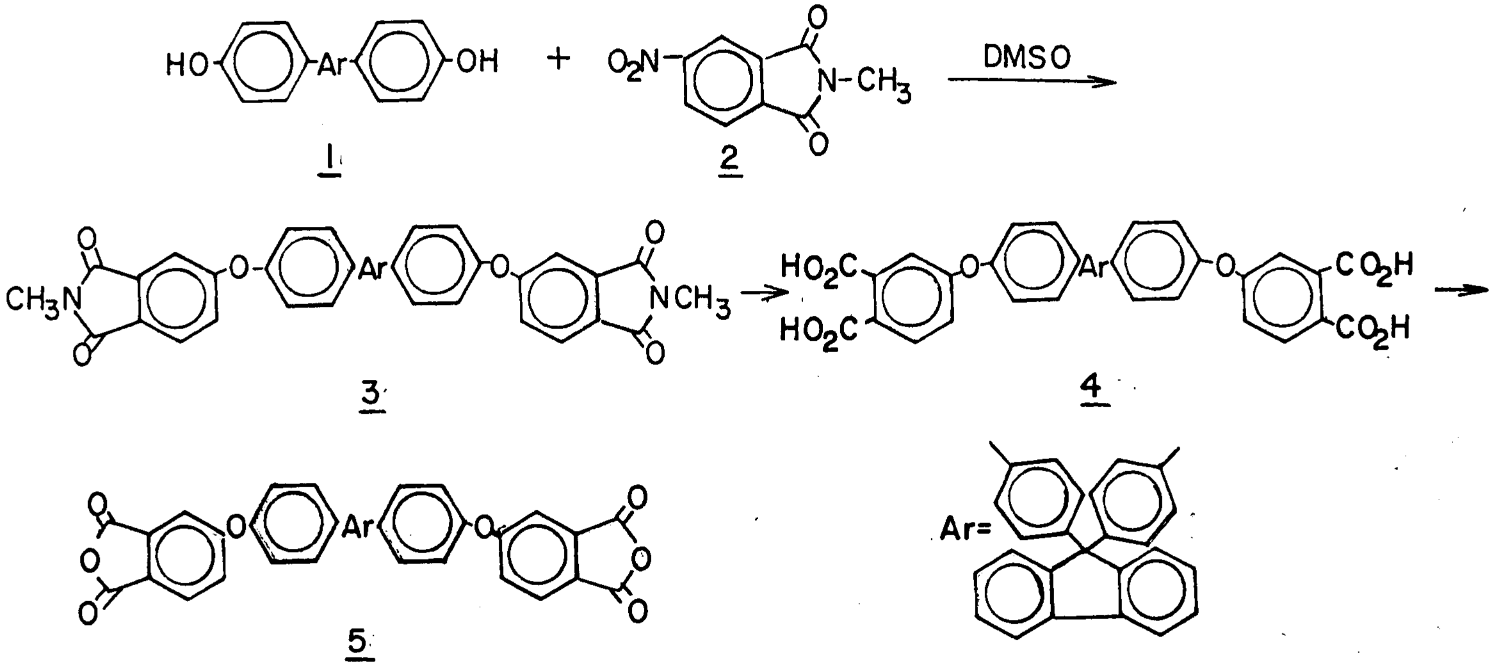
A second objective of this work was to complete our study of polyimides containing oxyalkylene linkages [6,7]. This study, which has resulted in several promising materials, was to be completed by investigating the effects of two additional structural modifications on the polymers' properties. In particular, 1,3-bis(4-aminophenoxy)-2,2-diphenylpropane, 2-(3-aminophenoxy)-2'-(4-aminophenoxy)diethyl ether, and 1-[2-(3-aminophenoxy)-ethoxy]-2-[2-(4-aminophenoxy)ethoxy]ethane were to be synthesized and polymerized with 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), pyromellitic dianhydride (PMDA), and 4,4'-oxydiphthalic anhydride (ODPA). It was anticipated that the polymers obtained from the first diamine would display considerably enhanced thermal stability. It was hoped that the morphology of the polymers obtained from the last two diamines would provide further insight into the effects of meta and para catenation on the polymers' ability to undergo crystallization.

A third objective of this work was to briefly investigate the effects of carrying out the preparation of poly(amic acid)s under non-equilibrium conditions. It was postulated that high-molecular-weight polymers could be obtained with relatively unreactive diamines and dianhydrides if the reverse reactions, i.e., depolymerization of the poly(amic acid), could be prevented. Approaches that were to be investigated included the in situ neutralization of the generated amic acid and its in situ esterification.

RESULTS AND DISCUSSION

Cardo Polyimides

The synthesis of the cardo dianhydride was carried out by the following route:



Considerable time was devoted initially to determining suitable reaction conditions for the coupling of 1 with 2. This work led to the cardo phthalimide 3 being prepared in DMAC at 80°C in 90% yields. Although the hydrolysis of this intermediate to the tetrasalt could be carried out readily in aqueous base, the conversion to the corresponding tetraacid (4) was complicated by the precipitation of partially neutralized salts. However, this conversion was affected in quantitative yields by heating the tetrasalt in dilute HCl at 60°C. The tetraacid was dehydrated in refluxing acetic anhydride.

The cardo dianhydride was polymerized with 4,4'-oxydianiline (ODA) (6) and 9,9-bis(4-aminophenyl)fluorene (8) in DMAC at ambient temperature (Table 1). Since the latter diamine appeared to be unreactive under these conditions, the polymerization was repeated at 60°C. The poly(amic acid) solutions were treated with an equimolar mixture of acetic anhydride and pyridine to affect conversion to the corresponding polyimides. The polymerization of diamine 8 with the cardo dianhydride was also carried

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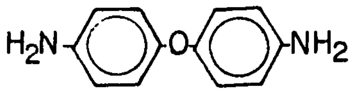

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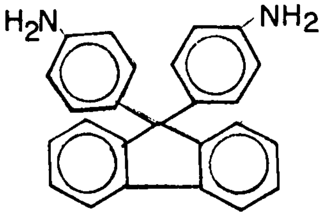

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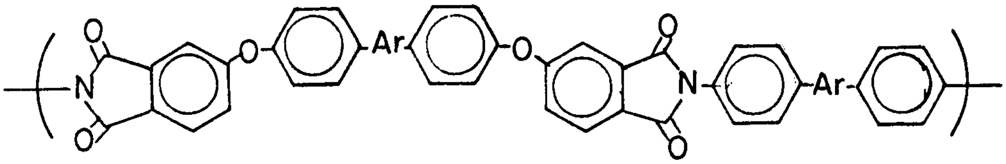


7 and 9

out in a toluene/m-cresol/isoquinoline mixture at elevated temperature. The water of imidization was distilled from the reaction mixture in the form of a water/toluene azeotrope.

The polyimides were soluble in polar aprotic solvents, THF, and chlorinated hydrocarbons. Tough, flexible films of 7 could be cast from chloroform solutions. The Tg's of 7 and 9 were 273°C and 316°C, respectively. Both polymers displayed outstanding thermal stability. Thermogravimetric analysis (TGA) showed 5% weight losses above 560°C in air and nitrogen atmospheres. (Figure 1).

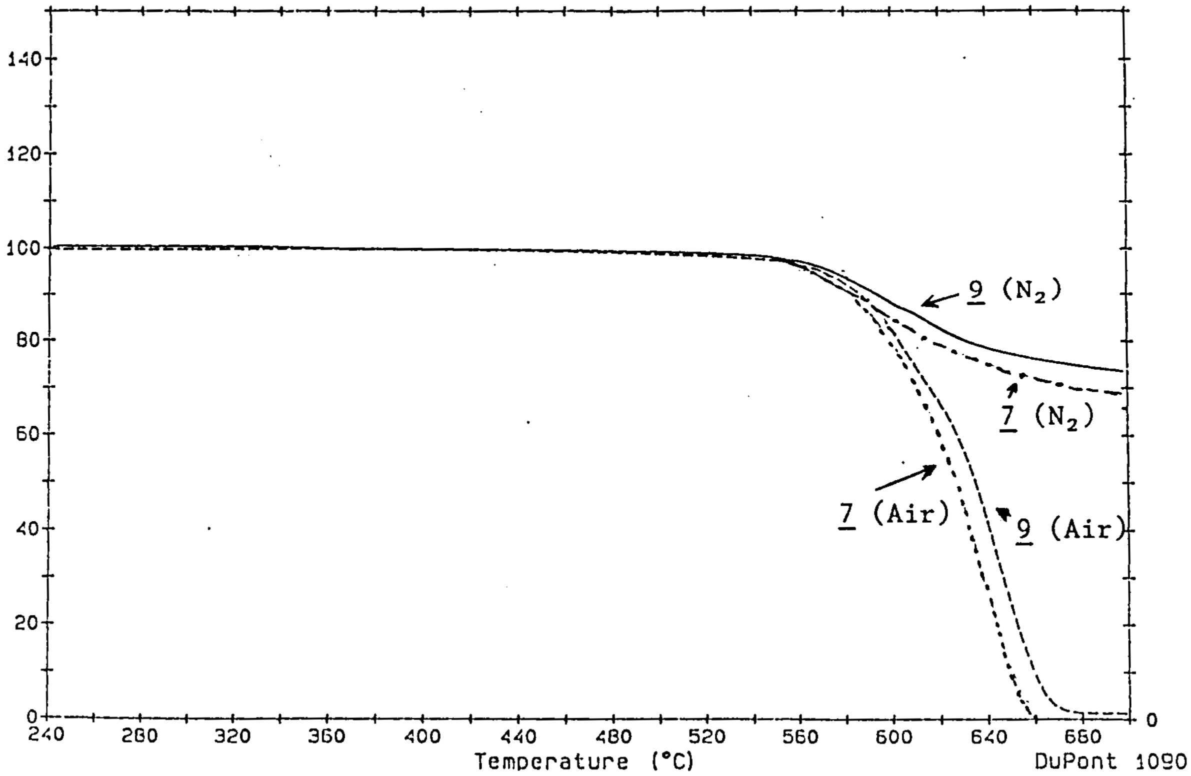


Figure 1. TGA thermograms of cardo polymers 7 and 9. (Heating rate 10°C/min).

TABLE 1

Physical Properties of Cardo Polymers

	Polym.	PAA[a]	PI		TGA[e]	
Polymer	Conditions	η	η	T_g	Air	N_2
7	DMAC, Ambient	0.58	0.52[b]	273	565	555
9	DMAC, 60°C	0.26	0.24	318	565	565
9	M-cresol/toluene/ isoquinoline reflux	-	0.32[c]	315	585	575

a. Inherent viscosity of poly(amic acid) precursor in DMAC at 30°C with a concentration of 0.5 g/dl.

b. Inherent viscosity of polyimide in DMAC at 30°C with a concentration of 0.5 g/dl.

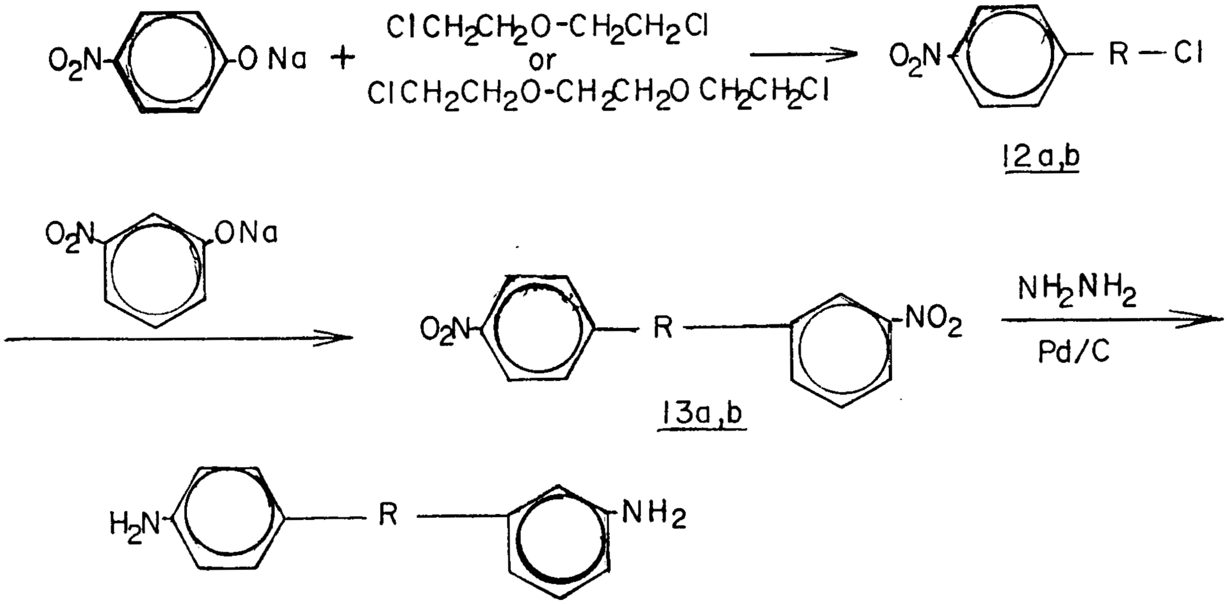
c. Inherent viscosity of polyimide in m-cresol at 30°C with a concentration of 0.5 g/dl.

d. Mid-point of change in slope on DSC thermogram obtained with a heating rate of 20°C/min.

e. Temperature at which 5% weight loss occurred with a heating rate of 10°C/min.

Polyimides Containing Meta- and Para-Catenated Oxyalkylene Linkages.

The syntheses of diamines that contain both meta and para catenation (14a,b) were carried out by the following reaction sequence:

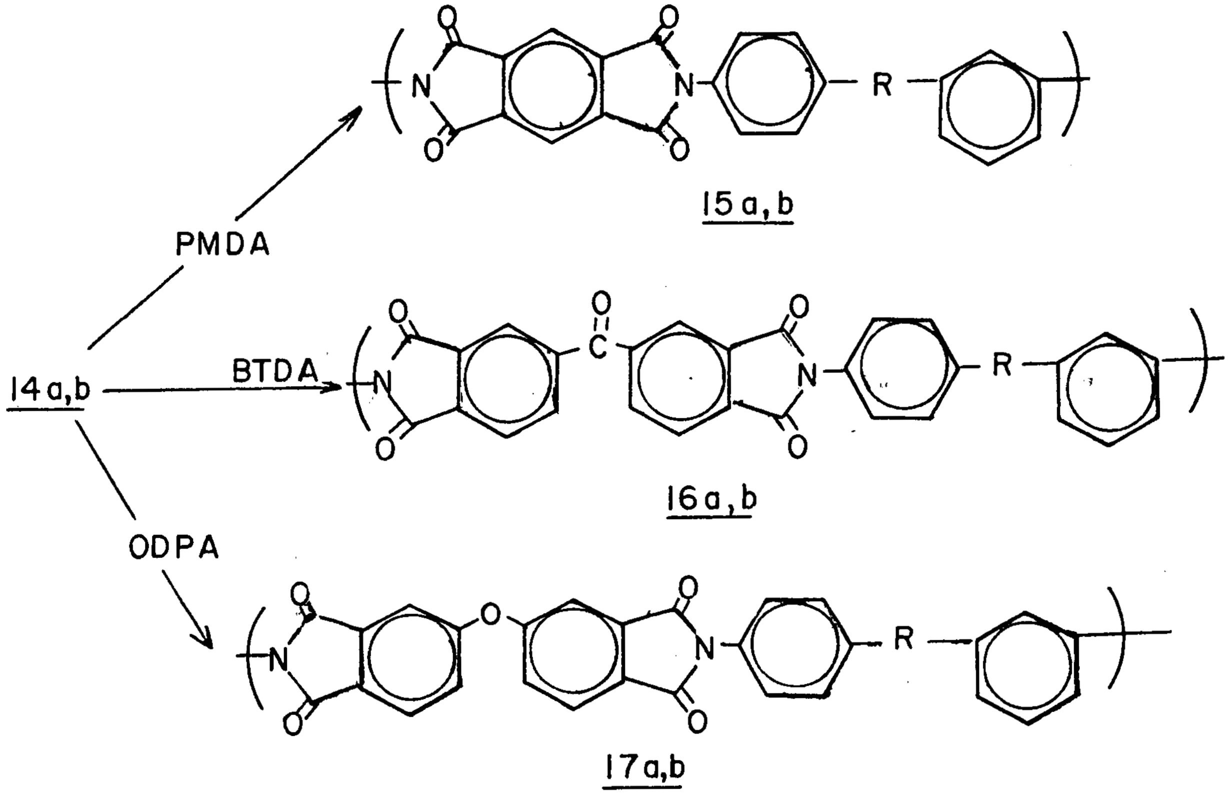


14 a R = $OCH_2CH_2O\text{-}CH_2CH_2O$

b R = $O\text{-}CH_2CH_2O\text{-}CH_2CH_2O\text{-}CH_2CH_2O$

Both diamines were polymerized with PMDA, BTDA and ODPA in NMP at ambient temperature. The inherent viscosities of the resulting poly(amic acid)s in NMP varied from 0.68 to 1.32 dl/g (Determined with a concentration of 0.5 g/dl at 30°C (Table 2).

The polymers were converted to the corresponding polyimides by treatment with equimolar mixtures of pyridine and acetic anhydride. With the exception of 17b, the polymers precipitated from the imidization solutions and could not be redissolved in organic solvents. Polymer 17b, which was isolated by precipitation in ethanol, readily redissolved in NMP.



The polyimides obtained from PMDA were highly crystalline, as witnessed by the strong melting endotherms displayed on their DSC thermograms near 380°C. Their thermograms also showed no discernible base line shifts that could be attributed to glass transitions, another indication of low amorphous content.

TABLE 2

Physical Properties of Polymers Containing Meta- and Para-Catenated Oxyalkylene Linkages

Polymer	PAA[a] η	PI[b] η	T_g[c]	T_m[d]	TGA[e] Air	TGA[e] N_2
15a	1.24	I[f]	ND[g]	380	386	450
15b	0.84	I	ND	375	415	448
16a	1.32	I	160	280,305	442	457
16b	0.91	I	140	290	428	443
17a	1.06	I	148	285	452	440
17b	0.68	0.66	108	100,250	410	440

a. Inherent viscosity of poly(amic acid) precursor in NMP at 30°C with a concentration of 0.5 g/dl.

b. Inherent viscosity of polyimides in NMP at 30°C with a concentration of 0.5 g/dl.

c. Mid-point of change in slope on DSC thermogram obtained with a heating rate of 20°C/min.

d. Minimum of melting endotherm on DSC thermogram.

e. Temperature at which a 5% weight loss occurred with a heating rate of 10°C/min.

f. Insoluble in organic solvents.

g. None detected.

The BTDA-based polymers 16a and b had Tg's of 160 and 140°C, respectively. Although the DSC thermograms of these polymers also contained melting endotherms near 300°C, the ΔH's of these transitions were less than those of the PMDA-based polymers. These results indicate that the polymers contained substantial amounts of both crystalline and amorphous regions.

The DSC thermogram of polymer 17a, which was obtained from 14a and ODPA, showed a strong Tg near 148°C and a weak melting endotherm near 285°C. Evidently, this polymer has a very low degree of crystallinity. Polymer 17b, which was prepared from 14b and ODPA, exhibited the most interesting properties. As mentioned earlier, the polymer was soluble in NMP and evidently highly amorphous. Upon heating to above its Tg of 108°C, it underwent exothermic crystallization to afford a highly crystalline material that displayed multiple melting endotherms (Figure 2).

Two samples of 17b were heated to 250°C. One sample was allowed to cool slowly to room temperature, while the other was cooled rapidly with ice water. The first sample did not redissolve in NMP at room temperature. (It did dissolve when the solvent was heated to approximately 100°C). The DSC thermogram of this sample did not show a Tg or a crystallization exotherm. This behavior is consistent with that of a highly crystalline

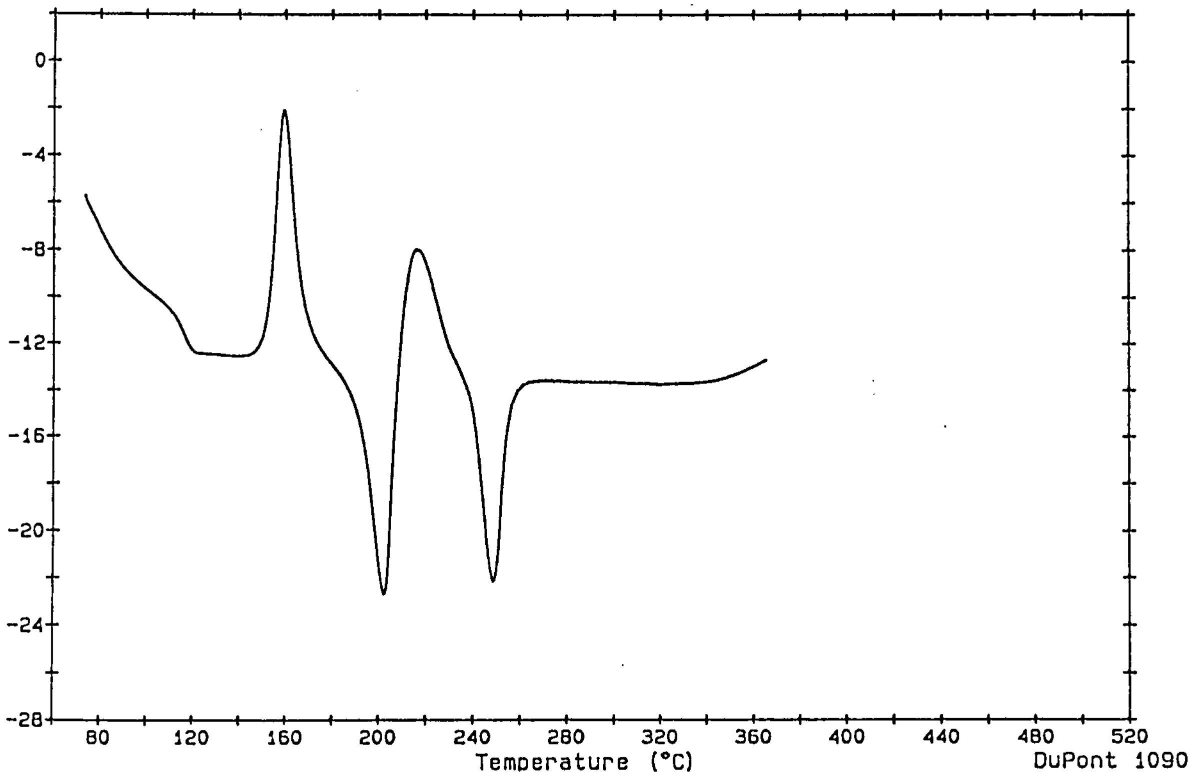


Figure 2. DSC thermogram of polymer 17b. (Heating rate 20°C/min).

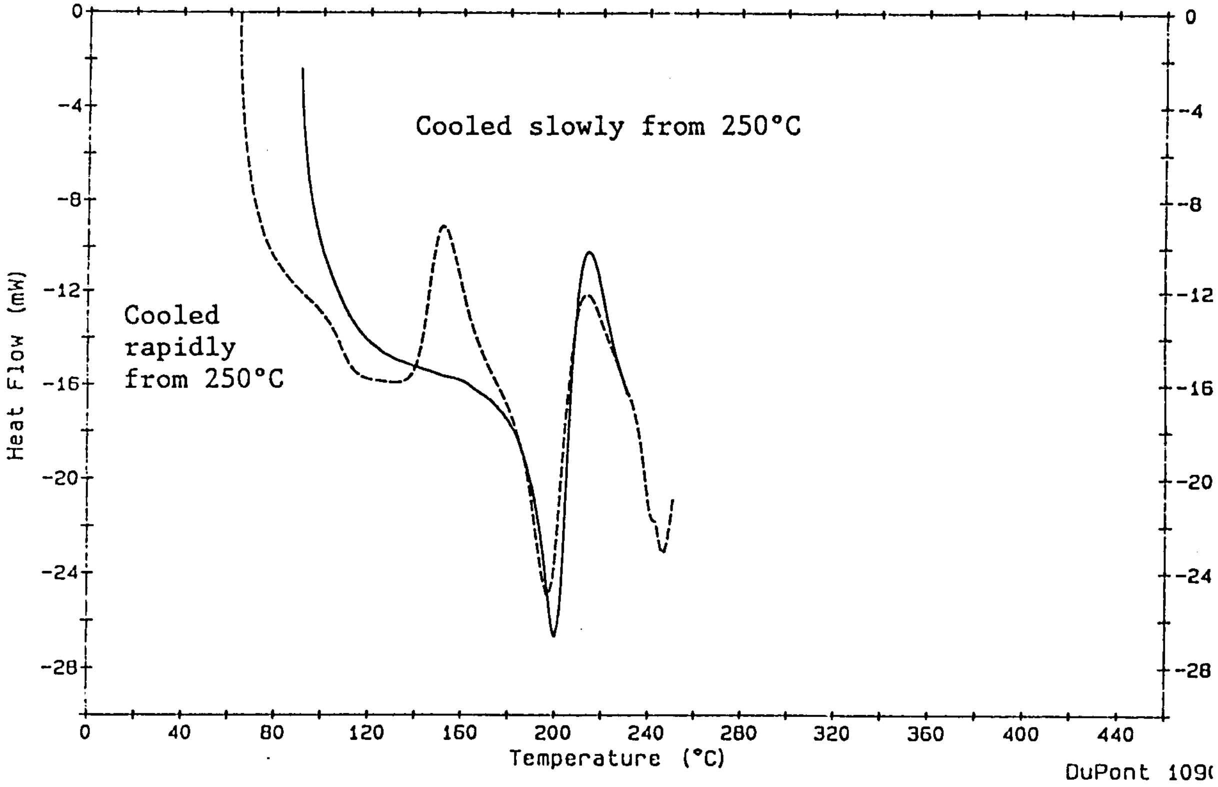
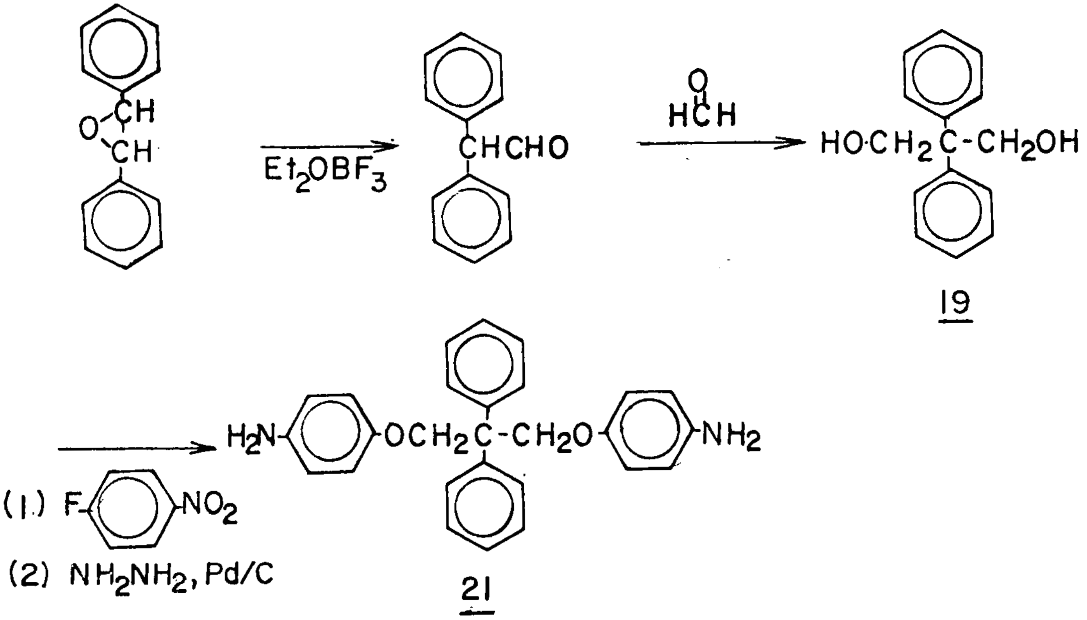


Figure 3. DSC thermograms of polymer 17b. (Heating rate 20°C/min).

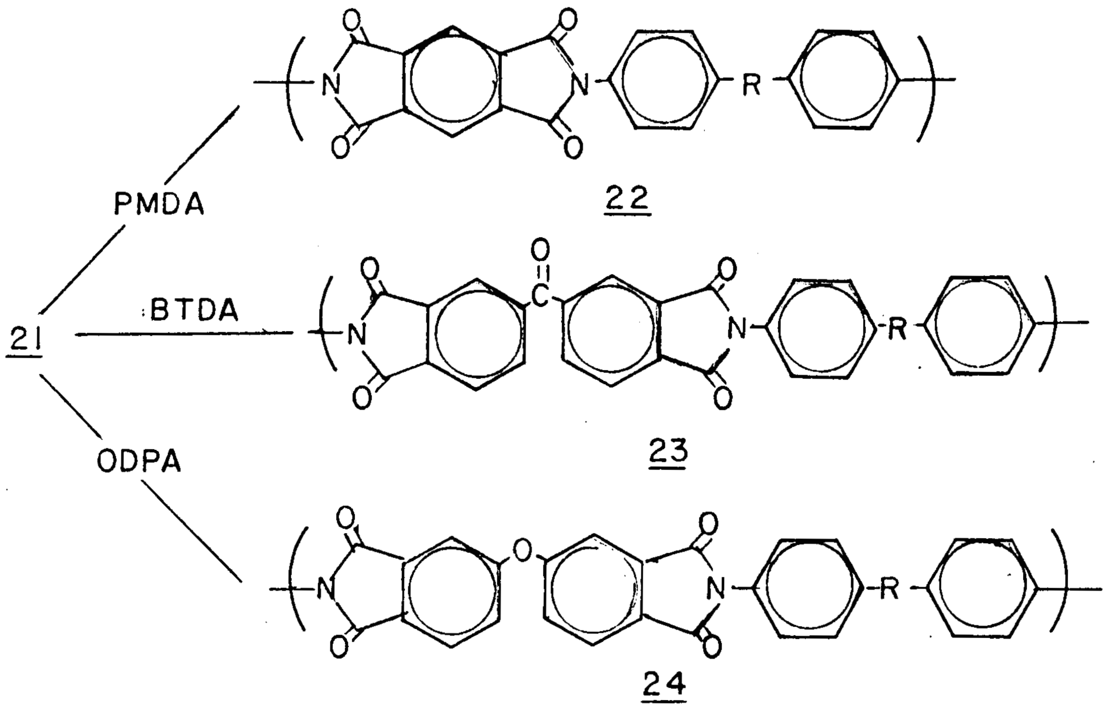
material. The second sample slowly redissolved in NMP at 30°C. The DSC thermogram of this sample showed a Tg and a crystallization exotherm (Figure 3). This indicates that the material was quinched in a highly amorphous state.

Polyimides Containing Phenyl-Substituted Oxyalkylene Linkages

The synthesis of 1,3-bis(4-aminophenoxy)-2,2-diphenylpropane (21) was carried out by the following route:



The diamine was polymerized with PMDA, BTDA and ODA in NMP at ambient temperature. The inherent viscosities of the resulting poly(amic acid)s in NMP varied from 0.64 to 1.12 dl/g (Table 3). The polymers were chemically imidized by treatment with an equimolar mixture of pyridine and acetic anhydride. Although the PMDA-based polymer (22) precipitated from the imidization mixture, 23 and 24 remained in solution and were isolated



by precipitation in ethanol. Polymer 22 could not be dissolved in common organic solvents. Polymers 23 and 24, however, were readily soluble in polar aprotic solvents, chlorinated hydrocarbons, and in THF. Tough, flexible films of these polymers could be cast from chloroform solutions.

The DSC thermogram of 22 indicated that the polymer was highly crystalline. No base line shift could be detected and a strong melting endotherm was present near 435°C. DSC analysis of 23 amd 24, however, showed them to be highly amorphous. Both showed strong base line shifts but no melting endotherms. The Tg of 23 was near 235°C while that of 24 was near 225°C (Table 3). Polymers 23 and 24 also displayed good thermal stability. TGA analysis showed that they retain 95% of their weight to near 450°C in air and to above 460° in nitrogen.

TABLE 3

Polymers Containing Phenyl-Substituted Oxyalkylene Linkages

Polymer	PAA[a] η	PI[b] η	Tg[c]	TGA[d] Air	TGA[d] N_2
22	0.64	I[e]	ND[f]	398	440
23	0.85	0.82	235	448	465
24	1.12	1.12	225	453	462

a. Inherent viscosity of poly(amic acid) precursor in NMP at 30°C with a concentration of 0.5 g/dl.

b. Inherent viscosity of polyimides in NMP at 30°C with a concentration of 0.5 g/dl.

c. Mid-point of change in slope on DSC thermogram obtained with a heating rate of 20°c/min.

d. Temperature at which a 5% weight loss occurred with a heating rate of 10°C/min.

e. Insoluble in organic solvents.

f. None detected.

Synthesis of Poly(amic acid)s

A brief study of the formation of poly(amic acid)s under nonequilibrium conditions was carried out. In one approach, polymers were prepared in the presence of bases that convert amic acids to salts and, thus, prevent any reverse reactions. As part of this study, the model reaction of phthalic anhydride with aniline was carried out in NMP at ambient temperature in the presence of lithium carbonate, potassium carbonate and triethyl amine. In all three cases, essentially quantitative yields (97-98%) of N-phenylphthalimide were obtained when the salt solutions were treated with acetic anhydride. In fact, the imidizations proceeded very quickly. In the case of lithium and potassium carbonate, the imide precipitated almost immediately after the addition of acetic anhydride. The imide precipitated from the triethylamine solution in approximately 20 minutes. The yields, however, were not significantly higher than that obtained when the phthalimide was prepared by the conventional method, i.e., when the amic acid was prepared and then treated with an equimolar mixture of pyridine and acetic anhydride.

The polymerization of BTDA and 2,2'-bis(3-aminophenoxy)-diethyl ether (25) was carried out in NMP at ambient temperature and at elevated temperatures in the presence of several different bases (Table 4). (This diamine was used because it is

TABLE 4

Polymerization of BTDA with 2,2'-Bis(3-aminophenoxy)-diethyl ether

Base	Temperature (°C)	$[\eta]^b$ (dl/g)
None	RT	0.48
$Li_2CO_3{}^c$	RT	0.59
$K_2CO_3{}^c$	RT	0.62
$K_2CO_3{}^c$	100	0.52
Et_3N	RT	0.61
Et_3N	65	0.40
C_6H_5N	RT	0.47
DMAP[d]	RT	0.25
$NaHCO_3{}^c$	70	0.43

a. Run in NMP with a 15% solids content.

b. Intrinsic viscosity determined in NMP at 30°C.

c. Salt did not dissolve completely in NMP.

d. 4-Dimethylaminopyridine.

less reactive than para-catenated diamines). All the salt solutions were treated with acetic anhydride to affect imidization. The polymerization that was carried out at ambient temperature in the presence of lithium carbonate and the polymerization that was carried out at 100°C in the presence of potassium carbonate afforded extremely viscous poly(amic acid) solutions. Such behavior is indicative of polyelectrolyte effects.

The intrinsic viscosities of several of the polyimides that were obtained from poly(amic acid)s prepared in the presence of bases were slightly higher than that of the control (Table 4). (The control polymer was prepared from the monomers by the conventional procedure, i.e., polymerization in NMP followed by imidization with an equimolar mixture of pyridine and acetic anhydride). Thus, the dramatic increase in molecular weight that was sought was not achieved.

The manner in which imidization was carried out did affect the morphology of the polyimide (Figures 4 & 5). A totally amorphous polyimide was obtained when the poly(amic acid) was prepared in the presence of potassium carbonate. When triethylamine was used an amorphous polyimide was obtained if the polymer was isolated by precipitation in ethanol. However,

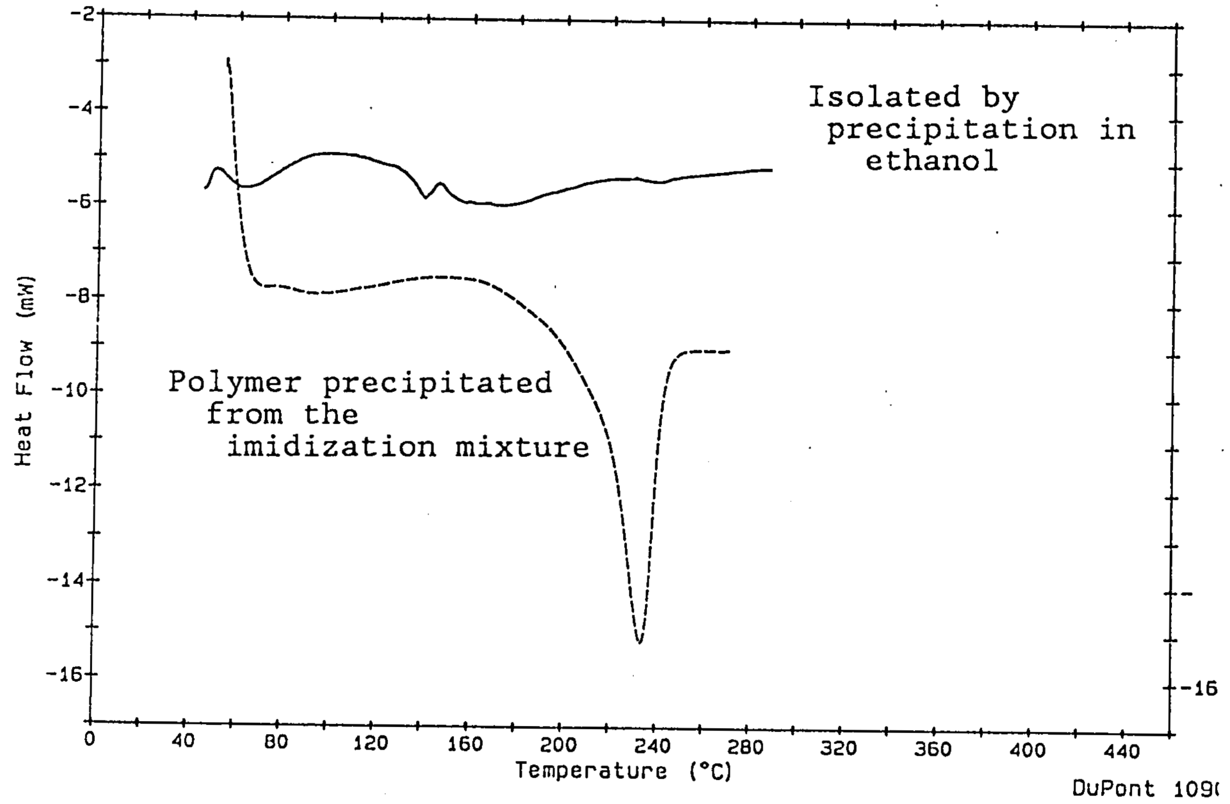


Figure 4. DSC thermograms of polyimide samples obtained from poly(amic acid)s that were prepared in the presence of triethylamine. (Heating rate 20°C/min).

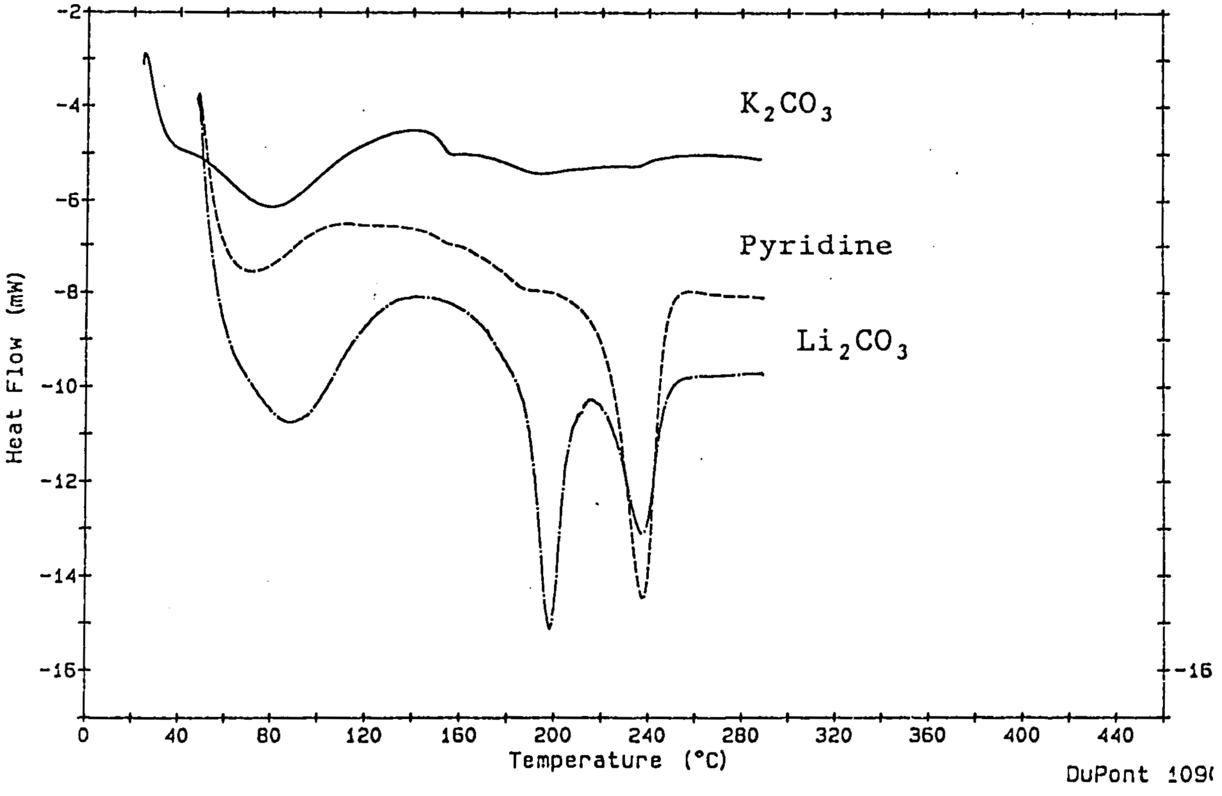


Figure 5. DSC thermograms of polyimide samples obtained from poly(amic acid)s that were prepared in the presence of various bases. (Heating rate 20°C/min).

if the imidization mixture was allowed to stir for 48 h after the addition of acetic anhydride, a semicrystalline product precipitated (Figure 4). Imidization of the poly(amic acid) prepared in the presence of lithium carbonate resulted in a polyimide that displayed two melting endotherms (Figure 5).

A brief attempt was also made to prepare a poly(amic acid) under conditions which would result in its immediate conversion to the corresponding poly(amic ester), thus, preventing any reverse reaction. As part of this study, the model reaction of phthalic anhydride and aniline was carried out in the presence of 2,2-dimethoxypropane, a methylating agent. Although several different sets of reaction conditions were used, the only product that could be isolated was the amic acid. Similar results were obtained when the polymerization of BTDA with <u>25</u> was carried out in the presence of the esterifying agent.

EXPERIMENTAL

9,9-Bis(4-hydroxyphenyl)fluorene (1)

9-Fluorenone was treated with phenol according to the known procedure[8] to give a 78% yield of white needles: mp 222-224°C (lit.[8] 222°C).

Cardo Bisphthalimide 3

A 3-necked, 5-L, round-bottom flask equipped with an overhead stirrer and a Dean-Stark trap was charged with 140.17 g (0.4 mol) of 1, 63.995 g (0.8 mol) of 50% aqueous NaOH, 2 L of DMAC, and 1 L of toluene. The mixture was heated to reflux, and the toluene/H_2O azeotrope removed by distillation. The distillation was continued for 3-4 h to remove all the water and the majority of the excess toluene. Approximately 30 mL of toluene was allowed to remain in the reaction mixture, which was air cooled to 80°C. 4-Nitro-N-methylphthalimide (164.93 g, 0.8 mol) was then added and the mixture stirred at 80°C for 4 h. (The blue solution darkened immediately upon the addition of the phthalimide.) After the mixture was allowed to cool to room temperature, it was slowly added to 4 L of 0.1 M aqueous HCl. The precipitate that formed was collected by filtration, washed several times with H_2O, and dried under reduced pressure to afford 243.4g (91%) of an off-white powder. This material was sufficiently pure to be used in the next reaction. A small sample was recrystallized from ethyl acetate and from ethanol to give a white powder: mp 262-264°C (lit.[9] 208-210°C); IR (KBr) 1765, 1702 (c=o), and 1620 cm^{-1} (aryl); NMR ($CDCl_3$) δ 3.1 (S, 6H, CH_3) and 6.8-7.8 ppm (M, 22H, aryl).

Cardo Bisphthalic Acid 4

A solution of 50.0 g (0.075 mol) of the bisphthalimide 3 and 24.0 g (0.60 mol) of NaOH in 50 mL of H_2O was stirred and heated at reflux for 18 h. The amber solution was allowed to cool to room temperature and then slowly added to 500 mL of cold 1 M HCl. The grey salt that precipitated was collected by filtration and stirred in 1 L of H_2O that was heated at 60°C for 30 min. During this time complete neutralization was affected. The suspension was filtered, and the product dried under reduced pressure overnight at 110°C to afford 49.4 g (96%) of a white, course powder: mp 196-198°C; IR (KBr) 3476 (COOH) and 1715 cm^{-1} (c=o).

Cardo Dianhydride 5

A solution of 30.54 g (0.045 mol) of the cardo bisphthalic acid (4) in 125 mL of acetic anhydride was stirred and heated at reflux for 4 h. The solution was then cooled to 0°C and allowed to stand. The pale yellow powder that precipitated was recrystallized twice from acetic anhydride containing activated charcoal to afford 24.3 g (84%) of light yellow crystals: mp 252-254°C (lit.[9] 237-238°C); IR (KBr) 1850 and 1775 cm^{-1} (O=C-O-C=O).

Polymerization of The Cardo Dianhydride with Diamines

To a polymerization vessel equipped with an overhead stirrer and purged with N_2, was added 1.0000 g (1.56 mmol) of the cardo dianhydride 5, 1.56 mmol of the diamine and 10 mL of anhydrous DMAC. After the solution was stirred for 8 h at ambient temperature, 0.64 g (6.2 mmol) of acetic anhydride and 0.5 g (0.62 mmol) of pyridine were added. The mixture was stirred for an additional 18 h and then added to 95% ethanol to afford light-yellow fibrous powders.

Polymerization of The Cardo Dianhydride with The Cardo Diamine at Elevated Temperature

To a solution of 0.2657 g (0.763 mmol) of 8 in 10 mL of *m*-cresol was added 0.4900 g (0.763 mmol) of 5. After the mixture was stirred for 2 h at room temperature, 10 mL of toluene was added. The solution was heated to approximately 120°C, and the toluene/water azeotrope distilled from the reaction mixture. Fresh toluene (10 mL) was added and the procedure repeated. After this process was repeated 5 more times over 2 h, the solution was heated to 180°C for 2 h, cooled, and added to 95% ethanol to afford a light-yellow fibrous powder.

2-Chloro-2'-(4-nitrophenoxy)diethyl ether (12a)

A mixture of 20.0 g (0.144 mol) of 4-nitrophenol, 12.6 g of 50% aqueous NaOH, 80 mL of toluene, and 300 mL of DMSO was stirred and heated to reflux under N_2. After the H_2O was removed by azeotropic distillation with the toluene, the dark red solution was added dropwise to 41.1 g (0.288 mol) of stirred 2-(2-chloroethoxy)diethyl ether. The resulting mixture was stirred overnight at 80°C. The dark solution was then slowly added to 4 L of ice H_2O. The brown precipitate that formed was collected by filtration, washed with 4 L of hot H_2O, and recrystallized from ethanol. The solid was stirred in 200 mL of diethyl ether and the resulting suspension filtered. The filtrate was evaporated to dryness under reduced pressure to afford 21.0 g (70%) of a white powder: mp 68-69°C; IR (KBr) 1530, 1345 (NO_2), 1260 (Ar-O-R), and 1120 cm^{-1} (R-O-R).

2-(3-Nitrophenoxy)-2'-(4-nitrophenoxy)diethyl ether (13a)

A mixture of 12.5 g (0.090 mol) of 3-nitrophenol, 7.6 g of 50% aqueous sodium hydroxide, 100 mL of toluene, and 300 mL of DMSO was stirred and heated to reflux. After the H_2O was removed by azeotropic distillation with the toluene, 20.0 g of 12a in 50 mL of DMSO was slowly added. The stirred mixture was heated at 80°C under N_2 overnight and then added to 2 L of ice H_2O. The yellow precipitate which formed was collected by filtration and recrystallized from ethanol to yield 18.5 g (60%) of yellow needles: mp 119-120°C; IR (KBr) 1510, 1345 (NO_2), 1260 (Ar-O-R) and 1120 cm^{-1} (R-O-R).

2-(3-Aminophenoxy)-2'-(4-aminophenoxy)diethyl ether (14a)

A stirred solution of 20.0 g (0.057 mol) of 13a in 250 mL of 95% ethanol was heated to reflux, and 1.0 g of palladium on activated carbon was added. Hydrazine hydrate (7.2 g, 0.144 mol) was then added dropwise. After the mixture was stirred and heated at reflux overnight, it was filtered hot through celite and allowed to cool. The white crystals that formed were collected by filtration and dried under reduced pressure at 60°C to afford 16.5 g (99.6%) of product: mp 101-102°C; IR (KBr) 3420, 3350 (NH_2), 1245 (Ar-O-R), and 1130 cm^{-1} (R-O-R).

1-[2-(3-Aminophenoxy)ethoxy]-2-[2-(4-aminophenoxy)ethoxy]ethane 14b)

Compound 14b was prepared from 1,2-bis(2-chloroethoxy)ethane, 3-nitrophenol, and 4-nitrophenol by the procedure described for 14a. The light-yellow oil was used as obtained from the reduction of the dinitro intermediate: IR (KBr) 3350, 3430 (NH_2), 1240 (Ar-O-R) and 1120 cm^{-1} (R-O-R).

2,2-Diphenyl-1,3-propanediol (19)

Treatment of diphenylacetaldehyde with formaldehyde according to the known procedure afforded a 90% yield of 19. The product was recrystallized from ethanol to yield white crystals: mp 102-103°C (lit.[10] 102°C-104°C).

1,3-Bis(4-Nitrophenoxy)-2,2-diphenylpropane (20)

To a stirred solution of 2.65 g (0.020 mol) of 4-fluoronitrobenzene and 3.3 g (0.024 mol) of K_2CO_3 in 150 mL of DMAC under N_2 was added 2.34 g (0.010 mol) of 19. The solution was stirred and heated at reflux overnight and then poured into 4 L of vigorously stirred ice H_2O. The yellow precipitate that formed was collected by filtration and washed with 1 L of H_2O. The crude product was extracted with hot ethanol to give 1.84 g (39%) of light-brown powder: mp 226-228°C; IR (KBr) 1510, 1350 (NO_2) and 1260 cm^{-1} (Ar-O-R).

1,3-Bis(4-Aminophenoxy)-2,2-diphenylpropane (21)

Compound 20 was reduced with hydrazine hydrate according to the procedure described for 14a to afford a 90% yield of white crystals: mp 76-77°C; IR (KBr) 3450, 3380 (NH_2) and 1250 cm^{-1} (Ar-O-R).

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