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# POLYIMIDES CONTAINING OXYETHYLENE UNITS, IV. POLYMERIZATION OF DIANHYDRIDES CONTAINING ETHER LINKAGES

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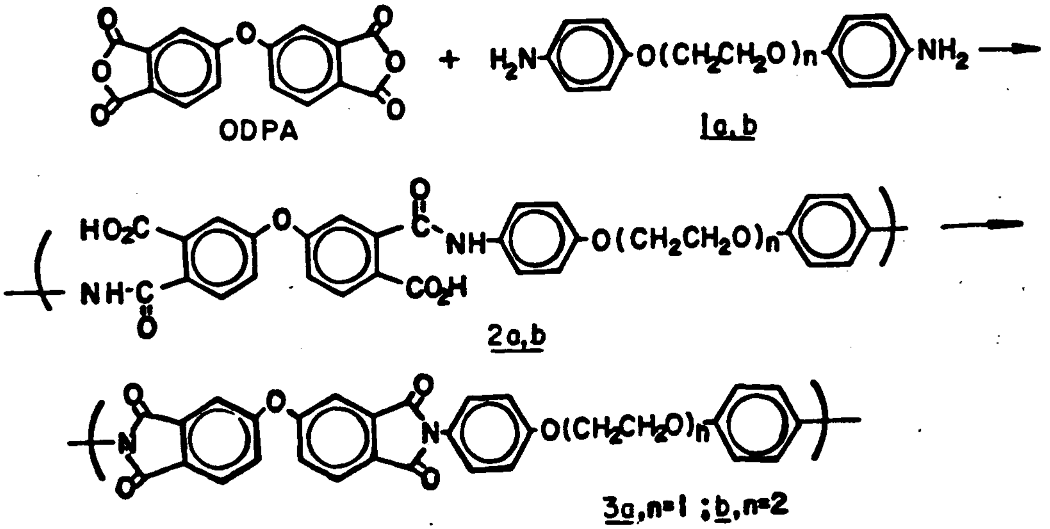
The overall objective of this ongoing research is the development of new composite resins for various aerospace applications. Although it is highly desirable that these polymers be soluble in order to facilitate processing, they must display considerable solvent-resistance in use. A recent approach has involved the synthesis of a new series of polyimides containing flexible linkages.[1-3] The polymers were prepared by the polymerization of aromatic dianhydrides with diamines containing oxyethylene linkages. For example, the polymerization of 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) with 1,2-bis(4-aminophenoxy)ethane (1a) and bis[2-(4-aminophenoxy)ethyl]ether (1b), afforded highly crystalline polyimides that were completely insoluble.[2] However, a polyimide that was amorphous and soluble was obtained from the polymerization of BTDA and an isomer of 1b, i.e., bis[2-(3-aminophenoxy)ethyl] ether (4b). In an attempt to obtain a soluble, amorphous polyimide that could be annealed into a crystalline state, block copolymers of 1b and 4b and BTDA were prepared.[3] Copolymers containing less than 20 weight % 1b were soluble in organic solvents. However, these polymers did not crystallize when heated above their Tg's. Copolymers containing higher levels of 1b were semicrystalline and insoluble.

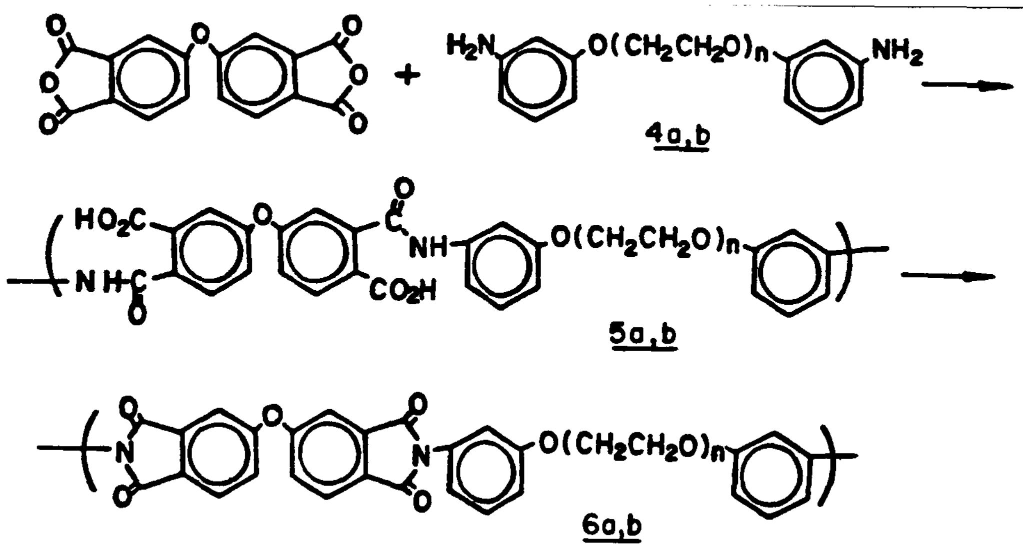
The objective of this work was to investigate the polymerization of the diamines containing oxyethylene linkages with 4,4'-oxydiphthalic anhydride (ODPA) and a new dianhydride, i.e., 4,4'-oxyethyleneoxyethyleneoxydiphthalic anhydride (OEDA). It was postulated that the use of these more flexible dianhydrides would result in more processable polyimides.

## RESULTS AND DISCUSSION

### Polymerization of ODPA

ODPA was polymerized with 1a,b and with 1,2-bis(3-aminophenoxy)ethane (4a) and 4b. The polymerizations were carried out under nitrogen in NMP at room temperature (Table 1). In the case of the para-linked diamines, the reaction mixtures became quite viscous within 15 minutes. The intermediate poly(amic acids) were treated with a mixture of acetic anhydride and pyridine to afford the corresponding polyimides.





4a,b

5a,b

6a,b

As was observed with analogous BTDA-based polymers, the polyimides prepared from the para-linked diamines were semicrystalline and insoluble in organic solvents. Their DSC thermograms, however, showed that their degrees of crystallinity were lower than those of the BTDA systems. The polyimides prepared from the meta-linked diamines were amorphous and soluble in NMP. As expected, all of the polymers displayed Tg's that were considerably lower than those of the corresponding BTDA polymers (Table 1).

TABLE 1

Polymers Based on ODPA

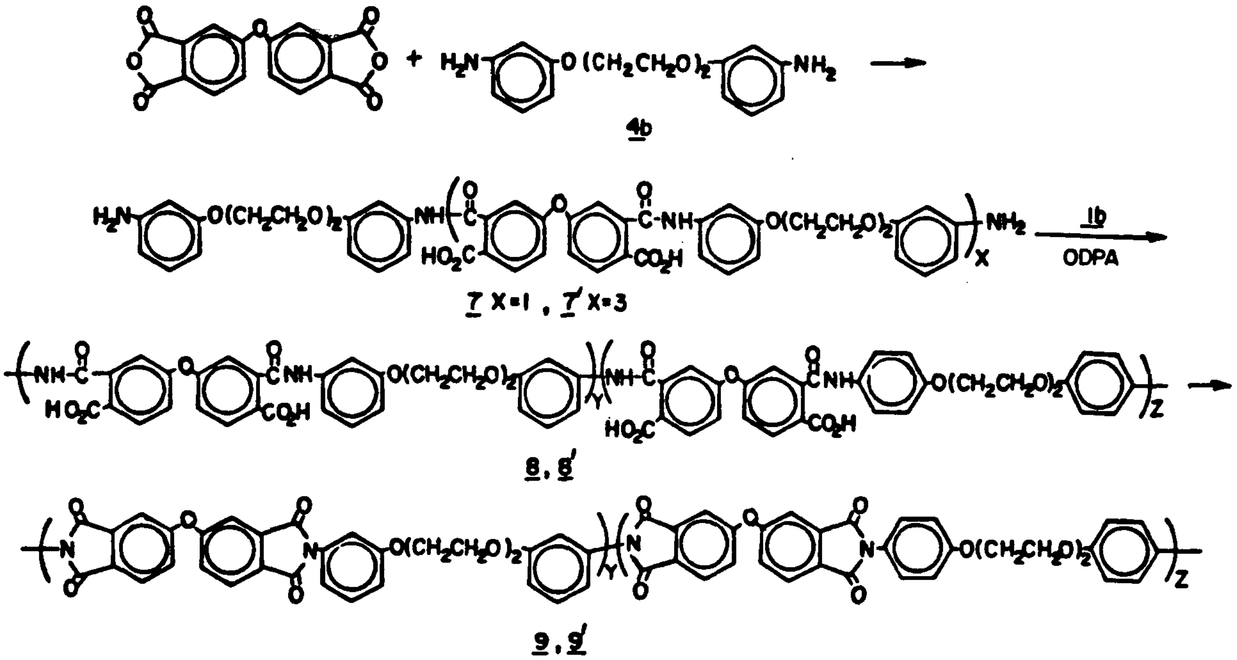
| Poly(amic Acid) | | Polyimide | | | | | |
|---|---|---|---|---|---|---|---|
| No. | {η}[a] | No. | {η}[a] | Tg(°C)[b] | Tm(°C) | TGA[c] | |
| | | | | | | Air | $N_2$ |
| 2a | 1.38 | 3a | d | 184 | 470 | 390 | 465 |
| 2b | 2.08 | 3b | d | 164 | 370 | 380 | 412 |
| 5a | 0.76 | 6a | 0.55 | 134 | - | 390 | 452 |
| 5b | 0.60 | 6b | 0.55 | 128 | - | 380 | 412 |

a. Inherent viscosity in NMP at 30°C with a concentration of 0.5 g/dl. Polymer was not isolated prior to determination.
b. Tg and Tm were determined by DSC analysis under $N_2$ with a heating rate of 20°C/min.
c. Temperature at which 5% weight loss occurred with a heating rate of 10°C/min.
d. Polymer was insoluble in NMP.

## ODPA-Based Block Copolymers

In our continuing effort to obtain a soluble, semicrystalline polyimide, block copolymers of 4b and 1b and ODPA were prepared. Thus, ODPA was treated with excess 4b in NMP at ambient temperature to afford amine-terminated oligomers (7). Molar ratios of ODPA to 4b of 1:2 and 3:4 were used. These oligomers were then polymerized with various amounts of 1b and additional ODPA to afford a series of block copoly(amic acids) (8) (Table 2). The poly(amic acid) solutions were then divided into two parts. One-half of each solution was heated to reflux in order to thermally imidize the poly(amic acid). The water generated by the cyclodehydration was removed by distillation. The remaining half of each solution was diluted with additional NMP to 6% solids and then treated with an equimolar mixture of pyridine and acetic anhydride. The resulting solutions were stirred overnight at ambient temperature to affect imidization.

The ODPA-based block copolyimides were considerably more soluble than the analogous BTDA-based copolymers. Copolymers containing up to 43 wt % para diamine remained soluble in NMP after imidization. As with the BTDA systems, thermal imidization in solution afforded more soluble polymers than did chemical imidization at ambient temperature. Polymer 9cT, which was obtained by thermal imidization, was the first copolyimide prepared in this investigation that displayed both a Tm and solubility in NMP.



## TABLE 2

ODPA-Based Block Copolymers

| Molar Ratio ODPA to 4b | Molar Ratio of Oligomer 7 to 1b | Wt % of 1b | $\{\eta\}^c$ | Thermal Imidization[a] | | | | Chemical Imidization[b] | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | No. | $\{\eta\}^d$ | Tg | Tm | No. | $\{\eta\}^d$ | Tg | Tm |
| 1:2 | 100:0 | 0 | 0.42 | 9aT | 0.29 | 132 | - | 9ac | 0.27 | 132 | - |
| | 75:25 | 14.3 | 0.43 | 9bT | 0.30 | 135 | - | 9bc | 0.38 | 134 | - |
| | 50:50 | 33.3 | 0.73 | 9cT | 0.39 | 133 | 266 | 9cc | e | 133 | - |
| | 25:75 | 60.0 | 0.85 | 9dT | e | 142 | 291 | 9dc | e | 135 | 330 |
| 3:4 | 100:0 | 0 | 0.47 | 9'aT | 0.23 | 124 | - | 9'ac | 0.40 | 128 | - |
| | 75:25 | 7.7 | 0.48 | 9'bT | 0.31 | 126 | - | 9'bc | 0.36 | 132 | - |
| | 50:50 | 20.0 | 0.54 | 9'cT | 0.36 | 122 | - | 9'cc | 0.48 | 136 | - |
| | 25:75 | 42.9 | 0.69 | 9'dT | e | 139 | 270 | 9'dc | e | 137 | 330 |

a. A solution of poly(amic acid) in NMP was heated to reflux, and the water of imidization was removed by distillation. (Fresh NMP was continuously added to replace the distillate). The distillation-addition cycle was carried out for 3 hr.

b. After the solution of poly(amic acid) in NMP was diluted to 6% solids with NMP, a two-molar excess of an equimolar solution of pyridine and acetic anhydride was added. The resulting mixture was stirred overnight at ambient temperature.

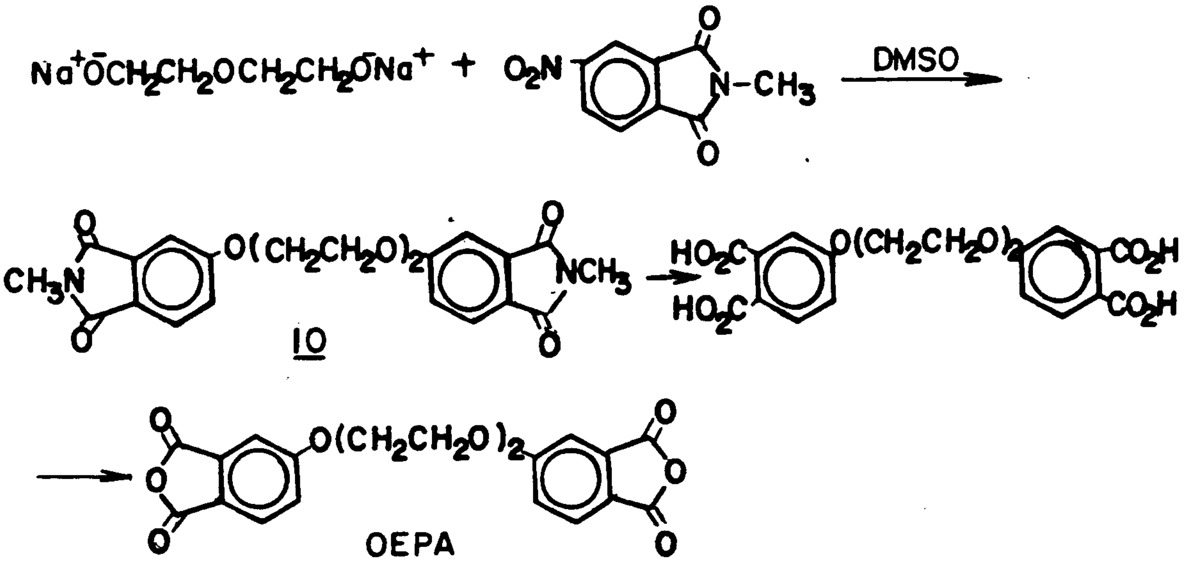
c. Inherent viscosity of poly(amic acid) in NMP at 30°C with a concentration of 0.5 g/dl.

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

e. Insoluble in organic solvents at ambient temperature.

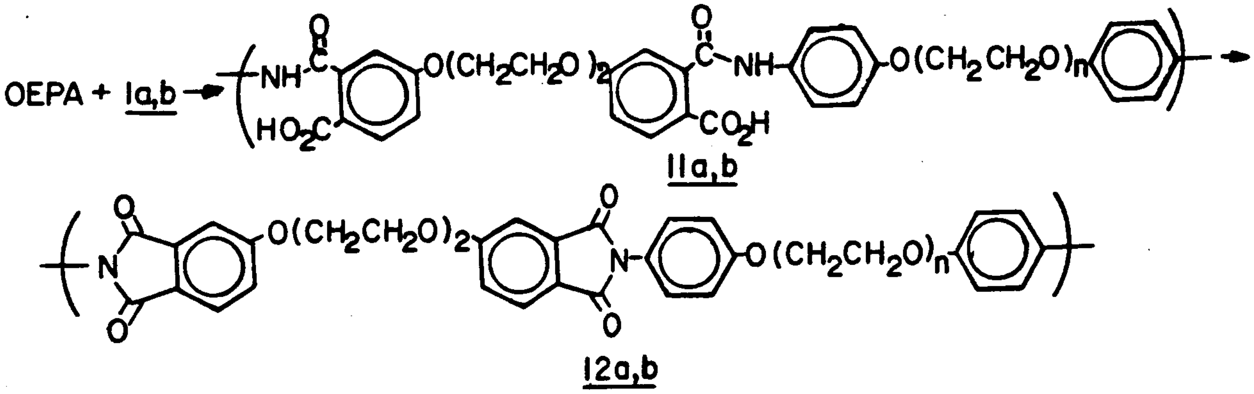
### Synthesis of OEDA

A dianhydride containing oxyethylene linkages, i.e., OEDA, was synthesized by the following route:



## Polymerization of OEPA

OEPA was polymerized with 1a,b and 4a under the conditions described for the polymerization of ODPA (Table 3). In this case, however, the poly(amic acid) intermediates displayed considerably lower inherent viscosities. This is probably due to the reactivity of OEPA, which should be considerably less than other dianhydrides due to the strong electron-donating alkoxy substituents on its phthalic anhydride moieties. (A study has been initiated to determine reaction conditions which will afford higher molecular weight materials). The poly(amic acids) were chemically imidized to give the corresponding polyimides. Similarly to all previous polymers prepared from the para-linked diamines, polymers 12a,b were semicrystalline and insoluble. Their Tg's were considerably lower than those of analogous ODPA polymers.



$\text{OEPA} + \underline{4a} \rightarrow \underline{13} \rightarrow \underline{14}$

TABLE 3

Polymers Based on OEPA

| Poly(amic Acid) | | Polyimide | | | |
|---|---|---|---|---|---|
| Sample No. | {η}[a] | Sample No. | {η}[a] | Tg(°C)[b] | Tm(°C) |
| 11a | 0.40 | 12a | c | 110 | -- |
| 11b | 0.31 | 12b | c | 88 | 204,216 |
| 11c | 0.33 | 12c | 0.20 | 108 | -- |

a. Inherent viscosity in NMP at 30°C with a concentration of 0.5 g/dl. Polymer was not isolated prior to determination.

b. Tg and Tm were determined by DSC analysis under $N_2$ with a heating rate of 20°C/min.

c. Polymer was insoluble in NMP.

## EXPERIMENTAL

General Procedure for the Preparation of Poly(amic Acids). A dry 50-ml, 3-necked, round-botton flask equipped with an $N_2$ inlet, a $CaCl_2$ drying tube and a magnetic stir bar was charged with the diamine (0.645 mmol) dissolved in NMP [15% solids (w/w)]. The dianhydride (0.645 mmol) was then added in a single portion, and the solution was stirred at room temperature under $N_2$ for 4 h.

General Procedure for the Preparation of Polyimides. After the poly(amic acid) solution was diluted with NMP to approximately 8% solids, a mixture of acetic anhydride (2.58 mmol) and pyridine (2.58 mmol) was added. The reaction mixtures was then stirred for 18 h under $N_2$ at room temperature. During this time, polyimides 3a,b precipitated from solution. Polyimides 6a,b were isolated by precipitation in 300 ml of rapidly stirred ethanol. The polymers were collected by filtration, washed several times with ethanol and hexane, and dried under reduced pressure at 110°C for 24 h.

4,4'-Oxyethyleneoxyethyleneoxybis(N-methyl phthalimide). To a 1 L 3-necked flask equipped with a Dean Stark trap, a condenser, an $N_2$ inlet, an overhead stirrer and a thermometer, were added 6.51 g (0.283 mol) of freshly cut Na metal and 75 ml of dry p-xylene. The mixture was heated at reflux for 0.5 h under $N_2$ and then cooled to room temperature. The p-xylene was decanted off and 250 ml of toluene was added. After the mixture was heated at reflux for 5 min and cooled to room temperature, 15.0 g (0.142 mol) of diethylene glycol was added. The resulting mixture was heated at reflux for 3 h. Upon cooling to room temperature, a greyish-white precipitate formed. DMSO (250 ml) was added and the toluene was removed by azeotropic distillation. After 58.3 g (0.283 mol) of 4-nitro-N-methyl phthalimide was added to the cooled reaction vessel, the mixture was heated at 60°C for 12 h. The mixture was allowed to cool and then poured into 1.2 N HCl. The precipitate that formed was collected by filtration, washed two times with water, and then extracted with methylene chloride. After a portion of the solvent had been removed under reduced pressure, an orange solid precipitated which was collected by filtration and dried to afford 34 g (56%) of product: m.p. 216-218°C; IR(KBr) 1705 $cm^{-1}$ (C=O) and 1250 $cm^{-1}$ (C-O-C).

4,4'-Oxyethyleneoxyethyleneoxydiphthalic Anhydride. A 500 ml, 3-neck flask equipped with a condenser and a magnetic stirring bar was charged with 25.0 g (0.059 mol) of 10 and a solution of 14.2 g (0.354 mol) of NaOH in 250 ml water. After the mixture was stirred and heated at reflux for 18 h, it was acidified with 28.2 ml of conc. HCl. The precipitate that formed was collected by filtration and stirred in 800 ml of refluxing $H_2O$ for 3 h. The solution was filtered, and the hot filtrate was acidified with 4 ml of conc. HCl. The solid was collected and dried under reduced pressure to afford 13.7 g (52%) of the white tetraacid: m.p. 177-180°C. A solution of 5.0 g (0.012 mol) of the tetraacid in 10 ml of acetic anhydride was heated at reflux for 4 h. The solution was allowed to cool to room temperature, and the creme precipitate that formed was collected by filtration. The product was recrystallized twice from acetone containing decolarizing carbon to afford 3.2 g (65%) of white crystals: m.p. 124-126°C; IR(KBr) 1846, 1775 (C=O) and 1294 $cm^{-1}$ (Aryl-O-$CH_2$).

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