THE SYNTHESIS OF A NOVEL POLYIMIDE PRECURSOR

by Peter Delvigs, Li-Chen Hsu, and Tito T. Serafini

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
ABSTRACT

A novel blocked polyimide precursor was synthesized by using diethylamine as the blocking reagent. The structure of the blocked precursor is the bis(N,N-diethylamide) of the polyamic acid derived from pyromellitic dianhydride and 4,4'-diaminodiphenyl ether. The blocked precursor was more resistant to thermal imidization than the corresponding polyamic acid. The weight-average molecular weight of the blocked precursor could be increased by solid-state polymerization. However, the molecular weight of the polyamic acid could not be changed from its initial value. Furthermore, the blocked precursor was still completely soluble after solid-state polymerization. The solvolytic stability of the blocked precursor in anhydrous N,N-dimethylacetamide was superior to that of the polyamic acid.
A novel blocked polyimide precursor (BPP) was synthesized by using diethylamine as the blocking reagent. Reaction of pyromellitic dianhydride (PMDA) with diethylamine gave a diamide-diacid, which was converted to the corresponding diamide-diacid chloride with sulfonyl chloride. Reaction of equivalent amounts of the diamide-diacid chloride and 4,4'-diaminodiphenyl ether (POP) in N,N-dimethylacetamide solution gave the soluble blocked precursor (BPP). Several properties of BPP were compared with those of the corresponding unblocked polyamic acid (PAA), prepared from PMDA and POP. The blocked precursor (BPP) was found to be more resistant to thermal imidization than PAA.

The weight-average molecular weight $\overline{M}_w$ of BPP was increased from 15 200 to 47 500 by the technique of solid-state polymerization, and BPP was still completely soluble after solid-state polymerization. In contrast, the $\overline{M}_w$ of PAA could not be increased from its initial value. Instead, PAA underwent thermal cyclization to the intractable polyimide.

The solvolytic stability of BPP at $25^\circ$C was superior to that of PAA. A solution of PAA in anhydrous N,N-dimethylacetamide showed a gradual decrease in viscosity over 500 hours. A BPP solution showed no viscosity decrease under identical conditions.

**INTRODUCTION**

Many current aerospace programs have established the need for polymeric materials which retain their useful properties at elevated temperatures. One important application of polymers is their use as matrix materials in fiber-resin composites. In recent years a considerable number of polyaromatic, polyaromatic-heterocyclic, step-ladder and ladder polymers which exhibit thermal stabilities (as determined by thermogravimetric analysis) in excess of $500^\circ$ C have been synthesized. These include such polymers as polyimides, polyimidazopyrrolones, polybenzimidazoles, polybenzothiazoles,
and polyquinoxalines. The molecular structures which confer thermal stability are also responsible for the inherent intractability of currently available thermally stable polymers. Among the polymers exhibiting outstanding thermal stability, the polyimides are probably the most highly developed.

Aromatic polyimides are synthesized in two steps (ref. 1). First, an aryl dianhydride is reacted with an aryl diamine in a polar solvent such as N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), or N-methyl-2-pyrrolidone (NMP). This reaction yields a soluble polyamic acid which is often referred to as a prepolymer (fig. 1). In the second step, water is eliminated from the polyamic acid, by thermal or chemical means, to form the cyclic polyimide. This polymer in its final form is infusible and insoluble in organic solvents. Therefore, in the manufacture of fiber-reinforced composites, the polymer must be used as a prepreg resin while it is still in the soluble polyamic acid state. Significant difficulties arise during the conversion of the prepolymer to a cured polymer. The difficulties stem mainly from the following factors: (1) evolution of volatiles due to vaporization of solvent and elimination of reaction byproducts, usually water, (2) susceptibility of the polyamic acid to hydrolytic degradation, and (3) the appreciable time required for staging and advancing the polyamic acid to its final stable polyimide state. The cyclization, or imidization, reaction occurs readily, and attempts to remove solvent prior to final staging usually result in conversion of the prepolymer into its intractable state. The evolution of the copious quantities of volatiles ultimately results in composites with high void contents which exhibit inferior mechanical properties and oxidation resistance.

We are currently studying means to improve processing characteristics of aromatic polyimides by chemical modification of the prepolymer. To minimize some of the processing problems, our approach in this study was to chemically block the free carboxyl groups of the polyamic acid with a suitable blocking group. Such a blocked prepolymer
offers several advantages over the free polyamic acid. The temperature at which imidization of the blocked prepolymer begins is expected to be higher. Consequently, it should be possible to remove the bulk of the solvent before appreciable imidization occurs. The blocked prepolymer can be isolated as a solid, and its molecular weight increased by the technique of solid-state polymerization. The higher molecular weight of the prepolymer can be expected to improve the thermomechanical properties of the final polyimide.

This report describes the synthesis of a blocked polyimide precursor (BPP), poly[4, 4'-oxydiphenylene-2, 5-bis(N, N-diethylcarbamyl)terephthalamide]. Diethylamine was used as the blocking reagent. Solid-state polymerization and solvolytic stability of BPP under various conditions were studied and compared with the behavior of the corresponding unblocked POP-polyamic acid (PAA).

**EXPERIMENTAL PROCEDURE**

**Reagents**

N,N-dimethylacetamide (DMAc). - Technical grade DMAc was distilled in dry equipment under nitrogen and stored over molecular sieve 5A.

Pyromellitic dianhydride (PMDA, compound I in fig. 2). - Technical grade PMDA was sublimed at 220° to 240° C and 10⁻² torr.

Diethylamine(II) and thionyl chloride. - These reagents were used as received.

4, 4'-Diaminodiphenyl ether (POP (VI)). - Technical grade POP was sublimed through silica gel at 180° to 200° C and 10⁻² torr.

![Synthetic scheme for POP-PI polyimide via blocked polyamide.](image-url)
Compound Synthesis

Poly[4,4'-oxydiphenyleneopyromellitamic acid](PAA). - PAA was prepared according to the method of Sroog et al. (ref. 2). A solution of POP (2.00 g, 1.00×10⁻² mole) in dry DMAc (20 ml) was placed in a flask fitted with a nitrogen inlet, a mechanical stirrer, and a drying tube; PMDA (2.18 g, 1.00×10⁻² mole) was added to the flask through a powder funnel with vigorous stirring. Residual traces of PMDA were washed in with 12 milliliters of dry DMAc. The mixture was stirred at room temperature under a slow nitrogen stream for 3 hours. The product was then precipitated by pouring the solution into rapidly stirred acetone (500 ml). The liquid was decanted. The yellow product was washed with 100 milliliters of acetone, filtered, and dried at 80°C for 2 hours to give 4.10 grams (98 percent) of PAA.

2,5-Bis(N,N-diethylcarbamyl)terephthalic acid (DCTA (IV)). - Diethylamine (87.6 g, 6.00×10⁻¹ mole) was added in drops to PMDA powder (13.1 g, 6.00×10⁻² mole) with vigorous stirring over a period of 30 minutes. The mixture was stirred at room temperature for another 3 hours. During this time the suspension thickened considerably and changed color from light yellow to colorless. The resulting bis-diethylamine salt of DCTA(III) was filtered off and dried in vacuum. The dry salt (27.8 g, 5.45×10⁻² mole) was dissolved in 200 milliliters of water, the solution was filtered, and the filtrate was acidified with concentrated H₂SO₄. On cooling in ice, colorless crystals of DCTA settled out. They were filtered off, washed thoroughly with water, and dried in vacuum to give a crude yield of 15.4 grams (71 percent), with a melting point of 217°C to 222°C. Crystallization from methanol-acetone (1:1 by volume) gave 5.4 grams of pure DCTA, with a melting point of 222°C to 223°C. One more crystallization did not change the melting point.

Analysis calculated for C₁₈H₂₄N₂O₆: C, 59.33 percent; H, 6.64 percent; N, 7.69 percent. Found: C, 59.40 percent; H, 6.63 percent; N, 8.23 percent.

2,5-Bis(N,N-diethylcarbamyl)terephthaloyl chloride (DCTC (V)). - DCTA (3.64 g, 1.00×10⁻² mole) was added in one portion to vigorously stirred thionyl chloride (14.3 g, 1.20×10⁻¹ mole), and the solution was stirred under reflux for 16 hours. Excess thionyl chloride was removed by distillation under reduced pressure to give 3.41 grams (85 percent) of crude DCTC. The acid chloride is very sensitive to atmospheric moisture. All attempts to purify the compound by crystallization resulted in hydrolysis to the starting material (DCTA), as determined by infrared spectroscopy. Consequently, DCTC was used in the subsequent step without purification.

Poly[4,4'-oxydiphenylene-2,5-bis(N,N-diethylcarbamyl)terephthalamide](BPP (VII)). - A solution of POP (1.60 g, 8.00×10⁻³ mole) in dry DMAc (10 ml) was placed in a flask fitted with a nitrogen inlet, a magnetic stirrer, a drying tube, and an addition funnel. A solution of DCTC (3.20 g, 8.00×10⁻³ mole) in 20 milliliters of dry DMAc was
added by drops through the addition funnel over a period of 15 minutes. A surge of temperature to 50° C occurred, but the temperature gradually returned to 25° C. The reaction mixture was stirred for 4 hours under a stream of nitrogen. The product was precipitated by pouring the solution into rapidly stirred acetone (500 ml). The orange-red precipitate was filtered and washed with 100 milliliters of acetone. The solid was filtered again and dried at 80° C for 2 hours to give a yield of 3.35 grams (79 percent) of BPP.

Analysis calculated for (C₃₀H₃₂N₄O₅)ₙ: C, 68.16 percent; H, 6.10 percent; N, 10.60 percent. Found: C, 68.29 percent; H, 6.14 percent; N, 10.38 percent.

Poly[4,4'-oxydiphenylene pyromellitimide](POP-PI (VIII)). - The polyimide was prepared by heating either PAA or BPP to 300° C at a rate of 4° C per minute, and maintaining the temperature at 300° C for 1 hour (ref. 2).

Solid-State Polymerization

The polymer was ground into a fine powder (60 to 80 mesh). The samples (100 to 200 mg) were packed into short glass columns having an inside diameter of 7.5 millimeters. The packed column was installed in a gas chromatograph oven. After the flow of the helium carrier gas was adjusted to the desired rate, the oven was heated and maintained at the reaction temperature for a specified time. The product was allowed to cool under flow of helium. It was then stored in a gas-tight container to avoid moisture absorption.

Viscosity Measurements

The intrinsic viscosity [η] and inherent viscosity ηₕ measurements were carried out at 25° C with a Ubbelohde viscometer. The solvent was dry DMAc, 0.1 N in LiCl.

Weight-Average Molecular Weight Determination

The weight-average molecular weights \( M_w \) of PAA and BPP were calculated from the Mark-Houwink equation:

\[
[\eta] = 1.85 \times 10^{-4} M_w^{0.80}
\]

determined by Wallach (ref. 3) for PAA.
Solvolytic Stability Studies

The polymer samples were dissolved in DMAc. The solvolytic stabilities were measured by observing the change in $\eta_{inh}$ of the polymer solutions as a function of time at the specified concentrations.

RESULTS AND DISCUSSION

Synthesis of Polymers

The general preparative method for aromatic polyimides involves, in the first step, the reaction of an aryl dianhydride with an aryl diamine in a polar solvent such as DMAc. This reaction produces the soluble prepolymer, a polyamic acid. The prepolymer is then cyclized to the intractable polyimide by thermal or chemical means with elimination of water (refs. 4 and 5).

A few variations of this procedure have been described in the literature. Angelo and Kreuz react the polyamic acid solution with a ditertiary aliphatic diamine to form a salt by crosslinking the polyamic acid through the carboxyl groups. The crosslinked prepolymer is then converted to the polyimide by application of heat (ref. 6). The polyamic acid can also be reacted with an N, N'-disubstituted carbodiimide to form a polyimino lactone, which is then converted by heating to the polyimide (ref. 7).

Aromatic polyimides have also been prepared directly from the monomers without isolation of an intermediate polyamic acid precursor. In one such procedure, a solution of an aryl diamine in a tetraester of an aryl tetracarboxylic acid is heated to form the polyimide in one step (ref. 8). Bell has prepared a salt of an aryl diamine and a dialkyl pyromellitate. Upon heating, the salt is polymerized directly to the polyimide (ref. 9). All these variations are suitable for preparation of polyimide films, but are not convenient for the manufacture of fiber-reinforced polyimide composites.

The starting material in our synthesis of the blocked polyimide precursor (BPP) was PMDA(I); I was reacted in a suspension of excess diethylamine(II) to form the salt III. Acidification of III gave the free diamide-diacid DCTA(IV); IV could also be prepared directly by reacting equivalent amounts of I and II in benzene or toluene solution, but the yields were poor.

Two structural isomers of IV are possible as a result of the aminolysis of I. The anhydride ring can be opened to form a product where the carbamyl groups are para to each other (as shown in fig. 2). Alternately, the reaction can yield a product with the carbamyl groups meta to each other. The reaction could also produce a mixture of both isomers. In our study we isolated only one principal product. In a similar reaction, the esterification of PMDA with methanol, Bell and Jewell (ref. 10) obtained
Figure 3. - Infrared spectrum of BPP and POP-PI in Nujol.
the para diester-diacid as the principal product. By analogy, the para isomer seems to be the more likely one in the aminolysis reaction. In addition, comparison of molecular models shows the meta isomer to be sterically hindered. On the basis of these factors, we have tentatively assigned the para structure to compound IV, as shown in figure 2. The possibility of compound IV having the meta structure cannot be excluded, however. The final polymer in the synthetic sequence, compound VIII, would be the same in either case.

Reaction of DCTA with thionyl chloride gave the diamide-diacid chloride (DCTC(V)). This compound was very sensitive to hydrolytic degradation.

The blocked polyimide precursor (BPP(VII)) was synthesized by solution polymerization of equivalent amounts of DCTC and POP(VI) at room temperature. The solvent used was DMAc, and the total solid content was kept at about 10 percent. The best results were obtained when a solution of DCTC was slowly added to a rapidly stirred solution of POP. The reverse mode of addition led to gel formation.

The unblocked precursor, POP-polyamic acid (PAA), was prepared by polymerization of PMDA and POP in DMAc solution (ref. 2).

The POP-polyimide (POP-PI(VII)) was obtained by thermal cyclization of either BPP or PAA at 300° C. The formation of the polyimide from either precursor can be monitored qualitatively by infrared spectroscopy. The polyimide samples obtained from BPP and PAA had identical infrared spectra. The spectra of BPP and POP-PI are shown in figures 3(a) and (b), respectively. Upon imidization, the amide N-H stretch peak of BPP at 3230 centimeters⁻¹ (fig. 3(a)) disappears, and the two imide carbonyl stretch peaks of POP-PI at 1775 and 1720 centimeters⁻¹ (fig. 3(b)) appear.

It is interesting to note that the blocked precursor (BPP) is more resistive to thermal ring closure than the unblocked precursor (PAA). When PAA was heated in air at 200° C for 1 hour, it was completely converted to the polyimide. However, BPP was only partially converted under the same conditions.

Solid-State Polymerization of Unblocked Polyamic Acid (PAA)

An important consideration in the manufacture of fiber-reinforced composites is the ultimate molecular weight of the polyimide. We can expect the thermomechanical properties of the composite to improve as the molecular weight of the polyimide is increased. One way to achieve a molecular weight increase is chain extension by means of solid-state polymerization of the soluble polyimide precursor (PAA or BPP). After chain extension the precursor should remain soluble, and could then be advanced to the final polyimide state in the usual manner. The degree of polymerization is not expected to change during the final curing step.

Solid-state polymerization of PAA and BPP was performed according to the technique of Hsu (ref. 11), who studied solid-state polymerization of poly(ethylene terephthalate).
No attempts were made to achieve an ultrahigh-molecular-weight product in this study. Rather, we were interested in ascertaining whether solid-state polymerization would proceed at all, even with precursors having low molecular weight. Therefore, we used samples with weight-average molecular weight $\bar{M}_w$ in the range of 15,000 to 17,000.

The starting material in the solid-state polymerization of PAA had an intrinsic viscosity $[\eta]$ of 0.45 deciliter per gram, which corresponds to an $\bar{M}_w$ of 17,100. Table I shows the effect of reaction temperature on $[\eta]$ of the final product. There was no further polymerization at 90°C or below. At 100°C, there was only a very modest increase of $[\eta]$. Likewise, when the helium flow rate was increased from 200 to 300 and 400 milliliters per minute at 100°C, only a very slight increase in $[\eta]$ was obtained. At 110°C and higher temperatures, appreciable cyclization of PAA to the polyimide structure began to occur, as determined qualitatively by infrared spectroscopy. As a result of the partial imidization, the product became partially insoluble in DMAc. The degree of imidization and the consequent insolubility increased with increasing reaction temperature above 110°C.

These results show that temperatures of 100°C or lower are not sufficient to effect chain extension of PAA. At temperatures of 110°C or higher, cyclization of PAA to the polyimide begins and becomes predominant with increasing temperature. Therefore, the chain extension of PAA by solid-state polymerization is not feasible from a practical viewpoint.

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<th>TABLE I. - EFFECT OF REACTION TEMPERATURE ON SOLID-STATE POLYMERIZATION OF POP-POLYAMIC ACID (PAA)</th>
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<tr>
<td>[Reaction time, 24 hr; He flow rate, 200 ml/min, except where indicated; initial intrinsic viscosity, 0.45 dl/g.]</td>
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<td>Reaction temperature, °C</td>
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aHe flow rate, 300 ml/min.  
bHe flow rate, 400 ml/min.
Solid-State Polymerization of Blocked Polyimide Precursor (BPP)

In contrast to the unblocked precursor (PAA), the solid-state polymerization of the blocked precursor (BPP) was successful. The parameters studied were (1) reaction temperature and (2) reaction time.

Effect of reaction temperature. - Figure 4 shows the relation between the reaction temperature and $[\eta]$ of the final product at a constant reaction time of 24 hours. The starting material had an $[\eta]$ of 0.41 deciliter per gram, which corresponds to an $M_w$ of 15 200. There was no further polymerization at 100°C or below. The reaction started at 110°C, and $[\eta]$ of the product increased with increasing temperature up to 140°C. At this temperature, $[\eta]$ of the product was 1.02 deciliters per gram, corresponding to an $M_w$ of 47 500. This represents a threefold increase in the degree of polymerization over the starting material. It is interesting to note that at 130°C and 140°C partial imidization of the product had occurred, but the samples were still soluble in DMAc. However, at temperatures of 150°C or higher, the degree of imidization was sufficiently high to render the product partially insoluble in DMAc. Therefore, the useful temperature range is 110°C to 140°C for the period of time studied.

![Figure 4. Effect of reaction temperature on solid-state polymerization of blocked polyimide precursor (BPP). Reaction time, 24 hours; helium flow rate, 200 milliliters per minute; initial intrinsic viscosity, 0.41 deciliter per gram.](image)
Figure 5. - Effect of reaction time on solid-state polymerization of blocked polyimide precursor (BPP). Reaction temperature, 150°C; helium flow rate, 200 milliliters per minute; initial intrinsic viscosity, 0.41 deciliter per gram.

Effect of reaction time. - Figure 5 shows the relation between the reaction time and $[\eta]$ of the final product at a constant temperature of 150°C. The starting material again had an $[\eta]$ of 0.41 deciliter per gram, or an $M_W$ of 15 200. There was no reaction at times of 2 hours or less. The polymerization started at 4 hours and gave a progressive increase of $[\eta]$ up to 8 hours. At 8 hours, the $[\eta]$ of the product was 0.84 deciliter per gram, corresponding to an $M_W$ of 37 300. Partial imidization was found to occur at 6 and 8 hours, but the products were still soluble in DMAc. At a reaction time of 10 hours, imidization was severe enough to preclude full solubility of the product.

Another solid-state polymerization study was carried out at a constant temperature of 175°C. At a reaction time of 1 hour, no increase of $[\eta]$ was observed. At 2 hours, the product became insoluble due to considerable imidization.

The solid-state polymerization studies of BPP show that the reaction is favored by an increase of reaction temperature and time. At the same time, increased temperature and time promote cyclization of BPP to the POP-polyimide structure. It is possible, however, to choose a range of reaction variables where chain extension occurs in preference to cyclization.

Solvolytic Stability Studies

One of the problems in the manufacture of polyimide-fiber composites is the sensitivity of the polyamic acid prepolymer solutions to solvolytic degradation. It has been
shown that the presence of water in DMAc solutions of PAA causes a gradual decrease in viscosity (refs. 2 and 12). The viscosity decrease indicates a hydrolytic degradation of the polymer chain. The proposed mechanism (ref. 13) of hydrolysis involves intramolecular cyclization of the o-carboxy group onto the amide linkage, with subsequent elimination of the amine. Even when PAA was prepared in anhydrous DMAc, the solutions showed a gradual viscosity decrease when kept at room temperature (refs. 2 and 12). The degradation was particularly severe for dilute solutions (approx. 0.5 percent). This phenomenon raises the practical question of shelf life. It has been found that polyamic acid solutions can be stored for longer periods only at relatively high concentration (10 percent) and low temperature (–15°C). In addition, moisture must be strictly excluded (ref. 1).

Reynolds and Seddon (ref. 14) studied the hydrolytic stability of solutions of PAA in aqueous triethylamine. They found the solutions to be stable over a period of 500 hours, as long as more than 100 percent of triethylamine required to neutralize the carboxyl groups was present. Such aqueous solutions can be dehydrated to prepare POP-polyimide films and coatings, but they are not well suited for the preparation of void-
free fiber-reinforced composites.

We studied the solvolytic stability of BPP solutions both in presence and absence of water, and compared the results with the behavior of the corresponding PAA solutions. The results are summarized in figure 6. The polymer solutions were stored at room temperature for the duration of the experiment, and inherent viscosity \( \eta_{\text{inh}} \) was measured at \( 25^\circ \)C. Comparison of PAA and BPP solutions in anhydrous DMAc showed a striking contrast in solvolytic stability. Curve 1 shows a gradual decrease of \( \eta_{\text{inh}} \) of the unblocked precursor (PAA) solution from an initial value of 0.494 to 0.464 deciliter per gram after 510 hours. In contrast, the blocked precursor (BPP) solution proved to be completely stable to solvolysis over the same time period (curve 3).

There was no great contrast in the behavior of PAA and BPP solutions in DMAc containing 1 percent by volume water. The PAA solution showed a gradual decline of \( \eta_{\text{inh}} \) from 0.434 to 0.406 deciliter per gram (curve 2). The corresponding BPP solution (curve 4) showed approximately the same rate of \( \eta_{\text{inh}} \) decrease. However, there was no \( \eta_{\text{inh}} \) decrease during the first 2 hours of the experiment.

CONCLUDING REMARKS

A blocked POP-polyimide precursor (BPP) was synthesized, by using diethylamine as the blocking reagent. The weight-average molecular weight of BPP was increased by the technique of solid-state polymerization. This reaction was studied at various temperatures and times. Under the most favorable reaction conditions of this study, \( 140^\circ \)C and 24 hours, the weight-average molecular weight \( M_w \) of BPP was increased threefold, from 15 200 to 47 500. In contrast, the \( M_w \) of the corresponding unblocked precursor, POP-polyamic acid (PAA), could not be increased appreciably from an initial value of 17 000. Instead, PAA underwent thermal dehydration to the intractable polyimide structure. The blocked precursor BPP was more resistant to thermal imidization than PAA. While BPP was only partially cyclized after heating in air at \( 200^\circ \)C for 1 hour, PAA underwent complete cyclization to the poliyimide (POP-PI) under the same conditions. At \( 300^\circ \)C, BPP underwent complete imidization to form POP-PI. The solvolytic stability of BPP was superior to that of PAA. A solution of BPP in anhydrous DMAc showed no decrease in inherent viscosity for 500 hours, while the inherent viscosity of a PAA solution decreased from 0.494 to 0.464 deciliter per gram under identical conditions.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, February 18, 1969,
129-03-09-02-22.
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