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Polyimide Thin Films Produced by Direct Solid-State Polymerization of an Amino Anhydride Monomer

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Polyimides make up an important class of high-performance polymers by virtue of their thermal stability, excellent electrical and mechanical properties, and their retention of such properties over a wide temperature range. Conventional condensation polyimides are made exclusively from a dianhydride and a diamine (AA + BB) by a one-step solution polymerization or by a two-step process involving solution polymerization and solid-state curing.[1] At present, almost all of the polyimide thin films used in microelectronics and optoelectronics applications are processed from solutions of precursor poly(amic acid)s, which often cause problems with the final material.

Attempts were made at the solution polymerization of an AB-type amino diester monomer, although it yielded only low molecular weight materials.[2] We have previously reported the successful synthesis and one-step solution polymerization of an AB-type amino anhydride monomer, 3-amino-5,6,9,10-tetrahydro[5]-helicene-7,8-dicarboxylic anhydride (**1**, Figure 1).[3] Herein we report the first case of a one-step solid-state polymerization of monomer **1** to produce a polyimide thin film. It is an attractive example of a solvent-free one-step route to polyimide thin film materials.

Thin films of monomer **1** can be formed by spin-coating from THF solution onto either silicon wafer or Pyrex glass. Thermal treatment[4] of the deposited film under argon atmosphere induces the monomer to first form oligoimides at 350 °C. Final thermal treatment at 450 °C above the glass transition temperature of the oligoimides[5] is necessary to effect complete transformation to high molecular weight polyimide **2**. There is no indication that this process is a melt process since the appearance of oligoimides of **2** can be verified with no visible signs of melting. A melting point can be observed by DSC[3] only for powdered samples of monomer **1** and not a spin-cast film of the same.

The stepwise transformation from monomer **1** to polyimide **2** can be confirmed using FT-IR spectroscopy, by monitoring the disappearance of the anhydride's carbonyl stretching at 1827 and 1761 cm^{-1} and the appearance of the imide's carbonyl peaks at 1764 and 1713 cm^{-1} (Figure 1). The spectra of powdered samples and deposited thin films of monomer **1** are identical (Figure 1a,b), indicating that the film is made of the monomer rather than the oligomer, and no polycondensation takes place during the spin-coating stage. After treatment at 350 °C the presence of both anhydride and imide functionality can be clearly seen (Figure 1c). Furthermore, GPC analysis indicated that there was only low molecular weight polymer formed ($n = 1-5$). Heating to 450 °C resulted in the complete disappearance of the anhydride peaks, and its IR spectrum (Figure 1d) is superimposable to that of high molecular weight polyimide **2** made by solution polymerization.[3] The films of monomer **1** and oligoimide of **2** were completely soluble in many solvents (e.g., chloroform) and can easily be scratched off of the substrate (silicon wafer). However, the final film of polyimide **2** was remarkably scratch resistant and was completely resistant to common organic solvents, such as boiling 1,1′,2,2′-tetrachloroethane, over a period of days. Upon examination of the surface topology, the spin-cast film of **1** (Figure 2a) is coherent and shows no signs of powdering but does show several topographical features. The film of polyimide **2** (Figure 2b) is free of defects, is of nearly uniform thickness, and does not show any signs of stress fractures. Heating of the polyimide to such elevated temperatures for prolonged periods may seem extreme. However, a film of polyimide **2**, produced by one-step solution polymerization, is thermally stable up to 490 °C under inert atmosphere (by TGA) and retains its mechanical properties (Young's modulus of 2.91 GPa at 25 °C) after treatment at elevated temperatures.[3] Furthermore, aging experiments of specifically synthesized oligoimides of **2**[6] have shown them to be stable for prolonged periods of time (up to 18 h at 350 °C by TGA).

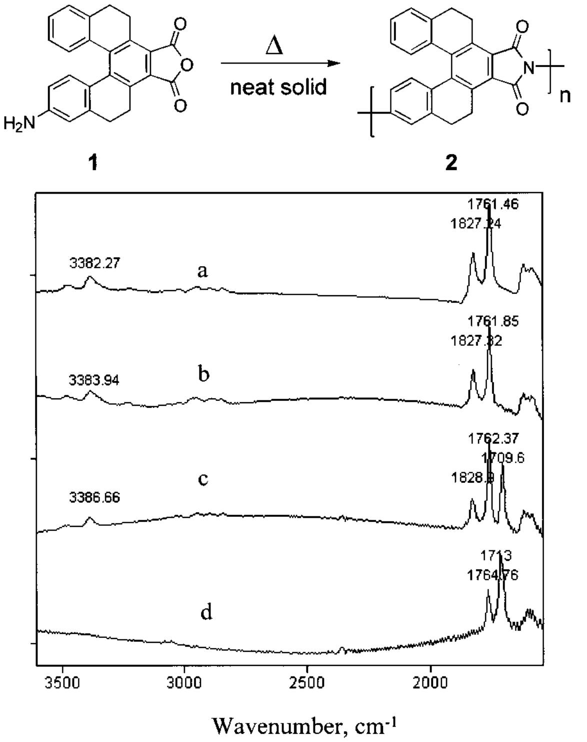

Figure 1. Solid-state synthesis of polyimide **2** from AB-type monomer **1**. IR spectra of (a) powdered monomer **1** in KBr, (b) spin-cast film of monomer **1** on surface-polished silicon wafer, (c) oligoimide **2** after heating at 350 °C, and (d) polyimide **2** after heating at 450 °C.

The presented method for the formation of a polyimide thin film has several advantages over traditional solution processes and other solid-state processes producing polyimides. Spin-coating proved to be an effective

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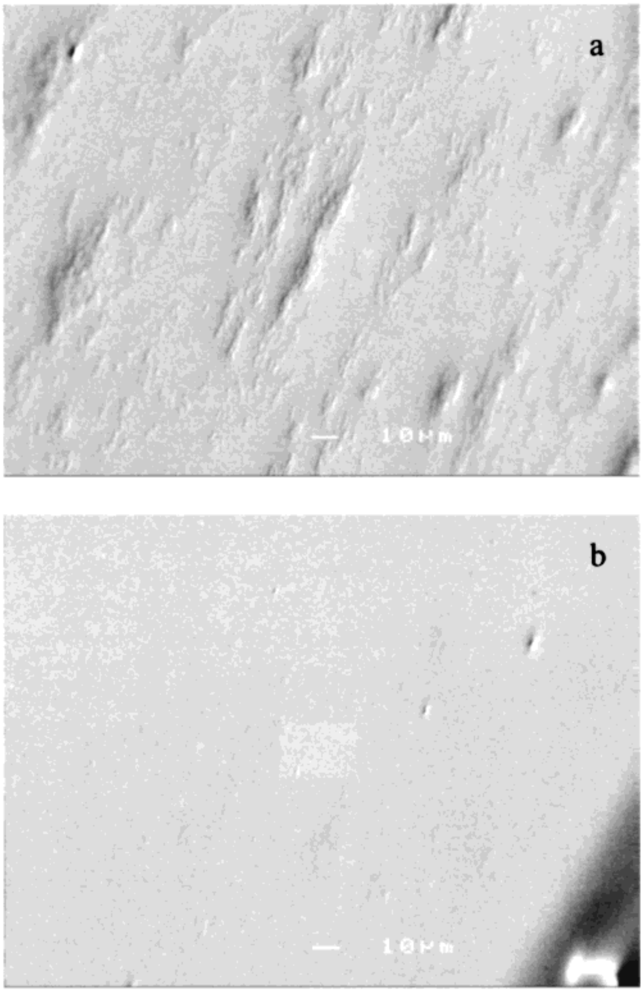

Figure 2. Electron micrographs of (a) monomer **1** as deposited on surface-polished silicon wafer and (b) polyimide **2** after thermal treatment to 450 °C. Both were taken at 60° inclination from the surface.

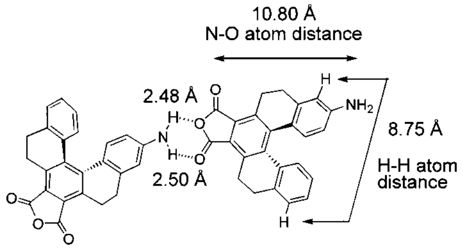

Figure 3. Arrangement of **1** within its single crystal with relevant distances marked.

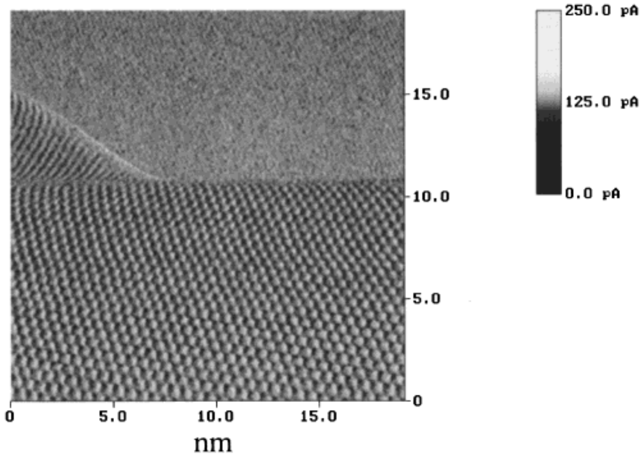

Figure 4. STM image of two intersecting monolayers of **1** (bottom and left) on the surface of graphite (top left).

way to deposit thin films of **1** onto the surface of the substrate and allowed for the control of the film thickness (typically 1−10 μm) simply based on the amount of monomer deposited on the substrate.[7] The use of volatile THF leaves the cast monomer films nearly free of solvent, thus making the polyimide film formation a nearly dry process.[8] Whereas a few examples of the formation of polyimide films using volatile solvents such as THF/methanol are known,[9] one-step solution polymerization is usually done in boiling *m*-cresol and poly(amic acid) solutions, used in two-step polyimide formation, containing typically 80 wt % of an amide solvent such as 1-methyl-2-pyrrolidinone. Imai et al were able to produce both aromatic and aromatic/aliphatic polyimides by thermal treatment of nylon salt-type monomers in the solid state.[10] Additionally, vapor deposition techniques at elevated temperatures have been used to form thin and ultrathin polyimide films.[11] However, the vapor deposition process requires the use of a specialized apparatus and is limited in general utility as only a few diamine and dianhydride monomers can be used such as pyromellitic dianhydride and 4,4′-oxydianiline.[12] In comparison with other cases of solid-state polymerization, the described monomer in this work is chemically unique in that it is an AB-type monomer. It therefore does not require careful stoichiometric balance, as does the system described by Imai et al. However, it is not the chemical uniqueness of monomer **1** that makes its solid-state polymerization possible.

The ability of monomer **1** to undergo a solid-state polymerization is twofold. First, it is a red solid with a clear melting point of 181 °C and is inert to self-polymerization in the solid state and in THF solution at ambient temperatures (e.g., 25 °C), thus making isolation and manipulation possible. Yet, we have previously shown that monomer **1** becomes reactive to polycondensation at elevated temperatures.[3] Second, this monomer has a tendency to form a film, due to the formation of a hydrogen-bonding entity between its amino and its anhydride functionalities.

X-ray diffraction analysis of a single crystal of **1** shows the amino and next anhydride functionalities forming a six-membered hydrogen-bonding entity (Figure 3), resulting in the formation of an extended array of self-assembled monomers across multiple unit cells within the single crystal.[13] The anhydride carbonyl involved in the hydrogen-bonding entity is the one that is para to the amino group across the biphenyl moiety. The distance between the oxygen and hydrogen atoms making up the hydrogen-bonding entity is approximately 2.50 Å.[14] Furthermore, using STM, an image of monomer **1** deposited on graphite from chloroform solution can be obtained (Figure 4), and it clearly shows the graphite surface (upper left) and two intersecting monolayers of monomer **1** (bottom and right). The thickness of the layer can be measured using STM, and its identification as such can be confirmed by verifying that the thickness of the layer falls between the expected range for monomer **1** (4−7 Å). Furthermore, the period of the monolayer (11.3 Å × 6.9 Å) corresponds well to the length and width of **1** (Figure 3). Such a regularity and breadth of molecular arrangement suggest that there is a method to its assembly.[15] On the basis of the arrangement of monomer **1** within a single crystal (also from chloroform), the method must be the formation of a hydrogen-bonding entity between the amino and anhydride functionalities. The use of hydrogen bonding in the design of a monomer with a self-complementary array of cooperative hydrogen bonds that leads to the formation of self-assembling linear polymers and reversible networks has been realized.[16]

As a result, given the close proximity of the amino and anhydride functionalities within a hydrogen-bonding entity, the polymerization at elevated temperatures occurring within the solid state must then be a result of the collapse of the hydrogen-bonding entity and the formation of an imide bond. Therefore, as is the case with its solution polymerization, monomer **1** also becomes activated to polymerization at elevated temperatures within the solid state. Furthermore, we have observed that coherent monomer films could not be spin-cast from solutions of monomer **1** in acetone or dichloromethane, indicating that the nature of the solvent plays a key role in the formation of the hydrogen-bonding entity and therefore the self-assembly of **1**. Additionally, since a clear melting point can be observed for dried powdered samples of monomer **1**,[17] the film formation must occur only on evaporation (or from spin-casting) of a relatively concentrated solution of monomer **1** in an appropriate solvent (100 mg mL^{-1} in THF).

The presented work provides a basis for the design and synthesis of other AB-type monomers that are able to undergo a solid-state polymerization to form a polyimide thin film with unique properties.

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Supporting Information Available: Atomic coordinates and unit cell parameters as determined by X-ray diffraction for compound **1**, rendering of four molecules of monomer **1** as positioned within the single crystal, and plot of aging experiment conducted on oligoimides of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Takekoshi, T. In *Polyimides—Fundamental and Applications*; Gosh, M. K., Mittal, K. I., Eds.; M. Dekker: New York; 1996; p 7.

(2) Feld, W. A.; Genez, B. J.; Friar, L. L.; Serico, L. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1978**, *19* (1), 552.

(3) Wang, Z. Y.; Qi, Y.; Bender, T. P.; Gao, J. P. *Macromolecules* **1997**, *30*, 764.

(4) Monomer films were heated to 350 °C over 1 h, held for 4−18 h and then heated to 450 °C, and held for 15 min and then cooled to room temperature.

(5) The glass transition temperature for the oligomer derived from **1** is 435 °C by DSC.

(6) Oligoimides of **2** are produced after treatment of monomer **1** at 350 °C in the solid state. Oligoimides of **2** were prepared by time-controlled polymerization and fractionated from chloroform/methanol. See Supporting Information. The polymerization conditions are described in ref 3, and they are characterized elsewhere: Bender, T. P.; Desjardins, P.; Qi, Y.; Wang, Z. Y. *Can. J. Chem.* **1999**, *77*, 1444.

(7) Monomer **1** (100 mg) was dissolved in 0.50 mL of THF. Typically, 1−10 drops of the monomer solution were deposited onto the surface of silicon wafers or Pyrex glass plates by spin-coating, which after curing resulted in the final polyimide film with thickness of 1−10 μm.

(8) Films contained less than 10% of THF by weight, as analyzed by TGA.

(9) (a) Echigo, Y.; Iwaya, Y.; Tomioka, I.; Furukawa, M.; Okamoto, S. *Macromolecules* **1995**, *28*, 3000. (b) Gaw, K.; Suzuki, H.; Jikei, M.; Kakimoto, M.; Imai, Y. *Polym. J.* **1997**, *29*, 290.

(10) (a) Itoya, K.; Kumagai, Y.; Kakimoto, M.; Imai, Y. *Macromolecules* **1994**, *27*, 4101. (b) Itoya, K.; Kumagai, Y.; Kakimoto, M.; Imai, Y. *Polymer* **1995**, *36*, 2827. (c) Inoue, T.; Kakimoto, M.; Imai, Y.; Watanabe, J. *Macromolecules* **1995**, *28*, 6368. (d) Inoue, T.; Kumagai, M.; Kakimoto, M.; Imai, Y.; Watanabe, J. *Macromolecules* **1997**, *30*, 1921. (e) Imai, Y.; Fueki, T.; Inoue, T.; Kakimoto, M. *J. Polym. Sci., Part A.: Polym. Chem.* **1998**, *36*, 1341.

(11) (a) Review: Kubono, A.; Okui, N. *Prog. Polym. Sci.* **1994**, *19*, 389. Specific examples: (b) Kubono, A.; Higuchi, H.; Umemoto, S.; Okui, N. *Thin Solid Films* **1993**, *232*, 256. (c) Yanagishita, H.; Nakane, T.; Nozoye, H.; Yoshitome, H. *J. Appl. Polym. Sci.* **1993**, *49*, 565. (d) Liberman, V.; Malba, V.; Bernhardt, A. F. *Thin Solid Films* **1997**, *305*, 26.

(12) Hutchings, C. W.; Grunze, M. *Rev. Sci. Instrum.* **1995**, *66*, 3943.

(13) For every molecule of **1** within the single crystal there is a molecule of chloroform present, but it occupies free space and is not near or involved in the hydrogen-bonding moiety. See the figure in Supporting Information.

(14) Hydrogen positions are calculated.

(15) The length and width of **1** shown in Figure 3 are the atom to atom distances and not the distances as would be projected onto the graphite surface.

(16) Beijer, F. H.; Brunsveld, L.; Folmer, B. J. B.; Hirschberg, J. H. K. K.; Langer, R. F. M.; Lowe, J. K. L.; Meijer, E. W. *Science* **1997**, *278*, 1601.

(17) For example, as would be made by precipitation of a solution of monomer **1** from THF into hexanes and drying the resulting powder.

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