Macromolecules **2006,** *39,* 7561−7565

Vapor Deposition and Curing of Polybenzoxazole Precursors

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Received March 6, 2006; Revised Manuscript Received August 10, 2006

ABSTRACT: Here we report on the vapor deposition polymerization of polybenzoxazole precursors. 3,3′-Dihydroxybenzidine and pyromellitic dianhydride were codeposited onto flat substrates to form poly(amic acid) films. As-deposited films contained poly(amic acid) species as well as unreacted dianhydride and diamine reactants. Quality films were obtained when reactant fluxes were well balanced. Coatings were cured under inert gas conditions and resulted in the conversion to polyimides (150−250 °C) and, at higher temperatures (500−550 °C), to semiaromatic polybenzoxazoles. Physical and chemical changes occurring during the curing process were studied with FT-IR, TGA, and nanoindentation experiments. The fully cured material is brittle and hard, and for thin films (<1 μm), films do not delaminate from glass substrates. Nanoindentation studies of both solution-prepared and vapor-deposited PBO precursors revealed that the elastic modulus improved upon conversion to the imide and benzoxazole forms, and polyimide showed the highest hardness value compared with poly(amic acid) and PBO.

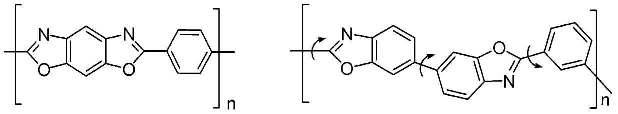
Introduction

Throughout the 1960s several new heterocyclic and aromatic polymers were developed to address the demands of the aerospace industry.[1] Rigid-rod macromolecules with high glass transition temperatures and high thermal stability were developed including polyimides,[2] polybenzimidazoles,[3] polybenzoxazoles[4] (PBOs), and polyquinoxalines.[5] PBOs in particular have been investigated over the past few decades because of their unusually high modulus and tensile strength in the fiber form, their excellent thermal stability, and their good hydrolytic and solvent resistance.[6−10] Fully aromatic PBO fibers (with commercial name Zylon) can be obtained by the condensation of 4,6-diamino-1,3-benzenediol dihydrochloride with terephthalic acid (TA) in the presence of poly(phosphoric acid) followed by dry-jet, wet-spinning process.[6] The resulting fibers exhibit an impressive tensile strength of 5.8 GPa and an elastic modulus of 270 GPa[8] and have a characteristic degradation temperature as high as 680 °C.[11]

Not surprisingly, there are enormous differences between the properties of fully aromatic PBO, i.e., poly(*p*-phenylenebenzobis(benzoxazole)) (**1**), and those of partially aromatic PBO, such as **2** (Scheme 1). PBO **1** is a rigid-rod macromolecule with a large perisistence length.[12,13] For PBO **1**, there are few opportunities for kinks in the polymer backbone, and free torsion rotation about C−C bonds has little effect on the overall polymer configuration. On the other hand, the bonding geometry of **2** permits several kinks in the backbone due to the various rotational isomeric states about C−C bonds. These rotations improve the solubility and processability of PBO **2** at the expense of mechanical properties.

Laboratory synthesis of semiaromatic PBOs, such as **2,** has been developed and involves the use of heterocyclic precursor polymers.[14,15] For example, the reaction between pyromellitic dianhydride and 3,3′-dihydroxybenzidine (Figure 1) results in polyhydroxyamide **3**, which can be thermally cyclodehydrated to form a polyimide. Upon further thermal treatment to ∼440 °C, biphenyllic hydroxyl groups react with the imide carbonyls to form new five-member, benzoxazole rings. At even higher temperature (∼550 °C) the material undergoes decarboxylation and releases carbon dioxide to form partially aromatic PBO **2**.[16] This synthesis strategy enables the precursor polyamide to be processed, and it does not require aggressive solvents such as methanesulfonic acid or poly(phosphoric acid).

Scheme 1. Structural Comparison of Fully Aromatic and Partially Aromatic PBO



1 **2**

Vapor deposition polymerization (VDP) is an alternative to melt-processing and solution-processing of polymer films. It is a one-step deposition−polymerization route to polymeric thin films that has several advantages over conventional film formation techniques. VDP is performed by the coevaporation of two or more reactive monomers onto a substrate under vacuum conditions. It is a solventless process whereby film thickness is easily modulated, conformal coatings can be achieved down to the nanometer length scale, and resulting coatings are free of defects associated with solvent evaporation. Over the past decade, full density, high performance polyimides,[17,18] polyquinoxalines,[19] and poly(oxadiazoles)[20] have been prepared using VDP techniques. Potential applications of these coatings include dielectric packaging, engineering of membranes for CO_2 sequestration or proton transport,[21,22] and electron transport layers in OLED devices.[20,23,24] VDP techniques have also been developed to study the deposition of polyimides for laser fusion targets.[25,26] Our laboratory is performing basic research to develop new technologies that will offer materials and processing options for future generations of laser targets. In this paper we explore the idea of using VDP as an approach to obtaining high performance PBO films.

Experimental Section

Materials. Pyromellitic dianhydride (PMDA) was purchased from Lancaster Chemicals (97% purity), and 3,3′-dihydroxyben-

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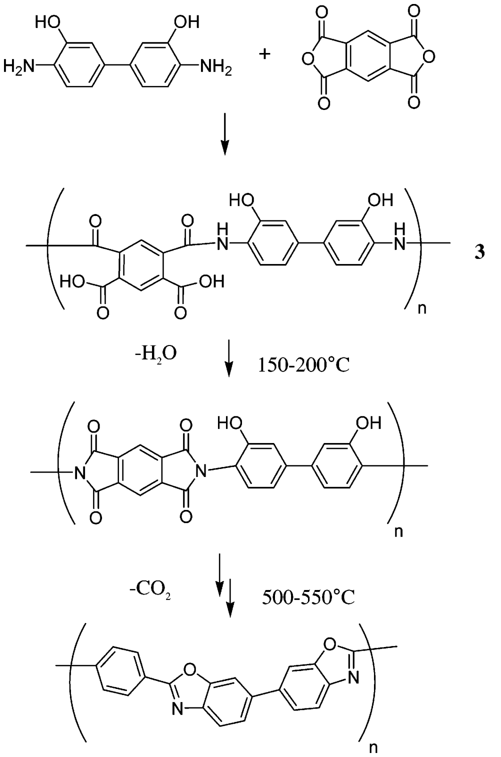

Figure 1. Synthesis of semiaromatic PBO involving thermal rearrangement of polyimide precursor.

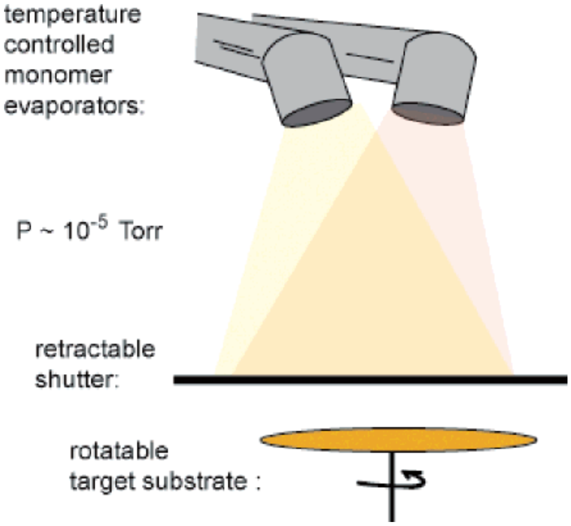

Figure 2. Drawing of deposition chamber.

zidine (DHB) was obtained from TCI America (99% purity). Prior to coating runs, PMDA and DHB were vacuum-dried overnight at 100 °C. For solution synthesis, PMDA was recrystallized twice before use according to ref 27, and DHB was used without purification. *N*,*N*-Dimethylacetamide (DMAc) was purchased from Alfa Aesar and was used as received. Potassium bromide disks (13 mm in diameter and 1 mm in thickness) were purchased from International Crystal Laboratories for FT-IR studies.

Vapor Deposition Polymerization of PBO Precursor 3. All attempts to vapor-coat PBO precursors were made using a custom-built vacuum deposition chamber. This chamber has been extensively used in studies of polyimide materials and is described in detail elsewhere.[26] A simplified drawing of the apparatus is shown in Figure 2. The chamber consists of two temperature-controlled monomer evaporators that are separated from the target substrate by 5.0 cm. A retractable shutter is used to shield the substrate from deposition until the monomer sources reach their steady-state evaporation rates. For each run, monomers were preheated to their deposition temperatures for 30 min prior to opening the shutter. The substrate was rotated at 20 rpm to improve film uniformity. The chamber pressure during deposition was observed to be between 2×10^{-6} and 5×10^{-6} mmHg. These conditions resulted in polymer deposition rates of about 3 μm/h. For this study films were vapor-coated to about 1 μm.

Table 1. Molar Loss Ratio at Different Operating Conditions

run	evaporator temp (°C) PMDA	evaporator temp (°C) DHB	molar loss ratio (PMDA:DHB)
1	153	163	8.2
2	153	203	4.0
3	158	213	1.5
4−9	153	213	1.14 ± 0.03[a]

[a] Reported error is indicative of reproducibility and was calculated as the standard deviation of six runs.

Solution Synthesis of PBO Precursor. Poly(amic acid) **3** was synthesized from the low-temperature reaction of PMDA with DHB in the presence of *N*,*N*-dimethylacetamide. DHB (2.5 g, 11.57 mmol) and DMAc (25 g, 26.60 mL) were placed in a 100 mL three-necked flask and stirred at 0 °C for 30 min under nitrogen purge. In a separate flask PMDA (2.52 g, 11.57 mmol) was dissolved in DMAc (25.2 g, 26.84 mL), and this solution was added to the stirring PMDA solution through an additional funnel. The reaction mixture was stirred vigorously at 0 °C for 1 h and then at room temperature for 24 h, yielding a 10 wt % solution of poly(amic acid) **3**. The resulting solution was spun-cast (3000 rpm) onto KBr optics and glass substrates for analysis.

Curing of PBO Precursors. As-deposited and solution-cast films were thermally cured to different temperatures (200 and 550 °C) using various heating rates (10, 1, and 0.1 °C/min) under argon gas. During the high-temperature cure, even small amounts of gaseous impurities (oxygen) were found to initiate thermal decomposition of films and were scrupulously avoided.

Characterization. The thickness of VDP films was measured using a film measurement device (Filmmetrics, model F20). FT-IR spectra were recorded using a Nicolet 20SXC infrared spectrometer. Vapor-coated films were examined using polarized optical microscopy. Thermal gravimetric analysis (Perkin-Elmer Pyris) was performed on as-deposited films at a heating rate of 10 °C/min. Mechanical properties (elastic modulus and hardness) were measured using nanoindentation techniques (MTS, Nanoindenter III). Loads were applied to the sample using a Berkovitch pyramidal diamond indenter until a specified displacement (~50 nm) was reached. The sample thickness was always at least a factor of 10 larger than the indenter displacement. Raw data gathered included load vs displacement curves. The hardness and elastic modulus were calculated and averaged from six different indents. For these calculations, the Poisson's ratio ν was taken to be 0.41 for poly(amic acid),[28] 0.33 for polyimide,[28] and 0.30 for poly(*p*-phenylenebenzobis(benzoxazole)).[29]

Results and Discussion

Several depositions were run to achieve a stiochiometric balance of monomer fluxes leaving the two evaporators, and results are summarized in Table 1. The molar-loss ratio (MLR) is defined as the ratio of moles (PMDA to DHB) leaving the evaporators during a 5 h coating run. Because molecular transport to the film depends on several factors, including reactor geometry, this ratio does not correspond directly to the molar composition of the as-deposited film.[30] Nevertheless, the molar-loss ratio is a useful quantity—it is simple to measure experimentally, and it serves as a good indicator of molar flux balance. To achieve a MLR near 1:1, temperatures were adjusted to 213 and 153 °C for DHB and PMDA, respectively. A slight excess amount of PMDA was intentionally used since excess diamine is known to cause undesirable side reactions and oxidation leading to general deterioration of film.[27,31] As expected, films

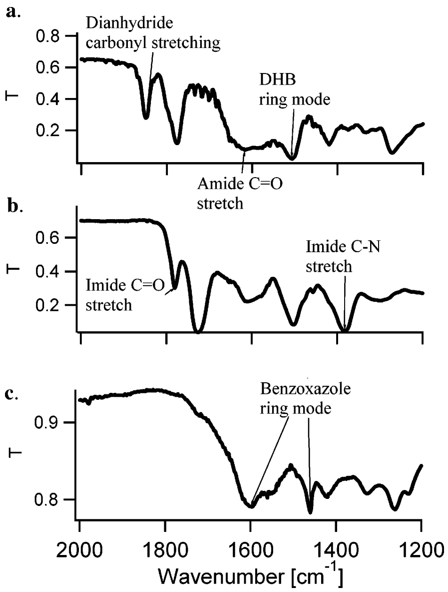

Figure 3. FT-IR spectra of (a) as-deposited film, (b) film cured at 200 °C for 5 h, and (c) film cured at 550 °C for 1 h. The spectrum in (c) was taken using reflective mode.

grown under these conditions were of higher quality—they were light-yellow in color, pinhole-free, and transparent and do not delaminate from glass substrates. However, films grown with large excess PMDA (MLR > 1.5) showed small white crystals on their surface (birefringence under polarized microscopy) and cannot withstand high temperature. Upon curing, these films have more pinholes and defects than those deposited near stoichiometric balance.

Selected FT-IR spectra obtained before and after thermal treatment are shown in Figure 3. It appears that the major component of as-deposited films is the PBO precursor, the *o*-hydroxypoly(amic acid), as evidenced, for example, by the intense and broad absorption band at 1650 cm^{-1} due to the amide C═O stretch. However, FT-IR data also indicate that unreacted monomers are also present. The sharp absorption at 1853 cm^{-1} is assigned to the symmetric carbonyl stretching mode of the dianhydride monomer, and the peak at 1503 cm^{-1} is partly attributed to the aromatic ring mode of free DHB. The presence of unreacted monomer was not surprising; in our prior study[25] of polyimide precursors we also identified unreacted monomers in as-coated films. Figure 3b shows an FT-IR spectrum of a PBO precursor film following heat treatment to 200 °C. The anhydride monomer absorptions were no longer present, and two new imide absorptions were present: at 1780 cm^{-1}, due to the symmetric C═O imide stretch, and at 1380 cm^{-1}, due to the imide C−N stretch. The last spectrum, shown in Figure 3c, was taken of a film heated to 550 °C and held there for 1 h. Medium-intensity absorption bands present at 1600 and 1460 cm^{-1} confirm the formation of benzoxazole rings.[16,32] The complete disappearance of imide peaks following the high-temperature cure suggests the thermal conversion from polyimide to PBO is complete.

A TGA scan of an as-deposited film (monomer loss ratio: 1.2) acquired under a N_2 atmosphere is shown in Figure 4. The sample continuously loses mass over the entire heating range, even as high as 600 °C. The continuous mass loss is believed to be associated with the evaporation of unreacted monomers. In addition to this continuous mass loss, discrete weight reductions were also observed and are associated with chemical transformations. A mass loss of about 14% was observed between 180 and 220 °C. This is larger than the theoretical mass loss (8%) occurring upon the loss of H_2O during cyclization. Additional mass loss is primarily attributed to evaporation of unreacted monomer but may also be due to partial film deterioration, i.e., emission of molecular fragments associated with branching and chain rupture events.[33,34] Samples also showed significant mass loss at temperature greater than 400 °C. This mass loss is attributed to decarboxylation from the PBO conversion, chain rupture, and end-group modifications.[33,34] The fully cured PBO had a residue at 650 °C that was about 50% of its original mass. This temperature is slightly lower than the characteristic half-decomposition temperature of commercial PBO fibers (670 °C) in nitrogen.[11] However, the thermal stability of the vapor-deposited PBO studied here far exceeds many common thermoplastics; for example, polystyrene decomposes at around 380 °C[35] and polyimide, also considered a high-performance material, begins to decomposes at 500 °C.[36]

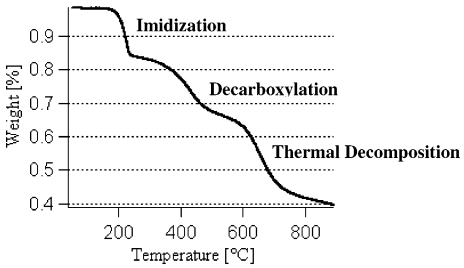

Figure 4. TGA thermogram of as-deposited poly(amic acid) film. The film was heated to 150 °C for 6 h before TGA investigation.

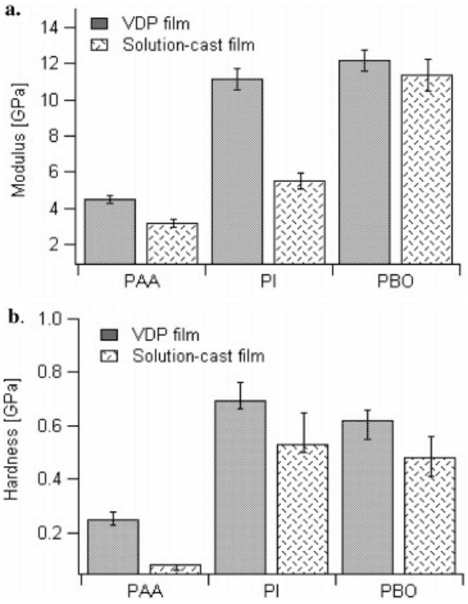

Figure 5. Modulus (a) and hardness (b) of vapor-deposited and solution-cast films at different stages of curing corresponding to poly(amic acid) (PAA), polyimide (PI), and polybenzoxazoles (PBO).

Nanoindentation results on as-deposited, solution-cast, and thermally cured films are compared in Figure 5. Compared to solution-cast films, as-deposited and cured VDP films always exhibit higher or comparable Young's modulus and hardness values. This result is a little unexpected since VDP films are believed to be of lower molecular weight[37] than solution-cast films. VDP involves a solid-state polymerization that, in the absence of solvent, is kinetically hindered due to low monomer and oligomer mobility.[25] However, vapor-deposited films show unique properties since VDP can be regarded as a layer-by-layer process. Prior X-ray studies on similar vapor-deposited polyimides have suggested that chain axes are preferentially oriented parallel to the surface.[38] In this study, differences in

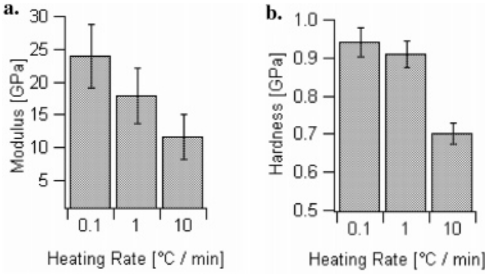

Figure 6. Effect of curing rate on the mechanical properties of cured polyimide: (a) modulus and (b) hardness.

Young's modulus between VDP and solution-cast films may be attributed to an overall higher degree of chain ordering and packing in the VDP form. It is difficult to assess, quantitatively, how chain anisotropy affects the Young's modulus parallel ($E_{\|}$) and perpendicular ($E_{\perp}$) to the surface. While nanoindentation is suitable for thin films, the measured modulus is a weighted average of $E_{\|}$ and $E_{\perp}$.

All heat-treated polymers show higher Young's modulus than as-deposited or as-cast polymers. The modulus of as-deposited films increased significantly upon converting to the polyimide and then increased slightly upon achieving PBO. The modulus improvement is attributed to the loss of chain flexibility as hydroxyamide chains are converted to more rigid, fully cyclized structures. PI and PBO films also exhibit higher values of measured hardness than their PAA precursors—regardless of whether they were solution-cast or vapor-deposited.

Mechanical properties also depend on curing rate (Figure 6). Since vapor-processed PBO films usually cracked after curing at high temperatures for long times (>1 h), we choose to focus on the properties vapor-processed polyimide to understand the influence of curing rate on mechanical properties. VDP samples imidized at a slower heating rate of 0.1 °C/min (longer annealing time) exhibit higher modulus values than those imidized at 1 and 10 °C/min. Films imidized at the slower rate even exhibited higher modulus than corresponding PBOs cured at 10 °C/ min. Slow curing may lead to chemical cross-linking and different mechanical properties as suggested by other authors.[26] Our results agree well with the study by Chang et al. on the curing reactions of solution-cast polyamide PBO precursors.[39] They found that mechanical properties strongly depend on the curing routine. In their study, the values of the tensile strength and modulus of the precursor films were enhanced remarkably by increasing the annealing temperature and time.

As mentioned in the Introduction, mechanical properties of fully and partially aromatic PBO should differ due to differences in bonding geometries. Indeed, the measured modulus of partially aromatic vapor-processed PBOs (12.5 GPa) is about 20 times lower than that of fully aromatic Zylon fibers (270 GPa). But the reported mechanical properties are still much better than most commodity polymers, and they exhibit outstanding thermal stability. For Zylon fibers, the alignment of molecules along the PBO fiber axis is extraordinarily high, and polymer chains become even more aligned when cured under a high stress field.[10,40] Clearly, chain alignment and ordering plays a crucial role in determining the mechanical properties of PBO. Mechanical processing of PBO such as heat treatment under uniaxial or biaxial stresses may be a strategy to improve mechanical properties of vapor-deposited PBO films.

Conclusions

In summary, we have demonstrated that VDP techniques can be applied to fabricate micron-thick PBO films. Curing of as-deposited poly(amic acid) under argon purge leads to the formation of polyimides at about 200 °C and subsequently to partially aromatic polybenzoxazoles at about 550 °C. FT-IR studies confirmed the existence of unreacted monomer and the formation of polyimide and PBO upon curing. TGA studies revealed mass losses due to imidization and decarboxylation as well as a continuous mass loss of unreacted monomer. Nanoindentation studies showed that the deposited film's Young's modulus and hardness can be improved by a factor of 3 after the conversion from poly(amic acid) to PBO and that the curing rate is an important process parameter. Most importantly, this study demonstrates, for the first time, that high-performance PBOs can be synthesized using a solventless, VDP approach. Further studies will target several other PBO precursors and will aim at understanding how stress treatment can affect molecular organization and mechanical properties.

Acknowledgment. The authors are grateful to Mark Bonino for assistance in setting up the vapor deposition apparatus. Xichong Chen acknowledges support from a Horton Fellowship administered through LLE. We also acknowledge start-up funding provided by the University of Rochester's Department of Chemical Engineering.

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MA0604993