Vapor-Deposition and Curing of Polybenzoxazole Precursors

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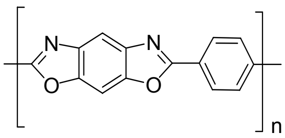
Polybenzoxazoles (PBOs) have been investigated over the past few decades because of their desirable properties: unusually high modulus and tensile strength (270 GPa and 5.8 GPa for fully aromatic PBO fibers), excellent thermal stability, and good hydrolytic and solvent resistance [1-3]. There are large differences between the properties of fully-aromatic PBO, i.e. poly (*p*-phenylenebenzo-*bis*-benzoxazole) (**1**), and those of partially-aromatic PBOs, such as **2**.



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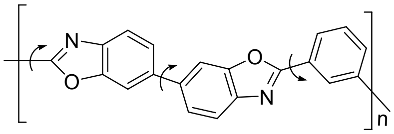

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Heterocyclic precursor polymers have been used to synthesize partially-aromatic PBOs (Figure 1) [4,5]. For example, the reaction between pyromellitic dianhydride and 3, 3'-dihydroxybenzidine results in polyhydroxyamide **3** which can be thermally cyclodehydrated to form a polyimide. Biphenyllic hydroxyl groups react with the imide carbonyls to form new five-member benzoxazole rings around 440°C. At higher temperatures (~550 °C) the material undergoes decarboxylation and releases carbon dioxide to form partially aromatic PBO **2**. This synthesis strategy enables the precursor polyamide to be processed, and it does not require aggressive solvents such as poly (phosphoric acid). In this study we explore the idea of using vapor deposition polymerization (VDP) as an approach to obtaining high performance PBO films.

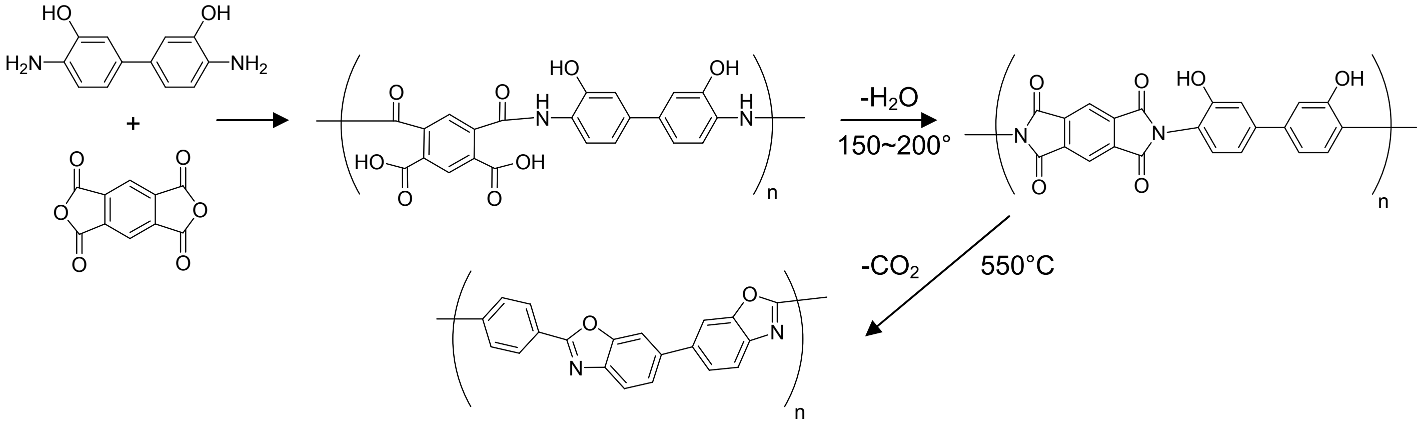

Figure 1. Synthesis of partially aromatic PBO through a polyimide intermediate

All attempts to vapor-coat PBO precursors were made using a custom-built vacuum deposition chamber. The chamber consists of two temperature-controlled monomer evaporators that are separated from the target substrate by 5.0 cm. The chamber pressure during deposition was observed to be around 3×10^{-7} Torr. These conditions resulted in deposition rates of 3 microns / hr. For this study films were vapor-coated to about 1 micron. Poly (amic acid) **3** was also synthesized through the low-temperature reaction of PMDA with DHB in the presence of N, N-dimethylacetamide according to reference [5]. 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.

Several depositions were run to achieve a stiochiometric balance of monomer fluxes leaving the two evaporators, and results are summarized in Table 1. The ratio of moles leaving the PMDA evaporator to the moles leaving the DHB evaporator is referred to as the molar loss ratio (MLR). In order to achieve a MLR near unity, temperatures were adjusted to 213 °C and 153 °C for PMDA and DHB, respectively. Vacuum-thermogravimetric experiments were performed to determine the relationship between temperature and vapor pressure of each monomer. These data are useful for determining the "optimal" evaporation temperatures for new monomers under consideration.

Table 1. Molar loss ratio at different operating conditions

	evaporator temp. (°C)		molar loss ratio
run	PMDA	DHB	(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.

Selected FT-IR spectra obtained before and after thermal treatment of VDP films are shown in Figure 2. It appears that the major component of the as-deposited film is *o*-hydroxy poly (amic acid). Unreacted monomers are also present in as-deposited films. The FT-IR spectrum of a PBO-precursor film following heat-treatment to 200 °C is shown in Figure 2b. 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 (Figure 2c) was taken of a film heated to 550 °C and held there for one hour. Medium intensity absorption bands present at 1600 cm^{-1} and 1460 cm^{-1} confirm the formation of benzoxazole rings [5, 6]. The complete disappearance of imide peaks following the high-temperature cure suggests the thermal conversion from polyimide to PBO is nearly complete.

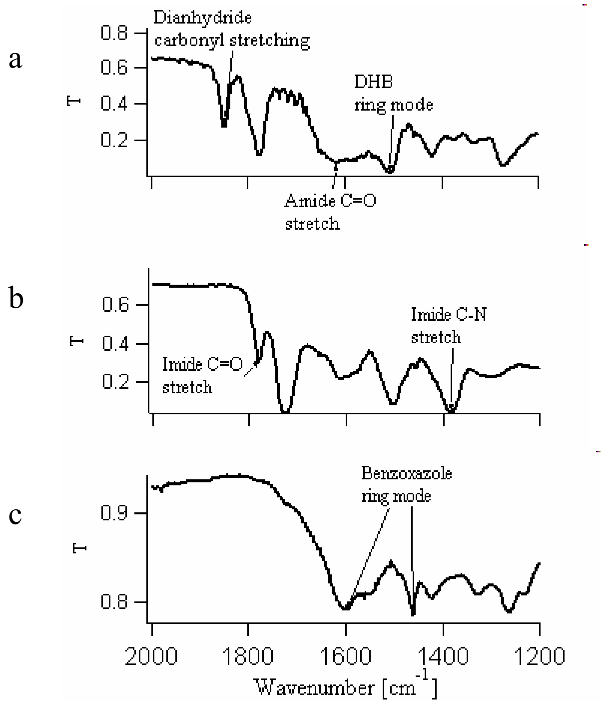

Figure 2. FT-IR Spectra of (a) as-deposited film (b) film cured at 200°C, and (c) film cured at 550°C. The spectrum in (c) was taken using reflective mode.

Nanoindentation results on as-deposited, solution-cast, and thermally cured films are compared in Figure 3. Compared to solution-cast films, Young's modulus measurements of cured VDP films were significantly (> 2x) lower, and measured hardness values of cured VDP films were moderately lower. These differences are likely due to differences in molecular weight. In addition, all heat-treated polymers have higher modulus and hardness than the as-deposited or as-cast polymers. Mechanical properties also depend on curing rate (Figure 4). In our study, VDP samples imidized at a slower heating rate of 0.1°C/min exhibit higher modulus values than those imidized at 1 °C/min and 10 °C/min. A slow curing rate may lead to chemical crosslinking and therefore different mechanical properties.

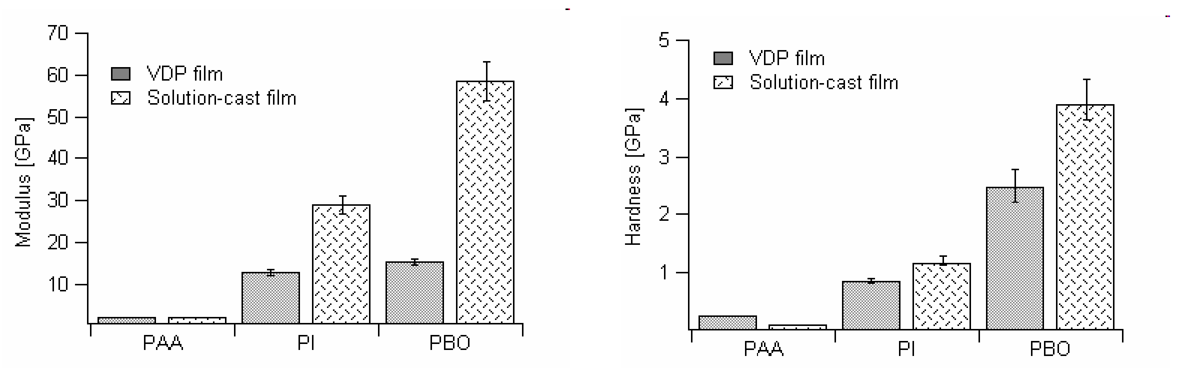

Figure 3. Modulus and hardness of vapor-deposited and solution-cast films at different stages of curing corresponding to poly(amic acid) (PAA), polyimide (PI), and polybenzoxazoles (PBO).

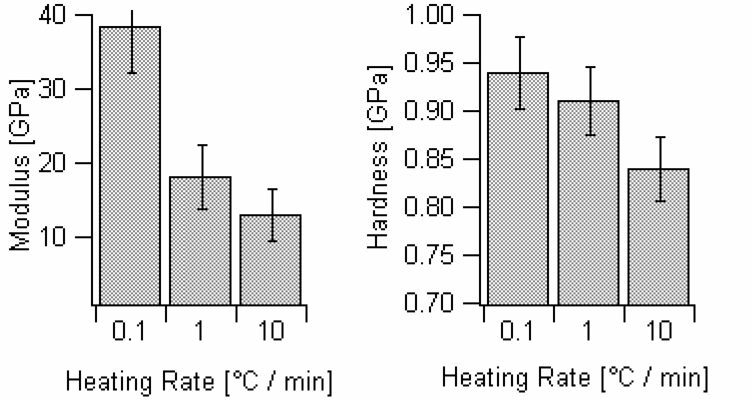

Figure 4. Effect of curing rate on the mechanical properties of cured polyimide

These experiments demonstrate, for the first time, that high performance PBO films can be prepared using VDP techniques. In our study, the measured modulus of resulting films modulus (15.4 GPa) is an order of magnitude lower in modulus than that of Zylon® fibers (270 GPa). However these mechanical properties are still much better than most commodity polymers.

References:

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