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Oxidative chemical vapor deposition of polyacenaphthylene, polyacenaphthene, and polyindane via benzoyl peroxide

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ABSTRACT

A method is presented to polymerize inexpensive and readily available electron-rich monomers via oxidative chemical vapor deposition. The process uses benzoyl peroxide, an organic oxidant, flash evaporated from a chloroform solution via direct liquid injection. The deposition temperatures ranged from 35 °C for indane to 125 °C for acenaphthylene and acenaphthene. These temperatures were determined by the volatility and melting point of the monomers, which were vaporized without the addition of a carrier gas. Benzoyl peroxide was not cracked into its respective free radical species but instead used as an oxidant at the substrate temperature. Polyacenaphthylene was deposited as a yellow film indicative of its highly conjugated polymer backbone, whereas polyacenaphthene and polyindane were both transparent dielectrics. Polyacenaphthylene and polyacenaphthene had higher average indices of refraction 1.6819 and 1.6640 (at 632.8 nm) than polyindane 1.5690, likely representing their higher density.

1. Introduction

Chemical vapor deposited (CVD) polymers have quite a few advantages over solution processed polymers such as their ability to be deposited as molecular layers [1], deposited without the use of solvents [2], superior optical quality when deposited as thin films, conformality [3], and their general suitability toward manufacturing processes. Although many polymers can be deposited via the use of plasmas (plasma-enhanced CVD) [4], their structure often suffers in these processes from a cross-linked structure giving rise to dangling bonds. These dangling bonds in turn may give rise to poor UV and oxidative stability compared to the analogous linear chain polymer [5]. Furthermore, thermal CVD methods have the advantage of preserving functionality in the polymer such that they can be used in, for example, “click” chemical reactions [6].

Thermal CVD polymers are generally deposited via a free radical addition polymerization. Of these polymers, parylene is the most common, where its monomer also acts as the initiator [7]. This initiator can be generated in situ via the high temperature, ~650 °C, “cracking” of [2.2]paracyclophane or functionalized derivatives thereof, or with leaving groups that generate the same *p*-xylylene intermediate [8]. Aside from the parylene polymers, thermal CVD polymers have been deposited via initiated-CVD (*i*-CVD) and hot-filament CVD (HF-CVD). *i*-CVD is where a free radical initiator is generated in situ over a filament array very near the substrate surface. This free radical initiator initiates polymerization very effectively with acrylate monomers or monomers that possess double bonds that are very electron poor (have adjacent electron withdrawing groups) [2]. Unfortunately, this method does not work with electron rich monomers. HF-CVD is equivalent to the parylene method of generating the free radical in situ, but it does this via a filament array rather than a remote pyrolysis tube in the case of parylene [9]. This method has been commercialized to deposit poly(tetrafluoroethylene).

Oxidative CVD has been undertaken with inorganic oxidants ($FeCl_3$ and Br_2) with the focus of polymerizing 3,4 ethylenedioxythiophene to produce its corresponding polymer, which is the preferential conducting polymer for organic electronics [2,10]. Unfortunately, both ferric chloride and molecular bromine are very aggressive toward vacuum systems, printed-circuit boards, and biomedical devices. In addition, the above methods for depositing polymers yield polymers with either poor UV and oxidative stability or their chemical process cost is high, for example, parylene AF-4 [11].

Ideally, a method would be developed to deposit thermal CVD polymers with inexpensive readily available chemistries (monomers or precursors), with a high manufacturing throughput, and upon polymerization yields polymers with a high UV and oxidative stability. If this process also retained functionality in the polymer chains, it would be a very powerful technique. The monomers in the current study, acenaphthylene (**A**), acenaphthene (**B**), and indane (**C**), have been polymerized via unique methods, including the following: electropolymerization[12], free radical polymerization [13,14], solid-state polymerization [15–17], chemical oxidative polymerization [18,19], emulsion polymerization [20], cationic polymerization [21], anionic polymerization [22,23], and oxidative polymerization via inorganic oxidants [24]. However, to date, these monomers have never

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been chemical vapor deposited. Acenaphthylene is of particular interest since it is photoluminescent (conducting when doped) and potentially a high-quality dielectric material respectively when polymerized. Polyacenaphthylene (undoped) is also yellow in color, which could be very useful for marketing purposes as a conformal coat. Of the aforementioned polymerization methods, chemical oxidative polymerization using benzoyl peroxide is the most adaptable to a vacuum environment where the technique has been called oxidative CVD (*o*-CVD) with the use of inorganic oxidants [2]. That terminology will be used in this paper here with the use of the organic oxidant benzoyl peroxide (**III**).

2. Experimental details

The CVD polymer thin films were deposited via a custom-built vacuum system with separate vaporizers for the monomers and the oxidant. The monomers, acenaphthylene (**A**) (T_m 92 °C), acenaphthene (**B**) (T_m 93 °C),and indane (C) (b.p. 176 °C), were purchased from Aldrich and used as-received. They were vaporized under vacuum (base pressure 0.5–0.7 Pa) at 100 °C, 105 °C, and, 40 °C, respectively. Acenaphthylene had much tar contained within it, but the clean chemical was easily vaporized with nearly all the tar left behind. The deposition time and temperature are shown in Table 1. The substrate was heated (or cooled) via a glycol loop with a substrate that had serpentine-like channels made of brazed copper. The deposition chamber was cold-walled but the front-end was heated via silicone heaters to at least the vaporization temperature of the monomers.

Benzoyl peroxide (**III**) (Aldrich) was dissolved in chloroform (Aldrich) and used as a 0.42-M solution. Chloroform was chosen as a stable non-reactive solvent toward benzoyl peroxide and Viton, used as both O-rings and tubing for direct liquid injection. Benzoyl peroxide is a solid and cannot be heated without an explosion in a closed system; therefore, it was dissolved in chloroform (direct liquid injection via a heated metering valve) then injected onto a hot manifold and flash evaporated. The vacuum system was pumped with a roughing pump/roots blower stack with an in-line foreline trap (organic vapor and particulate)

The thickness and the optical properties of the polymer thin films were measured via a J.A. Woollam variable angle spectroscopic ellipsometer (M-44 VASE) from 400 nm to 1000 nm, although the indices of refraction (in plane and out of plane) were reported at 632.8 nm. Polyacenaphthylene (**1A**) is photoluminescent (conductive when doped) and therefore strongly absorbing in the visible region. As a result, optical properties could only be measured away from their absorption edge. In all cases, a biaxial Cauchy model was used with Urbach absorption.

Substrates used for deposition, and all characterizations were floatzone (FZ) silicon <100 > double-side polished, n-doped with a resistivity of 2970–3210 Ω-cm (international wafer service). A Nexus 870 FT-IR (Thermo Scientific) was used for infrared spectroscopy measurements in transmission mode with a 4-cm^{-1} scan resolution, and 32 scans were undertaken both for background and samples scans after purging at least 10 min with dry nitrogen.

3. Can the monomers be free radical polymerized? Considerations of the organic initiators

The intention in this study is to use an organic oxidant, benzoyl peroxide (**III**), to oxidatively polymerize acenaphthylene (**A**), acenaphthene (**B**), and indane (**C**) under low pressure vacuum conditions and at low temperatures ≤125 °C; however, two questions arise.

1) Can these monomers undergo a free radical polymerization?
2) Does the oxidant itself, i.e., benzoyl peroxide, yield a polymer?

Certainly, acenaphthylene (**A**) has been polymerized in solution via AIBN [13] and ABCN [14] both carried out in THF; however, these initiators are much more aggressive than vacuum-derived free radicals mostly because their interaction time is greater in solution.

Two common free radical initiators were investigated *t*-butyl peroxide (**I**) and cumyl peroxide (**II**) using the method of *i*-CVD. Both of these free radical initiators will readily polymerize acrylate monomers via *i*-CVD such as glycidyl-methacrylate at a filament temperature of >175 °C and at a deposition temperature of ~35 °C [25]. This was confirmed experimentally although the data is not presented here. **I** can be metered through standard mass-flow controllers, whereas cumyl peroxide (**II**) is best delivered via bubbling argon through it using *t*-butyl cumyl peroxide (Trigonox T, AkzoNobel), which is a liquid and more convenient to use unlike dicumyl peroxide, which is a solid.

It is very important to match the proper surface concentration of the initiator with that of the monomer such that polymerizations will occur and high molecular weight (MW) polymer is achieved.

- If too much initiator is present at the substrate surface, then polymerization will occur but low MW polymer will result and the initiator will be found in high concentration in the thin film.
- If not enough initiator is present, then the deposition rate will be very slow and possibly not occur whatsoever.

The surface concentration is controlled by the flow of the chemical (initiator or monomer), the substrate temperature, and using the proper filament temperature in the case of *i*-CVD. These parameters need to be optimized for each chemical used. In the case of **I**, it has a high volatility (low MW) and therefore is not effective at polymerizing low volatility (high MW) monomers. As a result, **I** would be an effective initiator for indane (**C**) at 35 °C because they have matched volatility, whereas cumyl peroxide (**II**) is better matched with acenaphthylene (**A**) and acenaphthene (**B**) at a substrate temperature of 125 °C. When these experiments were undertaken in *i*-CVD mode at a filament temperature of 200 °C, no deposition occurred.

As a control sample, **II** was used to polymerize the low volatility *N*-phenylmaleimide (NMP) monomer (173 g/mol, Tm 86 °C) at a deposition temperature of 125 °C and at a filament temperature of 200 °C. NMP is an electron deficient monomer in contrast to **A**, **B**, and **C** and is therefore easy to polymerize via a free radical initiator. In summary, electron-rich monomers cannot be polymerized by the *i*-CVD method, i.e., using a free radical initiator; this is summarized in Fig. 1.

A set of control samples were also undertaken, where **I** and **II** were flowed over the filament array (*i*-CVD mode) heated to 200 °C and at a substrate temperature of 25 °C with no monomer was present. Again, no deposition was evident. The same sets of control experiments were undertaken with benzoyl peroxide (**III**) by itself delivered via direct liquid injection (DLI) in a chloroform solvent (0.42 M solution) both with heated filaments (~200 °C) and without heated filaments at a substrate temperature of 125 °C. In both cases, no deposition was evident. If **I**, **II**, or **III** yielded a deposited thin film without the presence of a monomer, then they would not be appropriate initiators. The caveat here is that the chemistry cannot always be well predicted a priori,

Table 1
Properties of the *o*-CVD polymers deposited in this study.

CVD polymer	Deposition temperature	Deposition time	Thickness	$n_{\text{in-plane}}$	$n_{\text{out-of-plane}}$	k
polyacenaphthylene	125 °C	15 min	118 nm	1.6758	1.6942	4.03E−03
polyacenaphthene	125 °C	20 min	469 nm	1.6663	1.6595	3.03E−03
polyindane	35 °C	10 min	74 nm	1.5799	1.5473	1.58E−03