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Full Paper

Thermomechanical Properties of Parylene X, A Room-Temperature Chemical Vapor Deposit- able Crosslinkable Polymer

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Poly(*p*-xylylene) has existed commercially for many years but has never gained widespread acceptance due to its poor thermal and optical properties. Parylene X, a new chemical vapor depositable polymer on the same process platform as poly(*p*-xylylene), is a copolymer of poly(ethynyl-*p*-xylylene) and poly(*p*-xylylene). It exhibits thermal stability to at least 420 °C, has a low coefficient of thermal expansion of 55 ppm after it is crosslinked, and exhibits low stress. It possesses a glass transition temperature of 73 °C and starts to crosslink at ~160 °C with a peak isotherm at 250 °C. The ethynyl functional groups crosslink to form the very stable phenyl moiety.

Keywords: Crosslinking, High thermal stability, Low stress, Parylene

1. Introduction

The first parylene-based polymer to be deposited was poly(*p*-xylylene) from *p*-xylene in 1948 by Szwarc.^[1] However, it was not until Gorham invented the deposition of poly(*p*-xylylene) (also called parylene N) from [2.2] paracyclophane that the method was commercially feasible due to the quantitative conversion from the precursor to the reactive xylylene intermediate at reasonable process temperatures.^[2] Cram won the Nobel prize in 1987 for his work with cyclophane chemistry; however, he never synthesized any cyclophanes with crosslinkable moieties. Hopf and co-workers have recently synthesized 4-ethynyl[2.2]paracyclophane and 4,12-diethynyl[2.2]paracyclophane from a 2-step synthesis via conversion from the formyl to acetylene moiety (Bestmann's synthesis^[3]).^[4,5] Chujo and co-workers also claimed to synthesize 4,12-diethynyl[2.2]paracyclophane via a Sonogashira cross-coupling reaction.^[6–9] Neither of these routes is scalable, even though Lahann and co-workers have used the Hopf route to polymerize 4-ethynyl[2.2]paracyclophane on a 50 mg scale.^[10] Poly(*p*-xylylene)-co-poly(ethynyl-*p*-xylylene), also called parylene X, was first presented at the Materials Research Society in

2005, having been synthesized from 4-ethynyl[2.2]paracyclophane.^[11]

By itself as a homopolymer, parylene N has nonexceptional properties. It has a thermal stability of <350 °C^[12,13] and an oxidative stability of <125 °C.^[14] Its Achilles heel is its aliphatic main-chain carbon bond that is susceptible to rupture with the presence of UV light, oxygen, or DC bias (applied voltage). Also, since the repeat unit is highly symmetrical, the polymer can crystallize with relative ease, especially above its α to β transition at 225 °C.^[15] Even at lower temperatures the polymer exhibits significant crystallinity that manifests itself as optical birefringence and scattering centers. The former is not desirable for dielectric applications. The latter prevents parylene N from being used as an optical material. Finally, parylene N possesses a low molar mass and therefore is not efficiently deposited in the CVD reactor. To deposit thick films (on the order of micrometers) at room temperature, deposition times are prohibitively long or much precursor needs to be used. In short, parylene N has a poor coating efficiency.

Despite the drawbacks parylene N is on a platform that is very desirable for the deposition of CVD films and especially polymers. Starting from the cyclophane precursor the polymerization is self-initiated, where the monomer is both the initiator and the monomer. The distribution between the monomer and the initiator is determined quantum mechanically between the triplet state (initiator) and the singlet state (monomer).^[16] Finally, the polymer is nonterminated, but can be terminated with relative ease with the presence of, for example, a forming gas. Due to the resonance stabilization of the intermediate (triplet versus singlet states), the intermediate can be transported to a remote site where deposition can occur at room tempera-

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ture. Room-temperature deposition allows the film to be deposited under a low stress state and on temperature-sensitive substrates. Room-temperature deposition is particularly important when the polymer is used as a barrier coating, where the coating process is the final manufacturing step, for example, when coating circuit boards.

Finally, the parylene process is unique because the lateral growth rate of the polymer can be controlled by the deposition pressure or temperature. Typically, the deposition pressure is controlled by an inert process gas for simplicity. Under low pressures, parylene is a highly conformal process. However, as the pressure is increased the interaction between the gas-phase intermediate and the substrate increases, allowing the polymer to exhibit a high lateral growth rate.^[17] This mode has been previously named 'caulking' mode since parylene can seal the surface of porous dielectrics.^[18]

It is the purpose of the current work to develop a cyclophane precursor that has the benefits of the parylene platform but overcomes the deficiencies of parylene N when it is deposited as a polymer. In particular, the goal of the current research is to improve the thermo-mechanical properties of parylene so that the new polymer can be used as an optical or dielectric material.

2. Thermal Stability and Crosslinking

Measuring the thermal stability of polymeric thin films is not necessarily trivial. A common method is to use a thermogravimetric analyzer (TGA) with a bulk sample. If a thick polymer film is deposited over a large area, it can then be peeled off, and analyzed by this technique. However, the primary drawback of this technique, besides being unable to analyze thin films (~ 2000 Å), is that a rate effect exists. Joesten analyzed the mass loss of parylene N by the TGA method, and found that parylene N is stable to 450 °C in a nitrogen environment.^[19] A more effective technique is to undertake isothermal anneals at increasingly higher temperatures using an optical technique with the thin film intact with its substrate. When this technique is undertaken with parylene N, it is apparent that it is thermal stable to 350 °C.^[20] The mass loss above 350 °C is also apparent in Figure 1 for a 250 Å film of parylene N. For all the films in Figure 1, there is an initial mass loss. This mass loss constitutes low molecular mass monomer and impurities that are present with the precursor. Of these two

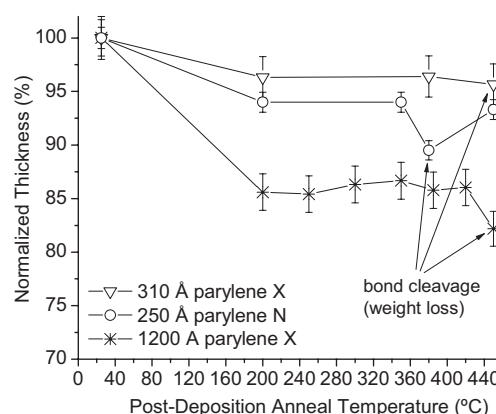


Fig. 1. Thermal stability of parylene N and parylene X measured by 30 min isothermal anneals in vacuum with an Ar purge of 200 mTorr.

factors, the volatile impurities are the dominant species, determined from repeating the experiment with a higher quality precursor with fewer impurities. The parylene N film has an apparent increase in thickness after the anneal at 450 °C; however, that can be attributed to the carbonization of the polymer backbone. The extinction coefficient for this film is 0.3 at 630 nm, which is three orders of magnitude higher than the undamaged film.

In contrast, parylene X, which is a copolymer of poly(*p*-xylylene) and poly(ethynyl-*p*-xylylene), exhibits much improved thermal stability over the poly(*p*-xylylene) homopolymer. From Fourier transform infrared spectroscopy (FTIR), the copolymer is roughly 80 % poly(ethynyl-*p*-xylylene) from the relative peak heights when the polymer is deposited at room temperature. Figure 2 shows the Gorham process starting with 4-ethynyl[2.2]paracyclophane to deposit parylene X. Note only the ethynyl intermediate is shown. The intermediate is resonance-stabilized between the benzoid (triplet state) and the quinoid (singlet state). Undertaking isothermal anneals with parylene X under an inert, gas-purged, vacuum environment results in a thin film with no thickness loss until 450 °C, where degradation was particularly evident for the thicker 1200 Å film. Films have been deposited at various thicknesses and with various purities of the precursor. In all cases, there is no mass loss to 420 °C.

Parylene N is a linear chain polymer. When the aliphatic main-chain bond is broken, a volatile fragment can be created with relative ease and hence there is a decrease in thickness. For a networked polymer, a broken bond does

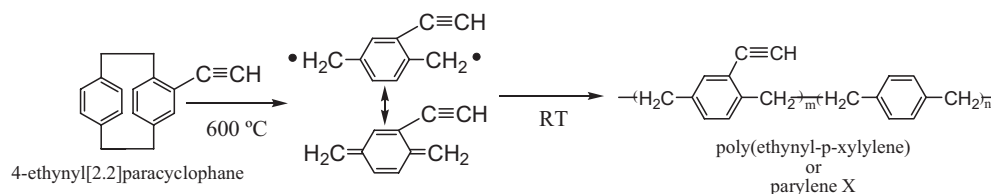


Fig. 2. Gorham process used to deposit parylene X from the 4-ethynyl[2.2]paracyclophane precursor.

not necessarily lead to a volatile fragment since each bond can have more than two connections. Figure 3 shows the FTIR data for parylene X as a function of thermal anneals for the same samples shown in Figure 1. From the FTIR

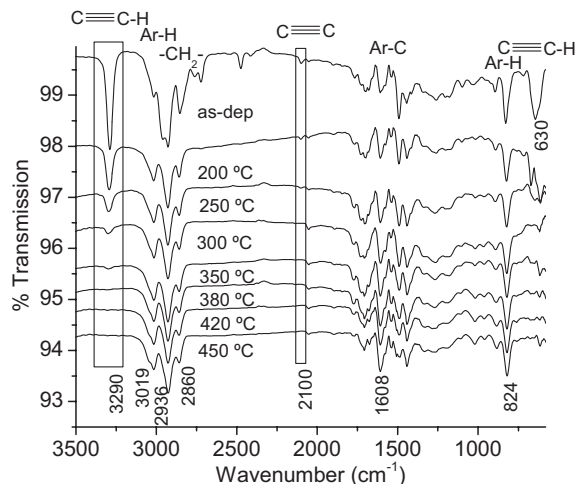


Fig. 3. FTIR spectra for parylene X annealed isothermally for 30 min each. Each sample is different.

data it can be seen that the C-H stretch associated with the alkyne moiety possesses a very strong peak at 3290 cm^{-1} . The C-C stretch at 2100 cm^{-1} , associated with the alkyne bond, is very weak because there is little change in the dipole moment of the bond; therefore, this is not a good bond to follow as crosslinking occurs. According to differential scanning calorimetry (DSC) (not shown) the precursor, 4-ethynyl[2.2]paracyclophane, starts to crosslink at about 160°C , with a peak exotherm at 250°C at a scan rate of $10^\circ\text{C min}^{-1}$. Parylene X was not analyzed by DSC since sample mass was an issue. However, The FTIR data in Figure 3 for parylene X reflects the DSC data for 4-ethynyl[2.2]paracyclophane pretty well. At 200°C there is a significant decrease in the C-H stretch at 3290 cm^{-1} , and at 300°C it is nearly gone. At 380°C , there is no peak associated with alkyne bonding in the polymer.

When the ethynyl moieties react with each other they can either dimerize to form a diene or trimerize to form a phenyl moiety. The formation of the moieties can be differentiated, with relative ease, based on DSC and FTIR. In FTIR, the phenyl moiety shows up at $\sim 1600\text{ cm}^{-1}$, whereas the diene shows up at $1900\text{--}2000\text{ cm}^{-1}$.^[21] In Figure 3 there is a clear, though small, increase at 1608 cm^{-1} associated with the phenyl moiety. Further, in the DSC spectrum for 4-ethynyl[2.2]paracyclophane, the exotherm is very strong, and more indicative of the formation of the phenyl moiety than the diene. The formation of the phenyl moiety liberates much heat due to the exceptional stability of the group. In conclusion, the crosslinking that is being undertaken with parylene X results in the stable phenyl moiety.

As part of undertaking thickness measurements with a variable angle spectroscopic ellipsometer (VASE), the in-

dex of refraction of the film can be measured with ease. Figure 4 shows the in-plane (*XY* plane) and out-of-plane (*Z* axis) indices of refraction for the 1200 Å parylene X film as a function of post-deposition anneal temperature.

The film exhibits a negative birefringence from the as-deposited condition through its degradation at 450°C . Even though there is no mass loss at 420°C , there is some evidence of bond cleavage from the increase in the optical constants in Figure 4, and from the relative peak heights in the FTIR spectra.

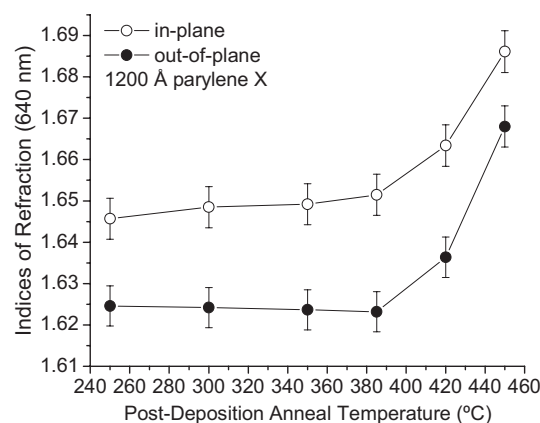


Fig. 4. In-plane (*XY* plane) and out-of-plane (*Z*-axis) indices of refraction at 640 nm derived from VASE measurements.

3. Coefficient of Thermal Expansion and Film Stress

One very effective method of determining the coefficient of thermal expansion (CTE) and glass transition temperature (T_g) of thin polymer films is with the use of a VASE with a hot stage. Beaucage et al. used a standard, non-spectroscopic ellipsometer with a hot stage to measure the CTE and T_g for polystyrene.^[22] Huang et al. used a VASE to measure the CTE and T_g for parylene C (chlorine on the phenyl group).^[23] It is not clear if either group measured the optical constants of the silicon substrate as a function of temperature, which is necessary to measure accurate thickness and optical constants of the thin film. Both studies were concerned with the thickness dependence on T_g among other properties.

For comparison sake, polystyrene has a volumetric CTE of $170\text{--}240\text{ ppm per }^\circ\text{C}$ below its T_g (glassy state) and $510\text{--}600\text{ ppm per }^\circ\text{C}$ above its T_g (rubbery state).^[24] In all cases, polymers have a significantly higher CTE above their T_g than below. The present work is no exception. After correcting for the optical constants of the silicon substrate, parylene X exhibits a CTE of $121\text{ ppm per }^\circ\text{C}$ below its T_g , and $217\text{ ppm per }^\circ\text{C}$ above its T_g . The break in the slope in Figure 5 occurs at 73°C , which represents the T_g of the thin film. Below 1000 Å , thickness effects can result in changes in the thermo-mechanical properties of the poly-

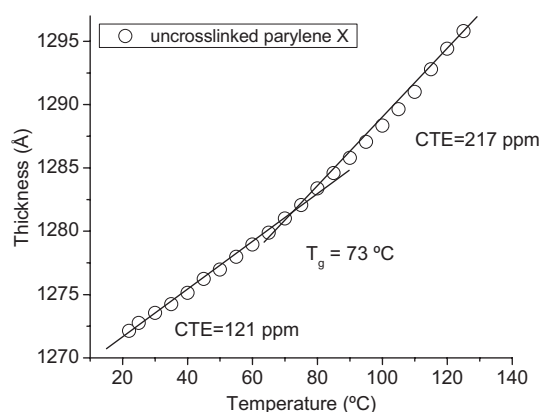


Fig. 5. Coefficient of thermal expansion for the *as-deposited* parylene X film. The break in the slope is indicative of the glass transition temperature of the polymer.

mer,^[23,25,26] as a result thicker films were analyzed in the current study. Also, the change in thickness with temperature is greater for thicker films, which allows more accurate measurements. After annealing the parylene X film at 380 °C for 30 min it became fully crosslinked. The CTE of the fully crosslinked thin film was 53 ppm per °C, as shown in Figure 6. In comparison, the Cyclotene variant of benzocyclobutene (BCB), which is used as a dielectric in many electronics applications, has a CTE of 52 ppm per °C.^[27] Cyclotene is also highly crosslinked, much like parylene X, but possesses weaker alkyl crosslinks rather than the phenyl moieties. The CTE of parylene N and parylene C have been previously published as 69 ppm per °C and 35 ppm per °C, respectively, with bulk samples.^[28] It is not clear how the measurement technique affects the final result, which is possibly the reason for the discrepancy of the reported values among the commercially available parylenes.

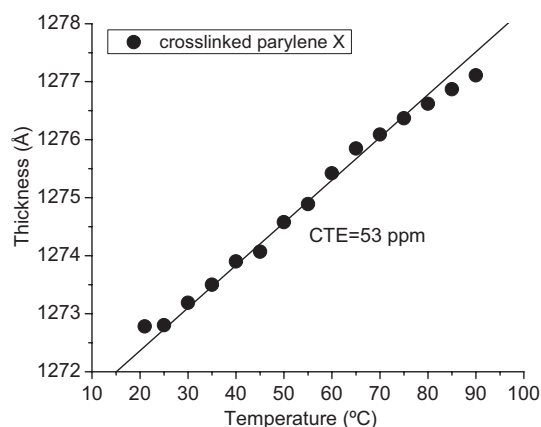


Fig. 6. Coefficient of thermal expansion for the *crosslinked* parylene X film. The film was annealed to 380 °C for 30 min.

The parylene polymers have a low stress state that is mostly attributed to their room temperature deposition. Parylene N, C, and AF-4 (aliphatic fluorinated parylene)

all show similar behavior in terms of their thin film stress as a function of temperature.^[29,30] The films start out with a compressive stress (10–20 MPa), and with heating there is little change in their stress state. However, during the cooling cycle the polymer possesses a tensile stress state, which increases to 20–60 MPa at room temperature. Figure 7 shows the thin film stress curve for parylene X as a function of temperature. The thin film was only heated to 170 °C (Fig. 7), but a similar result was found when the film was heated to 400 °C. The behavior seen in Figure 7 is very similar to previous results with the other parylene polymers and, in short, they all have very low tensile stress even after a post-deposition thermal anneal.

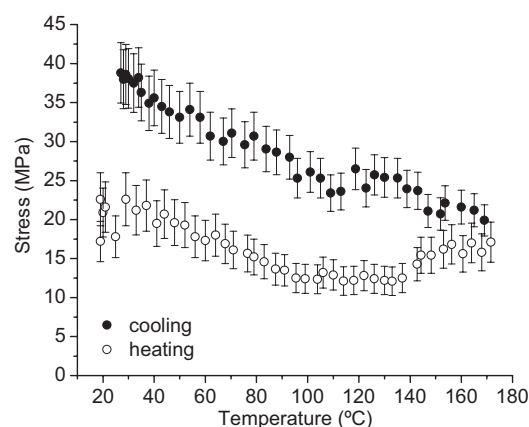


Fig. 7. Stress analysis of parylene X in the *as-deposited* condition. Much like the other parylene polymers, parylene X possesses low stress *as-deposited* and after post-deposition anneals.

4. Conclusions

A novel precursor, 4-ethynyl[2.2]paracyclophane, has been synthesized that results in a new polymer, parylene X, that is a copolymer of 20 % poly(*p*-xylylene) and 80 % poly(ethynyl-*p*-xylylene). Among hydrocarbon chemistries, the polymer has an exceptionally high thermal stability to >420 °C, which is also much higher than that of the poly(*p*-xylylene) homopolymer. The crosslinking commences at ~160 °C according to DSC results undertaken with the 4-ethynyl[2.2]paracyclophane precursor, and has a maximum exotherm at 250 °C. At 300 °C, there is very little ethynyl moiety left in the film according to FTIR results. In short, by crosslinking the parylene hydrocarbon chemistry, the thermo-mechanical properties of the polymer are greatly improved.

5. Experimental

All the films were deposited with a custom-built, 300 mm tool based on the parylene platform. The base pressure in the vacuum chamber was $<10^{-5}$ Torr, achieved with a turbomolecular pump backed with a roughing pump. The flow of the precursor was controlled with an all-metal regulating tip valve. The precursor was cracked at 650 °C, and deposition was undertaken

at room temperature under 1.5 mTorr with an unthrottled turbo pump. A 45 min deposition yielded a 248 Å film for parylene N. No carrier gas was used for these depositions. 4-ethynyl [2.2]paracyclophane was prepared according to the method of Chujo [6,9] and then sublimed at 110 °C. A 15 min deposition under 1.5 mTorr yielded a 312 Å copolymer parylene X film. It should be noted that the yield via the Chujo route is greatly affected by the presence of oxygen, and cross-coupling reactions go much better with the mono-brominated substrate, 4-bromo[2.2]paracyclophane. The thicker ~1200 Å film was deposited in 20 min without the use of the turbo-pump. Two samples were used for characterization of the ultrathin films, test grade <100> Si and double-sided polished float zone (FZ) <100> Si (>1000 Ω cm).

Chemical analysis was undertaken with a Nicolet Avatar 360 FTIR spectrometer at 8 cm⁻¹ resolution and 256 scans on FZ Si substrates. Thermal stability and optical characterization were undertaken with a M-2000 VASE (JA Woollam Co.) from 400–1000 nm at 72, 74, and 76° from the sample normal. A simple Cauchy fit was used to model the ellipsometric data amplitude (ψ) and phase (Δ) to generate thickness and optical constants for the ultrathin films.

The coefficient of thermal expansion measurements were undertaken with the same VASE with a custom-built hot stage. The hot stage was heated with polyimide tape embedded with heating elements. The optical constants of the Si substrate without the thin film were first measured in the temperature range 20–150 °C. Then the films were measured in 5 °C increments with the same substrate. Modeling was undertaken for each data point, which was a very laborious process. An anisotropic Cauchy model was used for each data point. The stress state of the films were measured by using a Flexus tool with 3" Si wafers. The radius of curvature of the wafers was first measured without a thin film and then after the thin film was deposited. The Flexus tool automatically converts the radius of curvature of the wafer to its stress state when the modulus of a film is entered along with its Poisson's ratio. The modulus was measured from nanoindentation measurements as 8.7 ± 0.5 GPa after an anneal at 250 °C, and 9.0 ± 0.5 GPa after an anneal at 380 °C. The corresponding hardness values for a 850 nm film were 0.88 ± 0.1 GPa after an anneal at 250 °C, and 0.96 ± 0.1 GPa after an anneal at 380 °C.

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