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Triptycene Polyimides: Soluble Polymers with High Thermal Stability and Low Refractive Indices

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Triptycene Polyimides: Soluble Polymers with High Thermal Stability and Low Refractive Indices

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Triptycene Polyimides: Soluble Polymers with High Thermal Stability and Low Refractive Indices

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Abstract

A series of soluble, thermally stable aromatic polyimides were synthesized using commercially available five and six membered ring anhydrides and 2, 6-diaminotriptycene derivatives. All of these triptycene polyimides (TPIs) were soluble in common organic solvents despite their completely aromatic structure, due to the three-dimensional triptycene structure that prevents strong interchain interactions. Low solution viscosities (0.07 to 0.47 dL/g) and versatile solubilities allow for easy solution processing of these polymers. Nanoporosity in the solid state gives rise to high surface areas (up to 430 m²/g) and low refractive indices (1.19- 1.79 at 633 nm), which suggest very low dielectric constants at optical frequencies. Polymer films were found to be amorphous. The decomposition temperature (T_d) for all of the polymers is above 500 °C and no glass transition temperatures can be found below 450 °C by differential scanning calorimetry (DSC), indicating excellent prospects for high temperature

1 applications. This combination of properties makes these polymers candidates for spin-on dielectric
2 materials.
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6 **Introduction**

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9 Aromatic polyimides have found widespread commercial application as a result of their thermal
10 stability, high glass-transition temperatures, chemical resistance, good mechanical properties and
11 dielectric properties. These materials are widely used in photoresists, alignment layers in liquid crystal
12 displays, and high temperature coatings.¹⁻³ However, many completely aromatic polyimides do not
13 display ideal properties, resulting from deficiencies in processability and solubility.⁴ To address these
14 problems, several previous approaches have been taken to increase the solubility, usually by adding
15 aliphatic segments^{5, 6} or bulky side groups.^{7, 8} However, these approaches either undermine the rigidity
16 of the backbone or disrupt the packing of the polymer chains, which generally lead to decreased
17 strength. In polyimide production it is common to prepare, characterize, and process the poly(amic acid),
18 which is thermally cured later.⁹ However, this also has disadvantages in that often thermally imidized
19 polymers are insoluble so an exact molecular weight can not be determined and incomplete imidization
20 may occur.
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37 To circumvent the limitations of current polyimides, we have designed polymers from this class that
38 include triptycene units in the backbone. Previous studies in our group have found that despite their
39 rigid, completely aromatic nature, triptycene units impart solubility to polymers.^{10- 12} This general
40 feature arises from the rigid 3-dimensional structure of triptycenes, which interrupts the close packing of
41 polymer chains and associated strong interpolymer interactions when placed in high frequency along the
42 polymer's backbone. It is also common for the triptycene containing polymers to exhibit good thermal
43 stability.¹³ Previous work from other groups has produced polyimide oligomers end-capped with
44 triptycene units, which were used for crosslinking. These polyimides exhibited thermal stability to
45 temperatures above 600 °C, but were insoluble in their thermally stable, crosslinked state.¹⁴ Linear
46 polyimides have also previously been synthesized containing triptycene in the repeat unit. Zhang et al
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1 synthesized triptycene polyimides with triptycene included in the dianhydride through the 1, 4 positions
2 and investigated the mechanical properties,¹⁵ however the optical properties of this material were not
3 reported. Other polyimides have been synthesized with 1, 4 or 1, 5-diaminotriptycene as a repeat unit,
4 however, the triptycene unit was only incorporated as a random copolymer¹⁶ or the optical properties
5 were not investigated.¹⁷ Triptycene incorporation has revealed dramatic enhancements in polymer
6 mechanical properties including increased stiffness, toughness, ductility, and ultimate tensile strength.¹⁸
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¹⁹ We also expect high triptycene content materials to have low dielectric constants based upon the internal free volume imparted by the triptycene.^{12, 20}

Polyimides have also been considered for use as dielectrics for integrated circuits²¹ due to their ease of processing, high thermal dimensional stability, and excellent electrical insulating properties.^{22, 23} Dielectric constants for non-fluorinated polyimides are in the range of 3.1 to 3.9.²¹ However, smaller integrated circuit feature sizes give rise to increased capacitive crosstalk between adjacent data lines and there is a need for new dielectric materials with dielectric constants of 2.0 or lower. Two major methods have been employed to further reduce dielectric constants (ϵ) in polyimides. One method is to incorporate fluorinated groups into the polyimide structure, which lowers the ϵ by localizing electron density in the C-F sigma bond and thereby reducing electronic polarizability.^{24, 25} Another method is to generate nanoporosity within the bulk polyimide, which has the effect of modulating the structure with the dielectric constant of air (≈ 1).²⁶ Perhaps the best known polymeric spin-on dielectric is SiLK, a highly crosslinked polyphenylene produced by Dow Chemicals. In the bulk, its dielectric constant is 2.65, with a refractive index of 1.63 at 633 nm,²⁷ and porous versions have been shown to exhibit dielectric constants as low as 2.0. Due to these impressive properties, IBM used SiLK as its dielectric material in its integrated circuits briefly in the early 2000s, however integration issues arose from the softness. Despite this, SiLK is still reported in hybrid devices.²⁶ Finding materials with requisite solubility, processability, thermal stability, and intrinsic dielectric constants below 2.0 continues to be a challenge, which if met, may allow for enhanced performance in small feature size electronics.²⁶

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In this report, we describe the synthesis and characterization of a class of soluble, aromatic polyimides based on commercially available dianhydrides and a 2,6-diaminotriptycene, which has never been incorporated in polyimides previously. We expected this unique connection, with the two of the three triptycene “paddles” parallel to the polymer backbone, to give rise to improved optical properties. Refractive indices were found to be extremely low for several of these triptycene polyimides (TPIs), suggesting suitably low dielectric constants (1.42- 3.20). BET (Brunauer-Emmett-Teller) surface area measurements reveal high surface areas (up to 430 m²/g), with greater surface areas roughly correlating with lower refractive indices. Polymer films were found to be amorphous by x-ray diffraction (XRD) and solution viscosities were also measured revealing lower viscosities than expected for polymers of reasonable molecular weights. We also show that they exhibit excellent thermal stability, with decomposition temperatures above 510 °C, no observable phase transitions below 450 °C, and high solubility in common organic solvents even once fully imidized. This combination of properties suggests that these polymers may be useful as solution processed spin-on dielectric layers.

33 **Results & Discussion**

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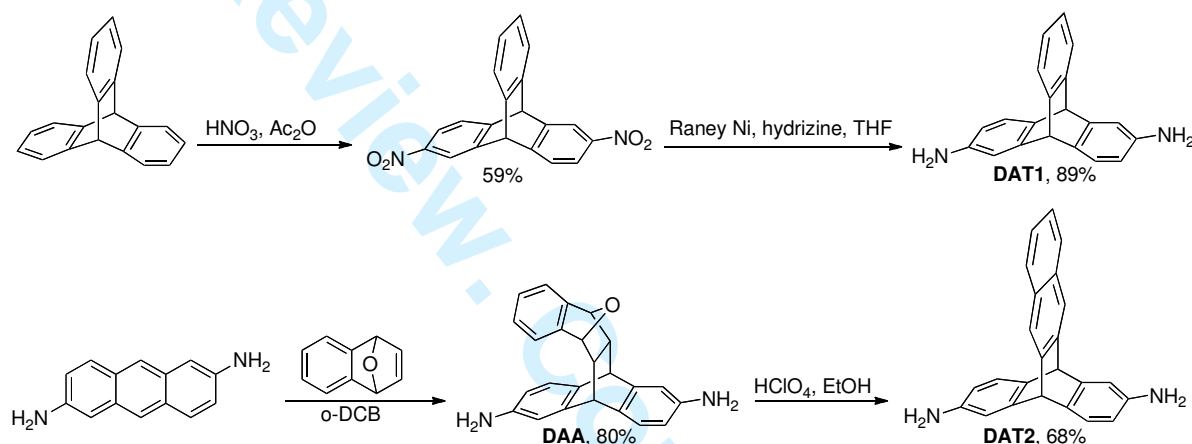
Synthesis. The synthesis of 2,6-diaminotriptycene has been previously reported²⁹ but was optimized to create higher yields of the dinitrotripcytence intermediates so as to minimize the amount of triaminotriptycene byproduct. Under-nitrated by-products can be subjected to further nitration, however over-nitrated products cannot be used for our purpose. A stoicheometric amount of nitric acid and increased reaction times allowed for the greatest yield of dinitrotriptycene (Scheme 1). The initial nitration produced a 1:1 mixture of regioisomers that could be separated to yield pure 2,6-dinitrotriptycene that was primarily used for diamine synthesis. Reduction of the purified 2,6-dinitrotriptycene with Raney-Ni and hydrazine in anhydrous THF yielded 2,6-diaminotriptycene (**DAT1**) nearly quantitatively.

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Synthesis of the extended iptycene structure **DAT2** is accomplished via a Diels-Alder reaction between 2, 6-diaminoanthracene and a benzofused 1,4-endoxide (Scheme 1), which has been proven to

be an efficient way for preparing various iptycene compounds.^{28,30} 2,6-diaminoanthracene is prepared as previously reported.²⁸ Reaction with 1,4-dihydro-1,4-epoxynaphthalene yields a single Diels-Alder adduct (**DAA**), which was dehydrated in the presence of perchloric acid, leading to **DAT2**. Both monomers were characterized by ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy as well as high-resolution mass spectrometry.

Scheme 1. Synthesis of **DAT1** and **DAT2**.

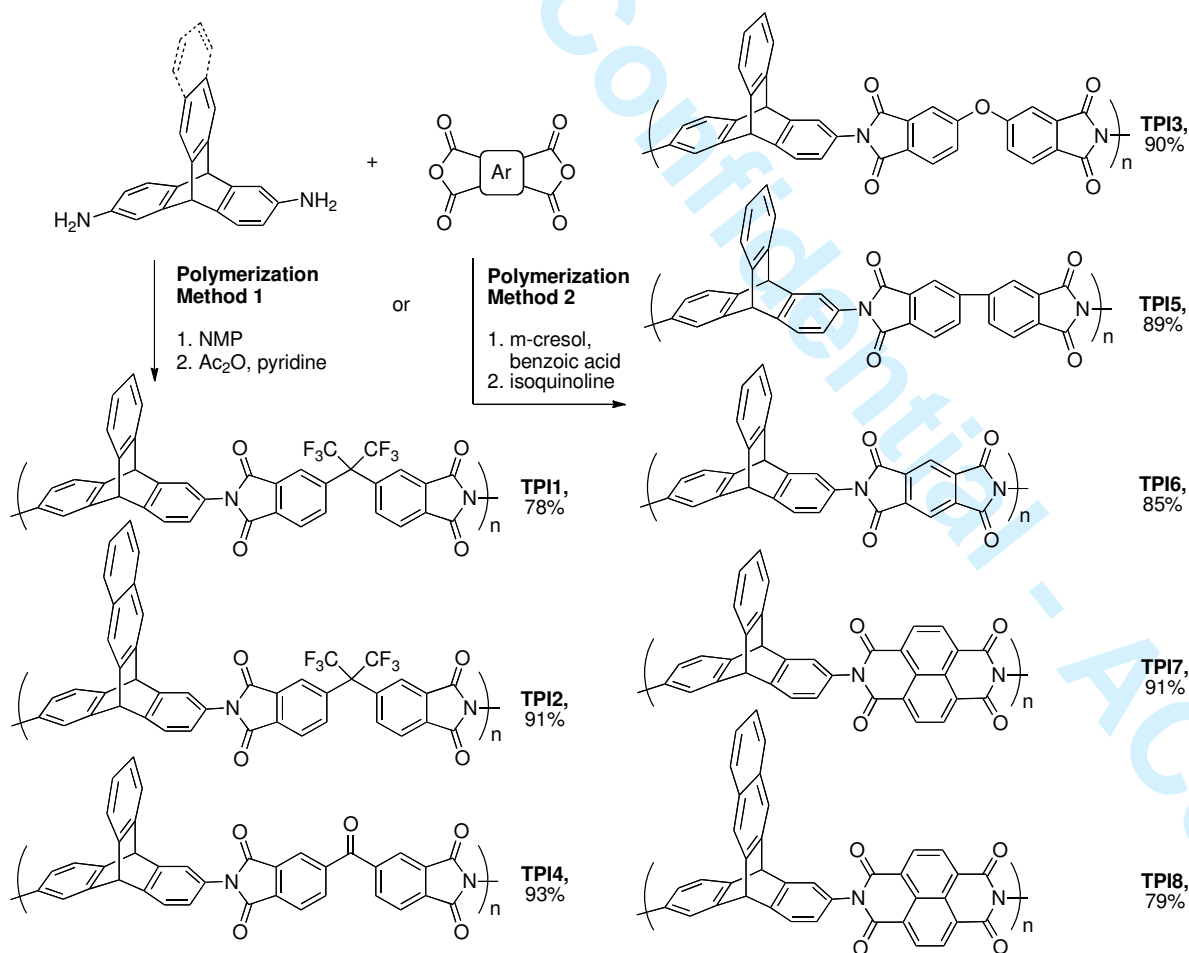


To produce high molecular weight polymers, two different polymerizations methods were utilized. Polymerization Method **1** involves a conventional two-step polymerization involving ring-opening polyaddition and then subsequent ring-closing dehydration. Initial step-growth polymerization of the diamine and dianhydride was carried out in *N*-methylpyrrolidone (NMP) to give the poly(amic acid) and pyridine and acetic anhydride were added in a second step as chemical dehydrating agents to facilitate ring closure. Polymer yields were 78- 93% after purification and this particular procedure was effective for the synthesis of the 5-membered ring polyimides (**TPI1- TPI6**). However, higher molecular weights were achieved for **TPI3**, **TPI5**, and **TPI6** using Polymerization Method **2**.

In Polymerization Method **2**, an acid catalyst is added in the initial polymerization and imidization is accomplished by addition of a base (Scheme 2). Specifically, freshly distilled *m*-cresol and benzoic acid were used in the first step, with isoquinoline acting as the base in the second step to drive the reaction to completion. Similar methods have been previously developed for 6-membered ring imides³¹ and our

1 highest molecular weights for **TPI3** and **TPI5- TPI8** were achieved by this method. Polymer yields
 2 from this method were 79- 91%. When the syntheses of 6-membered ring polyimides were attempted
 3 from this method were 79- 91%. When the syntheses of 6-membered ring polyimides were attempted
 4 using the first polymerization procedure, only oligomeric polyimide products were observed. It has been
 5 using the first polymerization procedure, only oligomeric polyimide products were observed. It has been
 6 suggested that this is because 6-membered ring polyimides go through an isoimide intermediate,³¹ rather
 7 than the poly(amic acid), in which case the classic chemical dehydrants would not facilitate imidization.
 8 However, in the polymerizations of our 5-membered ring dianhydrides, no evidence of the isoimide was
 9 observed in the FTIR spectra of polymer intermediates during Polymerization Method **2**. Instead, it is
 10 possible that the poly(amic acid) intermediate is more soluble in the acidic reaction conditions of
 11 Polymerization Method **2**, allowing polymer chains to grow longer. This theory would explain the
 12 higher molecular weights by Polymerization Method **2** for **TPI3**, **TPI5** and **TPI6**.
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24 **Scheme 2.** Polymerization Methods **1** (left) and **2** (right) and the structures of **TPI1- TPI8**.
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The polymers were characterized by $^1\text{H-NMR}$, fourier transform infrared spectroscopy (FTIR), and gel permeation chromatography (GPC). The $^1\text{H-NMR}$ spectra (Supplemental Information) show subtle upfield shifts of the aromatic imide protons from the dianhydrides and do not show any proton signals in the carboxylic acid region, suggesting complete imidization. For **TPI1** and **TPI2**, the $^{19}\text{F-NMR}$ shows only a single peak, also suggesting that there is only one polymeric species present. The FTIR spectra of the TPIs exhibit typical vibration features for a polyimide. Upon stopping the reaction of **TPI1** before the addition of the dehydrating agents, the poly(amic acid), **TPA1**, was isolated and a FTIR spectrum was taken for comparison (Figure 1). Dehydrative cyclization is accompanied by loss of the amide and carboxylic acid carbonyl stretching bands at 1654 cm^{-1} and 1718 cm^{-1} and gives rise to symmetric and asymmetric stretching bands of the imide carbonyl at 1726 cm^{-1} and 1785 cm^{-1} , respectively. FTIR data for the remaining TPIs can be found in the Supplemental Information. Molecular weights were determined by GPC in DMF versus polystyrene standards and are shown in Table 1. Number average molecular weights (M_n) ranged between 13 and 29 kDa, with the higher molecular weights being achieved for the most soluble polymers. Polydispersities of 1.5 to 2.1 are in accord with polymers produced by a step-growth mechanism with the lower PDIs reflecting some degree of fractionation with isolation and purification. Polymerization yields were good, suggesting that no major side products were present before purification.

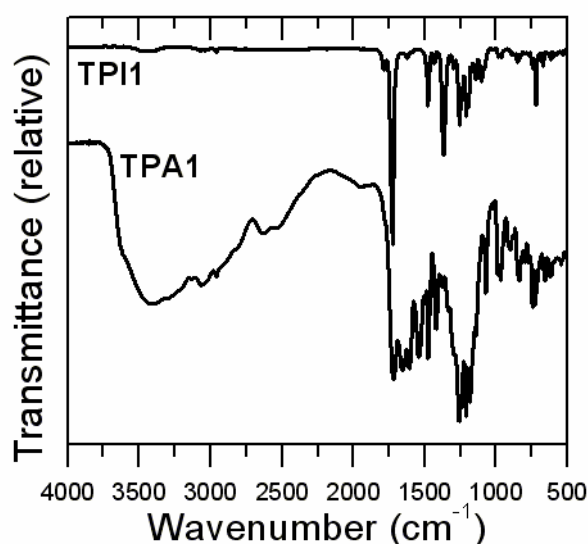
Table 1. Summary of the properties of **TPI1- TPI8**.

| | M_n (kDa) ^a | PDI | T_g (°C) | T_d (°C) ^b | Char Weight (%) | Inherent Viscosity (dL/g) | n | ϵ^c | n^{*d} | BET Surface Area (m ² /g) |
|-------------|-----------------------------|-----|---------------|----------------------------|-----------------------|---------------------------------|------|--------------|----------|-----------------------------------------------|
| TPI1 | 29 | 1.8 | >450 | 531 | 62 | 0.22 | 1.49 | 2.22 | 1.40 | 68 |
| TPI2 | 17 | 1.6 | >450 | 540 | 62 | 0.19 | 1.19 | 1.42 | 1.24 | 430 |
| TPI3 | 15 | 2.1 | >450 | 577 | 73 | 0.090 | 1.66 | 2.76 | 1.55 | 74 |
| TPI4 | 16 | 1.5 | >450 | 565 | 67 | 0.066 | 1.69 | 2.86 | 1.68 | 93 |
| TPI5 | 13 | 1.7 | >450 | 591 | 64 | 0.10 | 1.69 | 2.86 | 1.37 | 121 |

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|-------------|----|-----|------|-----|----|------|------|------|------|-----|
| TPI6 | 16 | 2.0 | >450 | 511 | 59 | 0.41 | 1.27 | 1.61 | 1.24 | 100 |
| TPI7 | 21 | 2.1 | >450 | 565 | 56 | 0.47 | 1.79 | 3.20 | 1.66 | 39 |
| TPI8 | 18 | 2.0 | >450 | 565 | 71 | 0.14 | 1.31 | 1.72 | 1.24 | 360 |

^a Number average molecular weight calculated by GPC in DMF versus polystyrene standards. ^b T_d reported as the 10% weight loss temperature under nitrogen. ^c Estimated from the refractive index using $n=\varepsilon^2$. ^d Refractive index of sample subjected to 200 hrs at 150 °C.

Figure 1. FTIR Spectra of **TPI1** and the intermediate poly(amic acid), **TPA1**. Transmittance scales offset for clarity.

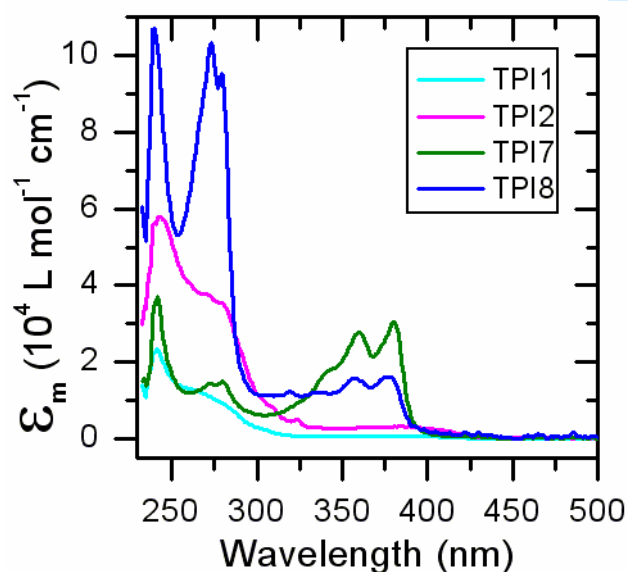


Solubility Properties. Previous work has shown triptycene containing polymers exhibit excellent solubility characteristics in comparison with their non-triptycene containing counterparts.^{12, 18} **TPI1-TPI8** were no exception and qualitative solubilities in common organic solvents are reported in the Supplemental Information. All polymers are soluble in dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO). **TPI1-TPI6** are soluble in toluene and xylenes, good solvents for spin coating applications. **TPI1** and **TPI2** are also soluble in tetrahydrofuran (THF), chloroform, dichloromethane (DCM), and even acetone. Several of the other polymers are soluble in these solvents as well. Solution viscosity measurements in DMF (at a concentration of 5 g/dL) reveal extremely low inherent viscosities in the range of 0.066- 0.47 dL/g (Table 1). Typically, the poly(amic acid)s that are processed due to the insolubility of the fully cyclized polyimide display inherent viscosities in the range of 1.0-1.79 dL/g.³²

Other triptycene-containing polyimides have been found to have inherent viscosities in the range of 0.45-0.74 dL/g.¹⁵ These viscosities are extremely low for polymers of reasonable molecular weights.

Optical Properties. All of the TPIs are yellow to orange in color, which is typical for aromatic polyimides. UV-Visible absorption spectra of the polymers (Figure 2) in dilute chloroform solutions confirmed that all of the polymers absorbed strongly in the near UV region with sharp absorptions at 239- 242 nm and low intensity broad absorption tails to approximately 400 nm that are assigned to charge transfer transitions. Polymers **TPI7** and **TPI8** containing the naphthalene diimide units also exhibited additional peaks at 274, 310 nm and 361, 381 nm respectively. Interestingly, the extension of the paddlewheel of the triptycene does not alter the absorption maxima, suggesting that it doesn't interact with the diimide chromophores. However, both polymers produced from monomer **DAT2** exhibit a stronger absorption around 280 nm.

Figure 2. UV-Vis Absorption Spectra. ϵ_m is the molar extinction coefficient per polymer repeat unit.



It has previously been demonstrated that high triptycene content in the polymer backbone increases the free-volume in the solid state; essentially creating molecular-scale pores in the material. These internal voids have been shown to substantially decrease the dielectric constant of insulating polymers^{12, 20} since the dielectric constant of the polymer is modulated with air ($\epsilon \approx 1$). To estimate the dielectric constant of these TPIs, the refractive index was measured by spectroscopic ellipsometry. In this technique,

1 linearly polarized light is reflected at a known angle (in this case, 70°) from the sample surface. The
2 change in the polarization of the light can be interpreted to give information about the thickness of the
3 film and its refractive index. Polymers spin cast from 5 mg/mL solutions of DMF on silicon wafer
4 yielded the thin films (3-47nm) used for the measurement. From the refractive index (n), the dielectric
5 constant (ϵ) at optical wavelengths can be estimated from
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$$\epsilon = n^2.$$

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15 Although this estimation often underestimates the dielectric constant of polyimides, it is clear that
16 incorporation of triptycene into these aromatic polyimides lowers their refractive index such that they
17 are comparable or better than those used commercially. Kapton NH™, a commercial leader, has a
18 refractive index of 1.70³³ at 633 nm and a dielectric constant of 2.7, and in comparison our triptycene
19 polyimides have refractive indices ranging from 1.19 to 1.79 at 633 nm, which gives approximated
20 dielectric constants of 1.42- 3.20 at optical frequencies (Table 1). The value of 1.42 is estimated for
21 **TPI2**, where both fluorine groups and the bulkier triptycene unit, **DAT2**, are incorporated. These results
22 warrant further investigations into **TPI2**'s use as a spin-on dielectric material. Other promising
23 candidates with estimated dielectric constants lower than 2.0 are **TPI5** and **TPI8** with an estimated ϵ of
24 1.61 and 1.72 respectively. These polymers may hold even more promise than **TPI2**, as there are
25 reservations towards use of fluorine-containing polyimides.²⁶
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41 To confirm that the internal free volume imparted by the triptycene was a plausible mechanism for the
42 lowering of the refractive index, BET surface area measurements were carried out. Previously, the
43 Swager group has reported a triptycene-containing polymer with a refractive index of 1.56 to have a
44 surface area of 400 m²/g.¹² This polymer included triptycene through a 2, 3 substitution and also
45 attached tert-butyl groups to 6 and 11 positions to enhance the bulkiness. **TPI2** and **TPI8** containing the
46 larger **DAT2** exhibit a similar surface area to this polymer (430 and 360, respectively) and lower
47 refractive indices. The TPis including **DAT1** as the diamine exhibit considerably lower surface areas
48 (39- 120 m²/g). Calculations suggested that pore sizes of the TPis were in the mesoporous range,
49 however, the shape of the isotherms suggest microporosity and that the model used for calculations may
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1 be inadequate. For mesoporous materials, the hysteresis loop of the isotherm should close at a relative
2 pressure of $p/p_0 \geq 0.4$, which is not the case for the TPIs.³⁴ The BET isotherms take a shape that most
3 closely resembles a Type II isotherm.³⁵ This type of isotherm, without hysteresis between absorption and
4 desorption, is usually characteristic of a non-porous material. In practice, however, it can describe
5 porous materials, as a Type IV isotherm, which is characteristic of porous materials and is a
6 modification of the Type II isotherm.³⁶ Additionally, the TPIs exhibit significant hysteresis between
7 adsorption and desorption, even at low relative pressures. This non-closed loop hysteresis can be
8 attributed to plasticization and swelling in a microporous structure.³⁴ Comparatively, most bulky
9 polyimides exhibit surface areas of 40- 68 m²/g^{37, 38} with only filled polyimides previously achieving
10 surface areas of 214- 1153 m²/g.^{39, 40} As expected, the magnitude of the surface area roughly follows a
11 reciprocal trend to the refractive index, with the highest surface area and lowest dielectric constant
12 found for **TPI2** (430 m²/g and 1.19) and the lowest surface area and highest refractive index found for
13 **TPI7** (39 m²/g and 1.79).

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31 **Thermal Properties.** Differential scanning calorimetry (DSC) analysis of the polymers showed no
32 glass transition temperatures (T_g) up to 450 °C and thermogravimetric analysis (TGA) indicated that the
33 decomposition temperatures (T_d) are above 510 °C (Table 1). This impressive thermal stability is
34 comparable to or better than leading commercial polymers, such as KaptonTM, which is recommended
35 for applications <400 °C.²¹ The polymer char weights at 800 °C are also shown as percentages and range
36 from 56-73%. This number provides an indication of the practicality of these materials as a high
37 temperature coating. To begin to probe the true thermal stability of the TPIs at elevated temperatures,
38 the refractive indices of thin films on Silicon were measured and then measured again after subsection to
39 200 hours at 150 °C. It was found that the films maintained their refractive indices within 20% of their
40 original value. In fact, the refractive indices decreased over the time period for all of the polymers
41 except **TPI2**. These values are reported in **Table 1** as n^* . The small changes in the refractive index can
42 be explained by a rearrangement of the polymers to their thermodynamic equilibrium since the original
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1 films were likely in a kinetic state due to the spin casting process. An annealing step should eliminate
2 this variability.
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4 **Conclusions**

5 We have synthesized a series of novel triptycene polyimides that exhibit high thermal stability and
6 solubility. The free volume imparted by the triptycene units enhances solubility, while retaining the
7 rigidity of a fully aromatic backbone. **TPI1** and **TPI2** are very soluble in toluene, xylenes, DMF,
8 DMSO, THF, chloroform, DCM, and acetone. Low inherent viscosities and solubility in a variety of
9 solvents suggest that these polymers may be ideal for solution processing. None of the polymers exhibit
10 glass transition temperatures below 450 °C and all of them decompose above 510 °C with the highest
11 decomposition temperature of 591 °C exhibited by **TPI5**. Char weights are around 60% and all polymers
12 are amorphous in thin films. Furthermore, low refractive of 1.31, 1.27 and 1.19 were found for **TPI8**,
13 **TPI6**, and **TPI2**, respectively. These values suggest dielectric constants at optical frequencies well
14 below 2.0 (1.72, 1.61, and 1.42 for **TPI8**, **TPI6**, and **TPI2**). The extremely low dielectric constant of
15 **TPI2** can be explained by the increase in nanoporosity as a result of the larger triptycene, **DAT2**, in
16 combination with the electronic effects of the fluorine groups.
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39 **Acknowledgements.** This work was supported by the U.S. Army through the Institute for Soldier
40 Nanotechnologies and the National Science Foundation through a Graduate Research Fellowship.
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43 **Supporting Information Available:** Experimental details including materials, instrumentation, and
44 detailed synthetic procedures. ¹H-NMR, ¹³C-NMR, and HRMS for **DAT1**, **DAA**, and **DAT2**. ¹H-NMR
45 spectra for **TPI1- TPI8**. FTIR spectra for **TPI2- TPI8**. ¹⁹F-NMR, ¹³C-NMR, and ¹H- gCOSY for **TPI1**
46 and **TPI2**. Complete solubility table for **TPI1- TPI8**. UV-Vis Spectra of **TPI3- TPI6**. Plots of TGA,
47 Spectroscopic Ellipsometry, and X-ray diffraction patterns for **TPI1- TPI8**. BET surface area reports for
48 **TPI1- TPI8**. This material is available free of charge via the Internet at <http://pubs.acs.org>
49
50
51
52
53
54
55
56
57
58

59 **References**

- 1 (1) Bessonov, M. I., Koton, M. M., Kudryavtsev, V. V., Laius, L. A. *Polyimides Thermally Stable*
2 *Polymers*; Consultants Bureau: New York, 1987; p 245-259.
3
4
5 (2) *Polyimides*; Wilson, D., Stenzenberger, H.D., Hergenrother, P. M., Eds; Blackie: London, 1990; p
6 57-78.
7
8
9 (3) *Polyimides: Fundamentals and Applications*; Ghosh, M. K., Mittal, K L., Eds.; Marcel Dekker:
10 New York, 1996; p 7-48, 71-120.
11
12
13 (4) Sroog, C. E.; *Prog. Polym. Sci.* **1991**, *16*, 561-694.
14
15
16 (5) Eichstadt, A. E.; Ward, T. C.; Bagwell, M. D.; Farr, I. V.; Dunson, D. L.; McGrath, J. E.;
17 *Macromolecules* **2002**, *35*, 7561-7568.
18
19
20 (6) Ghanem, B. S., McKeown, N. B.; Budd, P. M.; Al-Harbi, N. M.; Fritsch, D.; Heinrich, K.,
21 Starannikova, L.; Tokarev, A.; Yampolskii, Y. *Macromolecules* **2009**, *42*, 7881-7888.
22
23
24 (7) Kim, Y.; Kim, H.; Kwon, S. *Macromolecules* **2005**, *38*, 7950-7956.
25
26
27 (8) Liaw, D.; Chang, F.; Leung, M.; Chou, M.; Muellen, K.; *Macromolecules* **2005**, *38*, 4024-4029.
28
29
30 (9) Sroog, C. E.; Endrey, A. L.; Abramo, S. V.; Berr, C. E.; Edwards, W. M.; Olivier, K. L.; *J. Polym.*
31 *Sci. Part A* **1965**, *3*, 1373-1390.
32
33
34 (10) Williams, V. E.; Swager, T. M. *Macromolecules* **2000**, *33*, 4069-4073.
35
36
37 (11) Yang, J.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 11864-11873.
38
39
40 (12) Long, T. M.; Swager, T. M. *J. Amer. Chem. Soc.* **2003**, *125*, 14113-14119.
41
42
43 (13) Hart, H. *Pure & Appl. Chem.* **1993**, *65*, 27-34.
44
45
46 (14) Meador, M. A. B.; Meador, M. A.; Ahn, M.; Olshavsky, M. A. *Macromolecules* **1989**, *22*, 4385-
47 4387.
48
49
50
51
52
53
54
55
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57
58
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2
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47
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49
50
51
52
53
54
55
56
57
58
59
60
- (15) Zhang, Q.; Li, S.; Li, W.; Zhang, S. *Polymer*, **2007**, *48*, 6236- 6253.
- (16) Apithanawat, C.; Thongyai, S.; Praserttham, P.; Pulpoka, B.; Chantarasiri, N. *TISD Conf. Proc.* **2008**, 392-398.
- (17) Akutsu, F.; Saito, G.; Miyamoto, M.; Kasashima, Y.; Inoki, M.; Naruchi, K. *Macromol. Chem. Phys.* **1996**, *197*, 2239- 2245.
- (18) Tsui, N. T.; Paraskos, A. J.; Torun, L.; Swager, T. M.; Thomas, E. L. *Macromolecules* **2006**, *39*, 3350-3358.
- (19) Tsui, N. T.; Yang, Y.; Mulliken, A. D.; Torun, L.; Boyce, M. C.; Swager, T. M.; Thomas, E. L. *Polymer* **2008**, *21*, 4703-4712.
- (20) Amara, J. P.; Swager, T. M. *Macromolecules* **2004**, *37*, 3068-3070.
- (21) Maier, G. *Prog. Polym. Sci.* **2001**, *26*, 3-65
- (22) Ando, S. J. *Photopolym. Sci. Technol.* **2004**, *17*, 219-232.
- (23) Ree, M. *Macromol. Res.* **2006**, *14*, 1-33.
- (24) Murarka, S. P. *Solid State Technol.* **1996**, *3*, 83.
- (25) Van Krevelen, D. W. *Properties of Polymers*, 3rd ed; Amsterdam: Elsevier, 1990; p 321.
- (26) Volksen, W.; Miller, R. D.; Dubois, G. *Chem. Rev.* **2010**, *110*, 56-110.
- (27) Martin, S. J.; Godschalx, J. P.; Mills, M. E.; Schaffer, E. O., II; Townsend, P. H. *Adv. Mater.* **2000**, *12*, 1769-1778.
- (28) Rabjohns, M. A.; Hodge, P.; Lovell, P. A.; *Polymer*, **1997**, *38*, 13, 3395-3407.
- (29) (a) Klanderman, B. H.; Perkins, W. C. *J. Org. Chem.* **1969**, *34*, 630-633. (b) Chen, Z.; Swager, T. M. *Macromolecules* **2008**, *41*, 6880-6885.

- 1 (30) McNeil, A. J.; Müller, P.; Whitten, J. E.; Swager, T. M. *J. Am. Chem. Soc.* **2006**, *128*, 12426-
2 12427.
3
4
5 (31) Einsla, B. R.; 2005. PhD Thesis, Virginia Polytechnic Institute and State University. 69-84.
6
7
8 (32) M. Hasegawa, and K. Horie, *Prog. Polym. Sci.* **2001**, *26*, 259-335.
9
10
11 (33) Flaim, T.; Wang, Y.; Mercado, R; *Proc. of SPIE.* **2004**, *5250*, 423-434.
12
13
14 (34) McKeown, N. M. and Budd, P. M. *Macromolecules* **2010**, *43*, 5163- 5176.
15
16
17 (35) Rouquerol, F.; Rouquerol, J.; Sing, K. *Adsorption by Powders and Porous Solids: Principles*
18 *Methodology and Applications*; Academic Press: San Diego, 1999.
19
20
21 (36) Fagerlund, G. *Mat. and Struc.* **1973**, *6*, 239- 245.
22
23
24 (37) Sakodinsky, K. I.; Klinskaya, N. S.; Panina, L. I. *Anal. Chem.* **1973**, *45*, 1369- 1374.
25
26
27 (38) Ritter, N.; Antonietti, M.; Thomas, A.; Senkowska, I; Kaskel, S.; Weber, J. *Macromolecules*
28 **2009**, *42*, 8017- 8020.
29
30
31 (39) Min, C.; Wu, T.; Yang, W.; Chen, C. *Comp. Sci. Tech.* **2007**, *68*, 1570- 1578.
32
33
34 (40) Pang, J.; Qiu, K.; Wei, Y. *Chinese J. Polym. Sci.* **2000**, *18*, 469- 472.
35
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37
38
39
40
41
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