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Incorporation of Internal Free Volume: Synthesis and Characterization of Iptycene-Elaborated Poly(butadiene)s

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Introduction

Our research group has previously demonstrated that the "internal free volume" (Figure 1) swept out by iptycene moieties incorporated into polymeric sensors can be utilized to limit aggregation and provide binding cavities for analytes in explosives detection applications.[1] The reduction in aggregation also increases fluorescence in the solid state.[2] Such free volume has also been incorporated into the chemical structure of fluorescent and dichroic dyes, which have demonstrated enhanced anisotropic alignment in nematic liquid crystal displays.[3] A polymer that incorporates a large amount of internal free volume may also demonstrate a high degree of miscibility within another polymeric host, regardless of whether there is any affinity between the two polymers. The host polymer must fill this vacant space in order to minimize the energy of the system.[4]

While investigating the synthesis of new iptycene-containing materials, we found that butadiene-elaborated anthracene, tetracene, or iptycene scaffolds are transformed into high molecular weight polymers when heated to temperatures greater than 150 °C. The oligomerization of the simplest member of this series, the butadiene-elaborated anthracene, had been reported many years ago but was not characterized in detail.[5] As part of our efforts to develop methodology for the creation of materials with high degrees of free volume, we have investigated these materials further. Our results demonstrate a systematic approach to producing new materials with high degrees of free volume that can be used in applications benefiting from low densities such as high-performance (low-κ) dielectric materials for semiconductor devices.

In this report, the synthesis and characterization of a series of high molecular weight iptycene-containing polymers are presented. A thermally initiated radical polymerization of a butadiene-elaborated anthracene scaffold was utilized to yield polymer **1**. In a similar manner, radical polymerization of a butadiene-elaborated tetracene adduct yields polymer **2**, which should present an additional amount of internal free volume. Further synthesis, which employs an iptycene scaffold developed by Hart et al., incorporates an additional triptycene subunit, which contributes increased internal free volume to polymer **3**.[6] It should be noted that, due to the asymmetry of monomers **5** and **6**, polymers **2** and **3** contain random isomeric structures which, although undetectable spectroscopically, may result in added solubility or enhanced internal free volume.

Results and Discussion

The synthesis of monomer **4** is illustrated in Scheme 2.[7] The Diels−Alder adduct[8] of maleic anhydride and anthracene (95% yield) is reduced to afford the diol[9] (76% yield). Tosylation[9] (69% yield) followed by treatment with potassium *tert*-butoxide (92% yield) provides the desired monomer, **4**, in good overall yield (46%).

The diene monomer **4** was heated to slightly above its melting point, where it polymerized to form **1** (70%

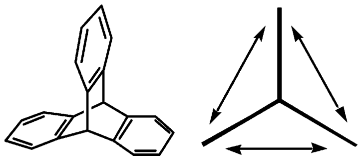
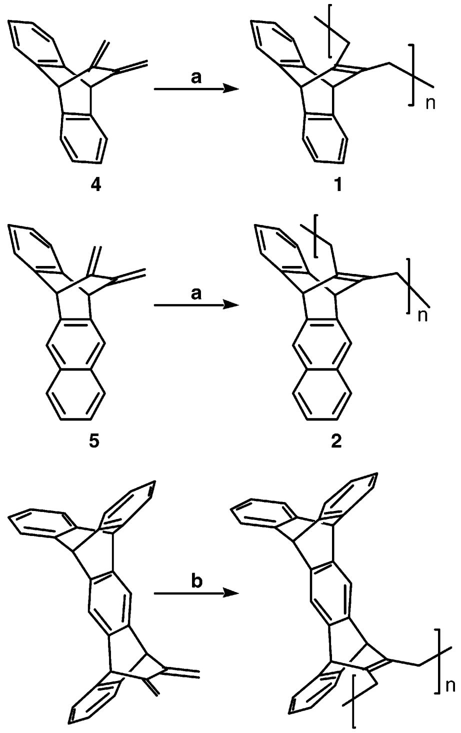


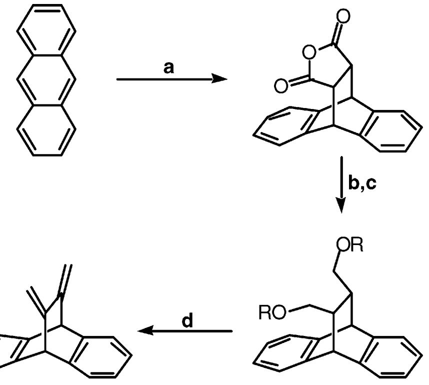
Figure 1. Triptycene and an illustration of its internal free volume.

Scheme 1. Synthesis of Iptycene-Containing Poly(butadiene)s[a]



[a] (a) 165 °C; (b) 165 °C, THF.

Scheme 2. Synthesis of Monomer 4[a]



[a] (a) Maleic anhydride, dioxane; (b) LiAlH$_4$, THF, R = H; (c) p-TsCl, pyridine, R = Ts; (d) KOtBu, THF.

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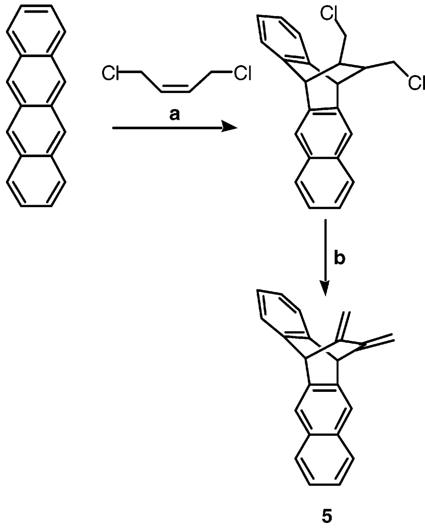
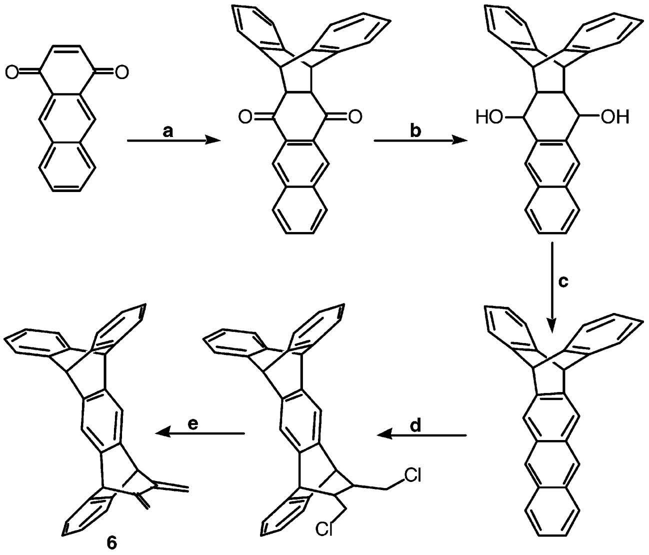
Scheme 3. Synthesis of Monomer 5[a]



[a] (a) 190 °C; (b) KOtBu, DMSO, THF.

Scheme 4. Synthesis of Monomer 6[a]



[a] (a) Anthracene, $AlCl_3$, CH_2Cl_2; (b) $LiAlH_4$, Et_2O; (c) *p*-TsCl, pyridine; (d) 1,4-dichloro-2-butene, 190 °C; (e) KOtBu, THF, DMSO.

yield) with high molecular weight. To confirm that the mechanism was a self-initiated radical polymerization, a radical inhibition experiment employing 1,4-benzoquinone as the inhibitor (5 mol %) was performed. Although some polymerization did occur when the reaction mixture was heated to 165 °C, the degree of polymerization was significantly reduced.

The synthesis of monomer **5** is illustrated in Scheme 3. The crude Diels–Alder adduct of tetracene and 1,4-dichloro-2-butene is treated with potassium *tert*-butoxide to yield monomer **5** (75% yield). Polymerization of monomer **5**, in the same manner as that of monomer **4**, affords polymer **2**. Although the reaction product is only sparingly soluble in common organic solvents, a soluble fraction (32% yield) can be taken up in THF with heating and vigorous sonication.

The synthesis of monomer **6**[6] requires five steps from 1,4-anthraquinone. The route pursued, which incorporates procedures from Patney et al., is outlined in Scheme 4.[10] The Diels–Alder adduct (87% yield), from the Lewis acid accelerated reaction of anthracene and 1,4-anthraquinone, is reduced with $LiAlH_4$ to give a diol. The crude product is used without additional purification. Tosylation and the subsequent elimination of *p*-TsOH gives the desired triptycene scaffold in acceptable yield (46%). The Diels–Alder adduct with 1,4-dichoro-2-butene (87% yield) is then treated with potassium *tert*-butoxide to give monomer **6** (80% yield).

Table 1. Physical Data for Polymers 1, 2, and 3

polymer	M_n[a]	PDI	T_g (°C)	*n* (633 nm)
1	310 000	2.0	145	1.572
2	86 000	1.4	233	1.635
3	18 000	3.0	204	1.533

[a] To rule out the possibility that polymer aggregation may result in inaccurate molecular weight determination by GPC (1 mg/mL sample concentration), additional runs were performed at higher dilution (0.5 and 0.1 mg/mL). In all cases, molecular weights determined by GPC gave good agreement to those reported above.

The melting point of monomer **6** (282 °C) is 125 °C higher than that of monomer **4** (157 °C). As a result, thermal polymerization of **6** in the melt does not occur without decomposition. For the polymerization, it was necessary to dissolve monomer **6** in a minimal amount of THF. Consequently, the degree of polymerization of **3** (55% yield) is considerably less than that of **1**.

In related work, we have shown that the incorporation of iptycene scaffolds in poly(aryl ethers) and polymers produced by ring-opening olefin metathesis polymerization produce materials with reduced dielectric constants.[11] We further found that the square of the material's refractive index provides a reasonable approximation of the dielectric constant of the material at optical frequencies. There are no strong electronic influences that should produce significant increases or decreases in the polarizabilities of the respective functional substructures (i.e., olefins, phenyls, naphthyls), and hence the observed trends in dielectric constants can only be accounted for by a systematic increase of the internal free volume of the iptycenes incorporated into the polymers.

Polymer **1**, a soluble fraction of polymer **2**, and polymer **3** were analyzed by GPC, DSC, and ellipsometry (Table 1). When compared to a polymer with similar functionality but minimal intrinsic internal free volume, such as polystyrene ($n_{633} = 1.756$), the refractive indices of the polymers were measured to give an indication of the amount of internal free volume incorporated by the iptycene scaffolds. From the data, it is apparent that polymer **3**, which presents an added triptycene moiety, incorporates the greatest amount of internal free volume, while polymer **2** incorporates the least. With its naphthalene arms enabling greater interpolymer π-associations, polymer **2** experiences poor solubility and reduced internal free volume in the solid state. The increased glass transition temperature of polymer **2** is likewise consistent with such an interaction.

Conclusions

Several high molecular weight iptycene-containing polymers have been synthesized through a thermally induced radical polymerization of butadiene monomers. Because of their iptycene-based superstructure, these polymers present internal free volume that could be utilized for the enhancement of miscibility and reduction of phase separation in polymer blends. Similar polymers could find potential as low-*K* dielectric coatings for electronics applications.

Experimental Section

General Methods and Instrumentation. All chemicals were of reagent grade from Aldrich Chemical Co. (St. Louis, MO) and used as received. All synthetic manipulations were performed under an argon atmosphere using standard Schlenk techniques unless otherwise noted. Glassware was oven dried before use. Column chromatography was performed using Baker 40 μm silica gel. All organic extracts were dried over $MgSO_4$ and filtered prior to removal with a rotary evaporator. Monomers **4**[7] and **6**[6] were synthesized according to literature procedures with a number of trivial modifications. NMR spectra were obtained on Varian Unity 300 MHz and Varian Mercury 300 MHz instruments. NMR chemical shifts are referenced to $CHCl_3$/TMS (7.27 ppm for ^1H, 77.23 ppm for ^{13}C). Mass spectra (MS) were obtained at the MIT Department of Chemistry Instrumentation Facility (DCIF) using a peak-matching protocol to determine the mass and error range of the molecular ion. All polymer solutions were filtered through 0.45 μm syringe filters prior to use. Polymer molecular weights were determined on a HP series 1100 GPC system in THF (1, 0.5, and 0.1 mg/mL sample concentrations) at room temperature vs polystyrene standards. Transition temperatures were determined by differential scanning calorimetry using a TA Instruments (New Castle, DE) Q1000 DSC at scan rates of 10 °C/min. Film thicknesses were measured using a Veeco (Woodbury, NY) Dektak 6M Stylus profilometer. Ellipsometry was performed on polymer films spin-coated onto silicon substrates with a Gaertner Scientific (Chicago, IL) three-wavelength variable-angle ellipsometer. Melting points were measured with a Meltemp II apparatus and are reported uncorrected.

13,14-Dichloromethyl-5,12-dihydro-5,12-ethanonaphthacene. Into a 100 mL heavy-walled glass tube were added tetracene (0.81 g, 4 mmol) and 1,4-dichloro-2-butene (13.35 g, 107 mmol) under Ar. The tube was sealed and heated to 190 °C for 48 h. The dark mixture was then cooled to room temperature. The solvent was distilled off (75 mTorr, 75 °C), and the black residue was purified by column chromatography (silica gel) with hexane−methylene chloride (2:1) as eluent to yield 1.36 g as a crude mixture of cis, trans, exo, and endo isomers. The compound was used without additional purification; mp 137−147 °C. ^1H NMR (300 MHz, $CDCl_3$) (note: the spectrum is too complex to assign the individual isomers): δ 2.52−2.64 (m, 2H), 2.86−3.02 (m, 2H), 3.48−3.53 (dd, 2H, J = 4, 11 Hz), 4.69−4.72 (dd, 2H, J = 1, 6 Hz), 7.18−7.25 (m, 2H), 7.36−7.50 (m, 4H), 7.76−7.85 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 43.9, 44.5, 44.6, 44.7, 46.6, 46.7, 122.2, 124.2, 125.8, 125.9, 126.0, 126.7, 126.9, 127.8, 132.6, 137.6, 139.8, 140.6, 142.6. MS (EI): calcd for $C_{22}H_{18}Cl_2$ (M^+), 352.0780; found, 352.0790.

13,14-Dimethylene-5,12-dihydro-5,12-ethanonaphthacene (5). Into a 250 mL round-bottom flask under Ar were added potassium *tert*-butoxide (1.24 g, 11 mmol), 13,14-dichloromethyl-5,12-dihydro-5,12-ethanonaphthacene (1.18 g, 3 mmol), THF (11 mL), and DMSO (22 mL). The dark green mixture was stirred at room temperature for 36 h. The reaction was quenched by pouring over ice water. The suspension was extracted with ether (300 mL), washed with brine (100 mL), and dried over $MgSO_4$. After filtration and evaporation to dryness, the product was purified by column chromatography (silica gel) with hexane as eluent to give 0.70 g (75% yield) as a white powder; mp 153−156 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 5.01 (s, 2H), 5.21 (s, 2H), 5.36 (s, 2H), 7.15−7.17 (dd, 2H, J = 3, 6 Hz), 7.36−7.43 (m, 4H), 7.76−7.79 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.3, 105.9, 121.7, 123.7, 125.7, 126.8, 127.8, 132.7, 139.8, 141.7, 144.1. MS (EI): calcd for $C_{22}H_{16}$ (M+), 280.1247; found, 280.1246.

Polymerization of 4. Into a 25 mL Schlenk tube under argon was added **4** (99 mg, 0.4 mmol). The compound was slowly stirred and heated to 165 °C for 1 h. After cooling to room temperature, the polymeric product was dissolved in a small amount of THF and then precipitated into MeOH. The white precipitate was isolated by centrifugation and dried under vacuum to give **1** (70% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 2.13 (s, 4H), 4.70 (s, 2H), 6.88 (m, 2H), 7.11 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 29.2, 55.4, 122.7, 124.6, 143.2, 146.4.

Polymerization of 5. Into a 25 mL Schlenk tube under argon was added **5** (102 mg, 0.4 mmol). The compound was slowly stirred and heated to 165 °C for 1 h. After cooling to room temperature, the sparingly soluble polymeric product was partially dissolved in THF by sonication. After removal of the insoluble polymer by filtration, the soluble fraction was then precipitated into MeOH. The white precipitate was isolated by centrifugation and dried under vacuum to give polymer **2** (32% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 1.91−2.15 (m, 4H), 4.55−4.70 (m, 2H), 6.84−6.96 (m, 2H), 6.99 (s, 2H), 7.02−7.22 (m, 2H), 7.28−7.46 (m, 2H), 7.54−7.70 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.3, 105.9, 121.7, 123.7, 125.1, 125.7, 126.8, 127.8, 144.1.

Polymerization of 6. Into a 25 mL Schlenk tube under argon were added **6** (58 mg, 0.1 mmol) and a minimal amount of THF (0.2 mL). The reaction was heated to 165 °C for 24 h. The reaction mixture was then cooled to room temperature, dissolved in additional THF, and slowly precipitated into MeOH. The white precipitate was isolated by centrifugation and dried under vacuum to give **3** (55% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 2.20 (m, 4H), 4.79 (m, 2H), 5.25−5.42 (m, 2H) 6.85−7.50 (m, 14H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 54.2, 118.1, 119.0, 122.4, 123.6, 125.3, 125.9, 142.1, 143.2, 145.7.

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