SYNTHESIS OF HETEROCYCLE TERMINATED TETRAYNES AS PRECURSORS FOR OPTOELECTRO-ACTIVE POLYMERS

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Abstract A new class of heterocycle terminated bis-*ortho*-diynyl arene (BODA) compounds have been synthesized via efficient ***in situ*** palladium catalyzed cross coupling reactions between tetra alkynyl silanes and aryl bromides and iodides. BODA monomers undergo Bergman cyclization upon heating and afford processable intermediates and ultimately network polymers. The new heterocycle terminated oligomers are compared to phenyl terminated derivatives and exhibit slight bathochromic shifts (25 nm) in their emission spectra due to the electron rich heterocycle.

Introduction

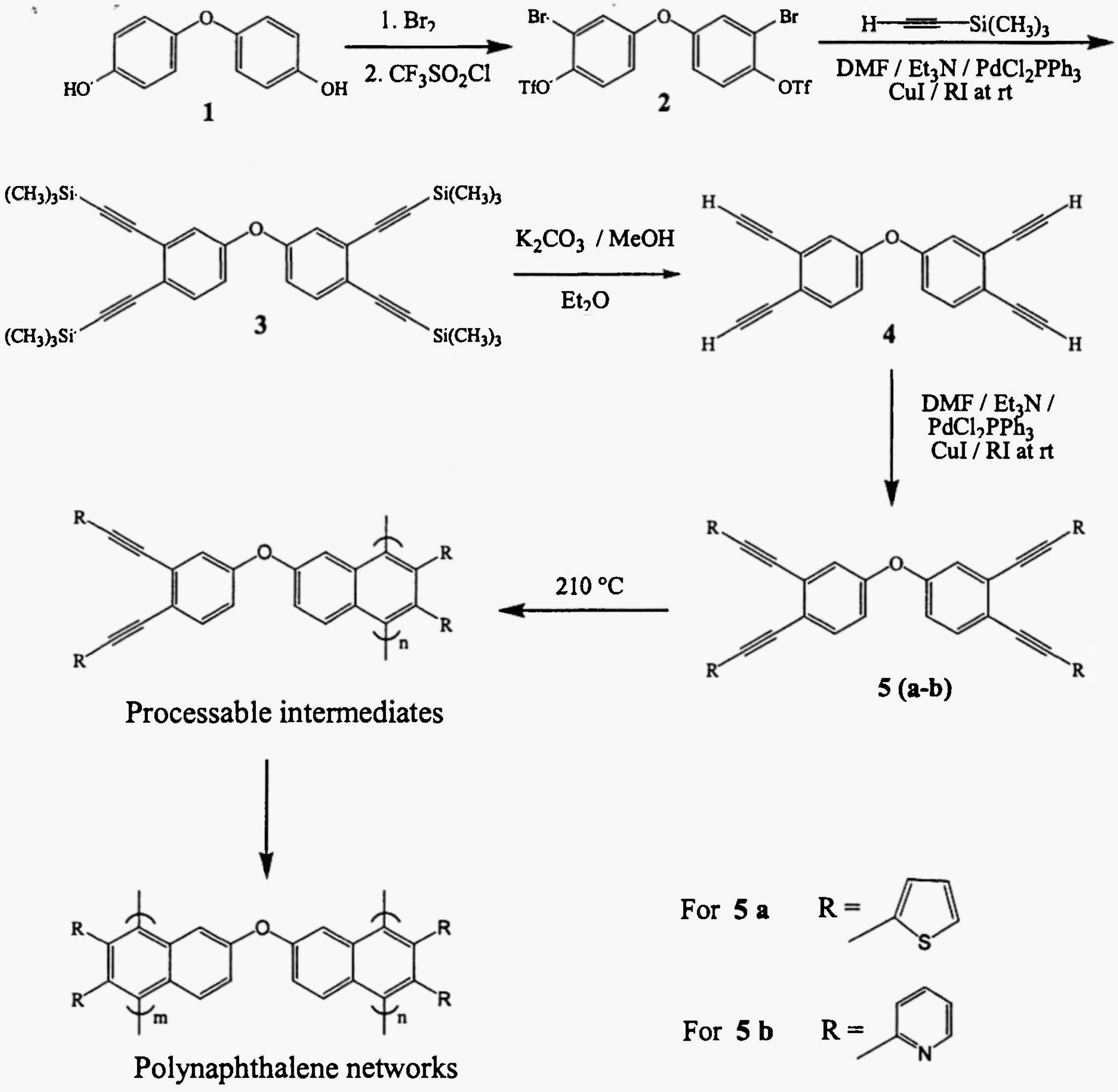
The thermal cyclo-rearrangement of enediynes,[1-2] known as the Bergman reaction,[1-5,9-11] has been established as a viable route for developing high performance polymers. [3-8] Although the simple aryldiynes lead to linear polyarylenes which are difficult to process, we focused on the synthesis of bis-*ortho*-diynylarene (BODA) monomers which polymerize to highly processable and reactive branched intermediates prior to final cure (Scheme 1).[5] BODA derived prepolymers can be easily coated or molded and are excellent precursors for microfabricated glassy carbon.[8]

Previously, BODA compounds were synthesized in a three-step synthetic protocol via selective ortho bromination of bisphenols followed by trifluoromethane sulfonato esterfication and subsequently Sonogashira[12] type Pd catalyzed coupling with monosubstituted terminal alkynes. Melt or solution polymerized BODA monomers gave polymers which exhibit higher thermal stability as well as optoelectronic properties.[6] However, to date BODA derived oligomers / polymers exhibit low to moderate emission intensities in the visible region. Here we report a new class of heterocyclic terminated BODA monomers synthesized via ***in situ*** desilylation followed by a Pd catalyzed cross coupling between alkynylsilanes and aryl iodides and bromides to enhance the optoelectronic as well as the thermal properties of the final network polymer (Scheme 1).

Results and Discussion

Our early work was focused on the synthesis of phenyl terminated monomers as precursors for high performance materials.[5] Our recent efforts, however, have focused on developing new monomers with heteroaromatic moieties as terminal groups (Scheme 1). Initially we attempted Sonogashira[12] type palladium coupling reactions between aryl triflates and bromides with monosubstituted acetylenes as reported for other BODA monomers previously.[5] However, the instability of the related pyridyl and thienyl acetylene derivatives redirected our approach to *in situ* direct cross coupling reactions between alkynylsilanes and aryl iodides. Alkynylsilanes were synthesized by Sonogashira type palladium coupling with aryl triflates and bromides with trimethylsilyl acetylene in high yield (> 85 %). Subsequent desilylation followed by *in situ* palladium catalyzed cross coupling afforded the heterocyclic terminated monomers in good yield (> 60 %) despite the tendency for oxidative homo-coupling. Isolation of the H-terminated tetraynes followed by coupling with aryl halides resulted in lower yields over the direct *in situ* coupling route.

Scheme 1



Upon heating neat above 200 °C for 2 hours, BODA monomers 3-5 formed branched polymers, which could be dissolved in THF and studied by UV-visible absorption and emission spectroscopy. Phenyl terminated BODA derived pre-networks and thermoset structures have been shown to exhibit photoluminescent properties.[6] In general, polymers prepared from 3-5 exhibit emission in the visible regions where thiophene and pyridine termination gave λ_{max} values of 440 nm and 425 nm, respectively, and ca. 100 nm peak width. These values represent only a slight (ca. 25 nm) bathochromic shift over phenyl terminated derivatives, yet are qualitatively much more intense than those previously prepared. Quantitative absorption and emission behavior for the fully cured networks in the solid state is currently underway and will be reported elsewhere.

Experimental

General TMS-acetylene coupling of BODA (3). The procedure for the preparation of bis-bromo and bis-bromo-bis-triflate starting materials are reported elsewhere.[5] To a 250 mL four neck flask equipped with thermocouple, N_2 purging tube, dropping funnel and magnetic stirrer was added 10.0 g (13.2 mmol) of the dibromotriflate, 50 mL DMF, and Et_3N. The solution was deoxygenated for 20 min and 0.687 g, (0.98 mmol) $[P(Ph)_3]_2PdCl_2$, and 0.11 g (0.98 mmol) CuI were added and the solution was heated to 90 °C. Deoxygenated trimethylsilyl acetylene 5.8 g, (59 mmol) was added dropwise over 15 min and the mixture was heated at 90 °C overnight. The crude product was purified by column chromatography using hexane / ethyl acetate 20:1 as the eluent.

General desilylation *in situ* coupling (5). To a three neck flask was added 3 and potassium carbonate (4 equiv. based on alkyne) and diethyl ether/ methanol (1 : 2). The flask was capped and the mixture was stirred overnight. Aryl halide (5 equiv. based on tetrayne), bis(triphenylphosphine) palladium (II) dichloride, and copper (I) iodide (0.011 equiv. based on tetrayne) were then added followed by addition of 20 mL of DMF and Et_3N at room temperature under nitrogen and the mixture was stirred overnight.

3,3', 4,4'-Tetra(trimethylsilylethenyl)phenyl ether (3). The crude product was purified by column chromatography (silica, hexane) giving yellow/red solid (84 %); mp 145 °C (by DSC); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.26 (s), 6.87 (d), 7.01 (s), 7.44 (d); ^{13}C NMR δ 0.01, 98.0, 98.0, 99.5, 102.3, 102.6, 119.3, 121.41, 122.1, 127.5, 134.0, 156.0; GC / MS *m/z* 554.00 (H^+).

3,3', 4,4'–Tetra(2-ethenylthienyl)phenyl ether (5a). The crude product was purified by column chromatography (silica, 10 : 1 hexane / ethyl acetate) giving an orange solid (68 %); mp 211 - 212 °C; FTIR (KBr disk) ν 689, 837, 1198, 1524, 1590, 2195, 2938, 3086 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.97 - 7.03 (m), 7.14 (d), 7.29 – 7.34 (m), 7.50, 7.53; ^{13}C NMR δ 86.7, 87.9, 91.2, 91.3, 119.3, 121.4, 127.2, 127.3, 127.6, 128.1, 132.1, 132.6, 133.2, 156.1 HRMS for $C_{36}H_{18}O_1S_4$ calcd (found) *m/z* 594.0240 (594.0231).

3,3', 4,4'-Tetra(2-ethenylpyridyl)phenyl ether (5b). The crude product was purified by column chromatography (silica, 9 : 1 hexane / ethyl acetate) giving an orange solid (64 %); mp 210 - 211 °C. FTIR (KBr disk) ν 732, 767, 815, 886, 1211, 1453, 1475, 1550, 1581, 2215, 2954, 3042 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (d), 7.09 (d), 7.22 - 7.26 (m), 7.31 (d), 7.65 - 7.72 (m), 8.62 - 8.63 (m); ^{13}C NMR δ 86.8, 87.1, 92.7, 93.6, 119.8, 121.1, 122.2, 122.8, 123.0, 127.0, 127.7, 128.8, 128.8, 132.0, 132.1, 134.1, 136.1, 143.1, 143.5, 150.0, 150.1, 156.4; FAB HRMS for $C_{40}H_{23}O_1N_4$ (M^+ + H) calcd (found) *m/z* 575.1873 (575.1871).

Conclusions

New bis-*ortho*-diynylarene (BODA) compounds with terminal heterocyclic rings have been successfully synthesized from available bisphenols and an *in situ* desilylation coupling method. Emission spectra of thiophene terminated oligomers in solutions indicated a slight bathochromic shift (25 nm) over phenyl terminated BODA monomers.

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