Polynaphthalene Networks from Bisphenols

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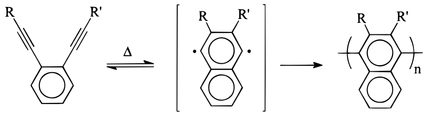
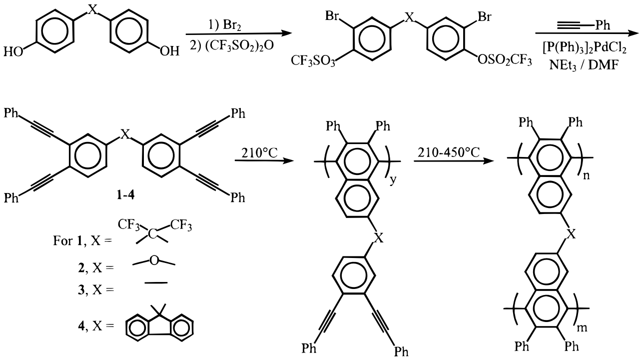
Enediynes were first studied by Bergman and are known to undergo thermal intramolecular cyclization to benzene 1,4-diradical or "dehydroaromatic" intermediates.[1] While the primary impetus for enediyne research remains focused on their biological activity as antitumor agents,[2] others have reported using enediynes in a polymerization scheme.[3,4] Tour detailed the synthesis of linear poly(phenylenes) and poly(naphthalenes) by thermolysis of substituted enediynes and 1,2-dialkynylbenzenes (Scheme 1).[3] This work extended earlier accounts[4] and revealed the Bergman cyclization as a viable polymerization reaction in detail.

Polynaphthalenes prepared by Bergman cyclopolymerization to date have been limited to linear systems of soluble, low molecular weight oligomers with fair thermal stability, or high molecular weight polymers exhibiting exceptional thermal stability yet are insoluble and not easily processed.[3,4] In addition, the preparation of 1,2-dialkynyl monomers is typically accomplished by the palladium-catalyzed coupling of terminal alkynes with difficult to prepare 1,2-dibromo or -diiodo aromatics.[3−5] We have found, however, that bis(*o*-di(phenylethynyl)phenyl) monomers **1**−**4** (Scheme 2) overcome both monomer synthetic obstacles and the processability/performance "tradeoff" issues common to linear polyarylenes.[6] We have developed a general multi hundred gram preparation of these compounds in three steps from commodity starting materials and reagents. When heated, monomers **1**−**4** undergo Bergman cyclopolymerization to reactive oligomers which can be melt or solution processed and thermally cured providing a new class of polynaphthalene networks. Other polymers containing naphthalene linkages are also known.[7] Our polynaphthalene networks were designed specifically to replace current dielectric materials used in integrated circuits.[8]

Scheme 1



Scheme 2



Monomer intermediates were prepared by selective *o*-bromination followed by quantitative trifluoromethanesulfonate (triflate) esterification of the corresponding bisphenols and gave aryl dibromide ditriflate intermediates in good yield (>75%). Sonogoshira-type[9] palladium coupling with phenylacetylene produced tetraynes **1**−**4** in isolated yields usually >80% (Scheme 2).[10] Our method does not use a copper cocatalyst, common to aryl alkyne couplings, thereby eliminating the potentially hazardous formation of copper acetylide.[11] All monomers were isolated as lightly colored crystalline solids with sharp melting points (Table 1).

Neat exothermic polymerizations of **1**−**4** are detected by differential scanning calorimetry (DSC, 10 °C/min) at 200−210 °C, giving reaction profiles consistent with known phenyl-substituted aryldiynes.[4] For example, the polymerization of 1,2,4,5-tetrakis(phenylethynyl)benzene and poly(arylene-1,2-ethynylene) each containing four acetylene linkages, gave a DSC-measured $-\Delta H = 29$ kcal/mol alkyne, whereas the thermolysis of **1**−**3** gave $-\Delta H = 27$, 29, and 27 kcal/mol alkyne, respectively. Fluorenyl monomer **4** exhibited a significantly lower $-\Delta H = 18$ kcal/mol alkyne, due to incomplete conversion.

Bergman cyclopolymerization kinetics, and thus rheological properties, are controlled by tetraphenyl substitution and provide

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(1) Bergman, R. G. *Acc. Chem. Res.* **1973**, *6*, 25−31. Bharucha, K. N.; Marsh, R. M.; Minto, R. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 3120. Lockhart, T. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4091. Jones, R. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 660.

(2) Nicolaou, K. C.; Dai, W.-M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1387−1416. Semmelhack, M. F.; Neu, T.; Foubelo, F. *J. Org. Chem.* **1994**, *59*, 5038. Grissom, J. W.; Calkins, T. L. *J. Org. Chem.* **1993**, *58*, 5422. Jones, G. B.; Mathews, J. E.; Li, A. *Tetrahedron Lett.* **1996**, *37*, 3643.

(3) John, J. A.; Tour, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 5011. John, J. A.; Tour, J. M. *Tetrahedron* **1997**, *53* (45), 15515.

(4) For tetrakis(phenylethynyl)benzene, see: Sastri, S. B.; Keller, T. M.; Jones, K. M.; Armistead, J. P. *Macromolecules* **1993**, *26*, 6171. Jones, K. M.; Keller, T. M. *Polymer* **1995**, *36* (1), 187. For poly(arylene-1,2-ethynylene), see: Grubbs, R. H.; Kratz, D. *Chem. Ber.* **1993**, *126*, 149−57.

(5) Zhou, Q.; Carroll, P. J.; Swager, T. M. *J. Org. Chem.*, **1994**, *59*, 1294. Ernst, A.; Gobbi, L.; Vasella, A. *Tetrahedron Lett.* **1996**, *37* (44), 7959−7962.

(6) For reviews, see: Scherf, U.; Müllen, K. *Synthesis* **1992**, 23. Tour, J. M. *Adv. Mater.* **1994**, *6*, 190. Kovacic, P.; Jones, M. B.; *Chem. Rev.* **1987**, *87*, 357. Schlüter, A.-D. *Adv. Mater.* **1991**, *3*, 282. Schlüter, A.-D.; Wegner, G. *Acta Polymer* **1993**, *44*, 59−69. Percec, V.; Bae, J.-Y.; Zhao, M.; Hill, D. H. *Macromolecules* **1995**, *28*, 6726. For water-soluble examples, see: Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 7411. Kim, S.; Jackiw, J.; Robinson, E.; Schanze, K. S.; Reynolds, J. R.; Baur, J.; Rubner, M. F.; Boils, D. *Macromolecules* **1998**, *31*, *1* (4), 964.

(7) For well-defined naphthalene polymers, see: Fahenstich, U.; Koch, K. H.; Müllen, K. *Makromol. Chem. Rapid Commun.* **1989**, *10*, 563. Pu, L.; Wagaman, M. W.; Grubbs, R. H. *Macromolecules* **1996**, *29*, 1138. Stenger-Smith, Sauer, J. D.; Wegner, G.; Lenz, R. W. *Polymer* **1990**, *31*, 1632. For poly(perinaphthalene), see: Lehmann, G. *Synthetic Metals* **1991**, *41*−*43*, 1615. Murkami, M. *J. Appl. Phys.* **1990**, *67* (1), 194. Naphthalene can be electrochemically polymerized, see: Shi, G.; Xue, G.; Li, C.; Jin, S. *Polymer Bulletin* **1994**, *33*, 325−329. Klamann, D. In *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed., Verlag Chemie: Weinheim, 1990; Vol. A15, p 423.

(8) For a recent status, see: *Mater. Res. Soc. Bull.* **1997**, *22* (10). *Low Dielectric Constant Materials III. Mater. Res. Soc. Symp. Proc.* Case, C.; Kohl, P.; Kikkawa, T.; Lee, W., Eds.; **1997**, *476*, 3−57. For low *k* polyimide development, see: Hedrick, J.; Carter, K.; Richter, R.; Miller, R.; Russell, T.; Flores, V. *Chem. Mater.* **1998**, *10*, 39.

(9) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *50*, 4467. Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, *8*, 627. Okita, T.; Isobe, M. *Tetrahedron* **1995**, *51* (13), 3737.

(10) Typical coupling procedure (**1**): To a deoxygenated solution of aryl dibromide ditriflate (102.4 g, 0.135 mol), DMF (400 mL), triethylamine (400 mL), and $[P(Ph)_3]_2PdCl_2$ (7.0 g, 0.01 mol) at 65 °C was added phenylacetylene (68.0 g, 0.667 mol) dropwise in 3−10 min. The mixture was heated at 90 °C for 2.5 h, diluted with CH_2Cl_2 (500 mL), washed with 10% HCl, evaporated, and cyrstallized giving 82.6 g (87%), mp 189−191 °C. IR (cm^{-1}): 2213.9 (-*CC*Ph). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30−7.40 (13H, br, m), 7.52−7.62 (13H, br, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 64.0 (hept, $C(CF_3)_2$, $J = 30$ Hz), 87.23, 87.48, 94.54, 95.38 (-*CC*Ph) 122.77, 126.16, 126.93, 128.36, 128.40, 128.71, 128.78, 129.4, 131.63, 131.72, 132.51, 133.11. ^{19}F NMR (376 MHz, $CDCl_3$): δ −63.84 (s). HRMS for $C_{47}H_{26}F_6$ calcd (found): 704.1939 (704.1926).

(11) Copper-free couplings have been reported, see: Alami, M.; Ferri, F.; Linstrumelle, G. *Tetrahedron Lett.* **1993**, *34* (40), 6403. Chen, Q. Y.; Yang, Z. Y. *Tetrahedron Lett.* **1986**, *27*, 1171.

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Table 1. Polymerization Events and Polynaphthalene Properties

monomer	T_m peak (°C)[a]	T_{exo} onset (°C)[a]	exotherm $-\Delta H$, J/g (kcal/mol)[a]	gel range at 210 °C (h)[b]	wt. loss at 450 °C (%/h)[c]	yield at 900 °C (%)[d]
1	190	210	650 (109)	3.5−5.0	1.5	88
2	108	205	848 (116)	3.2−4.3	1.0	90
3	173	200	789 (107)	2.9−4.3	0.5	98
4	105	210	413 (71)	1.6−3.7	1.2	93

[a] DSC (10 °C/min) in nitrogen. [b] Gel point to vitrification by dynamic mechanical spectroscopy (parallel plate). [c] TGA at 450 °C for 10 h in N_2. [d] TGA 900 °C for 3 h in N_2.

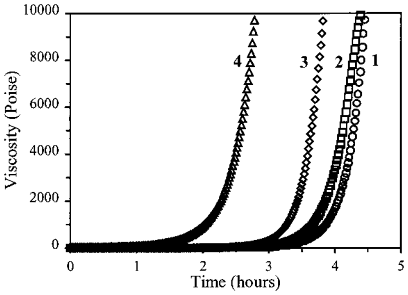

Figure 1. Complex viscosity of polymerization at 210 °C by parallel plate DMS.

large melt processing windows ranging 4−5 h at 210 °C as found by dynamic mechanical spectroscopy. For comparison, gel ranges (Table 1) are defined as the time between the gel point (initial increase in viscosity or modulus) and vitrification ($T_g = T_{cure}$). As shown in Figure 1, the structure dependent gel point decreases as flexibility decreases for monomers **1**−**4**, respectively.

For thin film preparation, monomers **1**−**4** were solution or melt polymerized at 200−210 °C and gave reactive oligomer/monomer mixtures of controlled molecular weight.[12] (*Caution! Temperatures required for spontaneous polymerization of bis-(o-(diphenylethynyl)phenyl) monomers can be lowered dramatically in the presence of Pd resulting in potential detonation.*)[13] Room-temperature solutions composed of 25−50 wt % solids were prepared from polymers of 3 000−24 000 M_w and polydispersities (M_w/M_n) of 3−11 by gel permeation chromatography (GPC vs polystyrene). In all cases, polymerization proceeded by an apparent step growth mechanism where molecular weight increased dramatically only after monomer fraction fell below 10% (Figure 2). Bergman cyclopolymerization neither requires catalysts or initiators nor produces side products, as similarly found for the linear polymerization of enediynes.[3] In contrast, however, the molecular weight distribution of oligomers from **1**−**4** grows with molecular weight (Figure 2, inset). This ability to solution or melt form branched pre-networks of broad molecular weight distributions is ideal for molding and coatings applications.

The IR spectra for the polymers show clearly that the alkyne stretch, common to **1**−**4** from 2210 to 2216 cm^{-1}, disappears upon heating. Further significant changes in the spectra are not observed, with the exception of subtle shifts in the prominent monosubstituted phenyl absorbances. Whereas the phenyl wagging vibration near 754 cm^{-1} remains unchanged, the monosubstituted phenyl bending signal is consistently 10−13 cm^{-1} higher in the polymers (698−700 cm^{-1}) vs the phenyl bend in the corresponding monomers (685−688 cm^{-1}) as predicted empirically and from model compounds.[14] Analysis of oligomer solutions by ^{13}C NMR revealed a relative decrease in the four noneqivalent alkyne signals (88−94 ppm for **1**−**4**) and the formation of adjacent broad signals. New alkyne carbons indicate pendant and branched terminal aryldiyne groups are formed as depicted in Scheme 2. The formation of multiple broad carbon signals from 124 to 134 ppm surrounding the aromatic methine and *ipso* monomer signals also indicate that only aromatic structures are formed during polymerization.

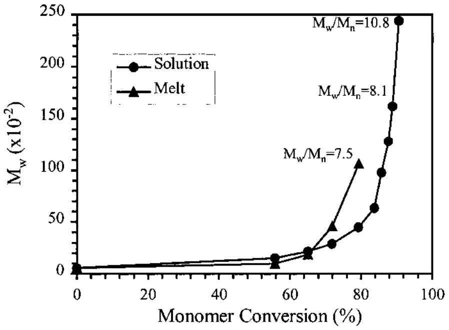

Figure 2. Step growth solution (50 wt % triisopropylbenzene) and melt polymerization of **1** at 210 °C by GPC.

After solution or melt application, the reactive oligomers were advanced by heating to 450 °C under nitrogen. Oligomer solutions were spin coated and cured on silicon substrates and gave visual defect-free films of controlled thickness (1−2 μm). In all cases, glass transition temperatures (T_g) were not detected by DSC or thermomechanical analysis below 400 °C. Dielectric constants ranging from 2.5 to 2.7 were measured for the cured films by parallel plate capacitance. Isothermal weight loss rates at 450 °C ranged from 0.5 to 1.5%/hour (Table 1), which places these polynaphthalenes among the most thermally stable organic polymers known.[15] This permits the use of high-temperature fabrication methods preferred for integrated circuits,[8] matrix composites,[15] and expected for developing π-conjugated optoelectronic materials exhibiting conductivity, photo- and electroluminescence, and nonlinear optical properties.[6,7]

Finally, after heating (TGA) for 10 h at 450 °C in nitrogen, the sample weights were reset to 100% and heated to 900 °C to assess densification of the networks and the carbon (char) yields.[16,17] An initial rapid weight loss from 500 to 900 °C ensued for each polymer before reaching equilibrium yields ranging from 88 to 98% (Table 1). The carbon products appeared as monolithic glassy solids and provide new examples of high carbon materials—currently sought for their extreme thermal, oxidative, and dimensional stability, hardness, and electrochemical properties.[17,18]

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Supporting Information Available: Detailed synthetic procedures and characterization data for the synthesis of monomers **1**−**4** and polymers listed in Table 1 (8 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(12) In a typical solution polymerization, **1** (1.5 g) and triisopropylbenzene (1.5 g) were deoxygenated and heated with stirring at 210 °C in a 25 mL Schlenk flask. Samples were analyzed by GPC over time and examined for their ability to form a coating. M_w = 3 000−10 000 prior to coating and cure to 450 °C. IR (cm^{-1}): 3059, 3026 (ArH), 1598 (Ar), 1493 (Ar), 1443 (w), 1253 (st, CF), 1206 (st, CF), 1135 (w, sh), 965 (w), 895, 827 (lone and adj. ArH), 756 (*m*-subst. Ph, wag), 700 (*m*-subst. Ph, bend).

(13) Monomer **3** containing 700 ppm Pd, reacted violently with gaseous decompostion upon melting. Metal-assisted enediyne activation is known. See: Warner, B. P.; Millar, S. P.; Broene, R. D.; Buchwald, S. L. *Science* **1995**, *269*, 814. Koenig, B. Hollnagel, H.; Ahrens, B.; Jones, P. G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2538.

(14) The phenyl bend for diphenylacetylene and *o*-terphenyl are 689 and 699 cm^{-1}, respectively. See: *The Aldrich Library of FT-IR Spectra, Edition I*; Pouchert, C. J., Ed., Aldrich Chemical Co.: Milwaukee, WI, 1985. Colthub, N. B.; Daly, L. H.; Wiberley, S. E. *Introduction to Infrared and Raman Spectroscopy, Third Ed.*; Academic Press: Boston, MA, 1990; p 270.

(15) Cassidy, P. E. *Thermally Stable Polymers: Synthesis and Properties*; Marcel Dekker: New York, 1980. Hergenrother, P. M. *Polym. J.* **1987**, *19* (1), 73.

(16) Mariam, Y.; Feng, K. In *Physical Properties of Polymers Handbook*; Mark J. E., Ed.; AIP Press: New York, 1996; Chapter 47, p 643.

(17) Jenkins, G. M.; Kawamura, K. *Polymeric Carbons*−*Carbon Fibre, Glass and Char*; University Press: Cambridge, U.K., 1976.

(18) Neenan, T. X.; Whitesides, G. M. *J. Org. Chem.* **1988**, *53*, 2489. Pocard, N. L.; Alsmeyer, D. C.; McCeery, R. L.; Neenan, T. X.; Callstrom, M. R. *J. Mater. Chem.* **1992**, *2* (8), 771.