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(phenylene)s and poly(naphthalene)s by thermolysis of substituted enediynes and 1,2-dialkynylbenzenes (Scheme 1). 3 This work extended earlier accounts 5 and revealed the Bergman cyclization as a viable polymerization reaction in detail.

Polynaphthalene networks 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, 5 In addition, the preparation of 1,2-dialkynyl monomers is typically accomplished by the palla-catalyzed coupling of terminal alkynes with difficult to prepare 1,2-dibromo or -diiodo aromatics. 3, 5 We have found, however, that bis(1-di(phenylethynyl)phenyl) monomers 1–4 (Scheme 2) overcome both monomer synthetic obstacles and the processability/performance “tradeoff” issues common to linear polarylenes. 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

Monomer intermediates were prepared by selective o-bromination followed by quantitative trifluoromethanesulfonate (triflate) esterification of the corresponding bisphenols and gave aryl dibromide triflate intermediates in good yield (75%). Sonogashira-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 alkylene 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).

Next 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 arylidyne. 4 For example, the polymerization of 2,4,5-tetraakis(phenylethynyl)benzene and poly(arylene-1,2-ethynylene) each containing four acetylene linkages, gave a DSC-measured −ΔH = 29 kcal/mol alkylene, whereas the thermolysis of 1–3 gave −ΔH = 27, 29, and 27 kcal/mol alkylene, respectively. Fluorenyl monomer 4 exhibited a significantly lower −ΔH = 18 kcal/mol alkylene, due to incomplete conversion.

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


(10) Typical coupling procedure (1): To a deoxygenated solution of aryl dibromide triflate (102.4 g, 0.135 mol), DMF (400 mL), triethylamine (400 mL), and [P(Ph)₃]·[P(Cl), 7.0 g, 0.01 mol) at 65 °C was added phenylacetylene (68.9 g, 0.667 mol) in 3–10 min. The mixture was heated at 90 °C for 2.5 h, diluted with CH₂Cl₂ (500 mL), washed with 10% HCl evaporated, and crystallized giving 82.6 g (87%), mp 189 °C, giving reaction profiles consistent with known phenyl-substituted arylidyne. 4 For example, the polymerization of 2,4,5-tetraakis(phenylethynyl)benzene and poly(arylene-1,2-ethynylene) each containing four acetylene linkages, gave a DSC-measured −ΔH = 29 kcal/mol alkylene, whereas the thermolysis of 1–3 gave −ΔH = 27, 29, and 27 kcal/mol alkylene, respectively. Fluorenyl monomer 4 exhibited a significantly lower −ΔH = 18 kcal/mol alkylene, due to incomplete conversion.
Table 1. Polymerization Events and Polynaphthalene Properties

<table>
<thead>
<tr>
<th>Monomer</th>
<th>$T_{im}$ peak (°C)$^a$</th>
<th>$T_{cure}$ (°C)$^b$</th>
<th>Exotherm (kcal/mol)$^b$</th>
<th>Gel Range at 210°C (%) at 450°C J/g</th>
<th>Wt. Loss at 450°C (%)</th>
<th>Yield at 900°C (%)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>190 210 650 (109)</td>
<td>-</td>
<td>-</td>
<td>3.5–5.0</td>
<td>1.5</td>
<td>88</td>
</tr>
<tr>
<td>2</td>
<td>108 205 848 (116)</td>
<td>-</td>
<td>-</td>
<td>3.2–4.3</td>
<td>1.0</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>173 200 789 (107)</td>
<td>-</td>
<td>-</td>
<td>2.9–4.3</td>
<td>0.5</td>
<td>98</td>
</tr>
<tr>
<td>4</td>
<td>105 210 413 (71)</td>
<td>-</td>
<td>-</td>
<td>1.6–3.7</td>
<td>1.2</td>
<td>93</td>
</tr>
</tbody>
</table>

$^a$ 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 mechanical 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! Temperature required for spontaneous polymerization of bis-(o-diphenyl-ethylthyl)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 ($M_w/M_M$) 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 nor initiators nor produces side products, as similarly found for the linear polymerization of enediyne.$^3$ 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 $\nu$(CC) at 2100 cm$^{-1}$, disappears with the exception of subtle shifts in the 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

Figure 2. Step growth solution (50 wt % trisopropylbenzene) and melt polymerization of 1 at 210 °C by GPC. 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 nonequivalent alkylene signals (88–94 ppm for 1–4) and the formation of adjacent broad signals. New alkylene 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.

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 compositions,$^5$ and expected for developing π-conjugated optoelectronic materials exhibiting conductivity, photo- and electrochromism, and nonlinear optical properties.$^6$ $^7$

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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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