

Comparison of "Polynaphthalenes" Prepared by Two Mechanistically Distinct Routes

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Since its discovery, the Bergman cyclization has suffered from the production of significant amounts of unidentified polymeric byproducts.¹ Subsequently, this isomerization of enediynes to produce aromatic rings was adopted as a method to generate conjugated aromatic polymers. Poly(1,4-naphthalene) (hereafter polynaphthalene),^{2–5} poly-*p*-phenylene (PPP),^{2,3} and poly(bis-*o*-diynyl arene) (BODA polymers)^{4,6} have all been reported using this preparative method. The exclusive production of a benzenic ring during these polymerizations requires either a step-growth mechanism or a highly regioselective chain growth polymerization (vide infra). Herein we report a comparison of polymers produced by an independent route and a "Bergman polymerization." Surprisingly, the latter route does not yield the expected 1,4-linked polyarene. This finding indicates the need for a reevaluation of the structure of this emerging polymer class and provides the first clues as to the identity of the polymeric byproducts arising in small-molecule cycloaromatizations.

Unsubstituted polynaphthalene was first prepared in 1983 by a Kumada reaction with the Grignard reagent derived from 1,4-dibromonaphthalene.⁷ After this work, the synthesis of polynaphthalene via the Bergman cyclization was reported (Figure 1).^{2,3} The color and IR absorption properties of this polymer produced through the diradical route disagreed with those reported for the product of the dehalogenative polymerization. To determine if the structures of these polymers differed significantly, both polymerizations were conducted according to published procedures,^{2,7} and the products were fully characterized. Each polymer displayed spectroscopic data in good agreement with those reported in the literature. However, these published data were not sufficiently detailed to allow the structural differences between the polymer products to be ascertained, and their total insolubility precluded their characterization in solution.

To contrast the ivory polymer prepared by the metal-catalyzed coupling and the red-brown material obtained via the diradical route, the products were analyzed by IR, solid-state NMR, and reflectance UV–vis spectroscopies; pyrolysis GC–MS; and MALDI-TOF MS and compared to a reference oligonaphthalene. α -Ternaphthyl was selected as the reference compound because it contains exclusively 1,4-linkages between the naphthalene residues, as are present in both proposed polymer structures. The IR absorption spectra of the poly(1,4-dibromonaphthalene), poly(*o*-diethynylbenzene), and α -ternaphthyl all displayed a peak around 760 cm^{–1} assigned to the out-of-plane vibrations of four contiguous hydrogens.⁸ Although the poly(1,4-dibromonaphthalene) and α -ternaphthyl displayed peaks in the region corresponding to two adjacent hydrogens, the poly(*o*-diethynylbenzene) had a weaker band at 874 cm^{–1} more closely associated with an isolated hydrogen. Differences between the polymers were further highlighted by the presence of weak

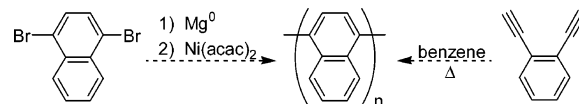


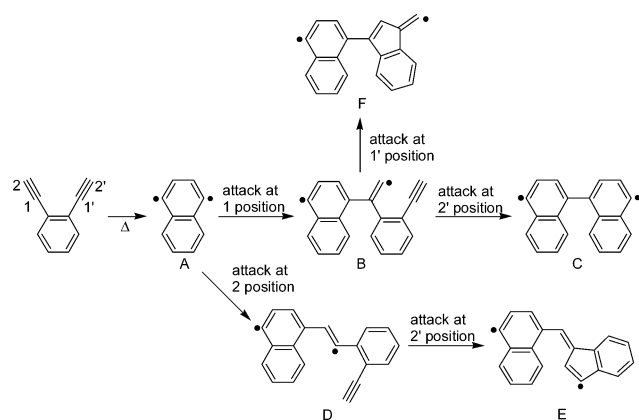
Figure 1. Two routes to polynaphthalene proposed in the literature.^{2,7}

terminal alkyne C–H and C≡C stretches at 3298 and 2104 cm^{–1} in the polymer produced by the diradical route.

Thermogravimetric analysis (TGA) of poly(1,4-dibromonaphthalene) revealed a 10% mass loss at 515 °C, while the poly(*o*-diethynylbenzene) trace showed a 10% mass loss at 435 °C, indicating a lower activation energy for chain scission in the latter, consistent with the presence of weaker bonds in the polymer backbone. This discrepancy prompted the use of pyrolysis GC–MS to obtain information about the decomposition products. This technique rapidly thermolyzes the polymer and then chromatographically separates and analyzes the released molecules by mass spectrometry to provide information about monomer identity and connectivity. The poly(1,4-dibromonaphthalene) gave rise to three types of molecules, accounting for 90% of the total area, corresponding to naphthalene (80%), two isomeric methylnaphthalenes (8.6%), and a dimethylnaphthalene (1.4%).⁹ Under the same conditions, the α -ternaphthyl displayed a large peak (91% of the total area) for naphthalene and two smaller peaks corresponding to methylnaphthalenes, comprising 4.4% of the total area. By contrast, the chromatogram obtained from the pyrolysis of poly(*o*-diethynylbenzene) had major peaks assigned to naphthalene (24% of the total area), methylnaphthalenes (20%), indene (22%), two isomeric methylindenes (24%), and dimethylnaphthalenes (6.5%). The observations of significant amounts of five-membered rings (indenes) and the increased percentage of methylnaphthalene released by the poly(*o*-diethynylbenzene) offer strong evidence that the structure of this polymer is not a simple 1,4-linked polynaphthalene.

A further difference in behavior between the two "polynaphthalenes" was discovered during routine characterization of their molecular weights by LDI-TOF and MALDI-TOF mass spectrometry. Here too, α -ternaphthyl was employed as a model compound to probe for potential fragmentation reactions. Analysis of the α -ternaphthyl, both as a neat powder and in matrix, resulted exclusively in molecular ion formation. The analysis performed on the poly(1,4-dibromonaphthalene) in a dithranol matrix yielded a spectrum with peaks spaced by one naphthalene unit ($M_n = 2000$ g/mol). Polymer chains consisting of up to 31 repeat units were observed under these conditions. In addition, all major species had hydrogen end groups, indicative of a hydrodebromination chain-termination process.¹⁰ Analysis of the poly(*o*-diethynylbenzene) under the same conditions used for that of poly(1,4-dibromonaphthalene) failed to cause polymer desorption and ionization. Though LDI-TOF performed on poly(1,4-dibromonaphthalene) resulted in

Scheme 1



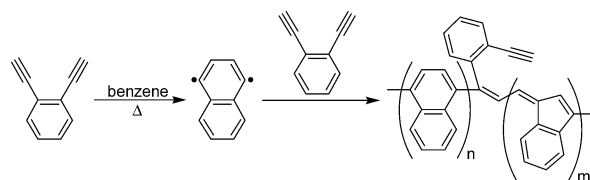
spectra showing intact polymer chains, analysis of poly(*o*-diethynylbenzene) at the same laser power leads to numerous peaks of odd mass (fragments) consistent with a polymer ablation process.¹¹

Additional insight into the structural differences between the polymers was obtained with ¹³C cross polarization magic angle spinning (CP-MAS) NMR. The poly(1,4-dibromonaphthalene) showed peaks in the NMR spectrum at 138 (1,4 positions), 133 (4a,8a positions), and 126 ppm (2,3,5,6,7,8 positions). Integration of these resonances provides a qualitative ratio of 1:1:3. The observed chemical shifts are comparable in position to those in α -ternaphthyl: 139 (1,4 positions), 134 (4a,8a positions), and 126 ppm (2,3,5,6,7,8 positions). By contrast, the spectrum of the poly(*o*-diethynylbenzene) contained a broad peak at 126 ppm and a very broad peak at 48 ppm.

Consideration of the mechanism of the diradical polymerization provides a likely explanation as to why the polymer generated through this route differs so substantially from the poly(1,4-dibromonaphthalene). The Bergman cyclization proceeds through a *p*-didehydroarene intermediate which, for the case of *o*-diethynylbenzene,¹² is 17.8 kcal mol⁻¹ higher in energy than the starting diyne. This energy difference ensures that the concentration of the 1,4-didehydronaphthalene intermediate will be very low and suggests that direct attack on the diyne is likely to occur in the high concentration of monomer (1 M) present during the polymerization. Thus, the generation of polynaphthalene by this route requires a highly regioselective attack at the 1 position, giving diradical **B**, and subsequent attack at the 2' position to yield naphthyl residue **C** (Scheme 1). However, intermediate **B** can cyclize on the 1' carbon to yield a benzofulvenyl residue (**F**).^{13,14} By contrast, if initial reaction with the monomer takes place at the less hindered 2 position, this yields diradical **D**. Internal cyclization of this diradical adds a benzofulvenyl residue to give **E**. Intermediates **F** and **E** are consistent with five-membered ring species observed in the pyrolysis GC-MS experiment of the poly(*o*-diethynylbenzene).

Scheme 1 is reasonable, provided that cyclization of **B** and **D** to **C**, **F**, and **E** occurs faster than the intermolecular addition of a radical to a carbon-carbon triple bond. However, during the reaction the monomer is present in high concentration and will be able to react with a growing polymer chain before **B** and **D** can cyclize, leaving an unreacted ethynyl group appended to the chain (Scheme 2). This accounts for the terminal triple bond observed in the IR spectrum of this polymer. Moreover, cross-linking could occur by addition to this unsaturation or to activated double bonds in the benzofulvene units or polymer backbone.¹⁵ These latter modes

Scheme 2



of reactivity provide an explanation for the presence of the sp³ carbons observed in the solid-state NMR experiment at 48 ppm. The inability to obtain intact chains in the MALDI-TOF MS experiment of poly(*o*-diethynylbenzene) is also suggestive of cross-linking. However, there is clearly a substantial amount of nonaromatic unsaturation remaining as evidenced by rapid bromine uptake (80 wt %) of suspensions of the polymer in CH₂Cl₂. (See Supporting Information.)

To conclude, the polymers prepared by a Kumada coupling and the Bergman cyclization are structurally distinct. Spectroscopic and spectrometric data indicate that the poly(1,4-dibromonaphthalene) is a poly(1,4-naphthalene), whereas the poly(*o*-diethynylbenzene) contains five-membered rings. In light of these dissimilarities, we suggest that these latter polymers not be represented as a poly-(1,4-naphthalene).

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Supporting Information Available: IR spectral data, TGA traces, ¹³C CP-MAS NMR spectra, MALDI-TOF MS data, reflectance UV-vis data, powder X-ray diffraction patterns, and synthetic procedures (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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