Synthesis of Polyphenylenes and Polynaphthalenes by Thermolysis of Enediynes and Dialkynylbenzenes

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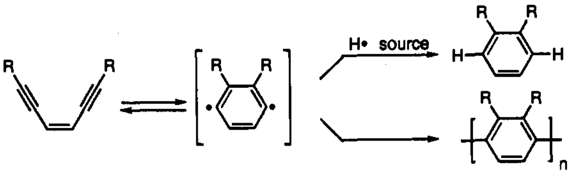
Bergman's study on the thermal cycloaromatization of enediynes led to the suggestion of a benzene 1,4-diradical intermediate.[1] Numerous synthetic and mechanistic studies were later performed to further investigate this reaction, and a variety of enediynes have been thermalized in the presence of radical terminators such as 1,4-cyclohexadiene (eq 1).[1,2] Even though large excesses of radical terminators were employed, the yields of the substituted benzenes were often moderate at best. The fact that the yields were diminutive kindled our interest because it suggested to us that polymerization may indeed be a preferred pathway and we could regard the intermediate benzene 1,4-diradical as a building block for substituted polyphenylenes. As suspected, deletion of the radical trapping source from the reaction mixtures allowed for the formation of substituted polyphenylenes (eq 2).[3]

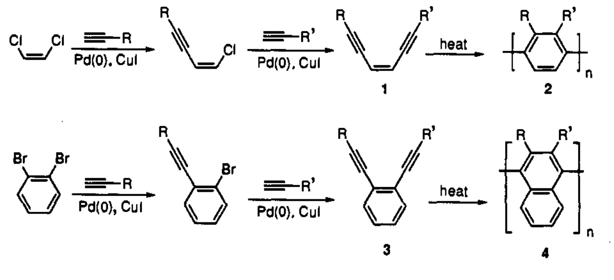


(1)

(2)

Substituted polyphenylenes have been shown to exhibit superb thermal and chemical resilience, interesting semiconducting properties upon doping, and applications in light-emitting diodes.[4,5] Therefore, this route to polyphenylenes and their derivatives is most attractive since (1) it requires no exogenous chemical catalysts or reagents for the polymerization; (2) heteroatomic coupling sites such as halogens are not necessary, and all atoms present in the monomer are also present in the polymer; and (3) the monomers can be rapidly prepared with a variety of substitution patterns to often afford soluble polyphenylene derivatives.

We could rapidly prepare numerous enediynes and dialkynylbenzenes by the Pd/Cu coupling protocol or an alkynylzinc chloride/Pd coupling.[6,7] Subsequent heating of the enediynes or dialkynyl aromatics led to polymerization products (eqs 3 and 4). The results of the polymerization are summarized in Table 1. We found that highest molecular weights could be obtained using benzene as a solvent and heating the monomers in thick-walled screw cap glass tubes[8] at 50–160 °C. In a few cases, when the polymerizations required higher temperatures, they were conducted on neat materials.



(3)

(4)

In general, monomers that had both R = H and R′ = H afforded insoluble polymers. Monomers that had either R = H or R′ = H readily polymerized to afford soluble polymers. In the cases where neither R = H nor R′ = H, the polymerizations were often slower and they required higher temperatures and neat reaction conditions, which likely caused polymer decomposition as flagged by the black color of the products (Table 1). The yields of the polymerized material were generally 50–90% after fractional precipitation. The obtained M_n values of 1500–2500 are quite typical for *p*-polyphenylene derivatives.[4] Note, however, that SEC-determined values of M_n versus polystyrene standards are inflated due to hydrodynamic volume differences of rigid rod polymers versus the randomly coiled polystyrene standards.

The superb thermal stabilities are apparent in that, in many cases, the unannealed polymers exhibited 10% weight loss only after exceeding 400–600 °C (Table 1). Being unannealed, some of the early weight loss could be attributed to occluded solvent; therefore, these values represent a lower limit for thermal degradation.

The IR spectra are most informative in confirming the structure of the proposed polymers.[9] For the monosubstituted polyphenylenes (Table 1, entries 1–7), the polymer repeat unit possesses a 1,2,4-substituted phenyl pattern. The most diagnostic bands at 935–810 cm^{-1} are assigned to the bending of a lone hydrogen at the 3-position, and the band at 880–795 cm^{-1} arises from the bending of two adjacent hydrogens at the 5- and 6-positions. Assignment of the disubstituted polyphenylenes can best be described using the bis(trimethylsilyl) derivative (Table 1, entry 9). The shoulder above 3000 cm^{-1} comes from the C–H stretching vibration. The band at 838 cm^{-1} results from out-of-plane C–H

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(1) Lockhart, T. P.; Comita, P. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4082. Lockhart, T. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4091. Bergman, R. G. *Acc. Chem. Res.* **1973**, *6*, 25. Jones, R. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 660.

(2) Lee, M. D.; Dunne, T. S.; Chang, C. C.; Ellestad, G. A.; Siegel, M. M.; Morton, G. O.; McGahren, W. J.; Borders, D. B. *J. Am. Chem. Soc.* **1987**, *109*, 3466. Golik, J.; Dubay, G.; Groenewold, G.; Kawaguchi, H.; Konishi, M.; Krishnan, B.; Ohkuma, H.; Saitoh, K.; Doyle, T. W. *J. Am. Chem. Soc.* **1987**, *109*, 3462. Beau, J. M.; Crevisy, C. *Tetrahedron Lett.* **1991**, *32*, 3171. Wender, P. A.; McKinney, J. A.; Mukai, C. *J. Am. Chem. Soc.* **1990**, *112*, 5369. Nicolaou, K. C.; Dai, W.-M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1387.

(3) (a) Recently, Bergman reported a double cycloaromatization based on a conjugated dienetriyne. See: Bharucha, K. N.; Marsh, R. M.; Minto, R. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 3120. (b) Likewise, recent tandem cyclizations have been accomplished by Grissom. See: Grissom, J. W.; Calkins, T. L.; McMillen, H. A. *J. Org. Chem.* **1993**, *58*, 6556. Grissom, J. W.; Klingberg, D. *J. Org. Chem.* **1993**, *58*, 6559. (c) Swager and Grubbs used a similar cascade sequence to cycloaromatize a poly(arylene–ethynylene). See: Zhou, Q.; Swager, T. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34*, 193. Grubbs, R. H.; Kratz, D. *Chem. Ber.* **1993**, *126*, 149.

(4) For some reviews on polyphenylene, see: (a) Kovacic, P.; Jones, M. B. *Chem. Rev.* **1987**, *87*, 357. (b) Noren, G. K.; Stille, J. K. *Macromol. Rev.* **1971**, 5, 385. (c) Elsenbaumer, R. L.; Shacklette, L. W. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Dekker: New York, 1986. (d) Tour, J. M. *Adv. Mater.* **1994**, *6*, 190. (e) Baughman, R. H.; Brédas, J. L.; Chance, R. R.; Elsenbaumer, R. L.; Shacklette, L. W. *Chem. Rev.* **1982**, *82*, 209(5) For use in light-emitting diodes, see: Grem, G.; Günther, L.; Ullrich, B.; Leising, G. *Adv. Mater.* **1992**, *4*, 36.

(6) (a) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467. Stephans, R. D.; Castro, C. E. *J. Org. Chem.* **1963**, *28*, 3313. Suffert, J.; Ziessel, R. *Tetrahedron Lett.* **1991**, *32*, 757. (b) The terminal alkyne units on the monomers were affixed to the alkenyl or aryl halides using (trimethylsilyl)acetylene followed by TMS removal with K_2CO_3/MeOH.

(7) In most cases involving alkyne coupling to 1,2-dibromobenzene, we could obtain higher yields using the Pd(0)-catalyzed coupling of the alkynylzinc chloride to the aryl bromide. See: Negishi, E.; Takahashi, T.; Baba, S.; Van Horn, D. E.; Okukado, N. *J. Am. Chem. Soc.* **1987**, *109*, 2393.

(8) CAUTION! The threaded glass tubes were obtained from Ace Glass Inc., product 8648. Though we experienced no explosions in more than 50 reaction runs studied, thermalization processes should be carried out behind protective shielding.

(9) (a) Bellamy, L. J. *The Infra-red Spectra of Complex Molecules*; Wiley: New York, 1975. (b) Lin-Vien, D.; Colthup, N. B.; Fateley, W. G.; Grasselli, J. G. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*; Academic: New York, 1991. (c) Mayer, R.; Kleinert, H.; Richter, S.; Gewald, K. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 115. (d) *The Aldrich Library of FT-IR Spectra, Edition I*; Pouchert, C. J., Ed., Aldrich Chemical Company: Milwaukee, 1985.

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Table 1. Thermal Polymerization of Enediynes and Dialkynylarenes To Afford Polyaromatics[a]

entry	monomer	R	R′	temp[b]	M_w[c,d]	M_n[d,e]	solubility[f]	$T_{10\%}$[g,h]	$T_{50\%}$[h,i]	color[j]
1	**1**	H	*n*-C_6H_{13}	120	3930	1570	soluble	287	472	brown
2	**1**	H	Ph	150	305 000[k]	9500	soluble	392	>900	tan
3	**1**	H	(*p*-C_6H_4)Ph	95	10 600	4100	soluble	438	>900	tan
4	**1**	H	(*o*-C_6H_4)Ph	50–90	3200	2000	soluble	432	791	tan
5	**1**	H	(*p*-C_6H_4)CMe_3	50–95	6500	2600	soluble	428	898	brown
6	**1**	H	1-naphthyl	115	5500	1450	soluble	416	>900	tan
7	**1**	H	9-anthryl	120	9400	800	partially soluble[l]	351	>900	orange[m]
8	**1**	*n*-C_6H_{13}	*n*-C_6H_{13}	140	980	810	soluble[n]	178	375	green
9	**1**	$SiMe_3$	$SiMe_3$	300[o]	2850	1040	soluble	248	490	black
10	**3**	H	H	140	–	–	insoluble	500	>900	brown
11	**3**	H	Ph	140	1200	850	soluble	380	617	tan
12	**3**	Ph	Ph	400[o]	–	–	insoluble	606	>900	black
13	**3**	*n*-C_6H_{13}	*n*-C_6H_{13}	340[o]	–	–	insoluble	507	>900	black

[a] Dashes signify that the value was not obtained or it was not clearly discernible during the analysis. Unless otherwise noted, all reactions were carried out in a thick-walled screw-capped tube in benzene (0.7–1.1 M) as the solvent. [b] Temperature in °C used for the polymerization. The reaction times were generally 24–48 h. [c] Weight average molecular weights. [d] Determined by size exclusion chromatography (SEC) in THF versus polystyrene standards. [e] Number average molecular weights. [f] Solubility in THF or CH_2Cl_2. [g] Temperature in °C at which 10% weight loss occurred. [h] Determined by thermogravimetric analysis (TGA) from 50 to 900 °C at 10 °C/min under an N_2 atmosphere. [i] Temperature in °C at which 50% weight loss occurred. [j] Color of neat polymer. [k] We presently have no explanation for the very broad polydispersity. [l] SEC data obtained on the soluble portion and TGA data obtained on the insoluble portion. [m] The monomer had an intense orange color. [n] Material was predominantly unreacted monomer. [o] The reaction was run without solvent.

bending of two adjacent hydrogen atoms bound to a phenyl ring. Analysis of the 1,2-dialkynylbenzene-derived polymers argued in favor of the 1,4-disubstituted naphthalene structure (eq 4). For example, for the simplest case where R = R′ = H (Table 1, entry 10), bands at 1595, 875 (two adjacent H atoms), and 754 (four adjacent H atoms) agreed with the literature values for 1,4-disubstituted naphthalenes.[9]

The mechanistic aspects of the polymerization process are intriguing.[10] Two general mechanisms are considered. First, a benzene 1,4-diradical may be attacking unreacted enediyne to generate a new biphenyl 4,4′-diradical intermediate. Continued reaction of this growing chain with enediyne should result in a chain growth like polymerization process in that the molecular weight of the polymer would increase rapidly even at low monomer conversions. Conversely, the benzene 1,4-diradical may predominantly couple with other radicals in solution to eventually form the polymer. In that case, the process should be step growth like where the polymer molecular weight would initially increase slowly, but then increase rapidly when monomer conversion was nearly complete. By monitoring consumption of **1** (R = H, R′ = Ph) (using capillary GC with terphenyl as an internal standard) and molecular weight (M_n by SEC), it was clear that the molecular weight increased slowly (M_n = 600 at 10% monomer consumption and 810 at 90% monomer consumption) until the monomer was nearly consumed (>97%), whereupon the molecular weight increased exceedingly rapidly. Therefore, the polymerization indeed resembles a step growth process. It should be noted, however, that a chain growth mechanism cannot be ruled out in that the propagating species may be unstable, giving rapid chain transfer and/or termination. Also, addition of small amounts of radical initiators did not increase the polymerization efficiency.

As a further confirmation of the radical coupling process described here, we carried out the thermalization process for two of the monomers in the presence of some of the radical trapping agent 1,4-cyclohexadiene. This was done with the hope of obtaining some small, characterizable dimeric species. Indeed, when **1** (R = H, R′ = Ph) was heated in benzene in the presence of 1,4-cyclohexadiene (33 mol %) at 150 °C, we observed the formation of polymeric material as well as several low molecular weight species detected by GC/MS analysis. The volatile material consisted of unreacted starting material, biphenyl (154 amu), and the desired dimeric adduct quaterphenyl (306 amu). Likewise, when **3** (R = R′ = H) was heated in benzene in the presence of 1,4-cyclohexadiene (21 mol %) at 150 °C, polymer was formed as well as several volatile species. The volatile material consisted of unreacted starting material, naphthalene (128 amu), 1,4-cyclohexadienyl addition/aromatization products, and the desired dimer 1,1′-binaphthalene (254 amu). The isotopic pattern and fragmentation pattern matched identically with the data base derived 1,1′-binaphthalene spectrum.

Finally, it has been shown that (*E*)-enediynes do not undergo the Bergman cyclization.[1] We therefore prepared (*E*)-1-phenylhex-3-ene-1,5-diyne. Heating this monomer to 150 °C for 2 days did indeed form a polymer, however, FTIR analysis verified that it was not a polyphenylene-derived material in that the two bands at 935–810 and 880–795 cm^{-1} were missing.

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Supplementary Material Available: Detailed synthetic procedures and characterization data for the synthesis of the monomers and polymers listed in Table 1 (16 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(10) Grissom, J. W.; Calkins, T. L. *J. Org. Chem.* **1993**, *58*, 5422.