

AD-A273 219



①

OFFICE OF NAVAL RESEARCH

GRANT : N00014-89-J-3062

R&T Code 4132084

Technical Report No. 15

Metal-Catalyzed Alkynylation of (Bromophenyl)oligophenylenes. A Rapid Route to
Thermoset Precursors of High Density Monolithic Glass-Like Carbon

by

E. B. Stephens and J. M. Tour

Accepted for Publication in

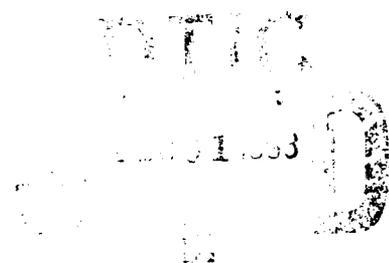
Advanced Materials

Department of Chemistry and Biochemistry
University of South Carolina
Columbia, SC 29208

November 22, 1993

Reproduction in whole, or in part, is permitted for any purpose of the United States Government

This document has been approved for public release and sale; its distribution is unlimited.



93 11 200 11

1993 93-29309



REPORT DOCUMENTATION PAGE			Form Approved OMB No 0704-0188	
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204 Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188) Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 11/22/93	3. REPORT TYPE AND DATES COVERED Technical Report		
4. TITLE AND SUBTITLE Metal-Catalyzed Alkynylation of (Bromophenyl)oligophenylenes. A Rapid Route to Thermoset Precursors of High Density Monolithic Glass-Like Carbon.			5. FUNDING NUMBERS G- N00014-89-J3062 R&T 4132084	
6. AUTHOR(S) Stephens, E. B.; Tour, J. M.				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry and Biochemistry University of South Carolina Columbia, SC 29208			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Department of the Navy Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5000			10. SPONSORING/MONITORING AGENCY REPORT NUMBER 15	
11. SUPPLEMENTARY NOTES <i>Adv. Mater.</i> 1992, 4, 570.				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Reproduction in whole or in part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The functionalization of (bromophenyl)oligophenylene with several alkynes is described. The bromide groups on the oligomer were replaced with terminal alkynes using a Pd/Cu catalysts system. Substitution of nearly all the original bromide locations was achieved. The functionalized oligomers, freely soluble in THF, exhibited high char yields on thermolysis to 900°C under a nitrogen atmosphere. Several of the functionalized oligomers flowed on heating. The oligomer that was functionalized with phenylacetylene exhibited a well-defined melting point at 190°C and acetylenic coupling did not take place until 310°C. The hot oligomer flowed to form a monolith of glassy carbon. Depending on the alkyne used, a range of densities from 1.39-1.95 g/cc could be obtained in the final carbon glass. The structure/property relationships and the material applications are discussed.				
14. SUBJECT TERMS			15. NUMBER OF PAGES	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	

Submitted as a communication.

DTIC QUALITY INSPECTED 1

Metal-Catalyzed Alkynylation of (Bromophenyl)oligophenylene.

Thermoset Precursors of High Density Monolithic Carbon Glass

Eric B. Stephens and James M. Tour*,¹
Department of Chemistry and Biochemistry
University of South Carolina
Columbia, South Carolina 29208

NTIS	CRA&I	<input checked="" type="checkbox"/>
DTIC	TAB	
Unannounced		
Justification		
By		
Date		
Number of Copies		
Dist	Availability or Special	

A-1

The functionalization of (bromophenyl)oligophenylene with several alkynes is described. The bromide groups on the oligomer were replaced with terminal alkynes using a Pd/Cu catalysts system. Substitution of nearly all the original bromide locations was achieved. The functionalized oligomers, freely soluble in THF, exhibited high char yields on thermolysis to 900°C under a nitrogen atmosphere. Several of the functionalized oligomers flowed on heating. The oligomer that was functionalized with phenylacetylene exhibited a well-defined melting point at 190°C and acetylenic coupling did not take place until 310°C. The hot oligomer flowed to form a monolith of glassy carbon. Depending on the alkyne used, a range of densities from 1.39-1.95 g/cc could be obtained in the final carbon glass. The structure/property relationships and the material applications are discussed.

Carbon materials produced by the thermolysis of organic polymers have been used for numerous applications in, for example, the aerospace, electronic, medical implant and automotive industries.² Phenolic resins have dominated as thermoset precursors to carbon; however, phenolics typically exhibit 35-40% weight loss on thermolysis and densities of the char are ~ 1.3 g/cc.² Since phenolics exhibit large weight losses and low density chars, the use of multiple impregnation cycles (usually 6-7) are required for the production of high performance carbon products possessing densities of 1.8-1.9 g/cc.^{2,3} In an effort to limit the number of impregnation cycles (the cost-determining step) necessary for high density carbon preparation, the development of high char yielding materials from alkyne-containing organics has been investigated by many.⁴ Unfortunately, the difficulty in preparing the alkyne-containing monomers and the explosive nature of the multi-alkynylaromatics have retarded the rapid development and commercialization of this process.

We describe here the synthesis of oligomers possessing two required features that make them suitable for thermoset precursors to high performance, high density glassy carbon materials. First, the oligomers have very low weight loss (high char yield, low outgassing) on conversion to glassy carbon so that significant void volume will not result in the molds. Second, the materials exhibit a well-defined melting point, even a gravity-induced flowing, prior to conversion to carbon so that processing in the melt is possible to produce carbon monoliths.

We previously described a one step synthesis of brominated oligophenylenes from 1,4-dibromobenzene in dioxane with HMPA.^{5,6} Recently, we described an alternative procedure that does not require the use of the cancer suspect agent HMPA and affords a 65% yield of an ether insoluble portion of **1a** ($n = m$) but possessing less *para* linkages than the oligomers prepared by the HMPA method (Figure 1).⁷

Figure 1

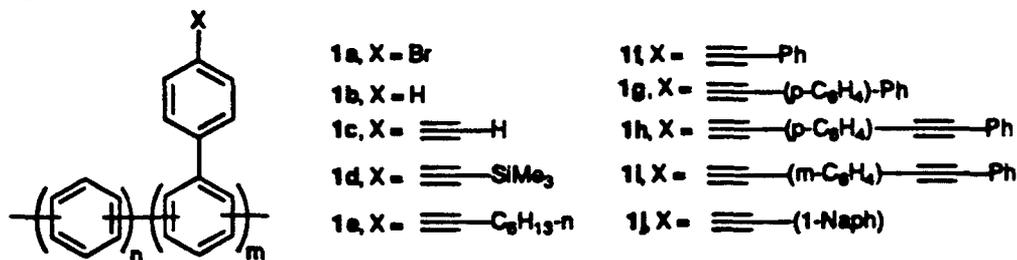


Table I

Compound	M_n^c	M_w/M_n^c	$T_{10\%}^d$	% Wgt Loss ^e	T_g^f , ^g	T_m^h , ^h	$T_{exo}^{g,i}$
1a ^a	500	3.9	400	48	---	155, 170	NA
1b	860	2.7	430	52	---	170, 225	NA
1c ^b	980	3.9	638	17.5	182	---	360
1d	570	6.6	378	27	---	140	160
1e	1010	3.3	430	33	---	140	170
1f	970	2.8	690	13.5	---	190	310
1g	1200	3.0	643	15.5	---	205	310
1h	1170	3.5	768	11.5	206	---	350
1i	1170	3.2	810	10.7	203	---	350
1j	1710	2.1	730	12.9	---	200	230

^aPrepared in THF without HMPA according to ref 7. All other compounds in this Table were prepared from 1a except 1e which was prepared from the brominated oligomer made with HMPA as in ref 5. ^bPrepared by treatment of 1d with K₂CO₃ in THF/CH₃OH. ^cDetermined by size exclusion chromatography (SEC) relative to polystyrene.⁹ ^dTemperature at which 10% weight loss occurred by thermogravimetric analysis (TGA) from ambient to 900°C at 20°C/min under an N₂ atmosphere. ^eTotal percent weight loss by TGA under the conditions listed in d. ^fOligomer glass transition temperature. ^gDetermined by differential scanning calorimetry (DSC) from 60°- 500°C at 20°C/min under an N₂ atmosphere. Dashed lines signify that these values were not clearly discernible by the DSC. ^hOligomer melt temperature. ⁱLarge exotherm characteristic of alkyne couplings. NA means not applicable.

All oligomers prepared were soluble in THF. Though 1a exhibits a high carbon to hydrogen (C/H) ratio, neither the brominated oligomer 1a nor the debrominated material 1b^g exhibited high char yields on heating (Table I).

In order to enhance the char yield, we needed to prevent volatilization on heating by appending a suitable thermo-activated cross-linking substituent. However, the moiety must not cross-link prior to the oligomer melting or else the desired flow properties would not be maintained. Additionally, the introduction of heteroatoms would be prohibited if a high char yield of carbon materials was to be achieved. Alkynes are known to form cross-linked alkenes and/or cyclotrimerize on thermolysis.⁴ Accordingly, we investigated the metal-catalyzed alkylation of **1a** that would concomitantly replace the bromide heteroatoms. Following the Stephans-Castro/Sonogashira protocol,¹⁰ **1a** was treated with various terminal alkynes in a THF solution containing diisopropylamine, both a CuI catalysts and Cl₂Pd(PPh₃)₂ or Pd(PPh₃)₄ catalyst (23°C for 1 h, 60°C for 10 h, and 100°C for 5 h in a threaded screw cap reaction tube) to produce **1d-j**. In most cases, complete bromide substitution was achieved as determined by elemental analysis.¹¹

Several structure/property relationships were clearly evident and allowed us to rapidly converge on thermoset precursors for glassy carbon. Though **1c** exhibited a high char yield, the terminal alkyne was too unhindered and the cross-linking event occurred without a well-defined melt by DSC analysis. Oligomers **1d** and **1e** which have more hindered alkynes than **1c**, exhibited well-defined melts; however, the introduction of the aliphatic material decreased the C/H ratio resulting in a lower char yield than desired. Remarkably, by simply substituting **1a** with phenyl acetylene to produce **1f** (amorphous by powder x-ray diffraction (XRD)), we obtained a very high char yield and the oligomer exhibited a well-defined melt at 190°C while the coupling event did not occur until 310°C by DSC analysis. *Hence a 120°C processing window exists for this glassy carbon precursor.* Gravity flow of the melted material occurred to form a glossy black monolithic disc of glassy carbon. The polydispersity of **1f** could be lowered by purification of the oligomers by fractional precipitation; however, the flow properties then decreased significantly. Likewise,

when we phenylacetylated a brominated oligophenylene having more *para* linkages prepared by the HMPA route,⁵ the flow properties on thermolysis were impaired. Thus more rigid oligomer backbones are inferior. Compounds 1g-j were also prepared and studied; however, they offered no significant char yield advantage over 1f.¹² Moreover, the reagent necessary for 1f, phenylacetylene, is commercially available. The densities of the charred compounds also varied significantly. Carbon materials derived from 1f, 1h, and 1i, had densities of 1.83, 1.95, and 1.39 g/cc, respectively.¹³ This represents an unusually large range of structural variability obtainable in the carbon material. The very high densities and char yields of 1f and 1h make these materials attractive for use as thermoset precursors to high performance carbon materials by limiting the needed impregnation cycles to 1-2. Powder XRD of the charred material from the thermolysis of 1f, 1h, and 1i confirmed the presence of glassy carbon with no signals for the graphitic crystallite.

Hence, organometallic methods permit a two step (oligomerization and functionalization) entry into thermoset precursors for high density glassy carbon.

Acknowledgements. This research was funded by the Department of the Navy, Office of the Chief of Naval Research, Young Investigator Program (N00014-89-J-3062), the National Science Foundation (RII-8922165, DMR-9158315, DMR-9101539), and generous industrial donors to the NSF/PYI award: Hercules Incorporated, IBM Corporation, Ethyl Corporation, and the Shell Development Company. We thank Dr. T. Keller of the Naval Research Laboratories for suggestions, and Dr. H. Jabloner of Hercules Incorporated for the density measurements and helpful suggestions.

Supplemental Material. Detailed experimental procedures for the preparation of the terminal alkynes and the preparation of 1a-j are provided as well as the TGA and DSC plots for 1a-j and the powder XRD plot of the char from 1f.

References and Notes

(1) Recipient of an Office of Naval Research, Young Investigator Award (1989-92) and National Science Foundation Presidential Young Investigator Award (1991-96).

(2) (a) Fitzer, E. In *Contemporary Topics in Polymer Science*, Vandenberg, E. J., Ed. Vol 5, Plenum: New York, 1984. (b) Wallenberger, F. T. *Angew. Chem. Internat. Ed. Engl.* 1964, 3, 460. (c) Fitzer, E.; Grieser, F. *Proceedings of the Fifth London International Carbon and Graphite Conference*, 1978, 1, 266. (d) Fitzer, E.; Geigl, K.-H.; Hüttner, W. *Proceedings of the Fifth London International Carbon and Graphite Conference*, 1978, 1, 493. (e) Bilow, N.; Miller, L. J. *J. Macromol. Sci. (Chem.)*, 1967, A1(1), 183. (f) Ehlers, G. F. L.; Fisch, K. R.; Powell, W. R. *J. Polym. Sci. Part A* 1969, 7, 2931. (g) Ried, W.; Freitag, D. *Angew. Chem. Internat. Ed. Engl.* 1968, 7, 835. (h) Fitzer, E. *Pure Appl. Chem.* 1980, 52, 1865. (i) Fitzer, E.; Kalka, J. *High Temp. High Press.* 1971, 3, 53. (j) Fitzer, E.; Mueller, K.; Schaefer, W. In *The Chemistry and Physics of Carbon* Vol 7, Dekker: New York 1971, p 237. (k) Noren, G. K.; Stille, J. K. *Macromolec. Rev.* 1971, 5, 385. (l) Keller, T. M. *Polym. Commun.* 1990, 31, 229. (m) Wallenberger, F. T. *Angew. Chem. Internat. Ed. Engl.* 1964, 3, 460. (n) Jenkins, G. M.; Kawamura, K. *Polymeric Carbons-Carbon Fibre, Glass and Char*; University Press: Cambridge, 1976. (o) Kinoshita, K. *Carbon: Electrochemical and Physicochemical Properties*; Wiley: New York, 1988. (p) Gupta, A. K.; Paliwal, A. K.; Bajaj, P. J. *Macromolec. Sci., Macromolec. Chem. Phys.* 1991, C31, 1.

(3) (a) Vinson, J. R.; Chou, T.-W. *Composite Materials and Their Use in Structures*, Applied Science: London, 1975. (b) Molyneux, M. In *Carbon Fibres in Engineering*, Langley, M., Ed., McGraw Hill: London, 1973.

(4) (a) Hay, A. S. *J. Org. Chem.* 1960, 25, 1275. (b) Neenan, T. X.; Whitesides, G. M. *J. Org. Chem.* 1988, 53, 2489 (c) Neenan, T. X.; Callstrom, M. R.; Scarmoutzos, L. M.; Stewart, K. R.; Whitesides, G. M.; Howes, V. R. *Macromolecules* 1988, 21, 3525. (d)

Callstrom, M. R.; Neenan, T. X.; Whitesides, G. M. *Macromolecules* 1988, 21, 3528. (e) Stille, J. K.; Rutherford, D. R. *Macromolecules* 1988, 21, 3530. (f) Hay, A. S.; *J. Polym. Sci., Polym. Chem. Ed.* 1969, 7, 1625. (g) White, D. M. U.S. Pat. 4 020 256, 1977. (j) Korshak, V. V.; Gribova, I. A.; Krasnov, A. P.; Sergeev, V. A.; Shitikov, V. K.; Elerdashvili, G. V. U.S. Pat. 3 765 982, 1973. (h) Jabloner, H. U.S. Pat. 4 070 333 and 4 097 460, 1978. (i) Economy, J. In *Contemporary Topics in Polymer Science*, Vandenberg, E. J., Ed. Vol 5, Plenum: New York, 1984. (j) Dawson, D. J.; Fleming, W. W.; Lyster, J. R.; Economy, J. In *Reactive Oligomers*; ACS Symposium Series 282; American Chemical Society: Washington, DC, 1982. (k) Hergenrother, P. M. In *Reactive Oligomers*; ACS Symposium Series 282; American Chemical Society: Washington, DC, 1986. (l) Baughman, R. H.; Eckhardt, H.; Kertesz, M. *J. Chem. Phys.* 1987, 87, 6687. (m) Baughman, R. H.; Yee, K. C. *J. Polym. Sci.: Macromolec. Reviews* 1978, 13, 219. (n) Callstrom, M. R.; Neenan, T. X.; McCreery, R. L.; Alsmeyer, D. C. *J. Am. Chem. Soc.* 1990, 112, 4954.

(5) Tour, J. M.; Stephens, E. B. *J. Am. Chem. Soc.* 1991, 113, 2309.

(6) For several reviews on polyphenylenes, see: (a) Kovacic, P.; Jones, M. B. *Chem. Rev.* 1987, 87, 357. (b) Tourillon, G. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Dekker: New York, 1986. (c) Elsenbaumer, R. L.; Shacklette, L. W. in ref 2c. (d) Baughman, R. H.; Bredas, J. L.; Chance, R. R.; Elsenbaumer, R. L.; Shacklette, L. W. *Chem. Rev.* 1982, 82, 209.

(7) Tour, J. M.; Stephens, E. B.; Davis, J. F. *Macromolecules*, 1992, 25, 499.

(8) The debromination was achieved by treatment of 1a with *tert*-butyllithium as described in ref. 5 and 7.

(9) The SEC-determined M_w of these oligomers versus polystyrene standards was within 5% of the M_w values determined using oligophenylenes standards. See ref 5.

(10) (a) Sonogashira, K.; Tobda, Y.; Hagihara, N. *Tetradedron Lett.* 1975, 4467.
(b) Stephans, R. D.; Castro, C. E. *J. Org. Chem.* 1963, 28, 3313. (c) Suffert, J.; Ziesel, R.
Tetrahedron Lett. 1991, 32, 757.

(11) Less than 0.5% Br was detected by elemental analysis in 1e-j. Compounds 1c and 1d showed 3.00% and 5.85% Br, respectively.

(12) The thermolyzed compounds had the following appearances after the TGA analyses: 1a was a glossy black porous disc; 1b, 1d, 1e, and 1g each formed several glossy black droplets; 1c was a black powder; 1h and 1i each formed dull gray meshes; 1j formed a single glossy black droplet; and 1f formed a glossy black monolithic disc. Thus, in addition to 1f, compounds 1g, 1h, 1i and 1j appear to be suitable for glassy carbon thermosets if a typical hot pressure system is employed.

(13) The densities were calculated using the very finely ground charred materials suspended in halocarbon solvent mixtures of known density.