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Thermoset Precursor to Monolithic Carbon Glass Prepared by the Pd/Cu-Catalyzed Alkynylation of Polyphenylenes.

by

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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 catalysis 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.

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Thermosets, glassy carbon, high density, polyphenylene, cross coupling

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Thermoset Precursor to Monolithic Carbon Glass Prepared by the Pd/Cu-Catalyzed Alkynylation of Polyphenylenes

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Carbon materials produced by the thermolysis of organic polymers have been used for numerous applications in, for example, the aerospace, electronic, and automotive industries.² Development of high char yielding carbon materials from alkyne-containing organics has been investigated by many; unfortunately, the difficulty in preparing the alkyne-containing monomers and the explosive nature of the multi-alkynylaromatics has retarded the rapid development and commercialization of this process.³

We describe here the synthesis of a polymer possessing two required features that make it suitable for a thermoset precursor to glassy carbon. First, the polymer has very low weight loss (high char yield) on conversion to glassy carbon so that significant void volume will not result in the molds. Second, the material exhibits 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. Though many carbon applications do not require these two features, they are a necessity if the material is to have uses as a thermoset precursor. Such precursors may have wide-spread applications ranging from uses in electronic components to rocket booster ablatives.^{2,3}

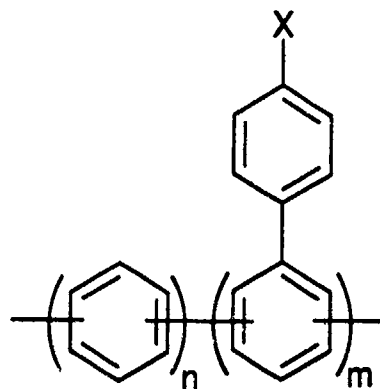
We previously described a one step synthesis of brominated polyphenylenes from 1,4-dibromobenzene in dioxane with HMPA.^{4,5} Recently, we described an alternative procedure that does not require the use of the cancer suspect agent HMPA and affords a 65% yield of an ether insoluble portion of 1a (n = m) but possessing less para linkages than the polymer prepared by the HMPA method (Figure 1).⁶ All polymers prepared were soluble in THF. Though 1a exhibits a high carbon to hydrogen (C/H) ratio, neither the brominated polymer 1a nor the debrominated material 1b⁷ 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.



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Figure 1



1a, X = Br

1b, X = H

1c, X = $\equiv$ -H

1d, X = $\equiv$ -SiMe₃

1e, X = $\equiv$ -C₆H_{13-n}

1f, X = $\equiv$ -Ph

1g, X = $\equiv$ -(p-C₆H₄)-Ph

1h, X = $\equiv$ -(p-C₆H₄)- $\equiv$ -Ph

1i, X = $\equiv$ -(m-C₆H₄)- $\equiv$ -Ph

1j, X = $\equiv$ -(1-Naph)

Table I

#	M_w^c	M_w/M_n	% Wt Loss ^d	$T_g^{e,f}$	$T_m^{f,g}$	$T_{exo}^{f,h}$
1a ^a	1944	3.89	48	---	155, 170	NA
1b	2323	2.68	52	---	170, 225	NA
1c ^b	3834	3.92	17.5	182	---	360
1d	3758	6.63	27	---	140	160
1e	3327	3.32	33	---	140	170
1f	2709	2.80	13.5	---	190	310
1g	3610	3.02	15.5	---	205	310
1h	4089	3.53	11.5	206	---	350
1i	3734	3.21	10.7	203	---	350
1j	3588	2.07	12.9	---	200	230

^aPrepared in THF without HMPA according to ref 6. All other compounds in this Table were prepared from 1a except 1e which was prepared from the brominated polymer made with HMPA as in ref 4. ^bPrepared by treatment of 1d with K_2CO_3 in THF/ CH_3OH . ^cDetermined by size exclusion chromatography relative to polystyrene. ^dTotal percent weight loss by thermogravimetric analysis (TGA) from ambient to 900°C at 20°C/min under an N_2 atmosphere. ^ePolymer glass transition temperature. ^fDetermined by differential scanning calorimetry (DSC) from 60°- 500°C at 20°C/min under an N_2 atmosphere. Dashed lines signify that the these values were not clearly discernable by the DSC. ^gPolymer melt temperature. ^hLarge exotherm characteristic of alkyne couplings. NA means not applicable.

However, the moiety must not cross-link prior to the polymer melting or else the desired flow properties would not be maintained. Moreover, the introduction of heteroatoms would be prohibited if a high char yield of carbon materials was to be achieved. Hence, we investigated the metal-catalyzed functionalization of 1a that would concomitantly replace the bromide heteroatoms. Following the Stephens-Castro/Sonogashira protocol,⁸ 1a was treated with various terminal alkynes in a THF solution containing diisopropylamine, both a CuI catalysts and $Cl_2Pd(PPh_3)_2$ or $Pd(PPh_3)_4$ 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.⁹

Several structure/property relationships were clearly evident and allowed us to rapidly converge on a 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. Polymers 1d and 1e had more hindered alkynes than 1c and they 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 polymer 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, void free monolithic disc of glassy carbon. Powder XRD of the charred material from the thermolysis of 1f confirmed the presence of glassy carbon with no signals for the graphitic crystallite. The polydispersity of 1f could be lowered by purification of the polymers by fractional precipitation, however, the flow properties then decreased significantly. Likewise, when we phenylacetylated a brominated polyphenylene having more para linkages prepared by the HMPA route,⁴ the flow properties on thermolysis were also impaired. Thus more rigid polymer backbones are inferior. Compounds 1g-j were also prepared and studied; however, they offered no advantage over 1f. Though the char yields were slightly better for 1h-j, the final carbon glass had not flowed as significantly as in the case of 1f.¹⁰ Moreover, the reagent necessary for 1f, phenylacetylene, is commercially available.

Hence, organometallic methods permitted a two step (polymerization and functionalization) entry into a thermoset precursors for glassy carbon that does not require the multi-step preparation of highly reactive and often explosive di- or trialkynylaromatics.

General procedure for coupling terminal acetylenes to 1a. The procedure by Sonogashira^{8a} was modified as follows. To a screw cap tube containing 1a (0.29 g, estimated 0.96 mmol of Br), copper(I) iodide (0.04 mmol, 4.0 mol%), dichlorobis(triphenylphosphine)palladium(II) or tetrakis(triphenylphosphine)palladium(0) (0.05 mmol, 4.5 mol%) in THF (3 mL) was added at room temperature a terminal acetylene (2.9 mmol, 3.5 eq) and diisopropylamine (2.9 mmol, 3.5 eq). The black reaction solution was stirred at room temperature for 1 h then warmed to 60°C for 10 h and 100°C for 5 h. The reaction mixture was allowed to cool to room temperature and poured into water (20 mL). The organic layer was separated and the aqueous portion extracted with methylene chloride (3x). The combined organic layers were washed with aqueous ammonium chloride (3x). Filtration and removal of the solvent *in vacuo* gave a brown oil which was usually stirred with ether and the ether insoluble solid was removed by filtration.

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

(10) 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 void-free disc. Thus, in addition to 1f, compounds 1g, and 1j appear to be suitable for glassy carbon thermosets if a pressure system is employed.