Table I. Cyclopolymerization of 1,5-Hexadiene in Toluene[a]

metallocene	(μmol)	*T*, °C	time, min	conversn, %	trans,[b] %
Cp_2ZrCl_2	(4.8)	21	60	11.1	80
Cp_2ZrMe_2	(4.8)	22	60	25.0	79
Cp_2ZrMe_2	(6.7)	0	270	56.0	84
Cp_2ZrMe_2	(14.3)	−78	420	0.6	91
$Cp^*_2ZrCl_2$	(3.4)	20	180	46.0	30
$Cp^*_2ZrCl_2$	(9.2)	−25	330	65.0	14

[a] Conditions: 5 mL of 1,5-hexadiene, Al/Zr = 2500. [b] From $C_{4,5}$ cis/trans ratio.

The trans selectivity in the presence of the Cp_2ZrX_2 catalysts can be rationalized by a preference of the growing polymer chain to adopt an equatorial position in a pseudo-chair transition state in the cyclization. However, inspection of molecular models suggests that a chair-type transition state is not readily accommodated in the presence of the more sterically hindered Cp* ligands. A twist-boat conformation could be accommodated, but placement of the polymer chain in the equatorial position in this case would lead to a cis ring.

In conclusion, homogeneous Ziegler–Natta catalysts are efficient for the cyclopolymerization of nonconjugated diolefins. High-molecular-weight polymers can be readily obtained from monomers which form strained olefins upon β-hydrogen elimination, and polymers with a range of microstructures can be obtained by choice of the appropriate catalyst precursor.

Acknowledgment. We gratefully acknowledge Himont Italia for salary support for L.R. and partial support from the NSF-MRL Program through the Center for Materials Research at Stanford. Differential scanning calorimetry was made possible by a gift from AT&T Corporation. R.M.W. is the recipient of a Du Pont Young Faculty Award, for which he is grateful. We thank J. Doug Meinhart of JEOL for assistance with the ^{13}C NMR spectra.

Registry No. Cp_2ZrCl_2, 1291-32-3; Cp_2ZrMe_2, 12636-72-5; $Cp^*_2ZrCl_2$, 54039-38-2; 1,5-hexadiene (homopolymer), 25067-96-3; polylmethylene-1,3-cyclopentanediyl, 40022-21-7; 1-hexene (homopolymer), 25067-06-5.

Supplementary Material Available: Polymerization procedures and ^{13}C NMR spectral data of polymer samples **1** and **2** (1 page). Ordering information is given on any current masthead page.

Doped Glassy Carbon Materials (DGC): Low-Temperature Synthesis, Structure, and Catalytic Behavior

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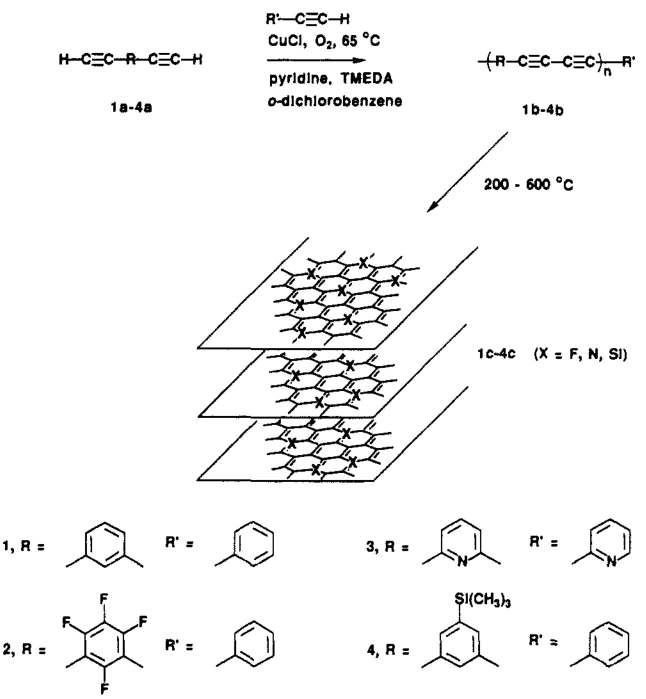
Glassy carbon has unique properties including chemical and thermal inertness, hardness, impermeability to gases and liquids, and electrical conductivity.[1] Current approaches to glassy carbon (GC) materials require high-temperature treatment (1000–3000 °C) of nonvolatilizing organic materials.[1-3] The extreme temperature requirements for these syntheses yield glassy carbon with <0.5% of any element other than carbon, independent of the precursor material.[4] Carbon electrodes are involved in a significant fraction of the more than $35 billion/year of U.S. products directly resulting from electrochemistry.[5] We felt that the homogeneous introduction of dopants would alter the electrochemical behavior of glassy carbon by modifying the adsorption of molecules to the electrode surface and by promoting catalytic activity.

Scheme I



As part of our program in the preparation and study of highly cross-linked organic solids, we have discovered a low-temperature route (600 °C) to doped (0–15 atom %) glassy carbon (DGC).[6] We report here the preparation, characterization, and catalytic properties of these doped glassy carbon materials. We chose four precursor diethynyl aromatics to demonstrate the versatility of our approach: 1,3-diethynylbenzene (**1a**),[7] the nondoped parent system; 1,3-diethynyl-2,4,5,6-tetrafluorobenzene (**2a**),[8] to ultimately generate a fluorinated glassy carbon surface; 2,6-diethynylpyridine (**3a**),[7,9] to incorporate a potential binding site in glassy carbon for metal complexes;[7] and 1,3-diethynyl-5-(trimethylsilyl)benzene (**4a**),[9] to probe the sensitivity of the thermal conversion reaction to an alkyl side chain. We prepared diacetylenes **1a**–**4a**, oxidatively coupled[10-12] these monomers in the

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[9] Spectral data for 1,3-bis[(trimethylsilyl)ethynyl]-5-(trimethylsilyl)benzene: mp 73–75 °C; IR (melt) 2942, 2882, 2143, 1570, 1369, 1273, 1246, 1160, 1130, 970, 799, 790, 755 cm^{-1}; ^1H NMR ($CDCl_3$, δ) 7.54 (s, 1 H), 7.50 (s, 2 H), 0.24 (s, 9 H), 0.23 (s, 18 H); ^{13}C NMR ($CDCl_3$, δ) 141.0, 136.4, 135.7, 122.7, 104.5, 94.7, −0.1, −1.3; HRMS, *m/z* 342.1613 (M^+, calcd for $C_{19}H_{30}Si_3$ 342.1655). Spectral data for **4a**: IR (neat) 3280, 3025, 2950, 2875, 2080, 1565, 1380, 1245, 1130, 870, 835, 805, 750 cm^{-1}; ^1H NMR ($CDCl_3$, δ) 7.60 (s, 3 H), 3.06 (s, 2 H), 0.25 (s, 9 H); ^{13}C NMR ($CDCl_3$, δ) 141.4, 137.0, 135.7, 121.9, 83.0, 77.7, −1.40; HRMS, *m/z* 198.0872 (M^+, calcd for $C_{13}H_{14}Si$ 198.0865). Spectral data for **3b**: IR (KBr) 3050, 2200, 2140, 2100, 1720, 1620, 1560, 1545, 1430, 1240, 1195, 1155, 980, 810 cm^{-1}. Anal. Calcd: C, 85.53; H, 2.72; N, 11.47. Found: C, 77.18; H, 3.39; N, 10.63. Spectral data for **4b**: IR (KBr) 3020, 2942, 2880, 2200, 1562, 1375, 1248, 1130, 870, 835, 750, 680, 620 cm^{-1}; ^1H NMR ($CDCl_3$, δ) 7.66 (s), 0.30 (s); ^{13}C NMR ($CDCl_3$, δ) 142.0, 137.9, 136.0, 132.6, 131.0, 128.5, 128.0, 121.7, 81.1, 74.6, −1.4. Anal. Calcd: C, 80.35; H, 6.07; Si, 13.59. Found: C, 79.30; H, 6.11; Si, 14.04.

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Table I. Conductivity (σ), Density (ρ), Young's Modulus (E),[a] Shear Modulus (S),[a] and Poisson's Ratio (ν)[a] of DGC Materials **1c–4c**

entry	sample	temp, °C	σ, S/cm	ρ, g/cm^3	E, MN/m^2	S, MN/m^2	ν
1	**1c**	200	$<1 \times 10^{-12}$	1.35	20 000	8040	0.241
2		400	3×10^{-7}	1.35	22 500	9200	0.223
3		600	0.7	1.50	28 500	10 800	0.326
4	**2c**	200	$<1 \times 10^{-12}$	1.27	11 900	5000	0.192
5		400	1×10^{-9}	1.64	12 300	5310	0.160
6		600	0.1	–	–	–	–
7	**3c**	200	$<1 \times 10^{-12}$	1.37	10 100	4000	0.288
8		400	3×10^{-8}	1.32	6000	2300	0.306
9		600	0.3	1.55	12 200	4550	0.336
10	**4c**	200	$<1 \times 10^{-12}$	1.11	10 000	4700	0.200
11		400	$<1 \times 10^{-12}$	1.01	5900	2300	0.256
12		600	9×10^{-7}	1.29	12 600	4950	0.272
13	glassy carbon[b]	–	100	1.46	29 400	12 000	0.233
14	graphitic carbon[c]	–	7	1.89	13 900	5860	0.185
15	diamond[d]	–		3.51	1 050 000	437 000	~0.200

[a] The modulus measurements were determined by the ultrasonic method described in the references listed in footnote 19. Uncertainty in the measurement is <5%. [b] V10, Atomergic Company. [c] Carbon P03, Pure Carbon Company, St. Mary's, PA. [d] The values were obtained from ref 21.

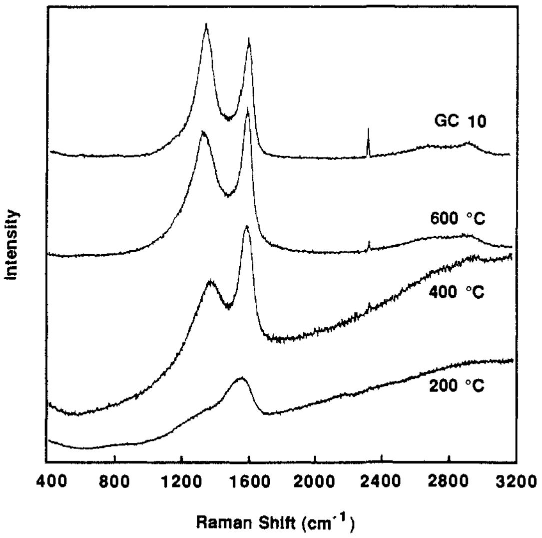

Figure 1. Raman spectra of **1c** thermally treated at 200, 400, and 600 °C (1 °C/min ramp rate; held at the final heat treatment temperature for 6 h) and 1000 °C heat treatment Tokai glassy carbon (GC10). Bands at 1200–1600 cm^{-1} show formation of sp^2-hybridized carbon lattice. Spectra were obtained with a Spex 1403 spectrometer at 515 nm.

presence of monoethynyl aromatics (RC≡CH) to control their molecular weight (and solubility), and thermally treated the compressed (4.5 kbar) oligomers to give the doped glassy carbon solids **1c–4c** (Scheme I).[13,14] These soluble oligomers (**1b–4b**)

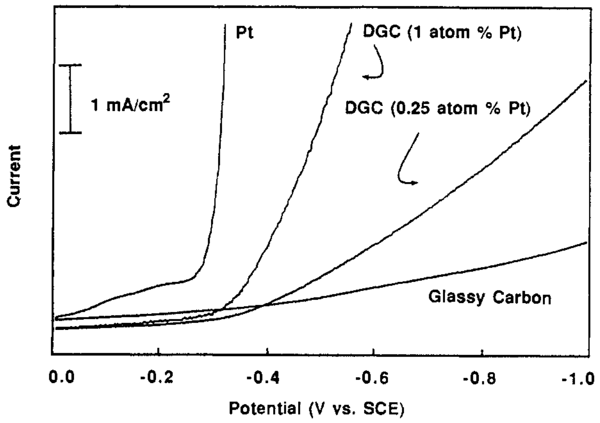

Figure 2. Reduction of 0.1 M sulfuric acid (pH 3) vs Ag/AgCl (3 M) on platinum, 1.0 atom % platinum doped **1c**, 0.25 atom % platinum doped **1c**, and **1c**. The doped glassy carbon electrodes were all thermally treated at 600 °C for 6 h.

also allow the immobilization of precious catalyst microparticles in glassy carbon. Addition of 0.25 and 1.0 atom % of platinum (as PtO$_2$) to **1b** prior to heat treatment immobilized the catalyst in glassy carbon. No loss of mass was detected for these samples throughout the thermal treatment. X-ray photoelectron spectroscopic analysis of **1c–4c** and of **1c** doped with platinum oxide confirmed the incorporation of dopants in these glassy carbon solids.[15]

Raman analysis confirms the glassy carbon microcrystalline structure of these carbon solids.[16] Figure 1 shows the Raman spectra of GC prepared at 1000 °C and **1c** thermally treated at 200, 400, and 600 °C. These spectra show the E$_{2g}$ fundamental at approximately 1580 cm^{-1} and the disorder mode at approximately 1360 cm^{-1}.[17] The intensity of the 1582-cm^{-1} band is correlated with the magnitude of the stacking dimension (L_c) and indicates the creation of an sp^2-hybridized lattice.[17,18] The intensity of the 1360-cm^{-1} band increases with greater carbon

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(10) In a typical procedure, oligomer **1b** was prepared in *o*-dichlorobenzene by the Cu(I)-catalyzed oxidative coupling of 1,3-diethynylbenzene containing phenylacetylene as the end-capping agent. Oligomers **2b–4b** were prepared analogously. **CAUTION**: *Compound **1a** and all other volatile polyethynyl aromatics should be distilled at high vacuum and at temperatures of less than 60 °C in well-shielded equipment. Only limited quantities should be distilled, stored, or manipulated as pure (undiluted) material.* For experimental detail, see: Hay, A. S. *J. Org. Chem.* **1960**, *25*, 1275–1276. Hay, A. S. U.S. Patent 3 300 456, 1967. Hay, A. S. U.S. Patent 3 332 916, 1967. Hay, A. S. U.S. Patent 3 519 611, 1970. See also: Dawson, D. J.; Fleming, W. W.; Lyerla, J. R.; Economy, J. In *Reactive Oligomers*; ACS Monograph 282; American Chemical Society: Washington, DC, 1982; pp 63–79. Jabloner, H. U.S. Patent 4 070 333, 1978. White, D. M. U.S. Patent 4 020 265, 1977.

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(13) Oligomers were prepared with a 3:1 or 10:1 ratio of the diacetylene aromatic to monoacetylene end-capping agent. In a typical preparation, approximately 200 mg of **1b** was compressed under pressure (4.5 kbar) in a 1-cm-diameter die while being heated to 200 °C. The die reached the final temperature in approximately 45 min. The black shiny disk obtained was subsequently thermally treated at the final temperature in vacuo (quartz vessel) or under an atmosphere of nitrogen. The properties of the organic solids were insensitive to the ratio of the diacetylene aromatic to end-capping agent. The location of the dopant atoms is not known in the carbon lattice, and the drawing depicts only a general structure for these carbon solids.

(14) Analysis of **1b–4b** by differential scanning calorimetry (DSC) found cure onset temperatures that ranged from approximately 150 °C (**3b**) to 200 °C (**1b**, **2b**, **4b**) with cure maximum temperatures of ~165 °C (**3b**) to 250 °C (**4b**) with cure energies from 70 to 230 cal/g. Thermal gravimetric analyses are characterized by a loss of less than 20% of their mass under nitrogen up to 1100 °C. Under dioxygen, the solids lost 10% of their mass between 380 °C (**3c**) and 500 °C (**4c**).

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disorder and may be used to estimate microcrystallite size, L_a.[17,18] The 1360-cm^{-1} mode has been attributed to disorder induced breakdown of Raman selection rules near graphitic edges and perhaps the presence of a vibration with A_{1g} symmetry.[18] The improved resolution of the disorder and E_{2g} modes on further heat treatment of **1c** at 400 and 600 °C indicates an increase in the crystallite dimensions (L_a and L_c) by an annealing process. The Raman spectra of the parent system (**1c**) thermally treated at 600 °C is remarkably similar to that of GC. *Clearly, an sp^2-hybridized carbon lattice is formed at 200–600 °C, as opposed to 1000–3000 °C when conventional GC is prepared from materials such as polyacrylonitrile.*

The density, elastic modulus, shear modulus, and Poisson's ratio of the solid prepared from poly(phenylenediacetylene) (**1c**) are strikingly similar to GC (Table I).[19] It is important to note that the Young's moduli of **2c**–**4c** (~12 000 MN/m^2) are less than half that found for **1c** (28 500 MN/m^2). The incorporation of dopants dramatically affected the elasticity of the organic solid.

Thermal treatment of **1c**–**4c** at 200 °C for 6 h gave only electrically insulating materials. However, the electrical conductivity of the organic solids increased with final heat treatment temperature (Table I).[20] With the exception of the silicon-doped solids, further heat treatment of these same solids at 400 °C for 6 h resulted in conductivities of approximately 10^{-8} S/cm. Further heat treatment at 600 °C for 6 h gave **1c**–**3c** with conductivities of approximately 1 S/cm. *Note that this conductivity is achieved even with* ***2c*** *which contains >30 wt % fluorine.*

These DGC materials function as practical electrodes. The voltammetry of the ferri/ferrocyanide [$Fe(CN_6)^{3-/4-}$] couple on GC prepared at 2000 °C (ΔE_p = 74 mV, $k°$ = 0.017 cm/s) and that of **1c** prepared at 600 °C (ΔE_p = 91 mV, $k°$ = 0.0075 cm/s) are remarkably similar.[22] With our approach, we have synthesized a homogeneously doped material which has catalytic properties similar to those of superficially modified electrodes.[23] Figure 2 shows the current vs potential curves for the reduction of proton to dihydrogen on glassy carbon (**1c**), platinum, and two platinum DGC (0.25 and 1 atom %) electrodes. These platinum DGC electrodes also exhibit excellent stability. *We have found no evidence for degradation of the electrode or loss of catalytic activity over several thousand reduction cycles.*

The elastic modulus, electrical conductivity, and Raman spectroscopy of these materials provide convincing evidence for a low-temperature synthesis of doped glassy carbon. This method of synthesis provides a new vehicle for the homogeneous immobilization of precious catalyst microparticles in a stable, conductive environment. We have also imparted catalytic electrochemical behavior to glassy carbon with our methodology. We are continuing to explore the preparation and electrochemical activity of these materials and also the preparation of thin films of these materials on various substrates.

Acknowledgment. We are grateful to Dr. Robert Haddon (AT&T Bell Laboratories, Murray Hill, NJ) for the electrical resistivity measurements, Bonnie J. Bachman (AT&T Bell Laboratories, Murray Hill, NJ) for the thermal analyses, and Howard Hutton (The Ohio State University) for the preparation of glassy carbon samples. We thank Professor Richard R. Schrock, Gui Bazan, and Steven A. Krouse (Massachusetts Institute of Technology, Cambridge, MA) for the donation of their gel permeation chromatography computer programs. We also thank Professor George Whitesides (Harvard University, Cambridge, MA) for useful discussions and encouragement and for the use of his ultrasonic measurement instrumentation.

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Studies on Tumor Promoters. 9. A Second-Generation Synthesis of Phorbol[1]

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Phorbol myristate acetate (PMA, **1a**) has long been recognized for its extraordinary ability to enhance the effect of various carcinogens in animal studies. The phorbol esters also elicit a wide variety of other biological responses, providing new opportunities for research on cancer, inflammation, cardiovascular disease, cystic fibrosis, AIDS, and memory development.[2,3] Our interest in the basic biochemistry of these compounds and their chemotherapeutic potential has recently led to the first synthesis of phorbol (**1b**).[4] We describe here a new route to phorbol and its analogues that features an unprecedented silicon transfer induced oxidopyrylium cycloaddition and transition metal mediated A ring synthesis.

The previous synthesis of phorbol was based on the potentially general tigliane, ingenane, and daphnane precursor **2**,[5] which was obtained by A ring annelation of the cycloadduct of zwitterion **3a** (Scheme I). Since this annelation was found to require a C4 ketone, a more direct route to **2** was envisaged through the oxidopyrylium–alkene cycloaddition of **3b**, a precursor incorporating a latent C4 ketone and potentially derivable from kojic acid.[6] To test this strategy, attachment of a secondary carbon of a tethered alkene to the C9 position (phorbol numbering) of kojic acid with provision for oxidation at C12 was required and was concisely accomplished by O-allylation and Claisen rearrangement.[7] Thus, addition of allylic bromide **5**,[8,9] prepared in three steps (62%) from

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