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35. We are grateful to P. Pulay, K. Wolinski, and J. F. Hinton for providing their TEXAS 90 program; to A. Warshel and F. S. Lee for providing a customized version of ENZYMIX; and to C. Jameson and P. G. Wolynes and the above for useful advice. Supported in part by the U.S. Public Health Service (USPHS) [grants HL-19481 and (in part) GM-40426], by the American Heart Association (grant AHA 92-013340), with funds provided in part by the Illinois Heart Association, Inc. and by the Graduate Research Board of the University of Illinois at Urbana-Champaign. J.G.P. was supported by a USPHS postdoctoral fellowship (grant GM-14545).

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Poly(phenylcarbyne): A Polymer Precursor to Diamond-Like Carbon

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The synthesis of poly(phenylcarbyne), one of a class of carbon-based random network polymers, is reported. The network backbone of this polymer is composed of tetrahedrally hybridized carbon atoms, each bearing one phenyl substituent and linking, by means of three carbon–carbon single bonds, into a three-dimensional random network of fused rings. This atomic-level carbon network backbone confers unusual properties on the polymer, including facile thermal decomposition, which yields diamond or diamond-like carbon phases at atmospheric pressure.

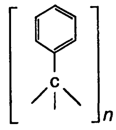
The polyacetylene class of polymers, of stoichiometry $(CR)_n$, has long been a focus of intense research owing to their conductive and electronic properties (*1*). These polymers have linear backbones consisting of alternating C–C and C=C bonds, each carbon bearing one substituent (*2–5*). Recently, inorganic backbone polymers of similar stoichiometry, but different structure, have been synthesized: the polysilynes $(SiR)_n$ and polygermynes $(GeR)_n$ and their copolymers (*6*). These polymers have a continuous random network backbone, each inorganic atom being tetrahedrally hybridized and bound by single bonds to three other inorganic atoms and one substituent. The properties of the network polymers are different from those of linear inorganic backbone polymers because of the network structure. We report an analogous carbon-based network polymer of $(CR)_n$ stoichiometry (*7*). That the linear structure is preferred in $(CR)_n$ polymers is to be expected, given the much greater strength of C=C over Si=Si or Ge=Ge bonds (*8*). However, appropriate synthetic conditions can produce a carbon network-backbone polymer of stoichiometry $(CR)_n$ (R = Ph; Ph, phenyl), which is analogous in structure to the polysilynes and germynes (*9–13*).

The synthesis (*14*) was accomplished by a procedure analogous to those used for the synthesis of the inorganic network polymers (*6*): the reduction of an appropriate $RCCl_3$ monomer with an ultrasonically generated emulsion of Na-K alloy and an ethereal solvent, tetrahydrofuran (THF) (Eq. 1).

$$PhCCl_3 + 3.0\ NaK \xrightarrow[THF]{475\text{-W, 20-kHz ultrasound}} \underset{\mathbf{1}}{(PhC)_n} + 3.0\ Na(K)Cl \qquad (1)$$

For R = phenyl, poly(phenylcarbyne) (**1**) is obtained from this reaction as a tan powder that is soluble in common organic solvents. Insoluble crosslinked material and low molecular weight oligomers are the only other products. Chemical analysis (*15*) of **1** was consistent with the empirical formula $(C_6H_5C)_n$, and gel permeation chromatography of the material gave a weight-averaged molecular weight of $\overline{M}_w$ = 4000 and a number-averaged molecular weight of $\overline{M}_n$ = 3077, which indicates that **1** is polymeric (*16*).

Infrared (IR) spectra of **1** show a complete absence of C=C stretching bands, which are characteristic of *cis*-polyacetylenes and are seen in the IR spectrum of poly(diphenylacetylene) (**2**), the linear polymer whose empirical formula is identical to that of **1** (*17*).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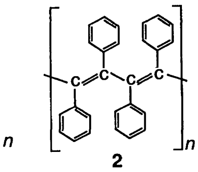
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The IR spectra also show bands consistent only with monosubstituted phenyl rings (*15*): no di- or trisubstituted phenylene-type aryl groups are present. The ^{13}C nuclear magnetic resonance spectroscopy of **1** exhibits a very broad resonance ($\delta\nu_{1/2}$ = 800 Hz) centered at a chemical shift δ of 51 parts per million (ppm) of the applied field, characteristic of quaternary carbon atoms (*7, 9–13*), and no resonances other than those of the phenyl rings were detected in the vinylic carbon region, where the resonances of the backbone carbons of phenyl-substituted acetylenes normally appear (*3, 4*). The resonance at 51 ppm is enhanced when **1** is synthesized with the use of 10 mole percent of α,α,α-trichlorotoluene monomer that has been labeled with ^{13}C in the α position. These data indicate that C=C bonds are not primary structural features of **1** and that this polymer therefore does not adopt the linear polyacetylene structure. The presence of quaternary α-carbons as a primary structural feature and the broadness of the ^{13}C resonances indicate that **1** consists of a randomly constructed rigid network of tetrahedral phenylcarbyne units in which each carbyne carbon forms three C–C bonds to the network and one to the phenyl substituent (Fig. 1). This structure corresponds to the network arrangements found in the analogous silicon and germanium polymers and

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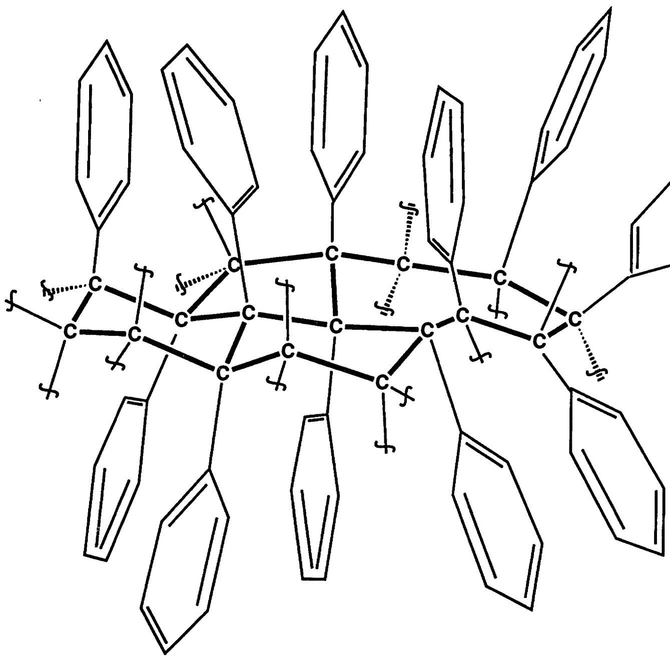

Fig. 1. Schematic representation of the proposed network structure of **1**.

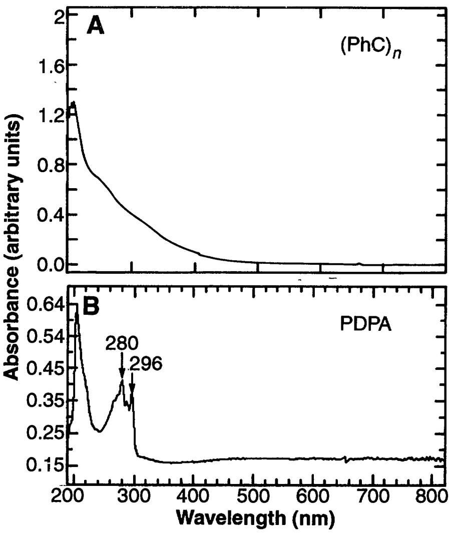

Fig. 2. Electronic spectra of (**A**) poly(phenylcarbyne) [(PhC)$_n$, **1**] and (**B**) poly(diphenylacetylene) (PDPA, **2**) in cyclohexane solution.

copolymers (6) and can be regarded as a geometrical isomer of the polyacetylenes.

The network microstructure of poly(phenylcarbyne) represents a potentially useful molecular architecture for chemically constructed carbon materials. Other examples of carbon-based materials with designed molecular architectures include network polymers of dendrimer, arborol, or hyperbranched structures (9–13), which consist of monomer units that successively branch off from a central core. Poly(phenylcarbyne) does not belong to this structural class, as it does not display the hierarchical dimensionality of branching from a multifunctional core that is characteristic of such materials. Also, all of the reported dendritic or hyperbranched types of carbon network polymers are composed of molecular units, such as aryl groups, which form the repeating units or monomers of the network.

An important difference in the poly(phenylcarbyne) structure is that the repeating or network unit is a single carbon atom only, making its backbone a three-dimensional (3D) network on the atomic, rather than the molecular, scale. Fullerenes also are composed of such atomic-level carbon networks (18), but the repeating units are formally sp^2 hybridized and π conjugated, although the geometry adopted by many of these carbon atoms actually deviates toward tetrahedral. Carbon-based small molecules in which formally tetrahedral carbon atoms, each bearing one substituent, are joined in fused-ring structures to form polyhedral shapes, such as the cubanes (C_8R_8) and dodecahedranes ($C_{20}R_{20}$) (7), can be regarded as oligomers of the poly(phenylcarbyne) structure. The carbon networks of the fullerenes, cubanes, and dodecahedranes, however, adopt symmetrical, regular polyhedral shapes, which significantly influence their properties, whereas the network of **1** is randomly constructed and therefore irregularly shaped.

The poly(phenylcarbyne) 3D atomic network is similar to the 3D atomic structure of solids, rather than to the polymer networks formed by molecular repeat units. The network backbone therefore displays solid-like properties (6), such as great rigidity, semiconductor-like electronic behavior, and easy conversion to solid-state phases (see below), more so than do organic networks formed by molecular repeat units. Such networks are often compared with, and display behavior characteristic of, micelles and membranes (9–13), whereas the structure and properties of poly(phenylcarbyne) are more analogous to those of small clusters of solid sp^3 carbon solubilized on their surfaces with aryl groups.

The physical properties of poly(phenylcarbyne) also indicate its structural similarity to inorganic network backbone polymers, the polysilynes and polygermynes (6). It is, like the inorganic polymers, amorphous, displaying no discrete glass transition temperature or melting point. It is stable in the presence of air and absence of light and can be cast from solution to form transparent films. Whereas the electronic spectrum of poly(diphenylacetylene) (17) (Fig. 2B) exhibits several sharp peaks at 296 and 280 nm, indicative of different lengths of conjugated C=C bonds (5, 19), the electronic spectrum of **1** (15) (Fig. 2A) is essentially identical to that of poly(phenylsilyne) (6), an intense broad absorption that starts at a wavelength $\lambda \leq 200$ nm and decreases into the visible to 450 nm. This absorption band in polysilynes and polygermynes has been attributed to extensive σ conjugation that extends across the 3D network backbone (6). Also, **1** exhibits an intense, broad fluorescence (λ_{max} = 460 nm) (15) similar to that of the polysilynes (20) and frequency-shifted from that of **2** (λ_{max} = 520 nm) (17). These features of the electronic spectra of **1** are analogous to those produced by long-range through-bond electron transfer by way of rigid nonconjugated C–C bonds in molecular species (21) and are presumed to arise in **1** from hole or electron transfer through a similarly hyperconjugated carbon framework, the rigid network backbone. In these electronic properties, poly(phenylcarbyne) again displays behavior more characteristic of solids than of non–π-conjugated organic polymer networks.

Compound **1** also undergoes the photooxidation reaction [insertion of O into the C–C σ-bonded network after ultraviolet (UV) irradiation], which has been found to be characteristic of the network backbone (6, 22) and has allowed the use of polysilynes as photoresists for submicrometer lithography (22). Exposure of **1** as a solid or solution to UV light centered at 254 nm in an ambient atmosphere results, after several hours, in the growth of strong C=O and C–O–C stretching bands in the IR spectrum, at 1720 and 1180 cm^{-1}, respectively. No reaction is seen in the IR spectrum when linear **2** is irradiated under identical conditions, again indicating the existence of a network rather than a linear backbone structure for **1**. This reactivity suggests that the polycarbynes, like their Si-based congeners, may be photopatternable and therefore potentially useful in photolithographic processes.

In one other important respect, poly(phenylcarbyne) displays unique reactivity owing to its sp^3 network backbone structure. Although both **1** and **2** are pyrolytic precursors to carbon, poly(phenylcarbyne) gives predominantly sp^3-carbon phases, including diamond or diamond-like carbon, whereas **2** produces principally graphite. When heated from room temperature to either 1000° or 1600°C over 7 hours under 1 atm of argon (*23*) (Eq. 2), **1** converts to a black, highly reflective, abrasive (*24*) solid that was found to contain only carbon by chemical analysis (<0.5% H) and x-ray fluorescence (EDX).

$$\underset{\mathbf{1}}{(\text{PhC})} \xrightarrow[\text{Ar, 1 atm}]{\Delta,\ 1000^\circ \text{ to } 1600^\circ\text{C}} \text{C} \qquad (2)$$

This material displays regions that are visibly transparent at thicknesses of 35 μm. The x-ray diffraction patterns (*25*) of this carbon vary from sample to sample: peaks that correspond to peaks found in the diffraction patterns of α- and β-carbyne (*26*) and cubic and hexagonal diamond (*27, 28*) have been observed in different combinations in different samples. Under the same conditions, **2** pyrolyzes to a dull gray powder, the x-ray diffraction pattern (*25*) of which shows peaks corresponding to poorly crystalline graphite and chaoite, a form of carbyne that contains a lower percentage of sp^3 carbon than α-carbyne (*26*).

Raman spectra (*29*) of the most transparent regions of the carbon obtained from the pyrolysis of **1** (Fig. 3, curve A) show a peak at 1336 cm^{-1}, indicative of diamond or predominantly sp^3-bonded diamond-like carbon (*28, 30–35*), as well as a peak at 1582 cm^{-1}, which corresponds to "nondiamond carbon" (*30*). Raman spectra of the carbon obtained from pyrolysis of **2** (Fig. 3, curve B) show only microcrystalline graphite (*30–34*). Atmospheric-pressure decomposition of poly(phenylcarbyne) at temperatures as low as 1000°C therefore produces sp^3-carbon phases, some of which display transparency and hardness, as well as characteristic spectral features, approaching those of diamond (*27, 28, 30–34, 36*). Such pyrolysis behavior is not seen in the chemically identical organic polymer **2**, which lacks the sp^3-carbon network backbone that is the unique structural feature of **1**.

The Raman spectra of the carbon obtained from these pyrolyses give further information about the structures of the materials. No first-order Raman bands are seen in the regions of 2900 to 3100 cm^{-1} or 2100 to 2300 cm^{-1}, strongly suggesting the absence of C–H and C≡C bonds in this material.

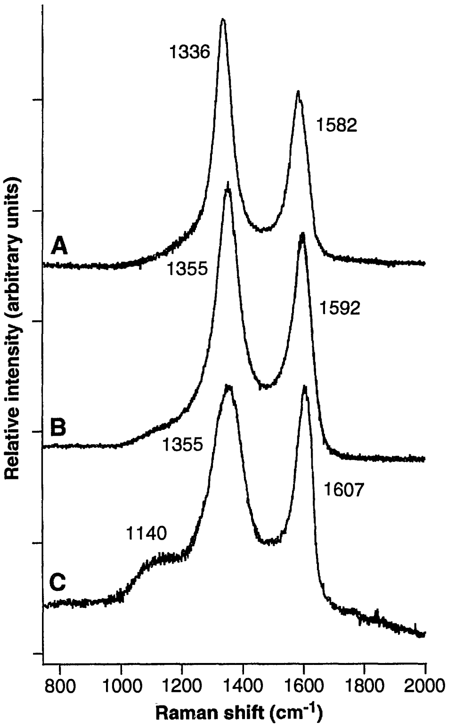

Fig. 3. Raman spectra of (A) the transparent carbon produced by pyrolysis of **1**, (B) the carbon produced by pyrolysis of **2**, and (C) the black, reflective carbon produced by the pyrolysis of **1**.

The Raman spectrum of the black, reflective regions of the carbon obtained from the pyrolysis of **1** (Fig. 3, curve C) shows peaks corresponding to microcrystalline graphite (1355 and 1607 cm^{-1}) and a broad shoulder centered at 1140 cm^{-1}, which is not seen in the carbon obtained from the pyrolysis of **2**. Many nanocrystalline diamond samples show this feature, which is thought to arise from the effects of small crystallite size or disorder in the tetrahedral carbon network (*30*). This feature has also been attributed to regions of amorphous or microcrystalline diamond or to a precursor to crystalline diamond (*31*). Its presence here suggests that even the predominantly sp^2 regions of this carbon may contain some percentage of sp^3 hybridization.

The char yield of **1** under the above pyrolytic conditions is 40 to 45%, a high yield typical of the network backbone structure (*37*); in comparison, a char yield of only 13% is seen for the linear polyacetylene **2**. After removal of the sp^2 hybridized carbon by wet etching (*27, 32, 33, 38*) (treatment with concentrated $HClO_4$ at 200°C for 5 hours), the carbon product obtained from pyrolysis of **1** retains 67% of its original weight, and the carbon obtained from the pyrolysis of **2** retains 45%. The overall yield of "hard carbon" (carbon that is resistant to oxidation by $HClO_4$) obtained from pyrolysis of **1** is therefore 30%, and the yield from pyrolysis of **2** is 6%.

The difference in the amount of sp^3 and sp^2 hybridized carbon in the pyrolysis products given by the stoichiometrically identical polymers **1** and **2** and the formation of diamond or diamond-like carbon by the atmospheric pressure decomposition of **1** presumably are attributable to the presence in the backbone of **1** of the 3D network of tetrahedral carbon atoms, as opposed to the sp^2 hybridized carbons that make up the backbone of **2**. During pyrolysis, conversion of this sp^3-bonded carbon network to predominantly sp^3-bonded carbon phases is therefore favored even at atmospheric pressure. High molecular weight carbon network polymers consisting of linear or "hyperbranched" sp^2-based molecules pyrolyze to give glassy (*12*) or amorphous carbon (*13*), not sp^3 phases, again confirming that the all tetrahedral carbon microstructure of poly(phenylcarbyne) is the critical feature that allows its facile conversion to diamond-like carbon, and not simply the presence of a carbon network. This suggests that this class of carbon-based network backbone polymers may find potential applications as precursors to diamond or hard carbon materials at lower pressures or temperatures than those used in some current deposition processes (*27, 28, 30–34, 36*). The conversion properties and yield of the polymers, and the quality of the diamond-like or hard carbon products obtained from them, could be optimized with the use of side groups other than phenyl and by more sophisticated processing techniques than simple pyrolysis. The easy processibility of these soluble, film-forming polymers could prove advantageous in the coating of substrates or in the formation of submicrometer features with high-resolution laser pyrolysis.

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14. In an inert atmosphere glovebox equipped with a high intensity (475 W, 20 kHz, and 0.5-inch tip) ultrasonic immersion horn, anhydrous THF (250 ml) was irradiated at full power by immersion of the horn, and Na-K alloy (50:50 mole percent, 9.3 g, 300 meq) was added, followed by three more minutes of sonication. A solution of α,α,α-trichlorotoluene (10.65 ml, 100 mmol) in 20-ml pentane was then added at a controlled rate over 20 min through an addition funnel, followed by sonication for 20 min. The reaction mixture was then moved from the drybox to a shielded hood, and 250 ml of water were added, after which the organic layer was separated from the aqueous. The organic layer was filtered and concentrated in volume to 50 ml in vacuum. Addition of methanol (200 ml) to the organic layer gave a tan precipitate, which was collected by filtration and purified by reprecipitation with ethanol from THF solution, giving 2.23 g (25%) of poly(phenylcarbyne) (**1**).
15. Spectral data for **1**: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.4 ppm (br, C_6H_5). $^{13}C\{^1H\}$ (50 MHz, $CDCl_3$): δ = 140, 125 (br, C_6H_5), and 51 ppm (br, $C_6H_5\mathbf{C}$). Infrared (KBr pellet): 3055(s), 3024(s), 2930(m), 1946(m), 1890(m), 1811(m), 1600(s), 1491(m), 1444(s), 1180(s), 1175(s), 1050(m), 900(w), 750(s), and 670 cm^{-1}(s). Gel permeation chromatography (GPC) (THF versus polystyrene): $\overline{M}_w$ = 4000, $\overline{M}_n$ = 3077, and polydispersity = 1.3. Electronic spectrum (cyclohexane): onset at 450 nm, increased gradually in intensity with decreasing wavelength to 200 nm. Emission spectrum (cyclohexane, excitation wavelength = 300 nm): λ_{max} = 460 nm. Elemental analysis: calculated: C, 94.34; H, 5.66; found: C, 94.95; H, 6.13. Electron spin resonance (ESR) (9.1 GHz, solid): g = 2.005.
16. Because the GPC molecular weight of **1** was determined with the use of linear polystyrene standards, the absolute value of the molecular weight is probably underestimated, as is seen in other network polymer systems (*5, 10, 11*) and should be regarded as an estimate and a lower limit only.
17. Compound **2** was synthesized by two different literature procedures (*3*). Additional samples of **2** were donated by T. Masuda of Kyoto University. Spectral data for **2**: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.4 ppm (br, C_6H_5); ^{13}C NMR (cross-polarization, magic angle spinning, 74.5 MHz): δ = 144.6, 140.5, and 125.5 ppm (C_6H_5); IR (KBr pellet): 3050(s), 1950(m), 1895(m), 1803(m), 1650(w), 1600(s), 1490(s), 1440(m), 1165(s), 1070(m), 1030(m), 800(m), 750(s), and 680 cm^{-1}(s); electronic spectrum (cyclohexane): λ_{max} = 280 and 298 nm; emission spectrum (cyclohexane, excitation wavelength = 300 nm): λ_{max} = 520 nm; ESR (*3*): g = 2.00185.
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23. Thermal gravimetric analysis shows that the thermal decomposition of **1** begins at 200°C and is complete at 450°C, reaching a constant weight of 40 to 45% of the initial. Annealing to 1000° or 1600°C improves the transparency of the product.
24. Though the upper limit of this material's hardness has not been established, we have observed that it easily scratches agate (hardness 6 to 7 Mohs); it is therefore much harder than graphite (0.5 to 1 Mohs).
25. The x-ray diffraction data were collected as powder patterns with use of Cu-Kα radiation on a Rigaku Geigerflex diffractometer equipped with a graphite monochromator or on a Debeye-Scherrer camera with a Ni-β filter. The following x-ray diffraction patterns (*d*-spacings in angstroms) were observed for different samples of pyrolyzed **1**: (i) 2.51, 2.49, 2.14, 1.54, 1.48, 1.31, 1.25, and 1.22; (ii) 2.43, 2.08, 1.49, 1.27, and 1.22; (iii) 2.54, 1.54, 1.32, 1.00, 0.98, 0.89, and 0.84; and of pyrolyzed **2**: 3.12, 2.56, 2.22, 2.08, 1.65, 1.58, 1.35, and 1.29.
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