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Synthesis and Characterization of Polycarbynes, a New Class of Carbon-Based Network Polymers

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Abstract: The synthesis and characterization of some polycarbynes, members of a new class of carbon-based random network polymers, are reported. The network backbones of these polymers are composed of tetrahedrally-hybridized carbon atoms, each bearing one organic substituent and linked via three carbon–carbon single bonds into a three-dimensional random network of fused rings. Poly(phenylcarbyne) (**1**), poly(methylcarbyne) (**2**), 75:25 poly(phenyl-*co*-methylcarbyne) (**3**), and 99:1 poly(phenyl-*co*-hydridocarbyne) (**6**) can be obtained by the reductive condensation of the appropriate $RCCl_3$ (R = Ph, Me, H) monomers in various ratios with ultrasonically-generated emulsions of sodium–potassium alloy and THF. Silyne/carbyne network copolymers such as 80:20 poly(phenylcarbyne-*co*-phenylsilyne) (**4**) and 78:22 poly(phenylcarbyne-*co*-*n*-butylsilyne) (**5**) are obtained from analogous reductions of $PhCCl_3$ and $RSiCl_3$ (R = Ph, *n*-Bu). Group 4 metals can be incorporated into the polymers by similiar reduction of $RMCl_3$ (R = Cp, Cp*, M = Ti, Hf) species with $PhCCl_3$, giving $[(PhC)_{0.98}(CpTi)_{0.02}]_n$ (**7**) and $[(PhC)_{0.95}(Cp^*Hf)_{0.05}]_n$ (**8**). The atomic-level carbon network backbone confers unusual properties on the polymers, including, in the case of **1**, facile thermal decomposition to form diamond or diamond-like carbon phases at atmospheric pressure.

Introduction

The polyacetylene class of polymers, of stoichiometry $[CR]_n$, have long been a focus of intense research due to their conductive and electronic properties.[1] These polymers have linear backbones consisting of alternating C—C and C═C bonds, each C bearing one substituent.[2–4] Recently, inorganic backbone polymers of similar stoichiometry but different structure have been synthesized: the polysilynes $[SiR]_n$ and the polygermynes $[GeR]_n$ and their copolymers.[5] These polymers have a continuous random network backbone, each inorganic atom being tetrahedrally hybridized and bound via single bonds to three other inorganic atoms and one substituent. The network polymers show novel properties compared to linear inorganic backbone polymers due to the characteristics conferred by the network structure. An analogous carbon-based network polymer of $[CR]_n$ stoichiometry has never been reported, although oligomers of this structure, the cubanes and dodecahedrnes, are known.[6] That the linear structure is preferred in $[CR]_n$ carbon polymers is to be expected, given the much greater strength of C═C over Si═Si or Ge═Ge bonds.[7] We recently reported, however, the synthesis and properties of poly(phenylcarbyne), the network backbone of which is composed of sp^3-hybridized carbon atoms which bear one phenyl group and are linked through three single C—C bonds into a random network of fused rings.[8] Poly(phenylcarbyne) is therefore analogous in structure to the polysilynes and germynes and constitutes the first member of a new class of carbon-based network polymers. We have shown that this network carbon backbone confers unique properties on these polymers, including facile conversion to diamond and diamond-like carbon at atmospheric pressure.[8] We report here full synthetic and characterization procedures on poly(phenylcarbyne) and other polycarbynes, as well as the syntheses of network copolymers of carbynes and inorganic-based monomers. Studies of the conversion of these polymers to diamond-like carbon and other ceramics will be reported elsewhere.[9]

Experimental Section

All syntheses were performed in an inert atmosphere glovebox equipped with a Heat Sytems-Ultrasonic Inc. W-485 ultrasonic processor and immersion horn with a $^1/_4$-in. titianium tip. Solvents used in the syntheses were Aldrich anhydrous grade and were distilled from sodium benzophenone prior to use. Liquid 1:1 mole ratio NaK alloy was prepared in the glovebox by adding solid potassium to an equimolar amount of molten sodium. α,α,α-Trichlorotoluene, 1,1,1-trichloroethane (Aldrich), phenyltrichlorosilane, *n*-butyltrichlorosilane (Silar), (pentamethylcyclopentadienyl)hafnium trichloride (Strem), cyclopentadienyltitanium trichloride (Aldrich), and Grignard reagents (Aldrich) were obtained from

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commercial sources and used as received. ^{13}C-Enriched α,α,α-trichlorotoluene was synthesized by MSD, Inc. Poly(diphenylacetylene) was synthesized according to two literature procedures,[3a,d] and additional samples were donated by Professor T. Masuda of Kyoto University. Solution-state NMR spectra were recorded at room temperature as saturated $CDCl_3$ solutions using a Bruker WP-200 spectrometer (50 MHz for ^{13}C). Solid-state ^{13}C cross polarization magic angle spinning (CPMAS) spectra were recorded on a Chemagnetics CMX-300 spectrometer resonating at 74.78 MHz for ^{13}C. Infrared spectra were recorded on a IBM FTIR-32 instrument. Electronic spectra were recorded on a Hewlett-Packard 8450A UV/vis spectrophotometer. Gel permeation chromatography (GPC) of polycarbynes was performed with a Waters 410 GPC/RI instrument equipped with a refractive index detector and three Waters ultrastyragel columns with pore sizes of 10^3, 10^4, and 500 Å. The GPC was interfaced with a NEC Powermate 386 computer with Millipore Millenium 2010 software. All GPC samples were run in a tetrahydrofuran (THF) flow of 1.0 mL/min at 35 °C and are reported versus polystyrene standards. ESR spectra were measured on a Varian E-Line Model EPR spectrometer at 9 GHz, with a modulation frequency of 100 kHz. Elemental analyses were obtained by combustion at 1600 °C in the presence of V_2O_5 from Galbraith Laboratories, Nashville, TN.

Poly(phenylcarbyne), $[PhC]_n$ (1). NaK alloy (50:50 mol %, 9.3 g, 300 mequiv) in 250 mL of THF was ultrasonically irradiated at full power for 3 min (***Caution*: The extremely pyrophoric nature of NaK alloy emulsions, combined with the greater likelihood of glassware breaking under ultrasonic irradiation, requires that this procedure be performed only in an inert atmosphere glovebox**). A solution of α,α,α-trichlorotoluene (10.65 mL, 100 mmol) in 20 mL of pentane was added dropwise to the reaction mixture over 20 min while sonication was continued. After the addition was complete, ultrasonic irradiation was continued for 20 min, with THF added as needed to replace that lost by evaporation. The reaction mixture was then removed from the drybox to a shielded hood, and 250 mL of water was added, after which the organic layer was separated from the aqueous layer. The organic layer was concentrated to 50 mL in vacuum. Addition of 200 mL of methanol gave a tan precipitate which was collected by filtration and purified by reprecipitation with ethanol from a THF solution, giving 2.23 g (25%) of poly(phenylcarbyne) (1): ^{1}H NMR δ 7.4 (br, $C_6\mathit{H}_5$); $^{13}C\{^1H\}$ NMR δ 140, 125 (br, C_6H_5), 51 (br, $\mathit{C}C_6H_5$); IR (KBr pellet, cm^{-1}) 3055 (s), 3024 (s), 2930 (m), 1946 (m), 1890 (m), 1811 (m), 1600 (s), 1491 (m), 1444 (s), 1175 (s), 1050 (m), 900 (w), 7 50 (s), 670 (s); GPC (THF versus polystyrene) $\bar{M}_w = 4000$, $\bar{M}_n = 3077$, polydispersity = 1.3; electronic spectrum (cyclohexane) onset at 450 nm, increasing gradually in intensity with decreasing wavelength to 200 nm; emission spectrum (cyclohexane, excitation wavelength = 300 nm) λ_{max} = 460 nm; ESR (9.1 GHz, solid) $g = 2.005$. Anal. Calcd. for C_6H_5: C, 94.34; H, 5.66. Found: C, 94.95; H, 6.13.

Poly(methylcarbyne), $[MeC]_n$ (2). 1,1,1-Trichloroethane (10 mL, 100 mmol) was reduced with NaK alloy (9.3 g, 300 mequiv) following the same procedure that was used to prepare **1**. After complete addition of the monomer and subsequent sonication, methanol (10 mL) was added to the reaction mixture while sonication was continued for 10 min. A vigorous reaction indicated that much of the NaK remained unreacted. The reaction mixture was then removed from the drybox to a shielded hood, where 200 mL of water was added. The red-brown organic layer was separated from the aqueous layer and concentrated in vacuum to 20 mL. Addition of 200 mL of methanol gave 95 mg (3.5%) of poly(methylcarbyne) (**2**) as a tan solid after filtration. ^{13}C NMR of the organic layer showed unreacted or partially reduced monomer as the only side products. Spectral data for **2**: ^{1}H NMR δ 1.0 (br, $C\mathit{H}_3$); IR (neat film on KBr, cm^{-1}) 2967 (s), 2930 (s), 2851 (s), 1638 (w), 1453 (m), 1375 (s), 1258 (vs), 1096 (w), 1024 (w), 850 (w), 752 (vw); GPC (THF versus polystyrene) $\bar{M}_w = 8096$, $\bar{M}_n = 4425$, polydispersity = 1.85; electronic spectrum (cyclohexane) onset at 400 nm, increasing gradually in intensity with decreasing wavelength to 200 nm. Anal. Calcd. for C_2H_3: C, 88.99; H, 11.11. Found: C, 64.96; H, 9.28.

75:25 Poly(phenyl-*co*-methylcarbyne), $[(PhC)_{0.75}(MeC)_{0.25}]_n$ (3). NaK alloy (50:50 mol %, 9.3 g, 300 mequiv) in 225 mL of THF was ultrasonically irradiated at full power for 3 min. A solution of α,α,α-trichlorotoluene (10.5 mL, 75 mmol) in 25 mL of pentane and a solution of 1,1,1-trichloroethane (2.5 mL, 25 mmol) in 25 mL of pentane were added dropwise simultaneously over 18 min with sonication, and sonication was continued for 10 min after the additions were complete. Methanol (100 mL) was added, and a vigorous reaction indicated that some NaK remained unreacted. Following the addition of the methanol, the red-brown reaction mixture was removed from the drybox, insoluble material was removed by filtration, and purification was carried out as described for **1**. This procedure gave 2.45 g (33%) of $[(PhC)_{0.75}(MeC)_{0.25}]_n$ (**3**) as a tan solid: ^{1}H NMR δ 7.2 (br, $C_6\mathit{H}_5$), 1.2 (br, $C\mathit{H}_3$), integration gives an empirical formula of $[(PhC)_{0.88}(MeC)_{0.12}]_n$; IR (KBr pellet, cm^{-1}) 3443 (w), 3061 (s), 3024 (s), 2926 (m), 1950 (m), 1890 (m), 1807 (m), 1599 (s), 1492 (vs), 1444 (vs), 1260 (s), 1074 (s), 1030 (s), 758 (s), 698 (s); electronic spectrum (cyclohexane) onset at 500 nm, in creasing gradually with decreasing wavelength to 200 nm; GPC (THF versus polystyrene) $\bar{M}_w = 6777$, $\bar{M}_n = 4912$, polydispersity = 1.37. Anal. Calcd. for $(PhC)_{0.75}(MeC)_{0.25}$: C, 93.88; H, 6.12. Found: C, 72.12; H, 6.19.

80:20 Poly(phenylcarbyne-*co*-phenylsilyne), $[(PhC)_{0.80}(PhSi)_{0.20}]_n$ (4). α,α,α-Trichlorotoluene (10.5 mL, 75 mmol) and phenyltrichlorosilane (3.9 mL, 25 mmol) were reduced with NaK (9.3 mL, 300 mequiv) following the same procedure that was used to prepare **3**. The product was purified by sequential precipitation from THF solution with water, methanol, and ethanol. This procedure gave 3.90 g (42%) of $[(PhC)_{0.80}(PhSi)_{0.20}]_n$ (**4**) as a yellow-orange powder: ^{1}H NMR δ 7.2 (br, $C_6\mathit{H}_5$); ^{13}C CPMAS NMR δ 135, 125 (br, C_6H_5), 65, 40 (br, $\mathit{C}C_6H_5$); IR (KBr pellet, cm^{-1}) 3036 (s), 2942 (s), 2937 (m), 1950 (m), 1870 (m), 1595 (s), 1484 (s), 1443 (m), 1419 (s), 1260 (m), 1114 (m), 1067 (m), 1020 (m), 990 (m), 732 (s), 690 (vs); GPC (THF versus polystyrene) $\bar{M}_w = 11\,381$, $\bar{M}_n = 4833$, polydispersity = 2.3; electronic spectrum (cyclohexane) onset at 450 nm, increasing gradually with decreasing wavelength to 200 nm. Anal. Calcd. for $(PhC)_{0.80}(PhSi)_{0.20}$: C, 88.50; H, 5.42; Si, 6.10. Found: C, 76.04; H, 5.43; Si, 6.10.

78:22 Poly(phenylcarbyne-*co*-*n*-butylsilyne), $[(PhC)_{0.78}(n\text{-}BuSi)_{0.22}]_n$ (5). α,α,α-Trichlorotoluene (10.5 mL, 75 mmol) and *n*-butyltrichlorosilane (4.1 mL, 25 mmol) were reduced with NaK (9.3 mL, 300 mequiv) following the same procedure that was used to prepare **3**. The product was purified by sequential precipitation from THF solution with water, methanol, and ethanol. This procedure gave 2.09 g (22%) of $[(PhC)_{0.78}(n\text{-}BuSi)_{0.22}]_n$ (**6**) as a yellow powder: ^{1}H NMR δ 7.2 ($C_6\mathit{H}_5$), 1.16, 0.85 ($C_4\mathit{H}_9$), integration gives an empirical formula of $[(PhC)_{0.61}(n\text{-}BuSi)_{0.39}]_n$; IR (KBr pellet, cm^{-1}) 3024 (s), 2924 (s), 1947 (m), 1850 (m) 1718 (m), 1598 (s), 1493 (vs), 1445 (s), 1376 (m), 1193 (m), 1078 (m), 1026 (s), 963 (s), 882 (m), 757 (s), 698 (vs); GPC (THF versus polystyrene) $\bar{M}_w = 9298$, $\bar{M}_n = 5830$, polydispersity = 1.59; electronic spectrum (cyclohexane) onset at 400 nm, increasing gradually with decreasing wavelength to 200 nm. Anal. Calcd. for $(PhC)_{0.777}(n\text{-}BuSi)_{0.223}$: C, 87.11; H, 6.24; Si, 7.16. Found: C, 74.70; H, 7.24; Si, 7.11.

99:1 Poly(phenyl-*co*-hydridocarbyne), $[(PhC)_{0.99}(HC)_{0.01}]_n$ (6). α,α,α-Trichlorotoluene (9.7 mL, 90 mmol) and chloroform (0.6 mL, 10 mmol) were reduced with NaK (9.3 mL, 300 mequiv) following the same procedure that was used to prepare **3**. The reaction mixture was purified by sequential precipitation from THF solution with water, methanol, and ethanol. This procedure gave 1.04 g (12%) of $[(PhC)_{0.99}(HC)_{0.01}]_n$ (**6**) as a tan powder: ^{1}H NMR δ 7.2 (br, $C_6\mathit{H}_5$), 2.0 ($C\mathit{H}$), integration gives an empirical formula of $[(PhC)_{0.99}(HC)_{0.01}]_n$; $^{13}C\{^1H\}$ NMR (10% ^{13}C-enriched at CH) δ 128, 114 (C_6H_5), 38 (CH); IR (KBr pellet, cm^{-1}) 3060 (s), 3025 (s), 2931 (m), 1950 (m), 1878 (m), 1805 (m), 1732 (w), 1595 (s), 1490 (s), 1443 (m), 1155 (s), 1114 (s), 1067 (s), 102 5 (s), 755 (s), 690 (vs); GPC (THF versus polystyrene) $\bar{M}_w = 5898$, $\bar{M}_n = 4168$, polydispersity = 1.41; electronic spectrum (cyclohexane) onset at 400 nm, increasing gradually with decreasing wavelength to 200 nm. Anal. Calcd. for $(PhC)_{0.99}(HC)_{0.01}$: C, 94.38; H, 5.62. Found: C, 86.45; H, 6.42.

98:2 Poly(phenylcarbyne-*co*-cyclopentadienyltitanium), $[(PhC)_{0.98}(CpTi)_{0.02}]_n$ (7). α,α,α-Trichlorotoluene (7.99 mL, 75 mmol) and cyclopentadienyltitanium trichloride (5.6 g, 25 mmol, in 10 mL of THF) were reduced with NaK (9.3 mL, 300 mequiv) following the same procedure that was used to prepare **3**. After complete addition of the monomers and subsequent sonication, water (200 mL) was added to the reaction mixture in a shielded hood, and the organic layer was separated from the aqueous. Addition of 200 mL of methanol to the organic layer gave a tan precipitate, which was collected by filtration and triturated with THF. This solution was filtered to remove 3.25 g of an insoluble brown solid. Addition of ethanol to the filtrate and refiltration gave 1.00 g (11%) of $[(PhC)_{0.98}(CpTi)_{0.02}]_n$ (**7**) as a yellow powder: ^{1}H NMR δ 7.2 (br, $C_6\mathit{H}_5$), 3.6 (br, $C_5\mathit{H}_5$), integration gives an empirical formula of $[(PhC)_{0.97}(CpTi)_{0.03}]_n$; $^{13}C\{^1H\}$ NMR δ 140, 125 (br, C_6H_5), 41 (br, $\mathit{C}C_6H_5$); ^{13}C CPMAS NMR δ 140, 128 (br, C_6H_5), 116 (br, C_5H_5); IR (KBr pellet, cm^{-1}) 3421 (w), 3061 (s), 3024 (s), 2908 (w), 1950 (m), 1866 (m), 1726 (m), 1620 (s), 1508 (vs), 1450 (s), 1145 (s), 1130 (s), 1074 (s), 1030 (s), 942 (m), 758 (s), 698 (s); GPC (THF versus polystyrene) $\bar{M}_w = 3327$, $\bar{M}_n = 2600$, polydispersity = 1.27; electronic spectrum (cyclohexane) onset at 450 nm, increasing gradually with decreasing wavelength to 200 nm, shoulder at 248 nm. Anal. Calcd. for $(PhC)_{0.976}(CpTi)_{0.024}$: C, 93.14; H, 5.58; Ti, 1.28. Found: C, 84.88; H, 6.12; Ti, 1.27.

95:5 Poly(phenylcarbyne-*co*-(pentamethylcyclopentadienyl)hafnium), $[(PhC)_{0.95}(Cp^*Hf)_{0.05}]_n$ (8). α,α,α-Trichlorotoluene (5.3 mL, 75 mmol) and (pentamethylcyclopentadienyl)hafnium trichloride (5.0 g, 25 mmol, in 25 mL of THF) were reduced with NaK (4.37 mL, 300 mequiv) following the same procedure that was used to prepare **3**. The product was purified by sequential precipitation from THF solution with water, methanol, and ethanol. This procedure gave 0.70 g (7%) of $[(PhC)_{0.95}(Cp^*Hf)_{0.05}]_n$ (**8**) as a tan powder: ^1H NMR δ 7.2 (br, C_6H_5), 1.9 (br, CH_3), integration gives an empirical formula of $[(PhC)_{0.94}(Cp^*Hf)_{0.06}]_n$; $^{13}C\{^1H\}$ NMR δ 140, 128 (CC_6H_5), 120 (C_5Me_5), 18 (CH_3); IR (KBr pellet, cm^{-1}) 3445 (w), 3023 (m), 2963 (m), 1952 (m), 1872 (m), 1720 (m), 1598 (s), 1492 (vs), 1443 (vs), 1066 (m), 912 (s), 756 (s), 697 (vs); GPC (T HF versus polystyrene) $\bar{M}_w = 5009$, $\bar{M}_n = 3965$, polydispersity = 1.26; electronic spectrum (cyclohexane) onset at 500 nm, increasing gradually with decreasing wavelength to 200 nm. Anal. Calcd. for $(PhC)_{0.9506}(Cp^*Hf)_{0.0494}$: C, 85.70; H, 5.49; Hf, 8.81. Found: C, 71.49; H, 5.56; Hf, 8.81.

Results and Discussion

Syntheses of Polycarbynes. In attempting to synthesize carbon-based analogues of inorganic network polymers, the much greater strength of C═C bonds over multiple bonds between inorganic elements had to be considered. Carbon polymers containing the tetrahedrally-hybridized carbyne unit (CR) were previously unknown, although many examples of oligomers of such units have been reported.[6] All other polymers of $[RC]_n$ stoichiometry adopt the polyacetylene structure, comprised of linear backbones of alternating C—C and C═C bonds. These polymers, however, are without exception synthesized by the polymerization of acetylene monomers, in which the carbon atoms are sp-hybridized. We theorized that rapid polymerization of monomers in which the carbon atoms were sp^3-hybridized might allow assembly of these atoms into tetrahedral arrays or network backbones analogous to those seen in the inorganic polymers. In our syntheses of inorganic polymers by Wurtz-type coupling of $RMCl_3$ monomers (M = Si, Ge), ultrasonically-generated emulsions of NaK alloy with organic solvents were demonstrated to be very fast and efficient reducing agents,[5] so an analogous synthesis of polycarbynes from $RCCl_3$ monomers using a similar reaction procedure was attempted. In a further attempt to avoid formation of polyacetylene-type structures, the phenyl group was chosen as the hydrocarbyl substituent to be used in initial attempts. The linear polyacetylene composed of the PhC unit, poly(diphenylacetylene), is known to be very sterically crowded, another factor which might favor formation of a carbyne-type structure.[3a,d]

We first attempted the synthesis of silyne/carbyne network copolymers, having seen from our previous work that the forming silyne network very efficiently incorporates monomers which cannot efficiently be polymerized alone under the reaction conditions, such as germanium, tin, and titanium species.[5] The syntheses were analogous to those which were successful for inorganic polymers: addition of varying ratios of $RSiCl_3$ and $PhCCl_3$ monomers to an ultrasonically-irradiated emulsion of THF and NaK (eq 1)

$$\underset{\textstyle R = Ph,\ n\text{-}Bu}{0.75PhCCl_3 + 0.25RSiCl_3} \xrightarrow[\text{475 W, 20 kHz ultrasound}]{\text{3.00NaK, THF}} [(PhC)_x(RSi)_y]_n \quad (1)$$

The syntheses of copolymers of $PhCCl_3$ with n-$BuSiCl_3$ and with $PhSiCl_3$ in 75:25 ratios were attempted by this method; the polymers were both obtained as soluble yellow-orange powders in yields of 20–40%, with empirical formulas of $[(PhC)_{0.80}(PhSi)_{0.20}]_n$ (**4**) and $[(PhC)_{0.78}(n\text{-}BuSi)_{0.22}]_n$ (**5**). Insoluble, cross-linked material and low-molecular-weight oligomers were the only other products. In both of these polymers (and in virtually all of those containing the carbyne unit), elemental analyses were significantly low in carbon (see Experimental Section). Since we have shown that carbyne backbone polymers are efficient pyrolyis precursors to diamond and diamond-like carbon at atmospheric pressure, a significant portion of the carbyne backbone may be converted to hard, oxidation-resistant carbon during combustion analysis, resulting in the low carbon values obtained. Similarly low values are seen in the combustion analyses of many molecular and polymer precursors to refractory ceramics.[10] Empirical formulas were therefore calculated from hydrogen and silicon analysis percentages. ^1H NMR integration gave an empirical formula of $[(PhC)_{0.61}(n\text{-}BuSi)_{0.39}]_n$ for **5**, but the inaccuracy of integration (see below) of the very broad peaks typical of network backbone polymers makes the analytically-derived formula more probable.

IR spectra of **4** and **5** show no bands at 1640–1655 cm^{-1}, which typically arise from *cis*-C═C double bonds in the backbones of polyacetylenes.[3,4] In the IR spectra of both polymers, bands characteristic of monosubstituted phenyl rings (1950, 1870–1850, 1718, and 750–730, 690 cm^{-1})[11] were seen, and no bands typical of phenylene structures (730–830 cm^{-1}) were present. The IR spectra therefore suggest that in both **4** and **5**, the [PhC] units are present as tetrahedral carbynes rather than as sp^2-hybridized species and that no cross-linking or reaction at the phenyl substituents has occurred. This is confirmed by the electronic spectra of the copolymers, which are virtually identical to those of polysilyne homopolymers,[5] indicating that the network backbone structure is present. The ^{13}C CPMAS NMR spectrum of **5** shows broad resonances between 40 and 65 ppm, in addition to the phenyl resonances at 125 and 135 ppm, which are typical of quarternary carbons (as seen, for example, in cubanes and dodecahedranes).[6] All spectral data on **4** and **5**, therefore, indicate that these materials are copolymers of silyne and carbyne units, each linked by three single bonds into a network backbone analogous in structure to those seen in the inorganic homopolymers.[12-17]

The successful extension of the reaction procedures used to prepare inorganic network polymers to the incorporation of carbyne backbone units led to attempts to prepare the first carbyne homopolymer, poly(phenylcarbyne) (**1**). The reduction of α,α,α-trichlorotoluene monomer with an ultrasonically-generated emulsion of NaK and THF (eq 2) gave **1** as a tan soluble powder in 25% yield. Very little insoluble material is produced in this reaction; the major side products are low-molecular-weight, alcohol-soluble oligomers. Chemical analysis of **1** was consistent with the empirical formula $[C_6H_5C]_n$, and gel permeation

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$$\mathrm{PhCCl_3} \xrightarrow[\text{475 W, 20 kHz ultrasound}]{\text{3.00NaK, THF}} [\mathrm{PhC}]_n + 3\mathrm{Na(K)Cl} \tag{2}$$

chromatography of the material gave $\bar{M}_w$ = 4000, $\bar{M}_n$ = 3077, indicating that **1** is polymeric.[18]

Infrared spectra of **1** (Figure 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)[3] (PDPA), the linear polymer whose empirical formula is identical to that of **1**. The IR spectra also show bands consistent only with monosubstituted phenyl rings (see above); no di- or trisubstituted phenylene-type aryl groups are present. The ^{13}C CPMAS NMR of **1** exhibits a very broad resonance ($\delta_{\nu 1/2}$ = 800 Hz) centered at 51–52 ppm (Figure 2), characteristic of quarternary carbon atoms, 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. The resonance at 51 ppm in the ^{13}C NMR spectrum of **1** is enhanced when **1** is synthesized using 10 mol % of α,α,α-trichlorotoluene monomer which has been labeled with ^{13}C in the α-position (Figure 2). These data indicate that C=C double 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 structure 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 single carbon–carbon bonds to the network and one to the phenyl substituent (Figure 3). This structure corresponds to the network arrangements found in the analogous silicon and germanium polymers and copolymers[5] and can be regarded as a geometrical isomer of the polyacetylenes.

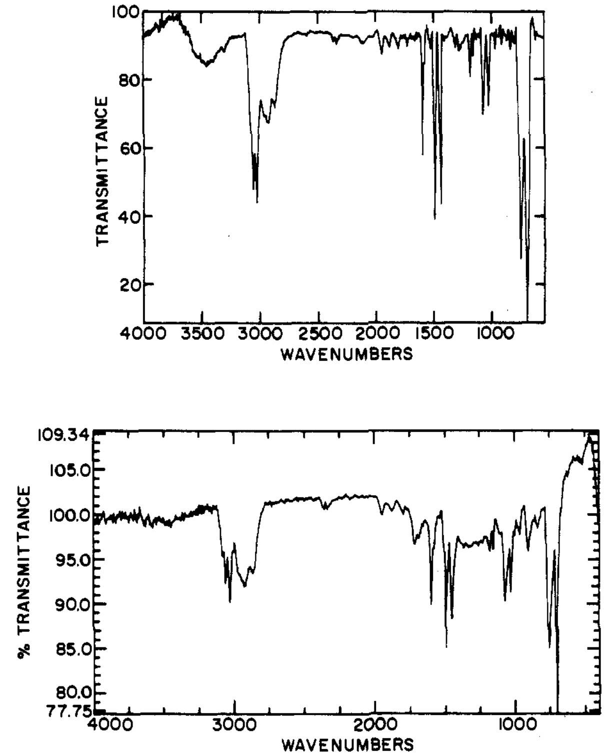

Figure 1. IR spectra of $[\mathrm{PhC}]_n$ (**1**, top) and $[(\mathrm{PhC})_{0.99}(\mathrm{HC})_{0.1}]_n$ (**6**, bottom).

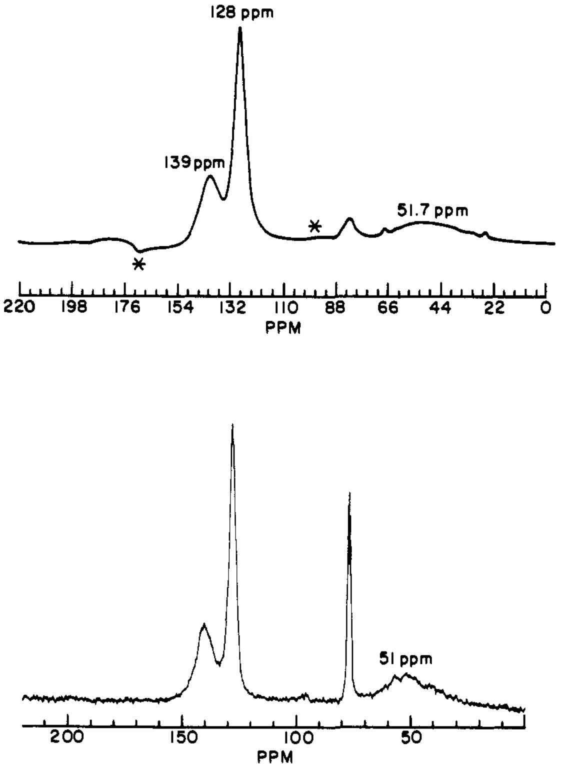

Figure 2. ^{13}C CPMAS NMR spectrum of $[\mathrm{PhC}]_n$ (**1**, top), and ^{13}C solution NMR spectrum of $[\mathrm{PhC}]_n$ which has been 10% enriched in ^{13}C in the backbone carbon.

Although spectral data indicate that the phenylcarbyne unit is the primary structural feature of **1**, some indications that impurities may be present are also seen. An aliphatic C–H stretching band at 2930 cm^{-1} is present in the IR spectra of **1**; this is attributed to some incorporation of THF into the polymer during the reductive condensation synthesis. This band is also present in the IR spectra of poly(phenylsilyne)[5e,g] and poly(phenylgermyne),[5f] which are also synthesized by a reductive condensation procedure in THF solution, and in the IR spectrum of **4**. Since no resonances attributable to incorporated THF appear in the ^{1}H NMR spectra of these polymers, and since the homopolymers give elemental analyses correct for their empirical formulas, the amount of THF incorporation into the materials must be small. A band at 3500 cm^{-1}, which sometimes appears in the IR spectrum of **1**, may arise from absorbed water (all the phenyl-containing polymers, as well as poly(diphenylacetylene), are hygroscopic), but also may be due to C–OH sites which arise from hydrolysis of unreacted C–Cl bonds during aqueous workup. A resonance sometimes seen in the ^{13}C NMR spectra of **1** (Figure 2) at ≈80 ppm may also indicate the presence of such sites, as this resonance has been attributed to C–OH functionalities in other carbon network polymer systems.[16] In addition, when **1** is synthesized with addition of the trichlorotoluene monomer to the NaK alloy emulsion over time periods longer than 25 min, the resulting polymer displays a weak band in its IR spectrum at 1642 cm^{-1}, indicating that C=C double bonds have formed. The intensity of this absorption increases with the time of monomer addition, suggesting that, although tetrahedral carbyne is the primary product of this reduction of an sp^3-hybridized monomer, the C=C double-bonded polyacetylene structure is the thermodynamic product and may be increasingly formed with longer reaction times and sonication. Whether the regions of polyacetylene structure which appear with long reaction times are incorporated into the primary reaction product or the polycarbyne network or form oligomers of poly(diphenylacetylene) homopolymer which are merely coprecipitated with the major product during purification is unknown. The characteristic spectral peaks of C=C bonds are seen, however, in the IR and NMR spectra

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(18) Because the GPC molecular weights of the polymers reported here were determined using linear polystyrene standards, the absolute value of the molecular weight is probably underestimated, as is seen in other network polymer systems,[5,13,14] and should be regarded as an estimate and a lo wer limit only.

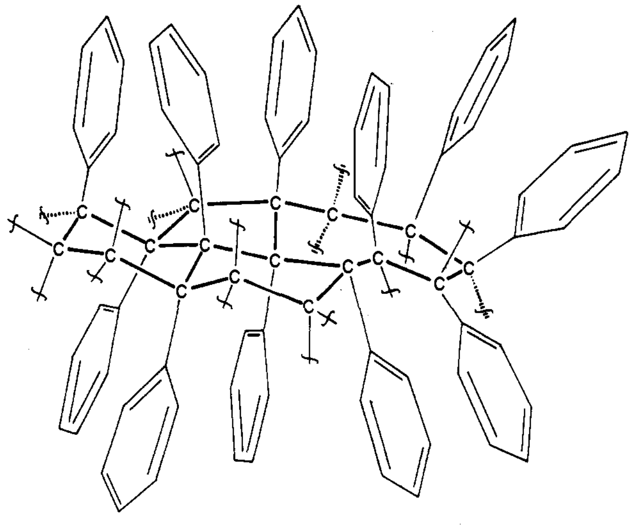

Figure 3. Schematic representation of the proposed network structure of **1**. Reference 8.

of crude samples of **1**, before the polymer has been purified by sequential precipitation, indicating that some oligomers containing the poly(diphenylacetylene) unit are produced by the polymerization reaction.

With the inorganic network backbone polymers, we have demonstrated that a substituent which extends at least three atoms out from the polymer backbone is necessary to solvate these networks;[5] for example, $[\mathrm{MeSi}]_n$ and $[\mathrm{EtSi}]_n$ are insoluble materials, and $[n\text{-}\mathrm{PrSi}]_n$ is only marginally soluble. However, since C–C single bonds are much shorter than those between inorganic elements (1.54 vs 2.34 Å for Si–Si single bonds), polycarbynes of the same degree of polymerization should form much smaller networks and therefore could possibly be solvated by shorter substituent groups. We therefore attempted the synthesis of poly(methylcarbyne) (**2**) by the reductive condensation of 1,1,1-trichloroethane (eq 3). The reaction proceeded

$$\mathrm{MeCCl_3} \xrightarrow[\text{475 W, 20 kHz ultrasound}]{\text{3.00NaK, THF}} [\mathrm{MeC}]_n + 3\mathrm{Na(K)Cl} \quad (3)$$

only to a small extent; the yield of soluble, polymeric product was only 3.5%, and the only side products observed were unreacted or partially reduced monomer. The amount of **2** obtained was too little to observe in ^{13}C NMR spectra, but GPC showed it to be polymeric, and its IR and ^{1}H NMR were consistent with those seen for other network polymers. Significantly, the electronic spectrum of **2** displays the characteristic network polymer absorption, confirming the presence of the carbyne network backbone (Figure 4) rather than the absorptions characteristic of poly(dialkylacetylenes).[3f] The presence of this absorption in an alkyl-substituted polycarbyne demonstrates that the apparent conjugation of these polymers' backbones (see below) does not arise from an extended π-system which might be formed during the reductive condensation of aryl-substituted monomers by reaction at the phenyl rings to give phenylene structures in the backbone.

The IR spectra of **2** show a band at 1638 cm^{-1} (see Figure 1), indicative of C=C double bonds, regardless of addition time of the monomer during the synthesis. The greater tendency for formation of the polyacetylene-type structure that is seen with this monomer is quite probably due to the relief of steric strain in the linear structure upon moving from the large phenyl substituent to the smaller methyl group. Similarly, the GPC weight-average molecular weight of **2** (8096 Da) is approximately twice that of **1** (4000 Da), demonstrating the increase in degree of polymerization with decreasing steric bulk of substituent which was found to be the critical factor in determining the molecular weight of the inorganic network polymers.[5]

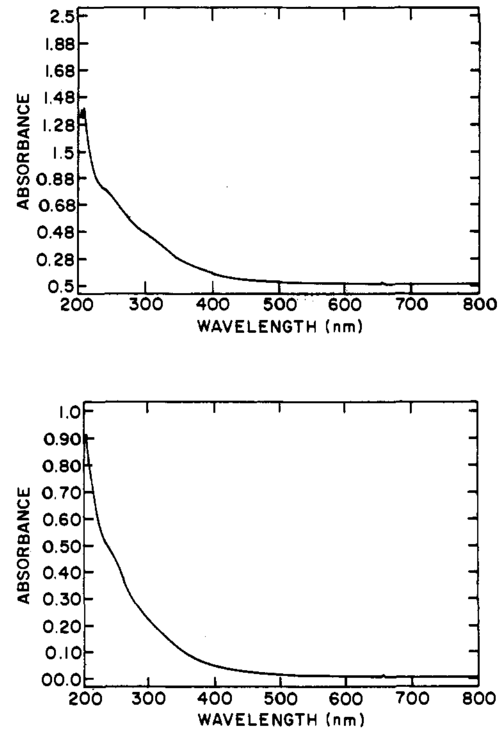

Figure 4. Electronic spectra (cyclohexane solution) of $[\mathrm{PhC}]_n$ (**1**, top) and $[\mathrm{MeC}]_n$ (**2**, bottom).

Since network copolymers of inorganic monomers have been easily synthesized and show useful variations in physical properties with variation in incorporated amounts of different monomers, we attempted to synthesize analogous polycarbyne copolymers. Reductive condensation of varying ratios of $\mathrm{PhCCl_3}$ with $\mathrm{MeCCl_3}$ and $\mathrm{HCCl_3}$ were performed, as shown in eq 4. In each case, soluble

$$\underset{\mathrm{R = Me,\ H}}{0.75\mathrm{PhCCl_3} + 0.25\mathrm{RCCl_3}} \xrightarrow[\text{475 W, 20 kHz ultrasound}]{\text{3.00NaK, THF}} [(\mathrm{PhC})_x(\mathrm{RC})_y]_n \quad (4)$$

polymeric materials were isolated as tan powders; each reaction also produced some insoluble cross-linked material, the amount of which increased upon increasing the percentage of the $\mathrm{MeCCl_3}$ or $\mathrm{HCCl_3}$ monomers. For monomer ratios of 75:25 $\mathrm{PhCCl_3}$ to $\mathrm{MeCCl_3}$ and 90:10 $\mathrm{PhCCl_3}$ to $\mathrm{HCCl_3}$, yields of soluble polymers ranged from 12 to 33% (for the calculated empirical formulas, see below). IR spectra show bands at 1640 and 1732 cm^{-1} for the $\mathrm{MeCCl_3}$- and $\mathrm{HCCl_3}$-derived copolymers, respectively (Figure 1); the intensities of these bands increase with increasing incorporation of MeC or HC units, again attrivutable to increased polyacetylene structure formation with increasing relief of steric strain. Similarly, the GPC weight-average molecular weights of the PhC/MeC copolymers are intermediate between those of the two homopolymers (see Experimental Section). Electronic spectra of the copolymers show the broad absorption band characteristic of the network backbone; also, the ^{13}C NMR spectrum of a 90:10 PhC/HC copolymer which was prepared using ^{13}C-enriched $\mathrm{HCCl_3}$ shows a strong, broad resonance in the quarternary carbon region (20–80 ppm), indicative of the carbyne structure.

Coreduction of 75% $\mathrm{PhCCl_3}$ with 25% $\mathrm{MeCCl_3}$ gives a copolymer which, by the hydrogen elemental analysis, has an empirical formula of $[(\mathrm{PhC})_{0.75}(\mathrm{MeC})_{0.25}]_n$ (**3**). Integration of the $\mathrm{CH_3}$ resonance at 1.2 ppm in the ^{1}H NMR spectrum of **3** with the phenyl proton resonance at 7.2 ppm gives an empirical formula of $[(\mathrm{PhC})_{0.88}(\mathrm{MeC})_{0.12}]_n$. This underestimation of the methyl protons in the ^{1}H NMR integration is consistent with the observed increase in rigidity and concomitant broadening and decrease in signal intensity which is seen in the NMR resonances of substituent carbon and hydrogen atoms of the polysilynes as the substituent atoms become closer to the rigid network backbone.[5] Similarly, coreduction of 90% $PhCCl_3$ with 10% $HCCl_3$ gives a polymer which, by proton integration, has an empirical formula of $[(PhC)_{0.99}(HC)_{0.01}]_n$ (**6**), which the hydrogen elemental analysis shows is an underestimation of the amount of HC units incorporated. Taking the empirical formulas given by integration as lower limits, the amount of MeC or HC units incorporated into copolymer with PhC is reasonably close to that introduced in the synthesis.

Physical Properties of Polycarbynes. The physical properties of the polycarbyne homo- and copolymers also indicate their structural similarity to inorganic network backbone polymers, the polysilynes and polygermynes. Like the inorganic polymers,[5] the polycarbynes are amorphous, displaying no X-ray diffraction patterns, discrete glass transition temperatures, or melting points. They are air-stable in the absence of light and can be cast from solution to form transparent films.

The electronic spectra of the polycarbynes are essentially identical to those of polysilynes, consisting of intense broad absorptions which start at $\lambda \leq 200$ nm and tail down into the visible to approximately 450 nm (Figure 4). This absorption band in polysilynes and germynes has been attributed to extensive σ-conjugation which extends across the three-dimensional network backbone. **1** also exhibits an intense broad fluorescence (λ_{max} = 460 nm) similar to that of the polysilynes and frequency-shifted from the emission of poly(diphenylacetylene) (λ_{max} = 520 nm). These features of the electronic spectra of polycarbynes are analogous to those produced by long-range through-bond electron transfer via rigid nonconjugated carbon–carbon bonds in molecular species,[19] or via tunneling,[20] and are presumed to arise in the polycarbynes from hole or electron transfer through a similarly hyperconjugated carbon framework, the rigid network backbone.[21] In these electronic properties, the polycarbynes are displaying behavior more characteristic of solids than of non-π-conjugated organic polymer networks, again demonstrating their similarly to their inorganic backbone congeners.

Like the polyacetylenes, poly(phenylcarbyne) exhibits a strong ESR signal which is characteristic in line shape and position of carbon-centered radicals. In sterically crowded polyacetylenes, this signal is attributed to formation of radicals by the twisting of the polymer backbone to relieve steric congestion, which disrupts the carbon–carbon π-bonds.[3] The ESR signal seen in **1** is presumed to arise from an analogous weakening or disrupting of the C–C single bonds of the network backbone in order to relieve steric strain, which again produces radicals. Molecular modeling has shown that the poly(phenylcarbyne) structure is indeed very sterically congested;[21] in contrast, poly(phenylsilyne) shows no ESR signal at all, indicating that the much longer Si–Si and Si–Ph bonds form a much less sterically crowded network, which can accommodate groups such as phenyl without disruption of the backbone's σ-bonds. A high degree of twisting of the backbone of polyacetylenes virtually destroys backbone conjugation; the position of the absorptions in the electronic spectrum of poly(diphenylacetylene) (298 and 280 nm) indicates average conjugation lengths of only 2–3 carbon–carbon double bonds.[4] In contrast, since the backbone of **1** is essentially σ-conjugated, analogous to those of inorganic networks, the radicals formed upon disruption of some C–C bonds can be transferred through the three-dimensional polymer network, producing the semiconductor-like electronic absorption spectrum. That this absorption arises from the carbon network backbone and not from any conjugated π-system formed by phenylene structures incorporated into the backbone is demonstrated by the appearance of an almost identical absorption in poly(methylcarbyne) (**2**). These electronic properties are analogous to those of the silyne and germyne polymers[5] and indicate that these atomic-level network systems can be regarded as behaving more like small clusters of solid sp^3-carbon (or silicon or germanium) solubilized on their surfaces with organic groups than like carbon-based network polymers which are composed of molecular repeating units.

Reactivity of Polycarbynes. Polymer **1** also undergoes the photooxidation reaction (insertion of oxygen into the carbon–carbon σ-bonded network upon UV irradiation), which has been found to be characteristic of the network backbone and which has allowed the use of polysilynes as photoresists for submicrometer lithography. 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 at 1720 and 1180 cm^{-1}, respectively. No reaction is seen by IR when linear poly(diphenylacetylene) 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 silicon-based congeners, may be photopatternable[22] and therefore potentially useful in photolithographic processes.

As was previously reported,[8] in one other important respect, carbyne-based polymers display unique reactivity owing to the sp^3-network backbone structure. Pyrolysis of **1** at atmospheric pressure under inert atmosphere gives predominantly sp^3-carbon phases, including diamond or diamond-like carbon, whereas other carbon-based polymers produce principally sp^2-hybridized carbon (as graphite, glassy carbon, or carbon black). Poly(diphenylacetylene), for example, the organic polymer which is chemically identical to poly(phenylcarbyne) but which lacks the sp^3-carbon network backbone which is the unique structural feature of **1**, was shown to produce principally graphite upon pyrolysis. The difference in the amount of sp^3- and sp^2-hybridized carbon in the pyrolysis products given by these stoichiometrically identical polymers 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 three-dimensional network of tetrahedral carbon atoms, as opposed to the sp^2-hybridized carbons that make up the backbon e of polyacetylenes. During pyrolysis, conversion of the 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 are reported to pyrolyze to give glassy[15] or amorphous[16] carbon, not sp^3-phases, again confirming that it is the already-present, all-tetrahedral-carbon microstructure of poly(phenylcarbyne) that is the critical feature in allowing its facile conversion to diamond-like carbon, and not simply the

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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 some current deposition processes. The conversion properties and yield of other polycarbynes and the quality of the diamond-like or hard carbon products obtained from pyrolysis are currently under investigation.[9]

Incorporation of Metals into Polycarbynes. Since network copolymers of silynes with group 4 metal monomers have been easily synthesized and show useful variations in physical properties with variation in incorporated amounts of different monomers,[23] we attempted to synthesize analogous metal-containing polycarbynes. Reductive condensation of varying ratios of $\mathrm{PhCCl_3}$ with $\mathrm{CpTiCl_3}$ and $\mathrm{Cp^*HfCl_3}$ were performed, as shown in eq 5.

$$\begin{array}{l} 0.75\mathrm{PhCCl_3} + 0.25\mathrm{RMcl_3} \xrightarrow[475\ \mathrm{W,\ 20\ kHz\ ultrasound}]{3.00\mathrm{NaK,\ THF}} \\ \qquad\qquad \mathrm{R = Cp, M = Ti} \\ \qquad\qquad \mathrm{R = Cp^*, M = Hf} \\ \qquad\qquad\qquad\qquad\qquad [(\mathrm{PhC})_x(\mathrm{RM})_y]_n \quad (5) \end{array}$$

In each case, soluble polymeric materials were isolated as tan powders; the reactions involving the titanium species also produced some insoluble cross-linked material, although the Hf reactions gave soluble oligomeric species as the only side products. For monomer ratios of 75:25 $\mathrm{PhCCl_3}$ to $\mathrm{CpTiCl_3}$ or $\mathrm{Cp^*HfCl_3}$, yields of soluble polymers ranged from 7 to 11% (for the calculated empirical formulas, see below). Because of the very great steric bulk of the Cp and Cp* substituents, it was not clear that any metal species would be incorporated or that any high-molecular-weight material would be obtained. Also, the extremely reducing conditions under which the polymerizations are carried out may have reduced the metal-containing species to colloidal metal before any could be incorporated into the polymers. As expected, the yields of soluble polymeric material were lower for reactions which involved the far bulkier Cp*Hf unit as opposed to the CpTi, although the GPC molecular weights of the Hf-containing polymers were higher.

Coreduction of 75% $\mathrm{PhCCl_3}$ with 25% $\mathrm{CpTiCl_3}$ gives a polymeric material which, by the elemental analysis, has an empirical formula of $[(\mathrm{PhC})_{0.98}(\mathrm{CpTi})_{0.02}]_n$ (**7**). The presence of the Cp ligand is confirmed by resonances in the ^{1}H and ^{13}C NMR spectra of **7**, at 3.2 and 116 ppm, respectively, which are characteristic of this ligand. Integration of the Cp resonance at 3.2 ppm in the ^{1}H NMR spectrum of **7** with the phenyl proton resonance at 7.2 ppm gives an empirical formula of $[(\mathrm{PhC})_{0.97}(\mathrm{CpTi})_{0.03}]_n$, confirming the empirical formula derived from elemental analysis. Polymer **7** shows all the characteristic spectral properties of the polycarbyne networks, including an absence of C=C stretches in its IR spectrum and the characteristic broad electronic absorption band. The polycarbyne network therefore appears to be present, with CpTi units incorporated. In copolymers of silynes with CpTi, sharp resonances in the ^{29}Si spectrum at −15 to −20 ppm indicate the presence of Ti—Si bonds,[23] suggesting that the CpTi units have been incorporated covalently into the silicon network backbone. No spectral data yet observed for **7** indicate how the CpTi units may be incorporated in the $[\mathrm{PhC}]_n$ macromolecules, but structures analogous to the silyne/CpTi polymers are indicated by the very similar NMR and electronic spectra of the materials.

Coreduction of 75% $\mathrm{PhCCl_3}$ with 25% $\mathrm{Cp^*HfCl_3}$ gives a polymeric material which, by the elemental analysis, has an empirical formula of $[(\mathrm{PhC})_{0.95}(\mathrm{Cp^*Hf})_{0.05}]_n$ (**8**). The presence of the Cp* lgiand is confirmed by resonances in the ^{1}H and ^{13}C NMR spectra of **8**, at 1.9 and 120 ppm, respectively, which are characteristic of this ligand. Integration of the Cp* resonance at 1.9 ppm in the ^{1}H NMR spectrum of **8** with the phenyl proton resonance at 7.2 ppm gives an empirical formula of $[(\mathrm{PhC})_{0.94}(\mathrm{Cp^*Hf})_{0.06}]_n$, confirming the empirical formula derived from elemental analysis. Polymer **8** again shows all the characteristic spectral properties of the polycarbyne networks, including an absence of C=C stretches in its IR spectrum and the characteristic broad electronic absorption band. The polycarbyne network therefore appears to be present, with Cp*Hf units now incorporated. The syntheses of **7** and **8** demonstrate that metals, as well as silicon, can be incorporated into polycarbynes, although the currently used synthetic procedures are not yet optimized for efficient incorporation of these monomers. The successful introduction of metals into the polycarbynes suggests that other elements may also be successfully used to tailor the reactivity, pyrolysis properties and products, and electronic behavior of the network carbon polymers.

Conclusions

The syntheses of the first $[\mathrm{RC}]_n$ network polymers, or polycarbynes, and of copolymers containing the carbyne unit were achieved by reductive condensation of $\mathrm{RCCl_3}$ and similar monomers using ultrasonically-generated THF NaK alloy emulsions in a procedure analogous to that which was successful in producing inorganic backbone network polymers. The new polymers are soluble in organic solvents and can be cast to form transparent films. All chemical and spectroscopic data indicate that the polycarbynes and their copolymers with inorganic and metallic elements are primarily composed of sp^3-hybridized alkyl or arylcarbyne units assembled via C–C single bonds into irregular networks. The atomic-level carbon network backbone confers unusual properties on the polymers, including, in the case of **1**, facile thermal decomposition to form diamond or diamond-like carbon phases at atmospheric pressure. Further studies on the optimization of polymer syntheses, the syntheses of new polymers containing the carbyne unit, and of the conversion of these materials to ceramics are in progress.

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