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Facile Synthesis of Poly(phenylcarbyne): a Precursor for Diamondlike Carbon

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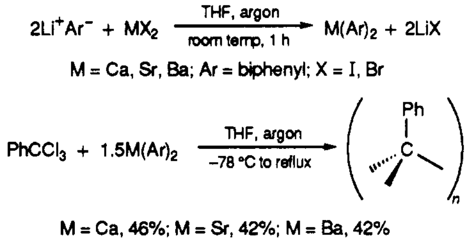
Man-made diamond processes are both unwieldly and expensive processes. The popular commercial process involves a transformation of graphite to diamond at 2500 °F under 50 000 atm of pressure. Another commercial method is a process of chemical vapor deposition (CVD) which yields a diamond film with high thermal conductivity, optical transparency, hardness, inertness, and even high electrical mobilities (semiconductivity).[1,2] Both processes are slow, expensive, and difficult to control.[3] Recently, Bianconi and Visscher[4] reported the chemical synthesis of a polymer precursor–poly(phenylcarbyne) which could be transformed to diamond-like carbon by simple pyrolysis. The report immediately attracted the attention of the media and the public since "the discovery implies there is a chemical means of forming diamond without hydrogen or a plasma. The discovery also implies a chemistry-based layer-by-layer growth of diamond is feasible."[5] However, the approach required a high-intensity ultrasonic immersion equipment and a sodium/potassium alloy[4] which could limit the industrial applications; moreover, the yield of poly(phenylcarbyne) is only 25% by this approach. Herein, we report a facile synthesis for poly(phenylcarbyne); the reaction can be completed under mild conditions, and the yield is almost double that of the previous method.

Highly reactive metals have been found to be a useful tool in the synthesis of special polymers, such as in chemical modification of halogenated polystyrene resins,[6] and in the synthesis of highly regioregular and high electroconductive poly(alkylthiophenes).[7] This experience encouraged us to investigate the synthesis of poly(phenylcarbyne) using these metals. The poly(phenylcarbyne) was synthesized by the following procedure:[8] Lithium (0.06 mol, ribbon from Aldrich) and biphenyl (0.066 mol) in a 100-mL flask were stirred in freshly distilled THF (40 mL) at room temperature under argon until the lithium was completely consumed (ca. 2 h). To a well-suspended solution of CaI_2 (0.03 mol, anhydrous from Cerac) in THF (40 mL) in a 250-mL flask, the preformed lithium biphenyllide was transferred via cannula at room temperature. The solution of Rieke calcium was stirred for 1 h at room temperature (the Rieke calcium is dark green and is apparently homogeneous in THF). A solution of α,α,α-trichlorotoluene (0.019 mol, 99+ % from Aldrich) in 10-mL of dry pentane was then added via a cannula at −78 °C. The reaction mixture was then warmed to room temperature and refluxed for 4 h. The reaction mixture was then cooled to room temperature and worked up[9] by the reported procedure.[4] The resulting tan powder was dried at 100 °C under vacuum for 24 h, giving 0.79 g (46%) of poly(phenylcarbyne). Using $SrBr_2$ or BaI_2 instead of CaI_2, following the same procedure described above gave the same product with 42% yield:



The spectral analysis (FTIR, ^1H and ^{13}C NMR, UV, fluorescence) proved the polymer obtained using this methodology was the same as the previously reported poly(phenylcarbyne).[4] The poly(phenylcarbyne) is a random three-dimensional polymer network. Infrared spectra[10] showed only monosubstituted phenyl groups present (the strong absorbance at 698 cm^{-1} ($\delta(mono_1)$) and 756 cm^{-1} ($\delta(mono_2)$) for two out-of-plane vibrations of a monosubstituted benzene ring).[11] No absorption bands of disubstituted benzene rings were found at 805 (for para-substituted),[11a,b] 790 and 870 cm^{-1} (for meta-substituted).[11c] No absorption bands of aliphatic C═C were found at 1650 cm^{-1}.[4,12] The ^1H NMR (500 MHz, $CDCl_3$) spectrum displayed a dominant aromatic proton resonance at δ 7.3 ppm. The very weak resonance around δ 3.5 ppm belonged to the terminal proton[13] of the polymer network. The ^{13}C NMR (125 MHz, $CDCl_3$) spectrum exhibited three resonances, one centered at 140 ppm was attributed to the

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(8) All manipulations were carried out under an atmosphere of argon on a dual manifold/argon system. Lithium ribbon, biphenyl, and MX_2 (M = Ca, Sr, Ba; X = I, Br) were weighed out and charged into reaction flasks under argon in a Vacuum Atmospheres Co. drybox. Tetrahydrofuran was distilled from Na/K alloy under an argon atmosphere immediately before use.

(9) Workup procedure: To the reaction mixture, distilled water (100 mL) was added. The mixture was then stirred for 30 min at room temperature. The organic layer was separated, filtered, and then concentrated to 30 mL in volume by vacuum. Addition of methanol (150 mL) to organic layer gave a tan precipitate, which was collected by filteration, washed by several portions of methanol (30 mL), and purified by reprecipitation twice from THF solution upon addition of ethanol. The biphenyl, which is soluble in ethanol and very soluble in methanol, and oligomer were washed out by the filteration and the purification above.

(10) FTIR spectral data (neat polymer film cast from $CHCl_3$ solution onto NaCl disk): 3053(s), 3024(s), 2924(m), 1946(w), 1882(w), 1803(w), 1599(s), 1492(s), 1444(s), 1180(m), 1155(m), 1030(m), 910(w), 756(s), 698(s), 667 cm^{-1} (w). The spectra show no absorption band for –OH group.

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(13) The chemical shift (δ) for methyl protons of toluene ($Ph\text{-}CH_3$) is 2.3 ppm; for methylene protons of bibenzyl ($Ph\text{-}CH_2CH_2\text{-}Ph$) is 2.9 ppm. In poly(phenylcarbyne), the terminal protons (>C(Ph)–*C*H(Ph)–C(Ph)<) are further deshielded since they bear more benzyl groups in the three-dimensional network of polymer. The chemical shift for these protons should be downfield to ~3.5 ppm.

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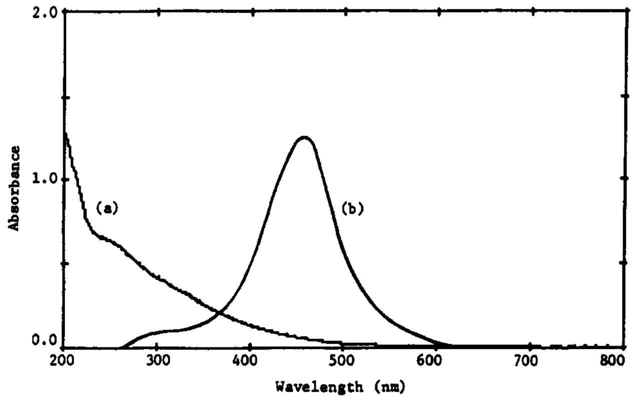


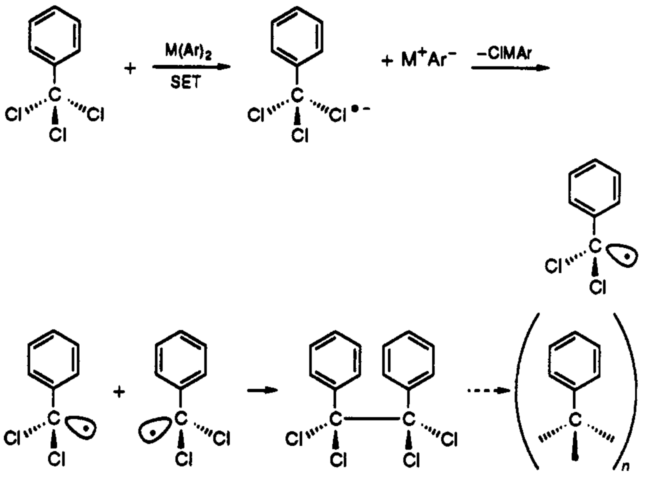
Figure 1. (a) UV–vis electronic spectrum (cyclohexane) and (b) fluorescence spectrum (cyclohexane, excitation wavelength = 300 nm) of poly(phenylcarbyne) obtained by this methodology.

ipso carbon of the phenyl ring, an intense resonance at 128 ppm was denoted to the other five carbons of the phenyl ring, a very broad resonance centered at 50 ppm was denoted to the quaternary carbon of poly(phenylcarbyne).[4]

The UV–vis electronic spectrum exhibited an intense broad absorption which started at a wavelength $\lambda \leq 200$ nm and decreased to 460 nm (Figure 1). Corresponding to the electronic absorbance, an intensive, broad fluorescence peak with λ_{max} at 460 nm was found in the fluorescence spectrum of polymer (Figure 1). Both UV–vis and fluorescence properties were consistent with the poly(phenylcarbyne) structure.[4]

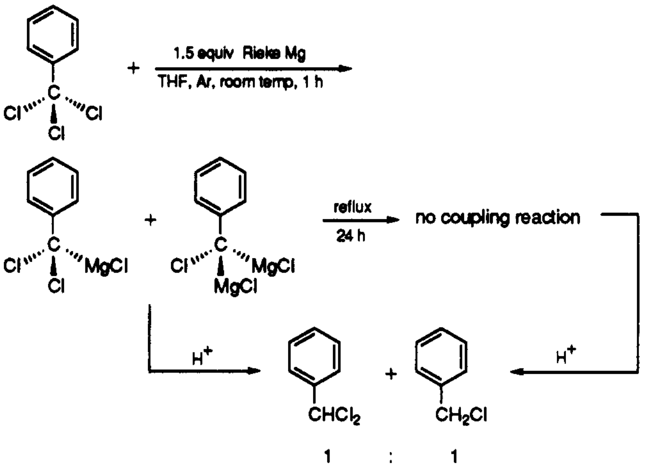
The elemental analysis of the polymer compared well with the empirical formula $(C_6H_5C)_n$ of poly(phenylcarbyne).[14] The molecular weight was determined by gel permeation chromatography (GPC, relative to polystyrene standard, THF as solvent), $\bar{M}_w = 4979$ and $\bar{M}_n = 2791$, corresponding to a polydispersity index of 1.81. The poly(phenylcarbyne) is soluble in common organic solvents, and a brown transparent film is easily cast from the solutions.

Scheme 1[a]



[a] M = Ca, Sr, or Ba. Ar = biphenyl.

The soluble and homogeneous forms[15] of highly reactive metals such as Rieke calcium, barium, or strontium are effective reagents for this type of polymerization. The polymerization failed when insoluble highly reactive metal powders such as Rieke magnesium[16] were used. The soluble biphenyl complexes $M(biphenyl)_2$ (M = Ca, Sr or Ba) were sufficiently active to facilitate polymerization. In contrast only oxidative addition of Mg* into the carbon–chlorine bond occurred and upon workup only α-chlorotoluene and α,α-dichlorotoluene were recovered quantitatively as products after 24 h of reflux. No coupling reaction or polymerization occurred:



these results suggest a free-radical mechanism for the polymerization of α,α,α-trichlorotoluene mediated by the homogeneous forms of highly reactive metals (Scheme 1). The polymerization is assumed to proceed by the coupling of free radicals which are generated by single-electron transfer (SET) between $M(biphenyl)_2$ and the carbon–chlorine bond[17] followed by exclusion of a chlorine anion. This novel approach to poly(phenylcarbyne) appears to be a general approach to several new materials. These results will be reported in due course.

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(14) Elemental anal. calcd for $(C_6H_5C)_n$: C, 94.36; H, 5.64. Found: C, 93.27; H, 5.79. No oxygen or chlorine was found, and no residue was detectable on combustion analysis of the sample.

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