# Platinum-catalyzed hydrosilylation of $C_{60}$: synthesis of a novel fullerene–siloxane polymer

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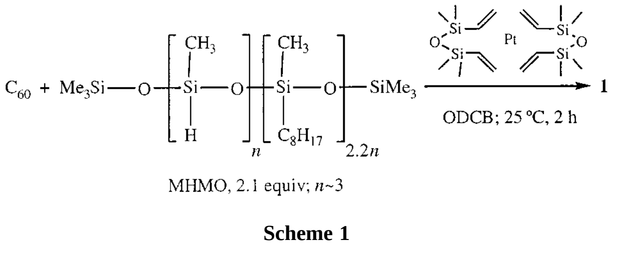
**The hydrosilylation of buckminsterfullerene with the oligomer poly(methylhydridomethyloctylsiloxane) produced a soluble, oxidation-resistant fullerene–siloxane copolymer, in which the siloxane oligomer is multiply attached to the $C_{60}$ moiety by covalent Si–C bonds essentially encapsulating the fullerene cage.**

With the development of a method for the preparation of macroscopic amounts of buckminsterfullerene, the chemistry of this closed shell molecule has been extensively investigated.[1,2] Finding useful chemical applications for $C_{60}$, however, has been met with limited success, partly due to its low solubility in common organic solvents.[3] Thus, much of the organic chemistry involving this molecule focuses on the synthesis, isolation, and characterization of its derivatives. It is hoped that some of these compounds will find useful application due to their increased solubility and unique electronic properties.

In 1991 Fagan *et al.* published the synthesis of $C_{60}$-$\eta^2$-bis(triphenylphosphine)platinum, the first fullerene–metal complex.[4] This landmark paper has led to further developments in fullerene–metal chemistry.[5] In addition, since platinum is the favored catalyst for hydrosilylation, it raised the possibility that $C_{60}$ might be derivatized by $R_3SiH$ addition reactions.[6] We report the metal catalyzed hydrosilylation of $C_{60}$ with poly(methylhydridomethyloctylsiloxane), MHMO, and characterization of the product, an unusual fluid.[7]

The original goal of this research was to synthesize a siloxane copolymer with pendant $C_{60}$ units. $C_{60}$ was synthesized using a modified graphite evaporation apparatus and was purified by continuous column chromatography.[8,9] The reaction of pure $C_{60}$ with 2.1 equiv. of MHMO ($M_w \approx 1470$; 3.1 Si–H/chain), and 0.05 equiv. of the platinum catalyst, (divinyltetramethyldisiloxane)platinum(0), afforded a shiny, black oil **1** in 83% yield (Scheme 1).† Product **1** was relatively viscous and displayed a low molecular weight, low dispersion pattern using size exclusion chromatographic analysis with an estimated molecular weight of *ca.* 4000 (Fig. 1). **1** was readily soluble in tetrahydrofuran, toluene, benzene, chloroform and carbon disulfide; slightly soluble in hydrocarbons such as hexane, cyclohexane and 3-methylpentane; and insoluble in water and alcohols. In contrast to many fullerenes and fullerene derivatives, **1** was resistant to air oxidation.[10] The IR absorption spectrum of the purified compound showed no absorption in the 2100–2300 $cm^{-1}$ region, indicating the absence of any Si–H functionality.



$$C_{60} + Me_3Si{-}O{-}\left[Si(CH_3)(H){-}O\right]_n{-}\left[Si(CH_3)(C_8H_{17}){-}O\right]_{2.2n}{-}SiMe_3 \xrightarrow[\text{ODCB; 25 °C, 2 h}]{} \mathbf{1}$$

**Scheme 1**

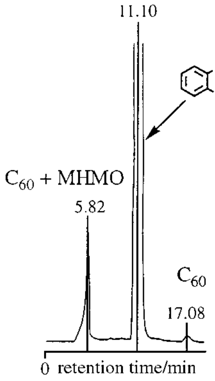


**Fig. 1** GPC chromatograph of the reaction mixture after 1 h; a small amount of unreacted $C_{60}$ is still present.

The UV–VIS spectra of the product and of unreacted $C_{60}$ in THF are shown in Fig. 2. The strongest absorption band observed in the spectrum of unreacted $C_{60}$ ($\lambda$ = 256 nm) has completely disappeared in the absorption profile of **1**, with a coincident increase in the intensity of the band at $\lambda$ = 220 nm. The intensity of the absorption at $\lambda$ = 333 nm is also reduced. These changes are characteristic of a highly derivatized $C_{60}$ moiety, where more than two π-bonds of the fullerene cage have been reduced.[11]

The $^1$H NMR spectra of unreacted MHMO and of the product are shown in Fig. 3.‡ The upfield signals in both spectra can be unambiguously assigned to alkyl substituents, shifted by $< 0.05$ ppm on going from the siloxane copolymer to the product. In the $^1$H NMR spectrum of unreacted MHMO, a characteristic Si–H resonance is found at $\delta$ 5.18. In the product this is replaced by a resonance at $\delta$ 3.99 which we attibute to hydrogen attached to the fullerene cage.[13] Integration of this signal with an internal standard suggests the incorporation of 5.9 protons per fullerene–siloxane adduct.

Analysis of the MALDI mass spectrum indicated an average parent ion mass of 3650 au. The $C_{70}$–siloxane adduct was also observed when a mixture of $C_{60}$ and $C_{70}$ was used. (Fig. 4).

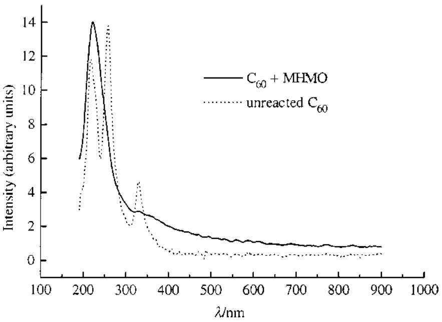


**Fig. 2** UV–VIS absorption spectra of **1** (THF) and of $C_{60}$ (toluene).

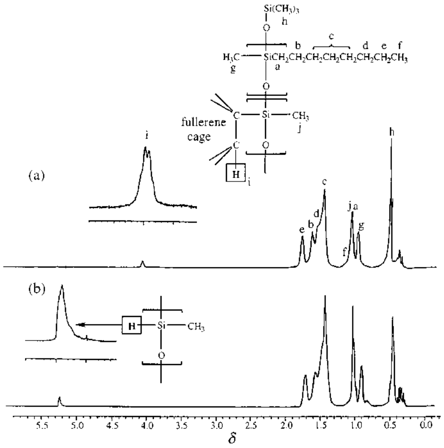


**Fig. 3** $^1H$ NMR spectra (500 MHz; [$^2H_6$]benzene) with designations of H and C atoms for tentative assignment of $^1H$ and $^{13}C$ NMR resonances. (a) polymer **1** and (b) poly(methylhydridomethyloctylsiloxane).

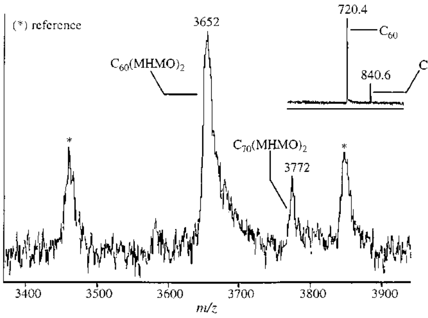


**Fig. 4** MALDI mass spectrum of **1**. Inset: unreacted $C_{60}$/$C_{70}$ mixture.

The analytical and spectroscopic data for **1** are inconsistent with the anticipated pendant structure. The molecular weight determination indicates that **1** is a 2 : 1 adduct of the siloxane copolymers with $C_{60}$. The lack of Si–H bonds in the product suggests that every Si–H silicon atoms in the polymer becomes attached to the fullerene cage. We propose a structure in which the $C_{60}$ moiety is surrounded and essentially encapsulated by two siloxane molecules, both multiply attached. A hypothetical representation of the structure is shown in Fig. 5. The sharp GPC peak and unusual resistance to air oxidation are also consistent with the proposed structure of this hybrid siloxane–fullerene fluid. The fullerene $^{13}C$ resonances are also highly indicative of a reduced fullerene cage.

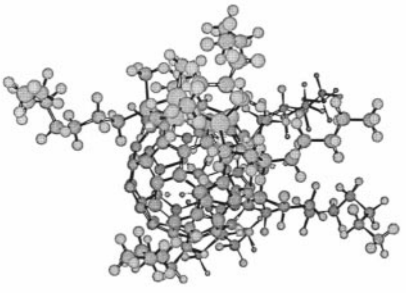


**Fig. 5** A schematic representation of 'shrink-wrapped' fullerene. One of the siloxane adducts has been removed to reveal the $C_{60}$ moiety.

The order of the addition of the platinum catalyst was found to be important.[14] If buckminsterfullerene was allowed to stir with the platinum complex before the addition of the poly(alkylhydridosiloxane), an insoluble precipitate would form; this precipitate, which we suppose to be a platinum–fullerene adduct, was unreactive towards the poly(alkylhydridosiloxane) and greatly reduced the overall yield of **1**.

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## Notes and references

† *Reagents and conditions*: MHMO polymer was obtained from Gelest, Inc. Chloroplatinic acid ($H_2PtCl_4 \cdot 6H_2O$), Aldrich, was used without further purification and stored under argon with refrigeration. The tetramethyldivinyldisiloxane platinum(0) complex was prepared by the reaction of chloroplatinic acid and 1,1,3,3-tetramethyl-1,3-divinylsiloxane ($(CH_2{=}CHSiMe_2)_2O$) (Gelest) to yield a 16 wt% platinum solution.

All experiments were carried out with Schlenk techniques under a dry argon atmosphere. All solvents were distilled immediately before use. NMR: Bruker AM-500 instrument, the solvent was used as an internal standard, with TMS as an external standard: [$^2H_6$]benzene ($\delta_H$ 7.15), $CS_2$ ($\delta_C$ 198), $CDCl_3$ ($\delta_{Si}$). IR: Mattson FTIR spectrometer (KBr plates, neat). GPC analysis: Waters Associates LC system {Shodex KF-802 column; THF: flow rate, 1.0 ml min$^{-1}$; UV detector, ($\lambda$ = 254 nm)}. UV–VIS: Perkin Lambda Array 3840 spectrometer (THF).

*Synthesis* of **1**: in a typical experiment, MHMO siloxane copolymer (130 mg, 0.087 mmol) was added to divinyldisiloxane Pt catalyst (2.5 mg, 0.013 mmol) dissolved in 5 ml degassed *o*-dichlorobenzene. The solution was stirred for 15 min at which point the clear, colorless mixture had become straw-yellow. A clear, purple solution of $C_{60}$ (30 mg, 0.042 mmol) in 24 ml of benzene was added. The reaction mixture immediately darkened and became opaque. After stirring for 2.75 h at 25 °C, the mixture was loaded onto an activated silica gel column and the amber-colored fraction was collected using benzene–MeOH (9 : 1) solution as the mobile phase (under 7.5 psi $N_2$). Some black, insoluble material remained on the column head. Removal of the solvent afforded 122 mg (80%) of a dark brown oil (**1**). GPC analysis indicated that no unreacted $C_{60}$ remained in the product. The material was then characterized as previously described. Exposure of **1** to air for several months led to no change in its spectra or its solubility.

‡ *NMR spectra*: see Fig. 3 for identification. Most resonances are multiplets. $\delta_H$, a, 0.91, b, 1.58, c, 1.36; d, 1.42; e, 1.64 f; 0.96; g, 0.84; h, 0.42; i, 3.99; j, 0.94. $\delta_C$ a, 21.7; b, 4.52; c, d, 27.5–34.8; e, 20.0; f, 9.9; g, j, 23.5, 23.6; h, −3.0; $C_{60}$, 125.5–147.5.[12] $\delta_{Si}$, $Me_3Si$, −5.9; (*n*-octyl)SiMe, −24.9; $MeSiC_{60}$, 6.2.

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