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Synthesis and characterization of tricarbonylmolybdenum-functionalized poly(methylphenylsilane)

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The synthesis and characterization of a new metal-functionalized polysilane is reported. Treatment of poly(methylphenylsilane) with $Mo(CO)_3(NC_5H_5)_3$ and $BF_3.OEt_2$ affords the novel copolymer, poly(methylphenylsilane-*stat*-methyl(η^6-phenyltricarbonylmolybdenum)silane). The synthesis and characterization of the model compounds, (η^6-phenyltricarbonylmolybdenum)trimethylsilane, 1-phenyl-2-(η^6-phenyltricarbonylmolybdenum)tetramethyldisilane and 1,2-di(η^6-phenyltricarbonylmolybdenum)tetramethyldisilane, are used to support a full structural characterization of the copolymer. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polysilanes; functionalization; molybdenumtricarbonyl)

INTRODUCTION

Polysilanes have attracted considerable interest in recent years owing to the unusual and interesting electronic properties arising from the delocalization of σ-electrons within the catenated silicon backbone[1,2]. This has led to a search for applications which have included; ceramic precursors[3], photoinitiators of vinyl polymerizations[4], resists in microlithography[5], photoconductors[6], and electrical conductors and other uses where charge transfer is effective[7].

Despite there being such a wide range of potential applications, their further development is limited by the polysilane structures that are easily accessible. Polysilanes can be prepared by a number of methods, including ring-opening polymerization, via masked disilanes, and sonochemically[1,2]; however, it is the Wurtz reductive-dechlorination reaction that is almost preclusively used for their synthesis. Unfortunately, the Wurtz synthesis limits the chain substituents to only alkyl or aryl groups as the majority of other substituents are unable to withstand the vigorous reaction conditions. As a consequence, there have been a number of methodologies developed for the introduction of functionalities following the polymerization reaction.

Such functionalization reactions include, a lengthy reaction sequence involving trimethylsiloxy protecting groups to introduce a phenolic substituent[8], the replacement of phenyl groups in poly(methylphenylsilane) (PMPS) with the triflate moiety[9], the introduction of chlorine groups in poly(dimethylsilane-*stat*-methylphenylsilane) at the expense of phenyl groups[10], and the chloro- and bromo-methylation of PMPS[11,12]. In this last instance the subsequent replacement of the chlorine or bromine atoms allows the introduction of other functionalities such as alkyl, amine, ester and diketone groups[13]. The acetylacetonoate group introduced in this manner has allowed the ready coordination of Fe(III) to PMPS[14]. However, on two counts this is not a particularly fruitful way of introducing the metals to a polysilane: (i) the product is intractable, and (ii) there is no direct interaction between the metal and the σ-electrons of the polymer chain. The incorporation of metals into polysilane structures so that there is an interaction of the metallic electron density with the σ-electrons of the backbone should result in a modification of their electronic properties. However, there are few reported syntheses that would facilitate such an investigation.

Pannell *et al.*[15] have utilized the chemically robust ferrocenyl group to copolymerize dichloroferrocenylmethylsilane and dichloromethylphenylsilane by using standard Wurtz-coupling-reaction conditions. Up to 14% of ferrocenyl groups were introduced, with a high-molecular-weight fraction being reported as part of a bimodal molecular-weight distribution. The glass transition temperature T_g and λ_{max} of the polymer were little changed compared to those of the poly(methylphenylsilane), although the incorporation of the ferrocenyl group did provide photostabilization of the polysilane backbone. Ratel and Pannell[16] also report the complexation of the chromiumtricarbonyl moiety on to PMPS, although no experimental details have been published.

Although not a polysilane, much interest has recently been aroused by the silicon-containing system developed by Manners and coworkers[17], who ring-opened the highly strained cycloferrocenyldimethylsilane to produce a polymer with a molecular weight of 500 000 Da and a polydispersity of 1.5. Ultra-violet (u.v.)–visible

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*To whom correspondence should be addressed spectroscopy revealed only a small difference in λ_{max} between the monomer and the polymer. Compared with the considerable red shift in the λ_{max} of the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) σ–σ^* transition of polysilanes with increasing molecular weight, this observation is disappointing. A number of metals (Al, B, Cr, Hf, Mo, Nb, Sm, Ta, Ti, V, W, Y, Zr) have been incorporated into a polysilane-type structure by oxidative addition across the Si–Si bond[18]. Although the starting materials are polysilanes, the metal-ligand fragments form part of the backbones in these structures, so that the products are no longer polysilanes. Little spectroscopic evidence was presented and the exact nature of the metallosilane materials was not determined. Chromium has been introduced into an oligomeric poly-silane by the dehydrogenative polymerization of a monomer containing the chromiumtricarbonyl moiety[19]. A molecular weight of only 1300 Da, corresponding to five repeat units, was achieved, and no unusual properties were reported.

The η^6-complexation of the molybdenumtricarbonyl moiety to polymers has been previously reported. Polystyrene beads were metallated by the direct thermal displacement of carbonyl groups from $Mo(CO)_6$[20], and poly(p-phenylene) was metallated via a $Mo(CO)_3(MeCN)_3$ intermediate and alternatively by the direct thermal reaction with $Mo(CO)_6$[21]. Poly(p-phenylene) that had been complexed with molybdenumtricarbonyl moieties showed an increased conductivity which was attributed to planarization of the polymer at the site of the complexation. The Fourier transform infra-red photoacoustic spectrum showed absorbances, albeit with a reduced intensity, in the same positions as those observed for doped poly(p-phenylene)[21].

This present paper is concerned with the incorporation of the $Mo(CO)_3$ moiety into PMPS and the characterization of the polymer product. As such, this is the first full report of the successful incorporation of a metal on to a high-molecular-weight polysilane using π-complexation to a phenyl substituent.

EXPERIMENTAL

Materials

All reactions were carried out in flame-dried glassware under an argon atmosphere. Solvents were freshly distilled from the appropriate drying reagents under a nitrogen atmosphere. Dichloromethylphenylsilane was freshly distilled before use, while all other reagents were used as supplied.

Apparatus and procedures

^1H and ^{13}C n.m.r. spectra were recorded on a JEOL GX 270 instrument, running at 270 and 68 MHz, respectively. The experiments were performed at 30°C in 5 mm diameter n.m.r. tubes with saturated solutions.

Molecular weights and polydispersities were determined against linear polystyrene standards over the molecular-weight range from 162 to 1 030 000 Da using a size exclusion chromatograph supplied by Polymer Laboratories, on a 5 μm particle size mixed-bed PL gel column. HPLC grade THF was used for the mobile phase.

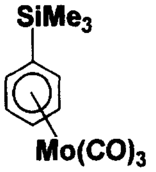
Atomic absorption spectroscopy was conducted on a Perkin-Elmer 1100B instrument. Measurements were calibrated against ammonium molybdate standards and were estimated to be accurate to within 1%. The samples were digested into aqua regia and were then diluted with distilled water to obtain ca. 2 M acid solutions.

Ultra-violet absorption spectroscopy measurements were recorded in THF with a Philips PU8470 spectrophotometer over the range from 190 to 900 nm. Elemental analyses were obtained at the University of Kent analytical centre.

The preparation of $Mo(CO)_3(pyridine)_3$

An excess of pyridine (py) (45 ml) was added to a jacketed Schlenk tube containing $Mo(CO)_6$ (6.3 g, 24 mmol) and the mixture was refluxed for 5 h to yield a red solution. Upon cooling to ca. −15°C large orange/yellow crystals were precipitated. These were isolated by filtration, ground to a powder, washed with light petroleum and dried under vacuum (yield = 8.16 g, 82%).

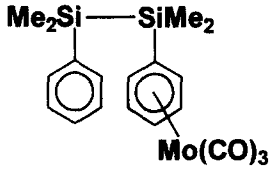
The preparation of (η^6-phenytricarbonylmolybdenum)-trimethylsilane 1



1

$Mo(CO)_3(py)_3$ (4.12 g, 9.87 mmol), phenyltrimethylsilane (1.70 ml, 9.87 mmol) and diethyl ether (70 ml) were placed in a Schlenk tube. Boron trifluoride diethyl etherate (3.64 ml, 29.60 mmol) was added very slowly dropwise and the mixture was stirred at room temperature for 2 h. The resultant yellow solution containing some black deposits was washed with cold distilled water (3 × 200 ml). The hexane/diethyl either layer was separated and the volatiles were removed under reduced pressure. The fine yellow needles were recrystallized from hexane and dried under high vacuum (yield = 2.10 g, 65%; m.p., 85–86°C (dec)). ^1H n.m.r. ($CDCl_3$) δ: 0.26 (s, 9H, $SiMe_3$), 5.44 (t, 2H, m-C_6H_5, $J = 6$ Hz), 5.65 (d, 2H, o-C_6H_5, $J = 6$ Hz), 5.74 (t, 1H, p-C_6H_5, $J = 6$ Hz). I.r., $\nu(C{\equiv}O)$ cm^{-1}: (KBr) 1946, 1865; (light petroleum) 1983; 1913. U.v. (λ/nm (ϵ/dm^{3}mol^{-1} cm^{-1})): 215 (18 800), 323 (13 000). Elemental analysis calculated, C 43.6, H 4.3; found, C 43.5, H 3.8%.

The preparation of 1-phenyl-2-(η^6-phenyltricarbonylmolybdenum)tetramethyldisilane 2 and 1,2-di(η^6-phenyltricarbonylmolybdenum)tetramethyldisilane 3



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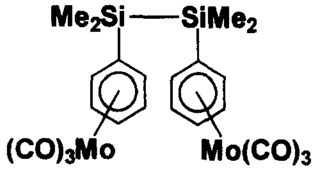


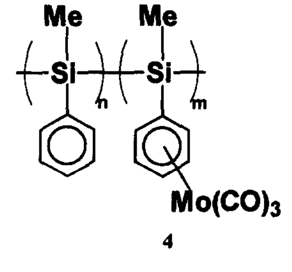
3

$Mo(CO)_3(py)_3$ (0.93g, 2.23 mmol), 1,2-diphenyltetramethyldisilane (0.60 g, 2.23 mmol) and diethyl ether (60 ml) were placed in a Schlenk tube. Boron trifluoride diethyl etherate (0.41 ml, 3.35 mmol) was added slowly dropwise and the reaction mixture was stirred at room temperature for 2 h. A further aliquot of boron trifluoride diethyl etherate (0.41 ml, 3.35 mmol) was added slowly and the reaction mixture as stirred for a further 2 h. The solution was filtered, diluted with hexane (60 ml) and washed with cold distilled water (3 × 100 ml). They yellow/green hexane/diethyl ether layer was separated and placed in a freezer (ca. −15°C) overnight to produce a small quantity of precipitate. This was filtered and washed with light petroleum to afford **3**. The washings were combined with the bulk filtrate. The volatiles were removed under reduced pressure to afford **2**. This was recrystallized from a diethyl ether/light petroleum (1 × 1 vol/vol) mixture to afford the yellow product. Compound **2**: yield = 0.59 g, 71%; m.p., 97–98.5°C (dec). ^{1}H n.m.r. (C_6D_6) δ: 0.14 (s, 6H, $SiMe_{2(coord.)}$), 0.21 (s, 6H, $SiMe_{2(uncoord.)}$), 4.46 (t, 2H, m-$C_6H_{5(coord.)}$, $J = 6$ Hz), 4.75 (t, 1H, p-$C_6H_{5(coord.)}$, $J = 6$ Hz), 4.82 (d, 2H, o-$C_6H_{5(coord.)}$, $J = 5$ Hz), 7.21–7.29 (m, 5H, $C_6H_{5(uncoord.)}$). I.r., $\nu(C{\equiv}O)$ cm^{-1}: (KBr) 1953, 1871. U.v. (λ/nm (ϵ/dm^3 mol^{-1} cm^{-1})): 213 (28 700), 327 (15 600). Elemental analysis: calculated, C 50.7, H 4.9; found, C 50.1, H 5.0%. Compound **3**: yield = 0.12 g, 9%; m.p. 106–110 °C (dec). ^{1}H n.m.r. (C_6O_6) δ: 0.06 (s, 6H, $SiMe_2$), 4.49 (t, 2H, m-C_6H_5), 4.75 (m, 3H, o,p-C_6H_5). I.r., $\nu(C{\equiv}O)$ cm^{-1}: (KBr) 1953, 1892; (THF) 1965, 1889. Elemental analysis: calculated, C 41.9, H 3.5; found, C 42.8, H 3.9%.

The preparation of poly(methylphenylsilane) (PMPS)

Freshly cut sodium (12.6 g, 0.54 mol) and mineral oil were added to a two-necked flask equipped with a nitrogen inlet. A fine dispersion of the sodium was prepared by heating until it became molten and then agitating with a homogenizer. The sodium dispersion thus prepared was washed four times with aliquots of diethyl ether (40 ml) to remove any traces of mineral oil before being transferred to a three-necked round-bottomed flask (2 l), equipped with a mechanical overhead stirrer, double-surface reflux condenser and dropping funnel. Diethyl ether (500 ml) and 15-crown-5 (6.1 ml, 0.03 mol) were added to the flask and the mixture was heated to reflux. Dichloromethylphenylsilane (40.6 ml, 0.25 mol) was added over a period of 90 min and the reaction mixture was further refluxed for 3 h. After cooling to room temperature, methanol (150 ml) was added very cautiously as a quenching reagent. After stirring for 20 h, distilled water (400 ml) was carefully added. The precipitated polymer was collected on a Buchner funnel and the oligomeric fraction removed by washing in hexane (300 ml). The solid fraction was decanted, dried and then dissolved in THF (200 ml), filtered through silver sand to remove any insoluble material and reprecipitated into methanol (600 ml). The white solid was isolated by filtration and dried under high vacuum (yield = 8.61 g, 27%; M_w = 73 000; polydispersity (p.d.) = 3.7). U.v. (λ/nm (ϵ/dm^3 mol^{-1} cm^{-1})): 223 (7 500), 338 (7 000).

The preparation of poly(methylphenylsilane-stat-*methyl (η^6-phenyltricarbonylmolybdenum)silane) 4*



4

PMPS (1.99 g, 16.6 mmol of repeat units), $Mo(CO)_3(py)_3$ (1.76 g, 4.2 mmol) and diethyl ether (160 ml) were placed in a Schlenk tube. Boron trifluoride diethyl etherate (1.56 ml, 0.012 mol) was added slowly dropwise and the reaction mixture was stirred at room temperature for 3 h. The product, a solid, was filtered off and the volatiles were removed under reduced pressure. The yellow polymer (2.4 g) was boiled in diethyl ether (80 ml) for 3 h to remove impurities, filtered off and dried under high vacuum (yield = 2.15 g, M_w = 68 000, p.d. = 3.1). ^{1}H n.m.r. ($CDCl_3$) δ: (−1.17)–(−0.75) (m, $CH_{3(coord.)}$), (−0.75)–(−0.34) (m, $CH_{3(uncoord.)}$), 3.95–5.90 (m, 16H, $C_6H_{5(coord.)}$), 5.95–7.55 (m, 84H, $C_6H_{5(uncoord.)}$). U.v. (λ/nm (ϵ/dm^3 mol^{-1} cm^{-1})): 224 (9500), 337 (7400).

RESULTS AND DISCUSSION

The synthesis and characterization of the three low-molecular-weight analogues undertaken prior to the metallation of the polymer, PMPS, had the dual purpose of testing the feasibility of metal–arene bond formation in the presence of a silyl substituent and of establishing the spectroscopic parameters which would guide the characterization of the metallated polymer. The synthesis and crystal structure of **1** were published[22] while this work was in progress, although no physical data were presented. Compound **1** was synthesized by the addition of a Lewis acid adduct, $BF_3 . OEt_2$, to a stoichiometric mixture of phenyltrimethylsilane and $Mo(CO)_3(py)_3$ at room temperature. The yellow crystals exhibit stability in the solid state to atmospheric oxidation when held at low temperatures with light excluded; however, in solution (THF) **1** quickly decomposes. The infra-red spectrum of **1** is dominated by two intense $\nu(C{\equiv}O)$ absorptions. The position of the absorptions in **1** (1983, 1913 cm^{-1}) (light petroleum) compared well to those of (η^6-benzene)tricarbonylmolybdenum (1985, 1912 cm^{-1}) (light petroleum)[23]. This indicates that in this particular environment the trimethylsilane group has little effect in its own right on the electron density in the arene ring, although it has been reported that the trimethylsilane group has a positive inductive effect[24]. The crystal structure of **1** is consistent with the published crystal structures of analogous molybdenumtricarbonyl-complexed, aryl-ring-containing systems, offering further evidence that the complexation of the molybdenumtricarbonyl moiety to PMPS would be feasible. The ^{1}H n.m.r. spectrum of **1** shows an upfield shift ca. 1.5 ppm for the phenyl protons and a smaller shift for the methyl protons, when compared with the starting material. This shift was anticipated, as the molybdenumtricarbonyl moiety lowers the bond order in the phenyl ring due to electron withdrawal[25]. The ultra-violet absorption spectrum shows a significant change upon complexation of the phenyl ring. The starting material, phenyltrimethylsilane, shows two peaks at 223 and 261 nm, which are assignable to $\pi \rightarrow \pi^*$ transitions in the phenyl ring. Compound **1** shows two peaks, namely a $\pi \rightarrow \pi^*$ transition at 215 nm and a molybdenum → phenyl π^* intramolecular charge transfer at 323 nm. The change in the $\pi \rightarrow \pi^*$ transition in the complexed phenyl ring is consistent with the shift that we observed in the n.m.r. spectra and with the known electron-withdrawing effect of the molybdenumtricarbonyl moiety[25].

The synthesis of a model compound containing only a single silicon atom does not allow the study of a significant factor involved in the chemical modification of high-molecular-weight polysilanes, namely the degradation of the molecular weight through silicon–silicon bond scission.

The compound 1,2-diphenyltetramethyldisilane, a dimeric 'building block' of PMPS, offers a silicon–silicon bond while still being small enough to be easily characterized. The mononuclear and binuclear metallated derivatives present the opportunity to study the likely consequences of having a neighbouring complexed phenyl ring. Compound **2** was synthesized in high yield (71%) by the staggered addition of $BF_3.OEt_2$ to a stoichiometric mixture of 1,2-diphenyltetramethyldisilane and $Mo(CO)_3(py)_3$, producing **3** as a by-product. The addition rate of the Lewis acid is crucial, as a rapid addition results in low yields, probably arising from degradation of the complex by the boron trifluoride diethyl etherate. Compound **2** was also formed by utilizing a $Mo(CO)_3(MeCN)_3$ intermediate, but this proved to be highly irreproducible; the high reflux temperature necessary for displacement of the acetonitrile ligand, coupled with the poor thermal stability of (η^6-arene)tricarbonylmolybdenum complexes, suggest *in situ* decomposition of the final product. As with **1**, the yellow **2** exhibits a partial stability to atmospheric oxidation. The solid-state infra-red spectrum of **2** shows two carbonyl peaks at 1953 and 1871 cm^{-1} (KBr). In comparison with the corresponding peaks of **1** (1946, 1865) this shows an increase in $\nu(C{\equiv}O)$. This increase is due to a decrease in the synergic back-donation from the molybdenum into π^*-carbonyl orbitals, which gives an indication that the phenyl rings of **2** are less electron-rich than the phenyl rings of **1**.

Compound **3**, formed as a by-product during the synthesis of **2**, possesses subtly different properties as a consequence of the extra coordinated molybdenumtricarbonyl moiety. The obvious method of synthesis for **3** would be to add an excess of the $Mo(CO)_3(py)_3$ intermediate to **2**, but this generally led to degradation. The addition of the extra molybdenumtricarbonyl moiety led to a change in colour, with the yellow of **2** being replaced by the green of **3**. Although stable in the dark in the solid state, **3** was observed by size exclusion chromatography (s.e.c.) analysis to degrade quickly to **2** in THF solution. The addition of a second molybdenumtricarbonyl moiety had a dramatic effect on the solubility, with **3** being insoluble in non-polar solvents. The ^1H n.m.r. spectrum shows just two peaks for the complexed aromatic region, which represent the three different proton environments. Analysis of the relative integration values of the two peaks and comparison with the ^1H n.m.r. spectrum of **2** enables the peak at 4.49 ppm to be assigned as the *meta*-protons and the peak at 4.75 ppm to the *ortho*- and *para*-proton environments. The clear separation of the *ortho*- and *para*-resonances observed with **1** and **2** is not seen for **3**.

As with **1**, **2**, and **3**, the copolymer **4** was synthesized by the removal of pyridine ligands from the $Mo(CO)_3(py)_3$ intermediate at room temperature in diethyl ether. The quantity of $Mo(CO)_3(py)_3$ added allowed for a theoretical loading of 25% of the phenyl groups. In fact, only a 15% loading was achieved (*vide infra*), an uptake of 60% of the theoretical value which is consistent with the yields achieved in the preparation of the model compounds. A quantitative recovery of polysilane would be expected, however, based on a 15% substitution level, polymer was recovered in only 88% yield. This suggests the possibility that some

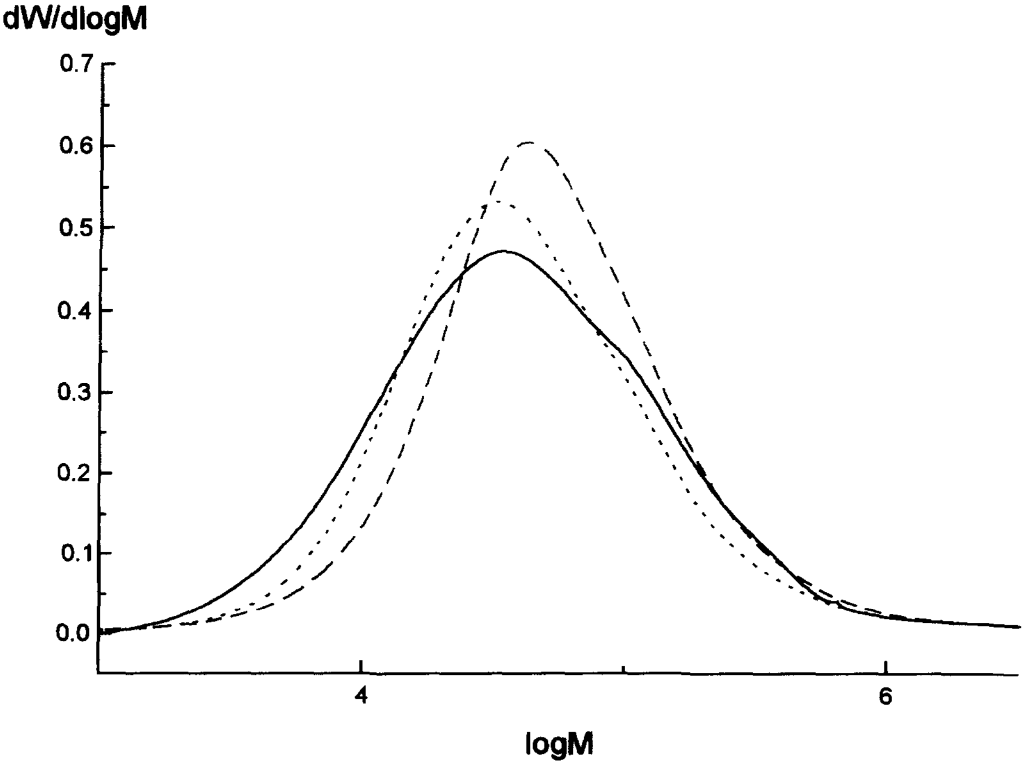


Figure 1 A comparison of the size exclusion chromatographs of: (—) PMPS; (···) **4** prepared in diethyl ether; (----) **4** prepared in diethyl ether/THF

degradation to oligomers occurred, with these being removed during purification of the final product.

A colour change from the white of the parent polymer to ochre yellow of the copolymer was analogous with the colour of the model compounds. In the dark, **4** is observed by infra-red analysis to exhibit a degree of stability to atmospheric oxidation in the solid state, but in THF solution the molybdenumtricarbonyl moieties oxidize on exposure to air to afford an intractable polymer, presumably through crosslinking. In comparison with the parent homopolymer, **4** was found to be only sparingly soluble in THF, CH_2Cl_2, $CHCl_3$ and toluene.

The loading of molybdenumtricarbonyl moieties was determined by atomic absorption spectroscopy and confirmed by analysis of the aromatic region of the ^1H n.m.r. spectrum. An overlay of the molecular-weight distribution of the starting material and **4**, depicted in *Figure 1*, indicates a small reduction in the molecular weight upon complexation at the 15% substitution level. The addition of the functionality would be expected to significantly increase the molecular weight and it seems likely that some degradation of the silicon backbone occurs. This could be due to weak siloxane linkages that can be formed during the workup in the preparation of the parent polymer which have been previously reported to degrade in the presence of Lewis acids[12]. These results, however, must be treated with some caution as s.e.c. does not provide an absolute molecular weight but merely measures the hydrodynamic volume of the compound. Metalled polymers with an increased molecular weight can be prepared by the use of a diethyl ether/THF mixed solvent system in which the THF (a Lewis base) is moderating the activity of the Lewis acid. Unfortunately, this methodology was less reproducible and the loading of molybdenumtricarbonyl moieties that was achieved was lower. A control experiment undertaken using an identical experimental procedure to the synthesis of **4**, but without the $Mo(CO)_3(py)_3$ reagent, yielded an intractable white product and a THF-soluble polymer fraction with a much reduced molecular weight of 18 000 Da, indicating that significant degradation had occurred.

The infra-red spectrum of **4** shows carbonyl peaks at 1966 and 1891 cm^{-1}, i.e. an increase in the $\nu(C{\equiv}O)$ stretching frequency compared with **1**, **2** and **3**. This is consistent with a raising of the carbonyl bond order due to decreased back donation from the phenyl π-orbitals into the carbonyl π^*-antibonding orbitals. This interesting observation may be evidence for the donation of electron density from the phenyl groups into the silicon backbone as this decrease in back-donation into the carbonyl π^*-antibonding orbitals indicates that electron density in the phenyl ring is depleted when compared to compounds **1** and **2**. U.v. spectroscopic data has been used to suggest that there is mixing of aryl π- and polysilane σ-electrons[2,26,27], although the evidence for this is far from clear[1]. The u.v. spectra of aryl substituted polysilanes shows an increase in the wavelength of the $\sigma \rightarrow \sigma^*$ transition when moving from dialkyl to alkylaryl to diaryl substituted polysilanes. This has been ascribed variously to either σ–π delocalization[2,26,27], or to an increased crystallinity within the polymer[1,2]. An allowed mechanism for the overlap of the phenyl π-electrons with the polysilane σ-electrons has been described by Takeda *et al.*[28] in terms of band mixing between the backbone σ-valence bond (VB) (Si-3p_x) and substituent phenyl π-HOMO (C-2p_x) orbitals.

When trimethylamine-*N*-oxide is added to **4** infra-red spectroscopic analysis of the product shows the absence of carbonyl resonances over the range 1800–2000 cm^{-1}, offering additional evidence for the presence of the molybdenumtricarbonyl moiety on **4**.

^1H and ^{13}C n.m.r. spectra were obtained for **4**. The poor solubility of the latter taken in conjunction with the characteristically broad spectra of polymers, limited the quality of spectra that could be obtained; however, the different environments in the molecule

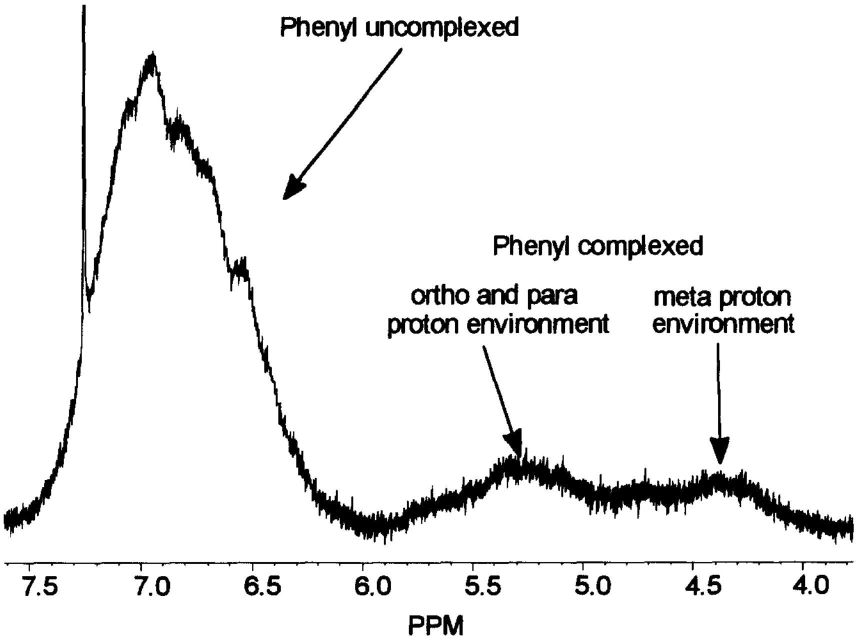


Figure 2 ^1H n.m.r. spectrum of copolymer **4** in $CDCl_3$, showing the aromatic region (3.8–7.6 ppm)

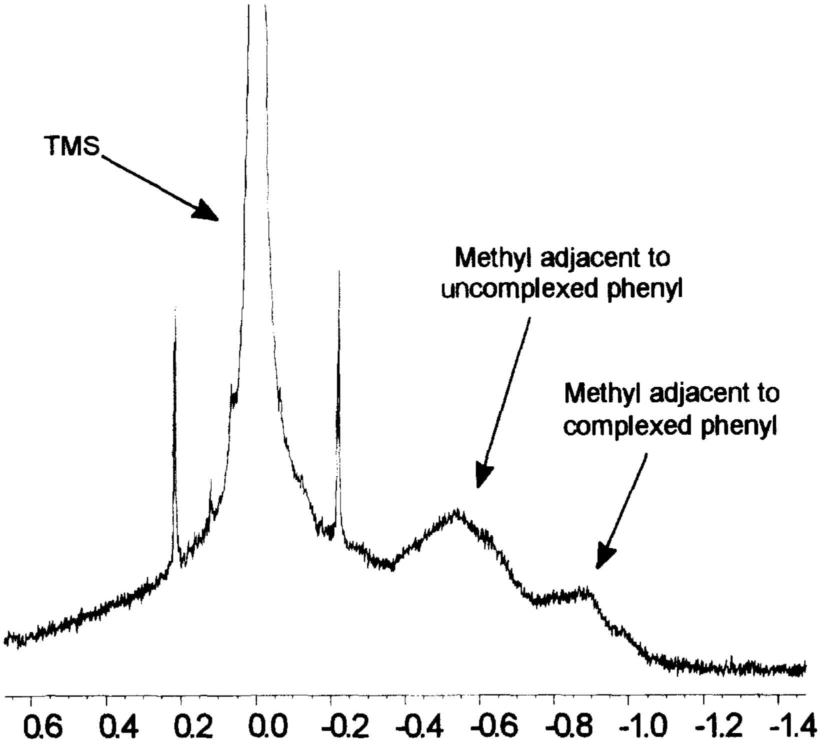


Figure 3 ^{1}H n.m.r. spectrum of copolymer **4** in $CDCl_3$, showing the methyl region ((−1.4)–0.6 ppm)

could be clearly distinguished (*Figures 2* and *3*). The protons of the complexed phenyl ring are observed in the same region that was observed with **1**, **2** and **3**, but due to the polymer substrate the fine splitting is not observed and the resonances are much broader. The resonances for the phenyl protons have a greater upfield shift than **1** and **2**. This indication of a decreased aromaticity in the phenyl rings fits in with the observed shift in the carbonyl stretches in the infra-red spectrum of **4**. As the electron withdrawal of the molybdenumtricarbonyl moiety would be expected to decrease with a decreased aromaticity, this may be additional evidence for σ–π mixing. The ratio of the integrals of the complexed to uncomplexed phenyl protons is 0.16, which is in close agreement with the loading of 15% calculated from the atomic absorption data. As with the ^{1}H n.m.r. spectrum of **3**, only two distinct environments can be observed for the three discrete complexes aromatic environments. Integration of the two peaks shows the ratio 3:2, and it is proposed (as in **3**) that the peak at 3.95–4.70 ppm represents the *meta*-proton environment, while the peak at 4.70–5.90 ppm represents the *ortho*- and *para*-proton environments. As expected, the ^{13}C n.m.r. spectrum displays a carbonyl resonance at 221.0 ppm, the uncomplexed ring carbons are represented by two broad peaks at 126.5–129.0 and 133.6–137.5 ppm, and the complexed ring carbons are at 90.2–95.8 and 98.3–103.0 ppm. The ultraviolet spectrum of **4** does not show the change upon complexation in the λ_{max} values that was observed for the model compounds, which is perhaps unsurprising considering the relatively low loading of molybdenumtricarbonyl moieties that was achieved and the significant σ–σ^* delocalization that already exists in the polysilane backbone. The extinction coefficients of the two peaks increase upon complexation due to the intense charge-transfer transition associated with the molybdenumtricarbonyl moiety.

CONCLUSIONS

Poly(methylphenysilane-*stat*-methyl(η^6-phenyltricarbonylmolybdenum)silane) can be prepared by treating PMPS with $Mo(CO)_3(py)_3$ and $BF_3.OEt_2$. A full characterization of this novel copolymer established that a 15% loading of molybdenumtricarbonyl units had been achieved. Copolymer **4** will be assessed for possible use as an electron-beam resist; however, its limited stability in solution makes routine handling of this material difficult. Work is currently in progress to establish whether poly(methylarylsilane)s with more electron-rich aromatic substituents than PMPS would produce more stable molybdenumtricarbonyl-functionalized polymers. Functionalization with other metal–ligand fragments is being explored and will be the subject of future publications.

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