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Silicon–oxygen bonding on diphenylsilane through palladium(II)-catalysed reactions

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The reactions of phenols with diphenylsilane are catalysed by palladium(II) catalysts such as Pd(TMEDA)Cl_2 (TMEDA = tetramethylethylenediamine), Pd(DEED)Cl_2 (DEED = *N,N′*-diethylethylenediamine), Pd(TEEDA)Cl_2 (TEEDA = *N,N′*-tetraethylethylenediamine) or $PdCl_2$ to form hydrated silanols with molecular formula $Ph_2Si(OR)OH{\cdot}nH_2O$ (when $R = C_6H_5$, $n = 3$; when $R = p\text{-}CH_3C_6H_4$ or $o\text{-}CH_3C_6H_4$, $n = 1$). The reaction of hydroquinone with diphenylsilane in the presence of catalytic amounts of Pd(TMEDA)Cl_2 forms an Si–O-bonded hydrated aggregate of composition $[(C_6H_5)_2Si(O\text{-}C_6H_4O).0.5H_20]_n$. *p*-Benzoquinone reacted with diphenylsilane in the presence of a catalytic amount of Pd(TMEDA)Cl_2 and the reaction proceeded via a multiple pathway involving quinhydrone as an intermediate charge-transfer complex which reacted further with diphenylsilane to give a linear siloxane. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: Pd catalysts; phenylsilane; phenol

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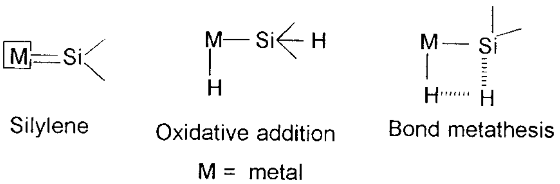
INTRODUCTION

The silicon–oxygen bond is used as a protecting group in organic chemistry.[1,2] Silicon–oxygen-bonded compounds also find applications in stereoselective transformations of organic compounds.[3] Polymers containing silicon–oxygen bonds in the main chain find an important place in everyday life.[4–8] The catalytic method for preparation of silicon-containing polymers has been successful due to advantages such as selectivity, mildness and continuous processing.[9–16] The dehydrogenative coupling reaction of silane is used to prepare silicon–silicon and silicon–heteroatom bonds.[2,17] Various transition-metal catalysts derived from copper,[18] palladium,[19,20] platinum,[21] rhodium,[22] iridium[23] and titanium[24] are used extensively for silicon–oxygen bond formation. σ-Bond metathesis,[5] formation of silylene intermediates[25] and oxidative additions[26,27] are the basic pathways described in these reactions (Scheme 1).

Siloxanes are abundant in nature and are formed under aerobic hydrolytic condition. Thus, an understanding of silicon–oxygen bond-forming reactions under ambient aerobic conditions with air-stable catalytic systems is desirable. Organosilicon compounds can form aggregates through hydrogen bonding.[28–30] Such aggregates may be considered as isolable or reactive intermediates in silicon–hydrogen bond activation reactions under hydrolytic conditions. The reactions of silicon-based compounds are usually carried out under an inert atmosphere and the hygroscopicity of silicon-based compounds becomes an important issue in forming the course of such reactions.[31] However, studies on such reactions under aerobic conditions are not being taken up in great detail, primarily because of the thermal instability of such aggregates.[32,33] In this paper reactions of silanes with phenolic compounds to synthesize some silicon–oxygen-bonded compounds from a dehydrogenative coupling reaction under aerobic conditions are described.



Scheme 1 Types of intermediates from dihydrosilane.

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EXPERIMENTAL

$PdCl_2$, $Pd(PPh_3)_2Cl_2$, *N*,*N*′-tetramethylethylenediamine, diphenylsilane, hydroquinone and *p*-benzoquinone were obtained from Aldrich (USA) and were used without further purification. IR spectra were recorded on a Nicolet-416 FT-IR instrument and UV–visible spectra on a Hitachi U-2001 spectrophotometer. Gas chromatography was carried out on a Hewlett Packard gas chromatograph 6890 using in SE-30 capillary column with flame ionization detection (FID); detector and injector temperatures were 250 °C and oven temperature was 200 °C, with nitrogen as a carrier gas. The resistance of the samples was measured on films made on mica plates using an apparatus comprising of a Hewlett Packard 34401 multimeter, a Kiethley 6512 programmable electrometer and an Agronics 93-C d.c. power supply unit. The films were prepared by dissolving 2 mg of the oligomers in acetone (0.5 cm^3) and then spreading the solution over a mica plate with the aid of a capillary tube and drying by an air drier. The molecular weights of the oligomers were determined in dimethylformamide (DMF) using a Toso HLC-8020 instrument. ^1H NMR was recorded on a JEOL 90 MHz NMR or in a Bruker 270 MHz NMR and 400 MHz NMR spectrometer.

Reaction of phenols with diphenylsilane catalysed by $Pd(TMEDA)Cl_2$

To a mixture containing diphenylsilane (186 mg, 1 mmol) and (1) phenol, (2) *p*-cresol or (3) *o*-cresol (1.5 mmol) in dichloromethane (2 cm^3), catalyst $Pd(TMEDA)Cl_2$ (5 mg 0.017 mmol) was added and the mixture was stirred at room temperature for 12 h. The solvent was removed under reduced pressure to obtain a paste, which was extracted with hexane (20 cm^3). The extract was evaporated under reduced pressure to obtain the corresponding silicon–oxygen-bonded aggregate in near-quantitative yield.

Spectroscopic analytical data

IR (neat): $\nu = 3327$ (bs), 3046 (w), 1591 (s), 1497 (s), 1485 (s), 1450 (s), 1234 (s), 1115 (s), 1064 (s), 700 (s), 689 cm^{-1} (s). ^1H NMR (DMSO-d_6): $\delta = 7$–7.8 (m), 3.5 (bs). Analysis for $C_{18}H_{16}O_2Si.3H_2O$: Calcd: C, 62.42; H, 6.35. Found: C, 62.69; H, 5.19%.

(2) IR (neat): $\nu = 3400$ (bs), 1600 (s), 1590 (s), 1506 (vs), 1421 (s), 1242 (s), 1123 (s), 825 (s), 706 (s), 519 cm^{-1} (s). ^1H NMR (DMSO-d_6): $\delta = 7.2$–7.9 (m, 14*H*), 3.6 (bs), 2.2 (m, 3*H*). Analysis for $C_{19}H_{18}O_2Si.H_2O$: Calcd: C, 70.37; H, 6.17. Found: C, 70.69; H, 5.72%.

(3) IR (neat): $\nu = 3400$ (bs), 1591 (s), 1489 (s), 1445 (s), 1421 (s), 1242 (s), 1115 (s), 843 (m), 749 (s), 698 (s), 511 cm^{-1} (s). ^1H NMR (DMSO-d_6): $\delta = 7.2$–8 (m, 14*H*), 3.6 (bs), 2.3 (m, 3*H*). Analysis for $C_{19}H_{18}O_2Si.H_2O$: Calcd: C, 70.37; H, 6.17. Found: C, 70.12; H, 5.58%.

Reaction of hydroquinone with diphenylsilane

A mixture of diphenylsilane (182 mg, 1 mmol), hydroquinone (101 mg, 1 mmol) and $Pd(TMEDA)Cl_2$ (5 mg, 0.017 mmol) were heated at 70 °C for 6 h. The resulting black mass was washed with petroleum ether to obtain 180 mg (64%) of *4*. ^1H NMR (DMSO-d_6): $\delta = 6.5$–8.3 (m). IR (KBr): $\nu = 3206$ (bs), 1516 (s), 1475 (s), 1347 (s), 1200 (bs), 1100 (s), 824 (s), 752 cm^{-1} (s). Analysis: Calcd for $[C_{18}H_{14}O_2Si{\cdot}0.5H_2O]_n$: C, 72.24; H, 5.01. Found: C, 72.45; H, 5.48%.

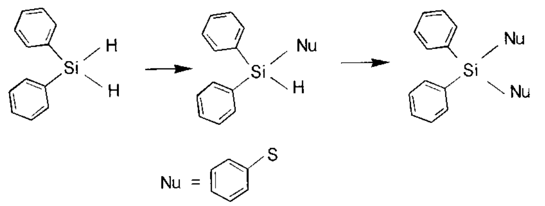
Reaction of *p*-benzoquinone with diphenylsilane

A mixture of diphenylsilane (182 mg, 1 mmol), *p*-benzoquinone (99 mg, 1 mmol) and $Pd(TMEDA)Cl_2$ (5 mg, 0.017 mmol) was heated at 110 °C for 0.5 h. The resulting black mass was washed with petroleum ether (10 cm^3) to obtain 200 mg (71%) of oligomer. ^1H NMR (DMSO-d_6): $\delta = 6.5$–8.3 (m), 2.75 (s). IR (KBr): $\nu = 3387$ (bs), 1591 (s), 1506 (s), 1123 (s), 1100 (bs), 697 cm^{-1}; (s). Analysis: Calcd for $[C_{18}H_{14}O_2Si\ 0.5H_2O]_n$: C, 72.24; H, 5.01. Found: C, 71.90; H, 5.65%.

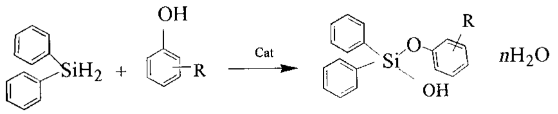
RESULTS AND DISCUSSION

We observed previously that the catalytic reaction of $Rh(PPh_3)_3Cl$ with diphenylsilane and thiols leads to a dehydrogenative coupling reaction.[9–11] The reaction proceeds through a sequential substitution at the Si–H bond (Scheme 2)

Similar catalytic reactions of diphenylsilane with phenolic compounds are also known to give monosilyl ethers.[12] Use of palladium catalysts for catalytic silicon–oxygen bond forming reactions on diphenylsilane have also been reported, but detailed investigations are not available.[34] We have ob-



Scheme 2



Scheme 3 Cat = Pd(TMEDA)Cl$_2$; the product is **1** (R = H, n = 3); **2** (R = o-Me, n = 1); or **3** (R = o-Me, n = 1).

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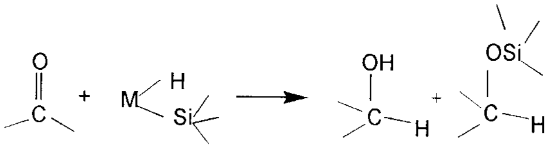
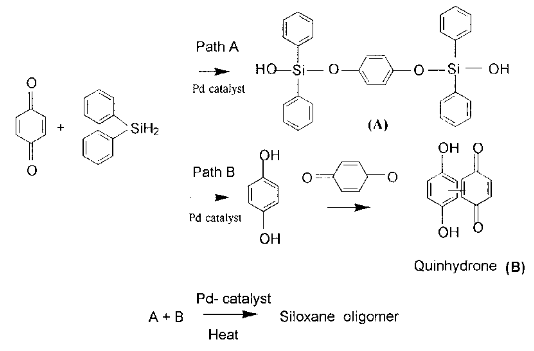
Scheme 4



Scheme 5

served that the reaction of phenols such as phenol, o-cresol and p-cresol with diphenylsilane in the presence of catalytic amount of palladium(II) complexes gives substitution reactions of which the products are colourless viscous liquids in which there are phenoxy and hydroxy groups with different amounts of water molecules attached to the molecule (Scheme 3). The number of water molecules in each compound varied from system to system. As the reaction proceeded, the Si–H frequency of the diphenylsilane that was originally present (at 2150 cm^{-1}) disappeared in the IR spectra of the products. Compounds **1–3** have a strong and broad O–H stretching frequency around 3350 cm^{-1}. Characteristic aromatic ring vibrations at 1625–1430 cm^{-1} for each compound were observed. In addition, the compounds have silicon–oxygen bond stretching around 1100 cm^{-1}. Dihydroxyphenol (hydroquinone) reacted with diphenylsilane at 80 °C, and gave the corresponding silicon–oxygen bonded ether as a silicon–oxygen bonded oligomer (Scheme 4). The oligomer had a unimodal gel permeation chromatograph with M_n 3327. The ^{1}H NMR spectrum (DMSO-d_6) of the compound had a multiplet in the region of $\delta = 6.5$–8.0 due to aromatic protons. Elemental analysis showed it to have composition $[(C_6H_5)_2Si(O\text{-}C_6H_4O)\cdot 0.5H_20]_n$. The IR spectrum has a strong absorption at 1110 cm^{-1} due to silicon–oxygen bond in the oligomer. In addition to these the characteristic IR absorption for a *para*-substituted aromatic ring was also observed. The common dihydroxy aromatic compounds contain water of crystallization and an alternative reaction that could maintain anhydrous conditions would give a better method for preparation of siloxanes. In addition to this, the solubility of dihydroxy aromatic compounds is poor in non-polar solvents, which makes them less attractive for homogeneous catalytic reactions. An alternative silicon–oxygen bond forming reaction is by reductive silylation of keto compounds[35] (Scheme 5). Quinonic compounds react in the presence of transition-metal catalysts such as RhCl(PPh$_3$)$_3$ with silanes and disilanes to give silicon–oxygen bonds.[36–39] Compounds containing a keto group can also be reduced by silane in the presence of a catalyst to give the corresponding alcohol, which can react further with a silane.[10] Another pathway in this reaction is silylation at the oxygen atom of a carbonyl group through a reductive reaction (Scheme 5).

We had observed that a smooth reaction between p-benzoquinone and diphenylsilane at 50 °C with Pd(TMEDA)$_2$Cl$_2$ (0.2 mol%) as a catalyst occurs to give a black solid which has an M_n value of 3260, with reference to polystyrene as standard. The compound is probably a mixture of **A** and **B** (scheme 6) and the molecular weight distribution observed in GPC could be due to the quinhydrone which exits in a linear extended form through charge-transfer interaction as well as hydrogen bonding.[40] The two components could not be purified completely. The ^{1}H NMR has a silicon–OH (Si–OH) signal at $\delta = 2.75$ from **A** in addition to the aromatic protons. A broad absorption at 3350 cm^{-1} appeared due to O–H stretching from solvated water molecules and the OH group. The product thus obtained on thermal treatment at 110 °C oligomerized further. The IR spectrum of the products obtained from a room-temperature



Scheme 6

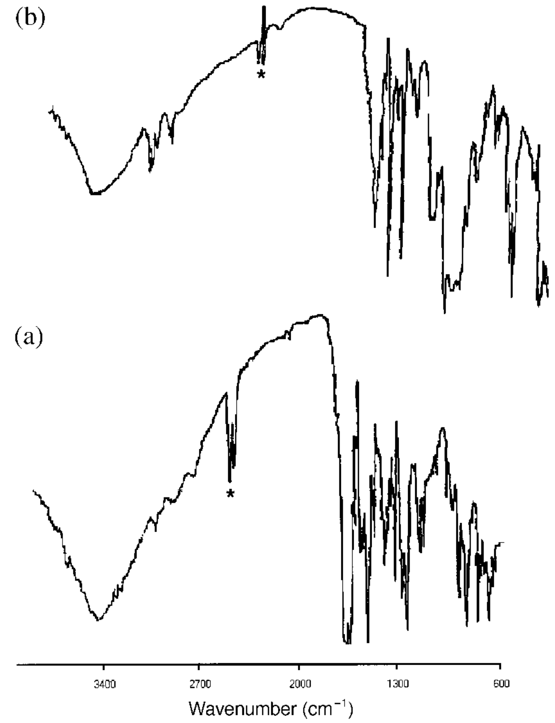


Figure 1 IR (KBr) spectra of the reaction mixture of benzoquinone with diphenylsilane catalysed by Pd(TMEDA)Cl$_2$. (a) At room temperature; (b) sample heated to 180 °C.* Background signals.

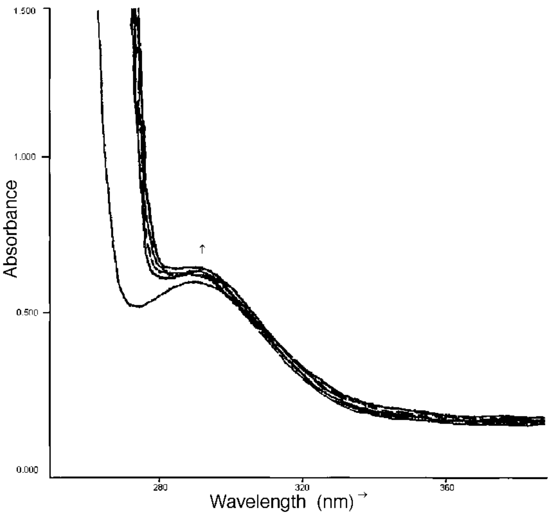


Figure 2 UV–visible spectra of a mixture of diphenylsilane (0.054 mmol) with *p*-benzoquinone (0.027 mmol) in dichloromethane (25 cm^3) recorded at time intervals of 8 min.

reaction is shown in Fig. 1(b). After heating this sample to 110 °C the IR spectrum (Fig. 1a) of the sample changed and showed a multiple set of absorbances at 1100 cm^{-1} due to silicon–oxygen bond formation. Further oligomerization of the mixture of products **A** and **B** was also reflected in gel permeation chromatography (GPC). GPC of the adduct of *p*-benzoquinone with diphenylsilane had one M_n value at 3328, whereas the sample heated above 110 °C showed two molecular weights having M_n values at 3328 and 5262. A similar reaction of *p*-benzoquinone with diphenylsilane in the presence of Pd(TMEDA)Cl$_2$ when performed at 110 °C gave the corresponding siloxane, an oligomer similar to that obtained from heating a mixture of **A** and **B**.

The interaction of diphenylsilane with *p*-benzoquinone in the absence and presence of a palladium catalyst was carried out in dichloromethane. In all cases it was possible to use the absorption at 292 nm as an index, as it is characteristic of a charge-transfer transition of the adduct of quinone and hydroquinone (**B** in Scheme 6). It was observed that there was slight increase in the absorption at 292 nm in the absence of catalyst, suggesting a small amount of reduction of *p*-benzoquinone by diphenylsilane and formation of **B** (Fig. 2). However, on addition of Pd(TMEDA)Cl$_2$ catalyst, absorption at 292 and 393 nm grew rapidly. Figure 3 represents the changes in absorbance with time of solutions containing diphenylsilane and *p*-benzoquinone with Pd(TMEDA)Cl$_2$ as catalyst. To confirm the formation of quinhydrone as a charge-transfer complex in the reaction, the reaction of diphenylsilane with quinhydrone itself was studied by UV–visible spectroscopy. Quinhydrone also interacted with

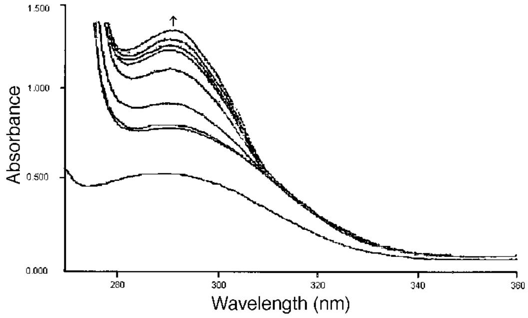


Figure 3 UV–visible spectra of a mixture of diphenylsilane (0.054 mmol) with *p*-benzoquinone (0.027 mmol) with Pd(TMEDA)Cl_2 (0.003 mmol) in dichloromethane (25 cm^3) recorded at time intervals of 8 min.

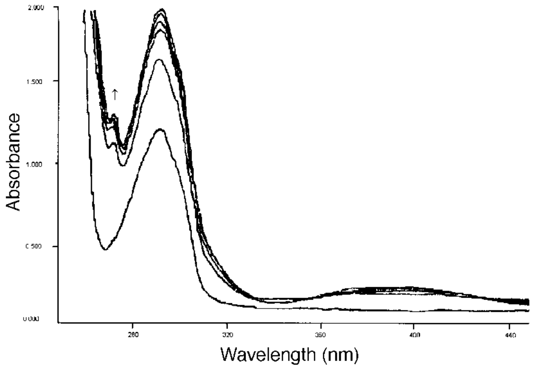


Figure 5 UV–visible spectra of a mixture of diphenylsilane (0.054 mmol) with quinhydrone (0.01 mmol) with Pd(TMEDA)Cl_2 (0.003 mmol) in dichloromethane (25 cm^3) recorded at time intervals of 6 min.

diphenylsilane without a catalyst giving a new absorption at 278 nm in addition to the original one at 292 nm (Fig. 4). The absorption peak at 278 nm probably occurs from product **A**. The intensity of 278 nm grew rapidly with time (Fig. 4). However, a solution containing *p*-benzoquinone and diphenylsilane with a catalytic amount of Pd(TMEDA)Cl_2 has a similar trend in the growth of the two absorptions, but in comparision with the earlier case, while growth at 278 nm is comparable there is a drastic enhanchment of absorption intensity at 292 nm (Fig. 5). This shows that the hydrogenation reaction shown in Path B of Scheme 6 is favoured by the palladium catalyst over Path A. This solution also had a new absorption maximum at 397 nm due to a metal-to-ligand charge-transfer transition of an intermediate species. Thus, the reaction of diphenylsilane with *p*-benzoquinone can pass through formation of quinhydrone via partial reduction of *p*-benzoquinone and further interaction with diphenylsilane. The charge-transfer complex of *p*-benzoquinone and hydroquinone can be formed either through a reduction of *p*-benzoquinone to hydroquinone or through the abstraction of a proton from the moisture present in the solvent. Proton

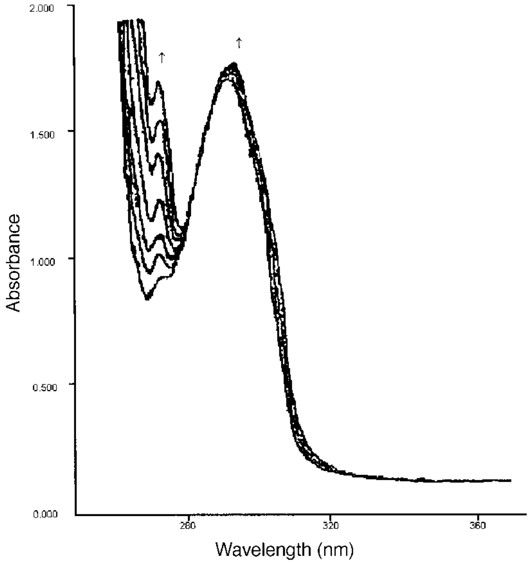


Figure 4 UV–visible spectra of a mixture of diphenylsilane (0.054 mmol) with quinhydrone (0.01 mmol) in dichloromethane (25 cm^3) recorded at time intervals of 6 min.

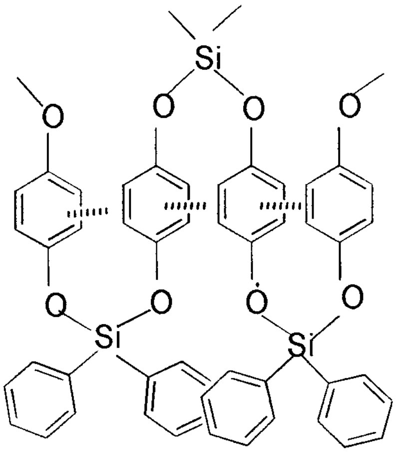


Figure 6 Possible π-stacking in the oligomer of diphenylsilane with hydroquinone.

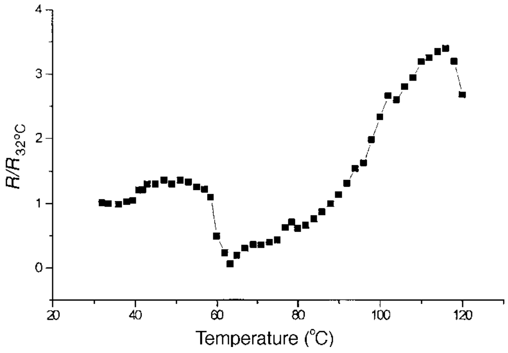


Figure 7 Variation of resistance (R) normalized to room-temperature resistance (R_{RT}) versus temperature of oligomer prepared from the reaction of diphenylsilane with hydroquinone.

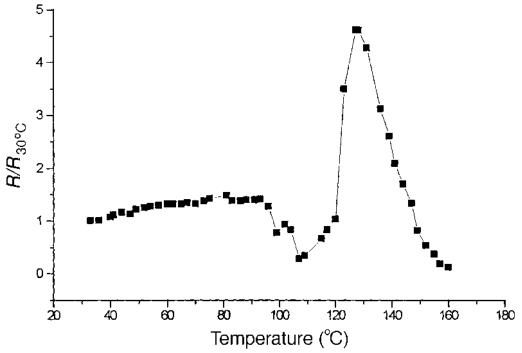


Figure 8 Variation of resistance (R) normalized to room-temperature resistance (R_{RT}) versus temperature of oligomer prepared from the reaction of diphenylsilane with p-benzoquinone.

abstraction from solvents by quinonic compounds with palladium catalysts are well studied.[32,33] The rate of change in absorbance at 292 nm is an index of formation of quinhydrone in the reaction and this reflects the relative reactivity of the palladium catalyst under consideration. The catalytic activities were determined in relative terms by monitoring the increase in the concentration of quinhydrone, which has an absorption maximum at 292 nm, and it was found that the relative rate of hydrogenation of quinone (Path B of Scheme 6) was in the order $Pd(TMEDA)Cl_2 < Pd(TEEDA)Cl_2 < PdCl_2 < Pd(PPh_3)_2Cl_2$.

Since the oligomers contain aromatic backbones π-stacking may be present in the molecules (Fig. 6). To ascertain such a possibilty, resistance of films of **4** was measured in the range 30–120 °C (i.e. below the melting point of 140 °C as determined by differential scanning calorimetry). A plot of resistance against temperature showed (Fig. 7) that the resistance of the sample increased initially and reached a maximum value around 116 °C. Although the magnitude of the resistance was in the order of gigaohms, the variation of resistance with temperature was similar to metallic properties attributable to π-stacking which cleaves on heating. Figure 8 shows a plot of resistance versus temperature of a film of oligomer prepared from the reaction of p-benzoquinone with diphenylsilane, recorded in the range 30–160 °C (below its melting point of (175 °C). There was also a fivefold increase in resistance around 100–127 °C, decreasing to the original value in the range 127–150 °C. Such a phenomenon probably occurs due to a change in the aggregated non-linear structure, which might have been present due to π-stacking of aromatic rings. (Fig. 6). Recently we observed similar effects on aggregation through hydrogen bonding in related systems.[41–44]

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