

Grafting and Polymer Formation on Silicon from Unsaturated Grignards: I— Aromatic Precursors

S. Fellah,[†] F. Ozanam,[†] J.-N. Chazalviel,^{*,†} J. Vigneron,[‡] A. Etcheberry,[‡] and M. Stchakovsky[§]

Laboratoire PMC, CNRS-Ecole Polytechnique, Route de Saclay, 91128 Palaiseau, France,
Institut Lavoisier, Université de Versailles St-Quentin-en-Yvelines, 45 av. des Etats-Unis,
78000 Versailles, France, Horiba Jobin-Yvon, Z.I. de la Vigne aux Loups, 5 av. Arago,
91380 Chilly-Mazarin, France

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Anodic decomposition of a phenylmagnesium halide at a surface-hydrogenated silicon electrode leads to formation of polymeric layers covalently anchored to the silicon surface. These layers have been characterized using spectroellipsometry, photoluminescence, infrared, and X-ray photoelectron spectroscopies. The phenyl ring appears preserved in the process, and the polymer formed is a polyphenylene. Contamination by aliphatic groups from the solvent may be minimized by using a solvent resistant to hydrogen abstraction by the phenyl radicals. Regioselectivity of the branching may be oriented to the para form by using 4-chlorophenylmagnesium bromide as the precursor.

Introduction

Organic functionalization of the silicon surface has been a very active field in recent years.¹ Organic species may be grafted to the hydrogenated silicon surface by various chemical and electrochemical methods. Covalent bonding through a direct Si—C link can be obtained, which gives the resulting surfaces a high chemical stability.^{1–3} Among the electrochemical methods,^{4–7} anodic reaction of the hydrogenated silicon surface in Grignard electrolytes has been found to be an especially fast and efficient route to the grafting of alkyl monolayers.⁷ In a further step, we have been trying to use this method for unsaturated organic species.⁸ Polymer films, rather than monolayers, were then obtained. This method may be regarded as a variant of electrochemical polymer synthesis, a synthetic route that can be applied to a variety of polymers and has been extensively considered in the literature.^{9–14} Among the electrochemical, however, the present method is specific in that context, as the chemically fragile hydrogen coating is attacked first, leading to formation of covalent bonds between the substrate and the formed polymer. It then represents an alternative to previously reported strategies aiming at anchoring polymers at the silicon surface through robust Si—C bonds. Previous strategies involve decomposition of unstable reactants at the hydrogenated surface,^{15,16} or a controlled chemical or electrochemical reaction after proper surface functionalization,^{17–21} a strategy successfully tested for a better control of the morphology of films electropolymerized on metal electrodes.¹² Our preliminary results on polymer formation by anodic reaction of unsaturated Grignard compounds have appeared elsewhere.⁸ Subsequently, we tried to characterize the layers obtained by this technique and to understand the mechanism intervening in their formation. These investigations were carried out using spectroellipsometry, infrared (IR), X-ray photoelectron (XPS), and photoluminescence spectroscopies. In addition, in situ IR

studies were made during the modification. We will report here on the anodic reaction of the hydrogenated silicon surface with aromatic Grignards, such as phenylmagnesium bromide in diethyl ether. We will first describe the experiments performed, then present the results, and finally discuss the mechanisms intervening in the surface modification and polymer formation.

Experimental Section

Silicon substrates were cut from p-type (6–10 Ωcm resistivity), (111)-oriented, float-zone-purified, double-side-polished Si wafers. Their dimensions were $15 \times 15 \times 0.5 \text{ mm}^3$. They were used for IR characterization in multiple-internal-reflection geometry. For that, they were polished in the form of prisms with 45° bevels, using an aluminum holder to which they were fixed with wax, which protects the faces of the sample during the polishing. Bevels were polished manually by using carborundum paper of grain size decreasing from $100 \mu\text{m}$ to $20 \mu\text{m}$, then with diamond paste down to $1 \mu\text{m}$ grain size. The silicon that we used was slightly doped to remain transparent to IR radiation. For the ellipsometric, XPS, and photoluminescence investigations, one-sided polished samples were used with typical dimensions of $15 \times 7 \times 0.5 \text{ mm}^3$.

Prior to the modification, the (111) silicon surface was prepared atomically flat and hydrogenated by cleaning in a hot (1:1 $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$) mixture and etching the oxide formed in deoxygenated 40% NH_4F solution.²²

The Grignard reagents were purchased from Aldrich and used as supplied. The modification was carried out in a nitrogen-purged glovebox, using the procedure described elsewhere.⁷ For the in situ IR studies, a leakproof cell, filled in the glovebox, was used, as also described elsewhere.⁷

The IR studies were performed with a Bomem MB100 Fourier transform spectrometer, using an external ATR arrangement and MCT cooled photovoltaic detector. Spectroellipsometric studies were made with a UVISEL NIR Horiba-Jobin-Yvon spectroellipsometer. The XPS studies were made with a VG Instruments ESCALAB 220i XL model, using monochromatized $\text{AlK}\alpha_1$ excitation (300 meV fwhm resolution). Constant

* To whom correspondence should be addressed.

[†] CNRS-Ecole Polytechnique.

[‡] Université de Versailles St-Quentin-en-Yvelines.

[§] Horiba Jobin-Yvon.

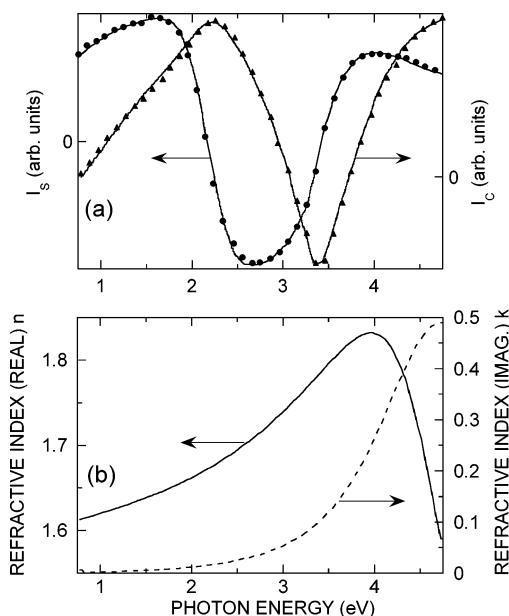


Figure 1. Analysis of a (111) Si surface modified with phenylmagnesium bromide in diethyl ether (0.5 mA/cm², 20 min) using spectro-ellipsometry. (a) Raw data (points) with fit (lines). (b) Model refractive index as a function of photon energy.

analyzer energy mode was used with a high resolution configuration (pass energy of 20 eV or 8 eV). The photoelectrons were generally collected perpendicularly to the surface sample. XPS profiling was performed using an Ar⁺ ion gun.

Results

Spectroellipsometry and Photoluminescence. Silicon surfaces modified by anodic treatment in an arylmagnesium bromide electrolyte for a few minutes at current densities on the order of 1 mA/cm² come out covered with a layer visible to the naked eye (from light brown to blue). A more quantitative characterization of the optical properties of these films in the visible range was obtained through spectroscopic ellipsometry and photoluminescence.

Figure 1a shows a typical set of ellipsometric data for a layer formed from phenylmagnesium bromide. These spectra were analyzed assuming a homogeneous film composition with a Forouhi–Bloomer form for the refractive index function²³ (a model often used in amorphous compounds, featuring an absorption edge and a dominant broad optical transition, with 5 adjustable parameters), and with some roughness of the outer surface (classically modeled as a surface porous layer through standard effective medium approximation²⁴). The obtained thicknesses are 91 nm for the film and 32 nm for the surface porous layer. The refractive index as a function of photon energy is shown in Figure 1b. Note that the imaginary part is very small, up to a photon energy on the order of 3 eV. The film material is then essentially transparent, and the color of the layers is just an “interference color”.

Table 1 summarizes the results obtained from the analysis of the ellipsometric spectra. In all the cases presented, the

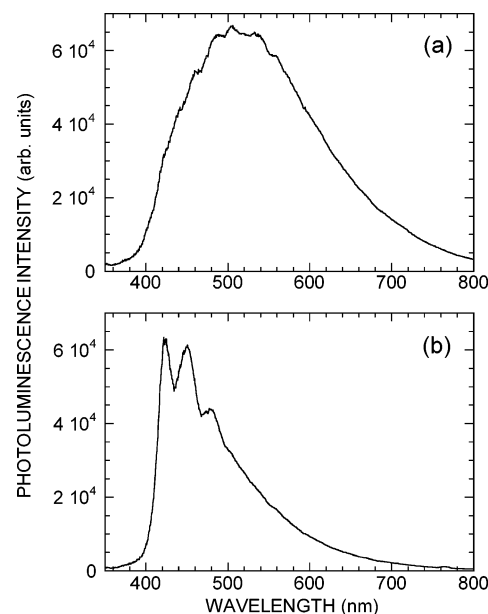


Figure 2. Typical photoluminescence spectra of Si surfaces modified (a) with phenylmagnesium bromide and (b) with 4-chlorophenylmagnesium bromide.

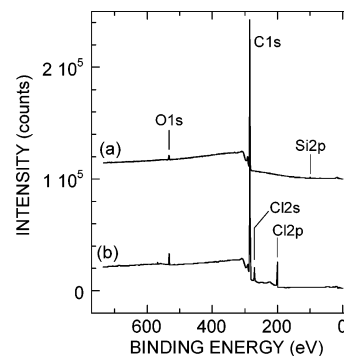


Figure 3. XPS survey of a (111) SiH surface modified (a) with phenylmagnesium bromide ($J = 0.5$ mA/cm² during 300 s) and (b) with 4-chlorophenylmagnesium bromide (in ether, $J = 0.5$ mA/cm² during 1000 s).

applied current density is 0.5 mA/cm². It is noticed that the layer formed with phenylmagnesium bromide is thicker if the solvent used is ether rather than dichlorobenzene.

These films exhibit a strong photoluminescence in the visible range (see Figure 2). Their transparency in the visible range, together with the similarity of their photoluminescence spectra with that of oligophenylenes and polyparaphenylene,²⁵ suggests that the film materials may be some form of polyphenylene.

XPS. X-ray photoemission enables us to follow the evolution of the chemical composition of the silicon surface after electrochemical modification. Figure 3a presents an XPS “survey” spectrum of a Si surface after modification in the presence of phenylmagnesium bromide. For anodic treatments of increasing Faradaic charge, the Si2p silicon signal in the 99.4–99.6 eV range progressively disappears as the polymer grows. Its intensity is always weaker than at the initial

TABLE 1: Thickness of the Polymeric Layer Obtained According to the Grignard Used and the Duration of Applied Polarization

Grignard used	duration of polarization	thickness of the polymeric layer	color of the polymeric layer
4-chlorophenylmagnesium bromide in ether	15 min	875 Å	blue-purple
phenylmagnesium bromide in ether	20 min	1066 Å	blue
phenylmagnesium bromide in dichlorobenzene	20 min	250 Å	light brown

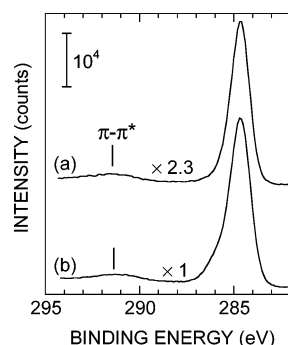


Figure 4. High-resolution XPS spectrum of a (111) Si surface modified (a) with phenylmagnesium bromide ($J = 0.5 \text{ mA/cm}^2$ during 300 s) and (b) with 4-chlorophenylmagnesium bromide (in ether, $J = 0.5 \text{ mA/cm}^2$ during 1000 s). Note the shoulder around 286 eV, ascribable to the carbon atoms substituted by chlorine.

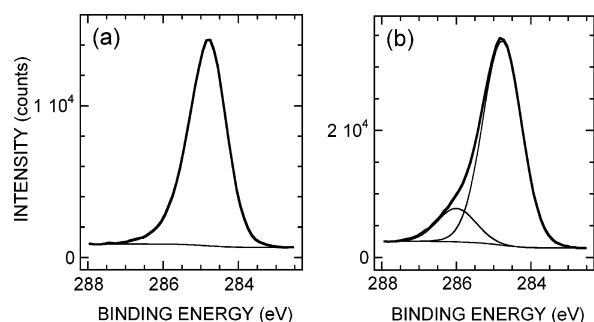


Figure 5. Fits of the C1s XPS spectra of Figure 4. (a) Case of phenylmagnesium bromide: superposition of a Shirley background and a single (slightly asymmetrized) Voigt function and (b) 4-chlorophenylmagnesium bromide: Shirley background and two Voigt functions.

hydrogenated Si surface. Finally, it completely vanishes, which is consistent with the formation of a rather thick polymer layer. However, for estimating the polymer thickness in the intermediate thickness range, the attenuation of the Si2p or Si2s signals must be used with care, because the presence of defects such as pinholes or small scratches may cause additional contributions to the signal, leading to strong underestimates of the thickness. Carbon is characterized by its peak in the 284–286 eV range. One also observes a small O1s oxygen peak around 532 eV. Very weak additional peaks of Br3d or Br3p, due to the presence of a very small quantity of bromine, are often found. They are sometimes associated with minute Mg2p or Mg2s peaks, which are still more difficult to detect, due to the lower values of the sensitivity factors. All in all, these observations indicate the formation of a rather thick polymeric layer at the surface of silicon, without significant side incorporation of the Grignard precursor, and with a weak oxygen external contamination, as will be demonstrated below.

High resolution spectra in the C1s region (see Figure 4a) show that the main peak essentially contains a single component. As shown in Figure 5a, the peak fitting needs only one contribution centered in the 284.7–284.8 eV range, with a fwhm close to 1.1–1.2 eV (for a pass energy of 20 eV). One notes the presence of a satellite centered at 291.4 eV, which contributes to the intensity of the spectrum at a level of 7.5%. This kind of satellite, attributed to a $\pi-\pi^*$ shake-up, is common for aromatic compounds.^{26,27} The reproducible position of the C1s peak at 284.7–284.8 eV, and of the shake up contribution,^{26,27} are consistent with the idea of a polyphenylene layer.

In an attempt to clarify the elementary composition of the polymer and the effects of incorporation of solvent residues in

TABLE 2: Values of the Atomic Percentages Obtained from Quantitative XPS Analysis for the Modification of the Silicon Surface Hydrogenated in the Presence of Phenylmagnesium Bromide According to Three Solvents Used: Ether, Tetrahydrofuran (THF) and Benzene ($J = 0.5 \text{ mA/cm}^2$ during 300 s)

	Si	C	O	Cl	Br
phenylmagnesium bromide in ether	0.63%	95%	2.6%	—	not detected
phenylmagnesium bromide in THF	19%	72%	8.0%	—	0.43%
phenylmagnesium bromide in benzene	1.9%	88%	8.0%	—	0.5%

the polymeric layer, we undertook XPS measurements on the surfaces modified in the presence of phenylmagnesium bromide in various solvents. We replaced the ether solvent by tetrahydrofuran and benzene. The results obtained are presented in Table 2. Keep in mind that the magnitude of the silicon contribution is an indication on polymer thickness, larger thicknesses are associated with smaller Si signals. These measurements show that, when THF is used, the thickness of the polymer film obtained is much lower. This result (consistent with the IR measurements to be reported later) can be reasonably ascribed to an increased recombination of the electrochemically generated radicals in THF as compared to other solvents. More importantly, the analysis of the intensity of the O1s peak does not make it possible to associate this contribution to the solvent residues. If such had been the case, one should have found an intensity minimum in benzene. The oxygen detected by XPS thus seems to come from a contamination and not from the reaction process itself, as will be demonstrated below with XPS profiling.

When the hydrogenated silicon surface is modified in the presence of 4-chlorophenylmagnesium bromide (in ether), the XPS survey spectra (Figure 3b) are rather similar to those obtained if the silicon surface is modified by phenyl groups, with an extra contribution due to chlorine at 200 eV. By applying a current density of 0.5 mA/cm^2 during 100 s, one forms a rather thick layer, and by increasing the duration of the anodic treatment, the quantity of carbon increases and the Si2p and Si2s peaks disappear. In high resolution (Figure 4b) the main carbon peak at 284.8 eV appears asymmetrical and exhibits a shoulder at 286 eV. This shoulder is attributed to the carbon atoms bound to chlorine. Curve fitting of C1s (Figure 5b) gives the position of the two contributions at 284.74 and 285.94 eV, with respective fwhm of 1.2 and 1.3 eV (pass energy of 20 eV). The area ratio is between 5/1 and 6/1. A similar fitting performed on the Cl2p peak shows that a one-contribution configuration can be proposed, with a perfect (1/2:3/2) spin–orbit coupling [ratio Area(1/2):Area(3/2) = 0.5]. The Cl2p_{3/2} peak is centered at 200.5 eV. These values agree with the parameters given for similar configurations in the literature.^{26,27} In addition, as in the preceding case, one notes the presence of a $\pi-\pi^*$ satellite at 291.4 eV. When the layers are thin, the intensity of the $\pi-\pi^*$ satellite is low, and in certain cases its presence becomes difficult to detect.

IR spectroscopy. IR spectroscopy has been used as a systematic tool to characterize the various types of bonds in the films formed, providing clear-cut information on their chemical nature.

The ex situ IR absorption spectra of the silicon surface modified with phenylmagnesium bromide show the presence of CH bonds of the aromatic type in the region 3000–3100 cm^{-1} (see Figure 6). These last ones are the proof that the polymeric film obtained incorporates monomeric units coming

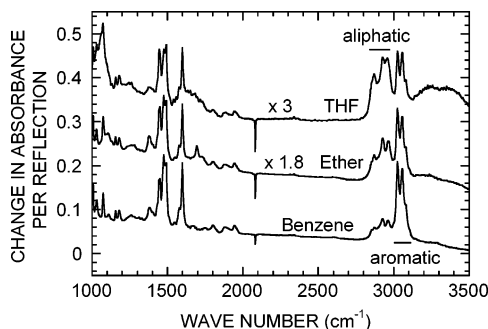


Figure 6. IR spectra of the (111) Si surface after anodic treatment in phenylmagnesium bromide in various solvents ($J = 0.5 \text{ mA/cm}^2$, during 5 min).

from the Grignard reagent, and not only decomposition products. The appearance of a negative νSiH peak is consistent with the grafting of the film by covalent bonds substituted to the initial Si–H bonds. The absence of any broad absorption in the region $1050\text{--}1200 \text{ cm}^{-1}$ stands as evidence that there is no significant oxidation of the Si surface.

However, the IR spectra also show an important contribution of CHs of the alkyl type in the region $2800\text{--}3000 \text{ cm}^{-1}$. Given the known robustness of the phenyl ring, it appears unlikely that this contribution could be due to breaking of the phenyl radicals before polymer formation.²⁸ Incorporation of fragments of solvent molecules into the polymer appears as a much more plausible explanation for this observation. This mechanism should be solvent dependent. To unambiguously confirm this interpretation, we replaced the diethyl ether solvent by tetrahydrofuran, toluene and benzene. This solvent replacement was carried out by adding the indicated solvent to the starting Grignard, initially in ether. The solution was then reconcentrated by evaporating the solvents using a vacuum pump. This operation was repeated twice in order to obtain a good substitution. This operation of solvent substitution must be made in this manner; one cannot dry the Grignard completely before adding the chosen solvent because the Grignard is not very stable in the absence of solvent.

The IR spectra of surfaces modified in these solvents show that the CHs of the alkyl type are more intense when one uses tetrahydrofuran and even more with toluene, but that their intensity clearly decreases in the case of benzene or 1,2-dichlorobenzene (toluene > tetrahydrofuran > diethyl ether > benzene = 1,2-dichlorobenzene). For the case of THF solvent, a band appears at 1060 cm^{-1} , possibly associated with the νCOC mode²⁹ (though an alternate explanation would be in terms of Si oxidation). More interestingly, the use of benzene or 1,2-dichlorobenzene thus makes it possible to obtain layers of greater purity. In the absorption region of the νCH modes, one obtains exactly the same IR spectrum if either benzene or dichlorobenzene is used. In practice, we preferred to work with dichlorobenzene because it has a higher boiling point, which makes it less volatile and thus less hazardous.

In Situ IR Spectroscopy. The in situ modification of the (111) atomically planar silicon surface with phenylmagnesium bromide (in diethyl ether) highlights the surface modification by the disappearance of the SiH bonds and the correlated appearance of νCH vibrations in the region $2800\text{--}3000 \text{ cm}^{-1}$. Vibrations of the benzene ring are apparent in the region $1000\text{--}1600 \text{ cm}^{-1}$. Figure 7 presents a series of in situ IR spectra during the electrochemical modification of the SiH surface in phenylmagnesium bromide. The current was applied as successive pulses of increasing duration, and the IR spectra were recorded between the pulses, following the method described in ref 7.

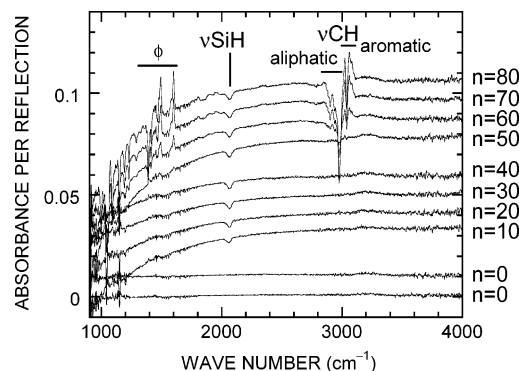


Figure 7. In situ IR spectra during the electrochemical modification of the SiH surface in phenylmagnesium bromide in ether. ($J = 100 \text{ mA/cm}^2$). For each spectrum, the number n of current pulses applied before the recording of the spectrum is indicated on the right-hand side. The current pulses have an increasing duration $\Delta t = \Delta t_0 \times \alpha^{n-1}$, where n is the spectrum number (on the right of each curve in the figure), with $\Delta t_0 = 0.1 \text{ s}$ and $\alpha = 1.05$. Mind that the cumulated Faradaic charge is an exponential function of n .

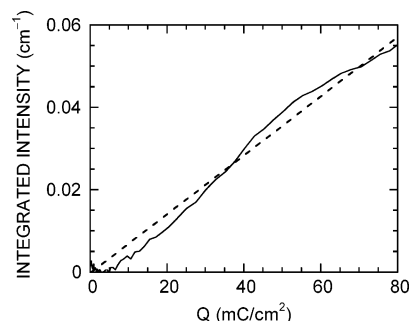


Figure 8. Growth of the intensity of the spectral band at $1475\text{--}1490 \text{ cm}^{-1}$, characteristic of the polymer formed from phenylmagnesium bromide.

The SiH band (negative) appears for a cumulated Faradaic charge on the order of $100 \mu\text{C/cm}^2$, which indicates the grafting of a first monolayer of aromatic species on the Si surface. Note that in situ observation of a negative νSiH band is a more clear-cut proof of the covalent grafting of the polymer than the ex situ observation, as the initial ex situ νSiH line is extremely narrow, and it is not always clear how much of it is preserved after the modification in the form of a broader line. Due to solvent broadening, the in situ line has a width comparable to that after modification, and the observed negative band unambiguously corresponds to a loss. In contrast to the behavior of the SiH band, the aromatic CH and phenyl-ring bands (positive) increase steadily with an increasing number of applied pulses, without any indication of a saturation. Note also the presence of negative contributions, associated with electrolyte displaced by the growing polymer film.⁷ A band characteristic of the formed polymer (at 1475 cm^{-1}) has been considered and analyzed quantitatively. Figure 8 illustrates the growth of its intensity as a function of the cumulated Faradaic charge Q . Its variation, which can be taken as an indication on the polymer thickness, is seen to be fairly linear. This demonstrates the possibility to control the polymer thickness by coulometry.

An interesting feature is the presence of a reproducible sloping baseline on the spectra (see Figure 7). This baseline can be fitted as a power law $\Delta I/I \propto -\lambda^\beta$, where λ is IR wavelength and $\beta \approx 3$. This shape, characteristic of free-carrier absorption, indicates a decrease in the concentration of free carriers probed by the IR beam. This can be attributed to the formation of a depletion layer at the Si/electrolyte interface. At the initial stage of the

surface modification, this depletion layer is plausibly due to the creation of interface states (Si dangling bonds).³⁰ The further increase in magnitude of the baseline indicates that the depletion layer becomes increasingly thick as the polymer grows. This may be associated with the presence of positive charges in the polymer, which may be due to trapped ions, or to charged defects as suggested, for example, by the presence of a band at 1595 cm⁻¹, often attributed to quinoid defects.³¹

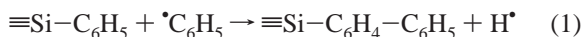
Discussion

The anodic decomposition of a Grignard is known to lead to the generation of active radicals.³² In the case of alkyl Grignards, it has been shown that the formed radicals can capture a hydrogen atom from the silicon surface, and the activated surface can become grafted with an alkyl group.⁷ Alternately, the radicals may recombine by dimerization or abstraction of a hydrogen atom from a solvent molecule.

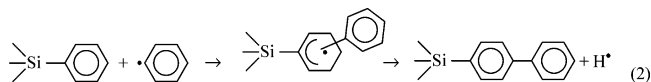
A phenyl radical is expected to react in much the same way as an alkyl radical, but, due to the higher binding energy of the CH bond (111 kcal/mol for ϕ -H as compared to an average of 99 kcal/mol for RCH₂-H²⁸), the phenyl radicals are expected to be more prone to solvent attack.³³ At a later stage, the generated solvent radicals can be incorporated into the polymer layer (this may take place before or after these radicals undergo reorganization reactions, e.g., for ether, CH₃CH•-O-CH₂CH₃ → CH₃CH=O + •CH₂CH₃;^{28,33} hence, the ether oxygen may or may not be incorporated into the polymer). This accounts for the observed solvent effects; the order for incorporation of aliphatic fragments (toluene > tetrahydrofuran > diethyl ether > benzene) exhibits indeed a fair correlation with that of Solv-H bond fragility (the corresponding enthalpies in kcal/mol are 83, 92, 92, 111²⁸). Good polymer purity, therefore, requires the use of a solvent with no labile H atoms. It is then clear that the phenyl group remains unaltered in the process, and the residual amount of aliphatic CHs in the polymer formed with benzene or dichlorobenzene solvent is due to ether molecules bound to the Grignard even after solvent substitution.³⁴

Phenyl Grafting. As far as the generation of solvent radicals may be avoided, the phenyl radicals abstract a hydrogen from the hydrogenated silicon surface. This reaction is expected to be irreversible, as the typical Si-H bond enthalpy is around 90 kcal/mol, far less than ϕ -H. (Note that the last figure is comparable to the enthalpy of the ϕ CH₂-H bond. This unusually low value for a C-H bond is due to the fact that the benzyl radical ϕ CH₂• is stabilized by conjugation.²⁸ We have found, indeed, that no reaction at all takes place with benzylmagnesium bromide. The subsequent step may be similar to that discussed for the alkyl groups,⁷ namely electrochemically with the Grignard or chemically with another radical, leading to formation of a phenyl-terminated Si surface. The vulnerability of surface SiH groups to phenyl-radical attack and the fact that these radicals are generated at the surface account for the high efficiency of the initial phenyl grafting step (evidenced by the ~100 μ C/cm² cumulated Faradaic charge needed to complete this first step, which corresponds to a Faradaic yield of ~100%).

Polymer Formation. The observed formation of a polymer layer shows that the phenyl-terminated surface is not stable in the presence of further electrogenerated phenyl radicals. Polymer formation may occur either by addition or substitution reactions. We have seen that, provided an appropriate solvent is chosen, all the CHs observed in the polymer are of the aromatic type. This confirms that the phenyl rings are preserved in the process, a clear-cut indication in favor of a substitution mechanism:



From general knowledge on free-radical reactions, it appears plausible that this substitution takes place via an addition-elimination process:²⁸



The elimination step from the cyclohexadienyl radical intermediate requires the participation of a co-reactant.²⁸ Here, the hydrogen released may be captured by another phenyl radical or a halogen radical (also generated in the anodic process) or else be transferred to the electrolyte as a H⁺ ion, after capture of a second hole.

At this point it may be useful to locate our approach among the many known synthetic routes for polyphenylene.^{35,36} The classical direct routes may be sorted out into two main classes. The oxidative routes, like Kovacic's method³⁷ and anodic electropolymerization from benzene,¹⁴ amount to an oxidation of benzene with elimination of two hydrogens. On the opposite, the reductive routes, like Yamamoto's,³⁸ start from a precursor disubstituted with electronegative groups (bromine,³⁸ chlorine,³⁹ methanesulfonyl,⁴⁰ etc.), which are eliminated by reduction (electrochemical⁴¹ or chemical by Mg or Zn in the presence of a catalyst³⁸⁻⁴⁰). Suzuki's method represents an intermediate between these two classes, as elimination occurs between an oxidizable and a reducible group born by the same precursor.⁴² The oxidative methods involve formation of positively charged intermediates.¹⁴ This is quite at variance with the present method, which then appears more related to the reductive methods, though it involves an anodic process.

One might question the possibility of a chain mechanism, similar to that reported for the classical Kovacic's synthesis of polyparaphenylene from benzene.³⁷ To test this possibility, we have made a specific in situ IR experiment. The anodic current was successively turned on and off, and the behavior of the IR signal associated with polymer formation was observed. It was found that the polymer growth starts as soon as the current is turned on and stops as soon as it is turned off. This tells us that if any chain reaction takes place at all, the lifetime of the involved radicals is very short and the chain stops very quickly. Also, if a chain mechanism were present, one would expect the number of monomer units incorporated into the polymer per elementary charge to be larger than unity. From the ellipsometric measurements and assuming a specific gravity of 1 for the polymer, this number appears to be on the order of 10⁻² in dichlorobenzene solvent and is always lower than 10⁻¹, i.e., much smaller than unity and consistent with the maximum value of 0.5 expected from eq 2 if no radicals were lost by dimerization. Furthermore, a convincing chain mechanism is difficult to work out. In the case of polyparaphenylene synthesis from benzene, both cationic and radical pathways have been invoked for sustaining the reaction.³⁷ However, transposing such mechanisms to phenylmagnesium bromide precursors seems difficult, especially because they both involve a final oxidation step for rearomatization, a condition uneasy to meet in a highly reducing medium such as a Grignard solution.⁴³ Therefore, in our opinion, eq 2 is rather firmly established as the dominant route to polymer formation.

Regioselectivity. In principle, eq 2 allows addition of the new phenyl unit in either ortho, meta, or para position with respect to the preceding link. Aromatic substitution on substituted benzene is known to favor ortho and para coupling. This

TABLE 3: Position of Vibrational Lines in the 1000–2000 cm⁻¹ Region for Our Samples (from phenylmagnesium bromide and from 4-chlorophenylmagnesium bromide) and from the Literature, for Disubstituted Phenyl Rings and for Polyparaphenylene (PPP)^a

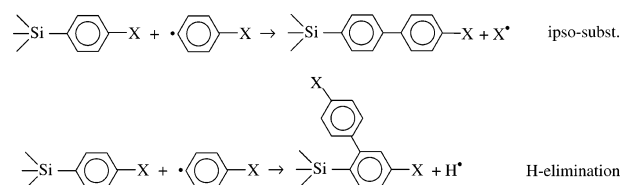
	our results ϕ MgBr	our results Cl ϕ MgBr	para [44]	meta [44]	ortho [44]	PPP [14,31,38]
summation bands	1945(w) 1900(w) 1880(w) 1800(w) 1750(w) 1670(w)	1905(w) 1780(w) 1650(w)	1900(m) 1800(w) 1650(w)	1930(m) 1870(m) 1810(sh) 1780(m) 1740(w) 1685(w)	1950(w) 1910(m) 1870(w) 1840(w) 1800(w) 1740(w) 1685(m)	
quadrant stretch	1595(s) 1578(w) 1550(w)	1595(m)		1630(s) 1600(w) 1580(v)	1600(s) 1580(v)	(1600) ^b
semicircle stretch	1490(m) 1475(s) 1450(s) 1400(w) 1380(m) 1260(w)	1490(w) 1480(s) 1465(m) 1400(m) 1380(w) 1355(w) 1255(w)	1500(v) 1410(m) 1355(w) 1255(w)	1490(v) 1445(m) 1160(w) 1100(m-w) 1080(w)	1490(v) 1445(m) 1160(w) 1130(m) 1030(m)	1480(s) 1390(m) 1250(w)
substituent-sensitive bands	1180(w) 1155(w) 1110(w) (ϕ -X) 1075(m) 1030(m) 1010(m)	1180(w) 1150(w) 1090(s) 1030(w) 1015(m) 1005(m)	1110(w) 1010(m)			(1070) ^c 1000(m)

^a s = strong, m = medium, w = weak, v = variable, sh = shoulder. ^b Not always observed, and likely associated with triphenylene or quinoid defects, according to refs 14 and 31. ^c Ph-Br vibration (observed only in PPP prepared from dibromobenzene according to ref 38). The band at 1075 cm⁻¹ in our experiments may also be associated with Br contamination, though the amount of Br found by XPS is below 1%. That at 1090 cm⁻¹ for the polymer obtained from 4-chlorophenylmagnesium bromide is certainly due to the presence of chlorine substituted phenyl groups.

is a consequence of the stabilization of the cyclohexadienyl radical (the intermediate state in eq 2) when the lone electron can be localized on the substituted carbon.²⁸ On the other hand, anodic synthesis of polyphenylenes from benzene or biphenyl is known to produce many structural defects, and not a pure para coupling like in the chemical synthesis under mild conditions.^{14,31} In the present case, from a detailed analysis of the IR spectra, we have tried to extract information on the stereochemistry of the obtained polymer. The 1000–2000 cm⁻¹ region is known to be especially sensitive to the stereochemistry of phenyl-ring substitution. Table 3 gives a list of the IR lines of our material, compared with those of polyparaphenylene, and those of molecules involving disubstituted phenyl rings.⁴⁴ It comes out that our data point to preferred ortho and para substitution. As already mentioned, this is in line with general trends of radical reaction on aromatic compounds substituted with a π -electron attractor group, according to eq 2, but also with results obtained on polyphenylenes electropolymerized from diphenyl.^{31,45} However, in contrast to the latter case where the polymerization reaction is thought to be initiated in solution in the vicinity of the electrode, here the ortho substitution is likely to be sterically hindered near the Si surface because of the covalent coupling of the first phenyl monomer to the Si substrate. However, in the bulk of the 3D film, rotation of the phenyl planes around the ϕ - ϕ bond largely relaxes these geometrical constraints.

Using 4-chlorophenylmagnesium bromide instead of phenylmagnesium bromide is expected to favor para substitution over ortho and meta. However, the so-called “ipso-substitution” mechanism,²⁸ which should favor para substitution like in the classical scheme of synthesis of polyparaphenylene (PPP) from

para-dibromobenzene,³⁸ is still in competition with hydrogen elimination:



The IR spectrum of the observed polymer (see Figure 9) appears substantially closer to that of PPP than in the case where phenylmagnesium bromide was used as the Grignard precursor. However, XPS data indicate that a significant amount of chlorine is present in the material (see Figures 3–5). The presence of chlorine is also responsible for the IR absorption at 1095 cm⁻¹, characteristic of chlorine-substituted phenyl rings.⁴⁴

The atomic Cl to C ratio can be extracted from the raw XPS data by two methods. From the two-component fitting of the

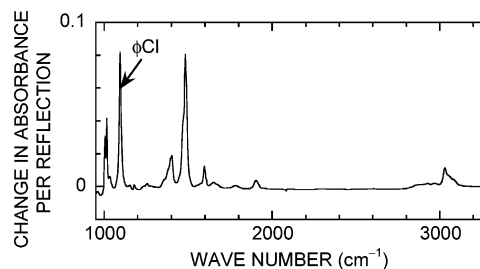


Figure 9. IR spectrum of a film obtained from 4-chlorophenylmagnesium bromide in benzene solvent.

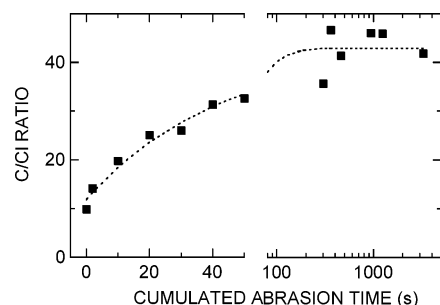


Figure 10. Carbon to chlorine atomic ratio as deduced from the XPS spectra, as a function of abrasion time. Note the change of the time scale from linear to logarithmic. The dotted line is an exponential fit. The abrasion rate is estimated to be on the order of 0.1 Å/s.

C1s spectrum and the obtained ratio of 1/6 between the two forms of carbon, an atomic Cl to C ratio of 1/7 is deduced. From the Cl2p to C1s area ratio and using standard XPS quantitative analysis, a Cl/C ratio of 1/9 is derived. If hydrogen substitution were the only reaction path, a ratio of 1/6 would be expected. On the opposite, if only ipso-substitution were taking place, this ratio should be about zero for the bulk polymer. However, terminal Cl atoms are to be expected at the end of the polymer chains, giving a local Cl/C ratio of 1/6. A careful XPS profile analysis using mild ionic abrasion of the layer has been made. The Cl signal is indeed found to decrease considerably from the surface to the bulk of the film. From the quantitative analysis of the Cl2p and C1s signals, it is found that the Cl to C ratio falls from 1/9 at the surface to a constant value of $\approx 1/45$ in the bulk of the polymer (see Figure 10). Furthermore, the absolute magnitude of the C1s XPS signal stays remarkably constant in this region, a good check of the homogeneity of the material, in agreement with the ellipsometric results. From the measured C/Cl ratio of 1/45, we can deduce the probability p of ipso-substitution from $1/45 = (1-p) \times 1/6$, which gives $p = 0.87$. This rather high value is in agreement with the qualitative findings from the IR data. It may be regarded as especially large, since there is only one available site for ipso-substitution, as compared to the four available sites for hydrogen elimination.

Chlorine substitution of the phenyl group, therefore, provides regioselectivity and favors formation of polyparaphenylene, though full regioselectivity has not as yet been reached.

Conclusion

Anodic decomposition of aryl Grignards at a hydrogenated silicon electrode has been shown to lead to the formation of polyphenylenes covalently anchored to the silicon surface. This electrochemical technique allows easy control of the reaction and of the polymer thickness. The mechanism has been analyzed. Though a detailed kinetic model has not been worked out, we feel that a reasonable level of understanding of the reaction mechanism has been reached. Improvement of polymer purity will require an optimization of the solvent, as THF or diethyl ether are not sufficiently resistant to hydrogen abstraction. One will be able to prepare pure polyparaphenylene if full control of regioselectivity can be obtained. This is a general problem of arylation in aromatic substitution. Here, a possible way to orient the substitution to the para position may be by using a better leaving radical than chlorine in order to favor the ipso-substitution pathway more efficiently.

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whence poor transport properties (they macroscopically appear rather insulating). In these conditions, it appears very unlikely that a charge-transfer reaction with the substrate could take place near the end of the chains.

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