Photochemistry at the Organosilane/Polymer Interface

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ABSTRACT: The surface modification of UV-absorbing (polystyrene)/nonabsorbing (polyethylene) polymers by chromophoric (hexamethyldisilane)/nonchromophoric (tetramethylsilane) organosilanes has been investigated by X-ray photoelectron spectroscopy (XPS). A strong correlation is found between the photochemical characteristics of the adsorbate/substrate and the amount of organosilicon species deposited during UV irradiation.

Introduction

Polymeric surfaces can be tailored to enhance a wide range of interfacial properties, such as wettability,[1] hydrophobicity,[2] adhesion,[3] and biocompatibility.[4] Such target surfaces may be attained in a variety of ways; these include using coronas,[5] plasmas,[6] and photochemical methods.[7] In the case of the latter technique, the most important criterion to bear in mind is that at least one of the reactants must be capable of becoming photoreactive during irradiation, i.e., either the incident moiety or the polymer substrate itself.

A systematic study has been undertaken with the aim of examining the relative photoreactivities of chromophoric (hexamethyldisilane)/nonchromophoric (tetramethylsilane) gaseous molecules with chromophoric (polystyrene)/nonchromophoric (polyethylene) substrates. Hexamethyldisilane ($[CH_3]_3Si-Si[CH_3]_3$) contains a weak Si–Si linkage which can readily undergo a $\sigma(Si-Si) \rightarrow \sigma^*(Si-Si)$ transition during UV absorption.[8] Tetramethylsilane ($Si[CH_3]_4$) is very similar to hexamethyldisilane in terms of molecular structure, except it does not possess a Si–Si bond and is therefore a relatively weak chromophore in comparison. Polyethylene is based upon extended alkane chains, $-(CH_2)_n-$, and is generally considered to be the simplest of polymers. Polystyrene is comprised of phenyl rings attached to alternate carbon centers along a polyethylene backbone; these aromatic centers absorb strongly in the UV region.[9] The various combinations of organosilane molecules with polymer substrates have been exposed to ultraviolet (UV) irradiation, and the resultant surfaces have been subsequently characterized by X-ray photoelectron spectroscopy (XPS). A pertinent aspect of this investigation is to address whether there is any mutual enhancement of the extent of surface modification, when both the organosilane gas and the polymeric substrate are strongly absorbing in the UV region.

Experimental Section

UV irradiation was carried out in a glass-walled reactor with a detachable quartz window (cut-off wavelength 180-200 nm).[10] A low-pressure Hg-Xe arc lamp (Oriel) was used as the photon source, operating at 50 W; this gave a strong line spectrum from 240 to 600 nm. Low-density polyethylene (ICI) and polystyrene (ICI) films were cleaned in an ultrasonic bath with isopropyl alcohol and subsequently dried in air. A small piece of polymer film was positioned in direct line-of-sight to the quartz window. The reactor was evacuated down to a base pressure of 3×10^{-2} Torr using a two-stage rotary pump equipped with a liquid-nitrogen trap and then valved off. A total of 0.4 Torr of hexamethyldisilane (Aldrich, 98% pure)/tetramethylsilane (Aldrich, 99.9% pure) vapor (both of which had been further purified by freeze–pump–thaw cycles) was introduced into the reactor from a monomer tube. The sample was then irradiated in this static atmosphere for a given time interval. Following completion of exposure, the lamp was switched off, and after a further 5 min, the reactor was evacuated back down to its base pressure.

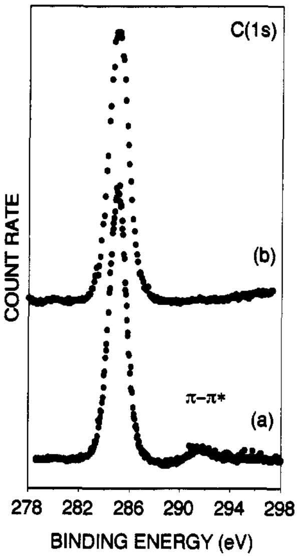

Figure 1. C(1s) XPS spectra of (a) clean polystyrene and (b) UV-irradiated polystyrene in the presence of hexamethyldisilane.

Core-level X-ray photoelectron spectra were acquired on a Kratos ES300 surface analysis instrument; this collected electrons in the fixed retarding ratio (FRR) analyzer mode. Mg Kα radiation (1253.6 eV) was used as the excitation source. XPS measurements were taken with an electron take-off angle of 30° from the surface normal. Data accumulation and component peak analysis were performed on an IBM PC computer. All binding energies are referenced to the hydrocarbon component ($-\underline{C}_xH_y-$) at 285.0 eV,[11] and the instrumentally-determined sensitivity factors are such that, for unit stoichiometry, the C(1s):O(1s):Si(2p) intensity ratios are 1.00:0.55:1.02.

Ultraviolet absorption spectra of the organosilicon monomers were recorded on a Perkin-Elmer Lambda 2 UV/vis double-beam spectrometer (190–1100 nm).

Results and Discussion

Clean polyethylene exhibits only one C(1s) peak at 285.0 eV, which can be attributed to the $-\underline{C}H_2-$ linkage in the basic polymer unit $-(CH_2)_n-$.[12] In addition to a hydrocarbon component at 285.0 eV, the XPS spectrum of clean polystyrene displays a distinctive satellite structure at ~291.6 eV (with 7% of the total C(1s) signal); this arises from low energy π–π* shake-up transitions of the phenyl rings accompanying core-level ionization[13] (Figure 1a). An

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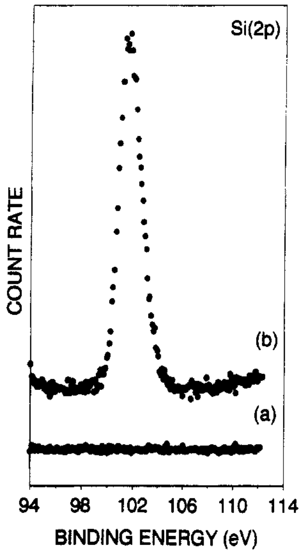

Figure 2. Si(2p) XPS spectra of (a) clean polystyrene and (b) UV-irradiated polystyrene in the presence of hexamethyldisilane.

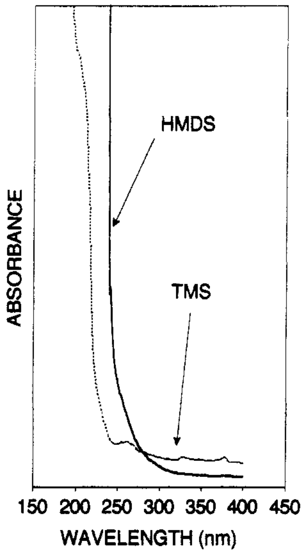

Figure 3. UV absorption spectra of hexamethyldisilane and tetramethylsilane.

absence of surface impurities was found for both of these polymers (Figure 2a).

Polystyrene absorbs light strongly below 280 nm via its phenyl ring chromophores,[9] whereas pure polyethylene is nonabsorbing above 200 nm.[14] UV absorption spectra of hexamethyldisilane (HMDS) and tetramethylsilane (TMS) are shown in Figure 3. HMDS absorbs strongly in the ultraviolet region at wavelengths shorter than ~250 nm, whereas the absorption threshold for TMS is shifted toward ~220 nm. Since the Hg-Xe UV lamp has a cutoff below 230 nm (with lines at 237.8, 248.2, and 253.7 nm), it can be assumed that only the HMDS molecule and the polystyrene substrate will undergo photoexcitation in these experiments.

Hexamethyldisilane/Polystyrene. Exposure of polystyrene to ultraviolet light in a hexamethyldisilane atmosphere results in the appearance of a Si(2p) peak at 101.4 ± 0.2 eV; this binding energy corresponds to silicon bound to carbon[15] (Figure 2b). The amount of silicon present at the polymer surface increases from zero up to a maximum value of ~17% after 40 min of UV irradiation (Figure 4). No further change was detected for longer exposure times. A corresponding attenuation in the C(1s) π–π shake-up satellite of polystyrene was observed (Figure 1b), thereby suggesting that the phenyl centers were participating in the ongoing photochemistry. A small amount of the O(1s) signal was also detectable afterward (~3%). However, this was not resolvable as oxygenated functionalities in either the C(1s) or Si(2p) envelopes and was therefore probably picked up during transfer of the sample from the irradiation vessel to the electron spectrometer. In the case of very long exposure times, a thin film of photopolymerized HMDS material was visible on the quartz window of the reactor; this was easily cleaned by wiping with a tissue soaked in isopropyl alcohol.

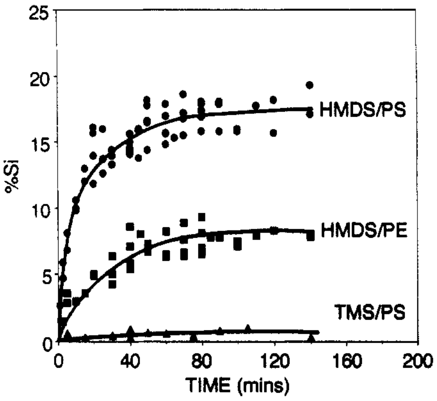

Figure 4. Photolytic uptake of silicon for (a) hexamethyldisilane/polystyrene, (b) hexamethyldisilane/polyethylene, and (c) tetramethylsilane/polystyrene (N.B. % C + % Si + % O = 100%, as determined by XPS).

Under the given experimental conditions both polystyrene and hexamethyldisilane absorb ultraviolet light and can therefore simultaneously undergo electronic excitation into a reactive state. The strong UV absorption by hexamethyldisilane may be attributed to the Si–Si bond acting as a chromophore for the σ(Si–Si) → σ^*(Si–Si) transition.[8] The photochemical decomposition of hexamethyldisilane leads predominantly to Si–Si bond homolysis and the production of trimethylsilyl radicals:[16]

$$(CH_3)_3SiSi(CH_3)_3 \xrightarrow{UV} 2(CH_3)_3Si\cdot$$

Once generated, silyl radicals may abstract hydrogen or add to vinyl or aromatic groups.[17] Therefore, one of the most likely reaction products expected would be $-Si(CH_3)_3$ functionalities grafted onto the polystyrene surface, i.e., $\sim C-Si(CH_3)_3$. On this basis, the maximum theoretical value for the percentage of silicon uptake would be 20%. Experimentally the amount obtained was ~17%; this is fairly close to the value predicted by this simple model. The loss in aromaticity at the polystyrene surface during reaction (as seen by the attenuation in the C(1s) π–π^* shake-up satellite) is consistent with this description.

Hexamethyldisilane/Polyethylene. A weak Si(2p) signal was measurable after UV irradiation of polyethylene under a HMDS environment. The extent of silicon incorporation into the surface increased toward a maximum value of ~7% over the first 40 min. This trend mirrors the behavior observed for polystyrene, except that the concentration of surface silicon species is greatly reduced. Again a weak O(1s) signal was measurable following reaction (~2%), and there was deposition of the organosilicon polymer onto the quartz window.

Polyethylene does not absorb ultraviolet light above 200 nm.[14] Therefore, the deposited silicon species must originate from the direct excitation and fragmentation of hexamethyldisilane (as is also found on the quartz window). The extent of reaction of HMDS with polyethylene (% Si = 7%) is much lower than that with polystyrene (% Si =

17%), reflecting the enhanced reactivity experienced by the photoexcited polystyrene substrate. Once generated, the trimethylsilyl radicals may react directly with the polyethylene substrate via abstraction of hydrogen atoms, or alternatively disproportionation could occur in the gas phase,[16,18,19] leading to silanes and highly reactive silenes:

$$2(CH_3)_3Si\cdot \xrightarrow{UV} (CH_3)_3SiH + (CH_3)_2Si{=}CH_2$$

The latter may subsequently undergo photopolymerization.

Tetramethylsilane/Polystyrene. Only a very small amount of silicon was detected at the polystyrene surface following exposure to UV light in the presence of TMS (~0.6%). This value remained constant over the whole range of exposure times, thereby indicating a relative lack of reactivity of polystyrene toward TMS compared with HMDS. Subsequent to reaction, the surface oxygen content was found to be as high as 7%. This was probably due to the photoactivated polystyrene surface reacting with the laboratory atmosphere during transport to the XPS spectrometer. In this case, no polymeric deposit was found on the reactor window following completion of an experiment.

TMS does not absorb strongly over the wavelengths accessible in these experiments (230–600 nm; Figure 3). Therefore, the only photosusceptible species in this study will be the polystyrene surface, which upon excitation could react with a TMS molecule, possibly via hydrogen abstraction (a process which is reported to occur during the photolysis of polystyrene):[20,21]

$$PS{-}H \xrightarrow{UV} PS\cdot + H\cdot \xrightarrow{Si[CH_3]_4} PS{-}CH_2Si[CH_3]_3 + H_2$$

Tetramethylsilane/Polyethylene. Polyethylene was found to be completely inert toward TMS under UV irradiation, even over long exposure times. As neither polyethylene or TMS absorb at the wavelengths used in these studies, no reaction would be expected for this combination of reactants. This is precisely what was found.

Conclusions

Polystyrene and hexamethyldisilane are strongly absorbing in the UV region and therefore couple to generate the greatest degree of organosilicon incorporation into the polymer surface. In the case of polyethylene, which is a nonchromophoric substrate, much less surface modification was attained; this can be attributed to either hydrogen atom abstraction by trimethylsilyl radicals at the substrate or the photopolymerization of silene (a disproportionation product of trimethylsilyl radicals). Tetramethylsilane is incapable of absorption at the UV wavelengths employed in these experiments; this leads to only a minor extent of reaction with polystyrene (probably via hydrogen atom abstraction by the photoexcited substrate); and no interactions at all are observed with a polyethylene surface.

In the future, this highly novel HMDS/polystyrene photochemistry may prove to be more effective than using polysilane coatings[22] for direct photochemical imaging during the production of submicron structures for integrated circuits, since the pattern can be generated in one simple step.

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