

Mechanism of RF Plasma Induced Fragmentation of SiCl_4 and Surface Functionalization of Polymeric Substrates from SiCl_x Species

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SYNOPSIS

The generation of extremely reactive species of silylium (silicinium) ions under plasma conditions opens up new ways for surface modification, even of the most inert polymeric surfaces. To control the plasma-induced chemistry and to tailor new molecular surface architecture, the mechanism of formation of the active species of the discharge must be understood. In this work the plasma-induced molecular fragmentation of SiCl_4 was studied and the surface functionalization of cellulose paper (CP), polyester (PET), polypropylene (PP), and polytetrafluoroethylene (PTFE) substrates with silicon atom based active species was evaluated. Gas chromatograph mass spectroscopy (GC-MS) and low Energy Electron MS (LEEMS) measurements carried out both on SiCl_4 and on the molecular mixture resulting from the recombination of plasma generated species indicate that the most predominant fragments are SiCl_3^+ cations accompanied by SiCl_2^+ and SiCl^+ species. Survey and high-resolution electron spectroscopy for chemical analysis (ESCA) data collected from plasma functionalized surfaces show significant silicon and oxygen atom content regardless of the nature of the substrates. © 1996 John Wiley & Sons, Inc.

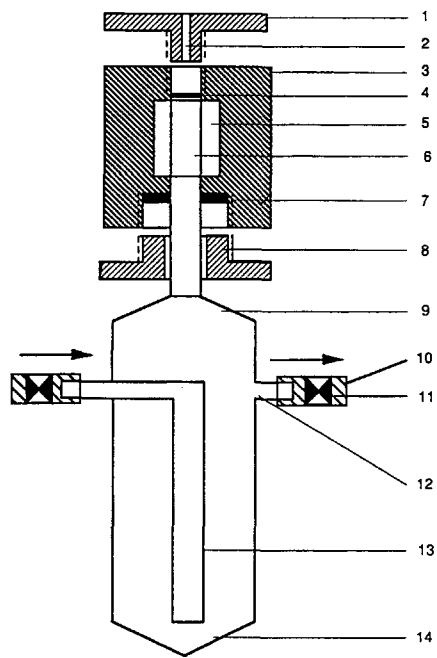
INTRODUCTION

Advanced technologies require high-performance polymer-based composites in which properties like high modules, high tensile strength, and low specific gravity (high strength/weight ratio values) are essential. Unfortunately, some of the best polymeric candidates in this field (PP, PTFE, etc.) exhibit chemical inertness, and conventional chemistry does not offer adequate solutions for surface functionalization. Macromolecular plasma chemistry, a relatively new branch of polymer chemistry, is a very promising approach to this problem. The active species of inert- or reactive-gas plasmas (ions of either polarity, free radicals, excited neutrals, electrons, photons) can efficiently interact with surface molecular layers of polymers, leading to new

functionalities or active sites (e.g., free radicals) capable of interacting through physical or chemical forces with various chemical derivatives or macromolecular counterparts. As a result, the new surface characteristics (polarity, adhesion, reactivity, etc.) can be further utilized in subsequent steps to give surface graft copolymers or advanced composites.^{1–6}

The possibility of generating extremely reactive silylium ions under electrical discharge conditions makes this plasma technique very attractive. The silylium ion is a cation in which the silicon atom is bound only to three other atoms instead of four, as in conventional silicon compounds. The trigonal silylium ions (SiCl_3^+) are stable species only in the gas phase^{7–10}; they have not yet been produced in the condensed phase^{11,12} and the existence of their reactive intermediates in solutions has been only suggested.¹³ The trigonal planar structure of these ions makes them extremely unstable and consequently reactive. A distortion, for instance, of only

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(1) Brass septum fastening threaded cap; (2) 0.5-mm diameter cylindrical channel for inserting syringe needle; (3) main body of stainless-steel special sealing; (4) Teflon-coated silicon-rubber septum; (5) window for monitoring the level of collected liquid; (6) cylindrical upper part of Pyrex tubing; (7) silicon-rubber O-ring; (8) stainless-steel threaded lower cap; (9) main body of pyrex trap; (10) silicon-rubber elastic coupling; (11) valve; (12) lateral glass tubing connection; (13) gas-guiding glass tubing; (14) conic bottom glass trap.

Figure 1 Specially designed liquid nitrogen trap for collecting plasma-generated molecular mixture.

3 degrees from the ideal silylium angle of 120 degrees determines more than half of the total out-of-plane displacement of the silicon atom during

the conversion from a trigonal planar to a tetrahedral structure.⁷ In this article the mechanism of plasma-induced molecular fragmentation of SiCl₄ is discussed as well as the role of silylium ions in the surface functionalization of CP, PP, PTFE, and PET.

EXPERIMENTAL

Materials and Methods

Commercially available silicon tetrachloride (Silicon-IV-chloride, 99%, packed under nitrogen) was used in all of the experiments. The silicon tetrachloride was handled in a glovebox under an argon blanket. Additive-free Fortiline PP film, Whatman-1 filter paper, Kodak PET film, and PTFE sheets were employed as substrates with 50 mm × 80 mm surface areas. High-purity argon (Liquid Carbonic) was used to decontaminate the reactor before each experiment.

The surface atomic composition of plasma-modified polymeric substrates was analyzed using X-ray photoelectron spectroscopy (ESCA, Perkin-Elmer Physical Electronics 0 5400 Small Area System; *M_g* source; 15 kV, 300 W; pass energy 89.45 eV; angle 45 degrees). The ESCA analysis involved the determination of carbon (C1s), oxygen (O1s), chlorine (Cl2p), fluorine (F1s), and silicon (Si2p). All samples were stored under open laboratory conditions until the measurements were started. The dynamic equi-

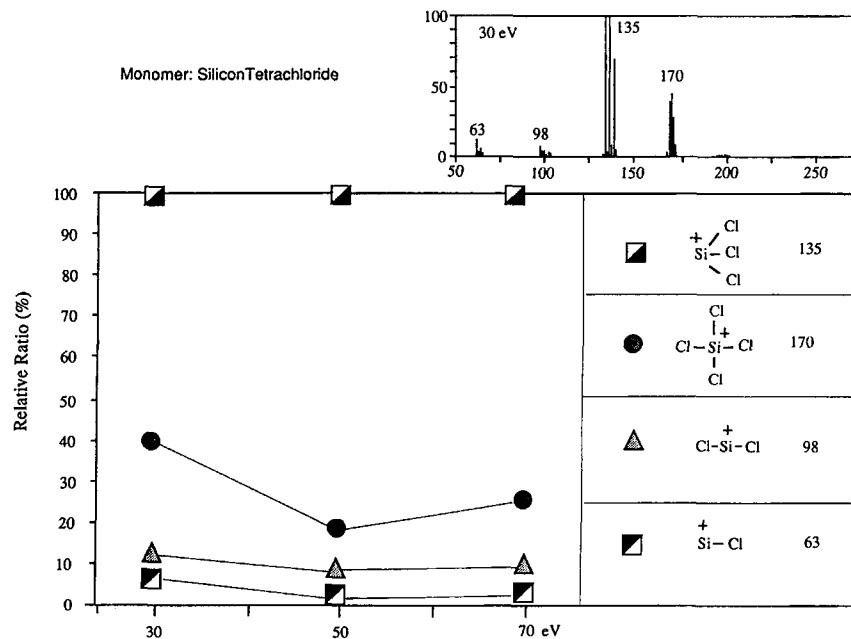


Figure 2 MS simulation of SiCl₄ at different electron energy levels.

Table I Comparison of Silicon Model Compounds with Trapped Plasma Species on Ion and Isotopic Contributions of SiCl⁴⁺ and SiCl³⁺

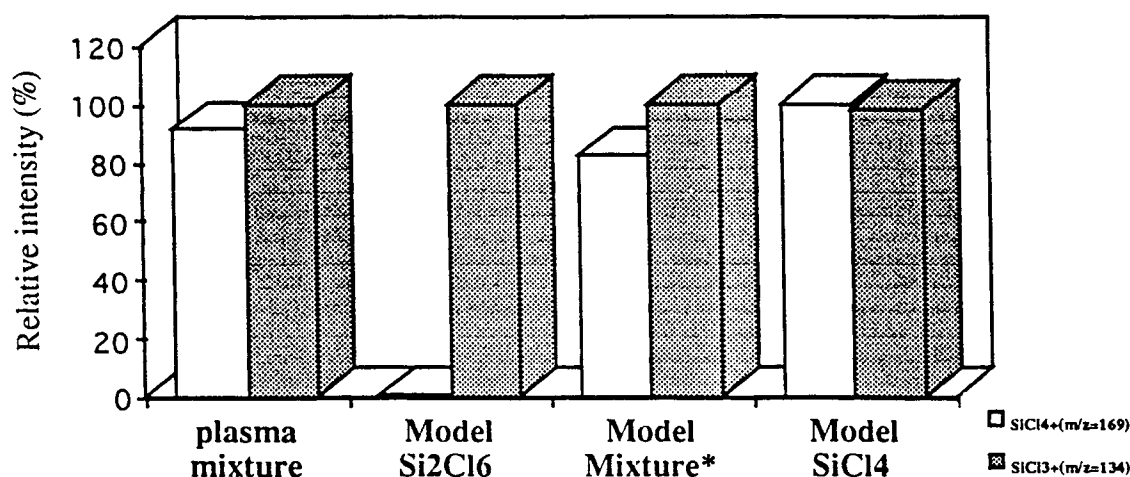
Nature of Ion	Theoretical		Trapped Mixture		Model Si ₂ Cl ₆		Model Mixture ^a		Model SiCl ₄	
	m/z	%	m/z	%	m/z	%	m/z	%	m/z	%
SiCl ⁴⁺	173.84	11.82	173.84	12.81	—	—	173.84	11.93	173.84	10.99
	171.84	50.64	171.84	48.17	—	—	171.84	41.37	171.84	45.05
	169.85	100.00	169.85	100.00	—	—	169.84	100.00	169.84	100.00
	167.85	75.22	167.85	74.62	—	—	167.85	73.12	167.85	71.95
SiCl ³⁺	136.87	34.56	136.88	36.29	136.87	24.78	136.87	36.30	136.87	29.78
	134.88	100.00	134.88	100.00	134.87	100.00	134.88	100.00	134.87	100.00
	132.88	99.46	132.88	99.16	132.88	98.70	132.88	93.85	132.88	93.38

^a Model mixtures refers to the model silicon compound containing 70/30 (vol %) of SiCl₄ and Si₂Cl₆ mixture.

librium established under ESCA X-ray irradiation conditions of polymeric layers or metal samples insulated from the spectrometer probe produces an overall positive charge on the samples' surfaces (due to insufficient charge carriers) and results in a retardation of leaving electrons, which is manifested by lower kinetic energy values (higher bonding energies). Photoionization and photoconductivity responsible for this phenomenon are both structure and insulating layer thickness dependent. Consequently, to eliminate surface charging, special measures must be applied (use of electron guns or low-power/low-pressure ultraviolet [UV] irradiation) or calibration corrections must be performed (by referring to a known binding energy value) for proper comparative analysis of untreated and modified

substrates. During the measurements, charge neutralization techniques were not employed; instead, recalibrations of binding energy values were performed with reference to the C1s peak.

The mixtures of neutral molecules from the recombination of plasma-generated active species were collected for analytical purposes in a specially designed Pyrex glass liquid nitrogen trap (Fig. 1). The trap is composed of a Pyrex glass collecting part (9) and a specially designed metallic sealing system (3). The gas-guiding tubing (13) located in the interior of the trap assures the collection of the samples in the conical-shaped lower end of the vessel (14), permitting an easy evaluation of retained sample volumes. Connecting Pyrex glass side tubings and elastic couplings (10, 12) and valves (11) permits both



*: Model Mixture contains 70/30 (vol%) of SiCl₄ and SiCl₆ compounds

Figure 3 HR-MS generated SiCl₄⁺ and SiCl₃⁺ composition of trapped plasma mixture, model Si₂Cl₆, 70%/30% mixture of model SiCl₄ and Si₂Cl₆ and model SiCl₄.

the convenient connection and isolation of the trap from the plasma reactor. The metallic sealing system, connected to the trap through the sampling tubing (6) of the glass vessel, is composed of a hexagonal stainless steel main body (3), a Teflon-coated silicon septum (4), a silicon O-ring (7), and fastening threaded caps (8, 1). The sealing is provided with two cavities (windows) on two opposite faces of the main body, permitting the monitoring of the liquid levels of the collected samples. It is noteworthy that the Teflon-coated septum closes (with the Teflon face) the open end of the tubing (6), which does not allow any contact of the collected materials with the rest of the sealing and the environment. After sample collection, the whole trap is vertically positioned with the sealing system on the lower end, permitting the transfer of the sample in the sampling tubing (6) and convenient sampling through the cylindrical channel (2) by means of a syringe. Both the silicon O-ring and the septum are located far away from the liquid nitrogen zone, which prevents low temperature induced rigidization and vacuum-leaking problems.

The chemical derivatives resulting from the recombination in the trap of plasma-generated active species were analyzed with GC-MS (GC—Carlo Erba Fractovap 4162; MS—Kratos MS × 25; experimen-

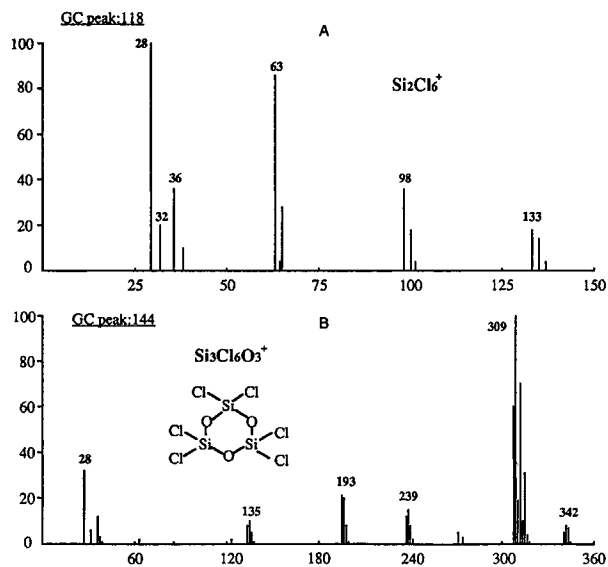


Figure 5 MS diagrams corresponding to GC peaks (A) 118 and (B) 144.

tal conditions—column-fused silica, length, 30 m, ID, 0.32 mm; coating, 0.25 μm of 5% phenyl and 95% vinyl polysiloxane; injector-splitter temperature 25°C; temperature profile of the column, 10 min at room temperature, then heated up to 250°C at

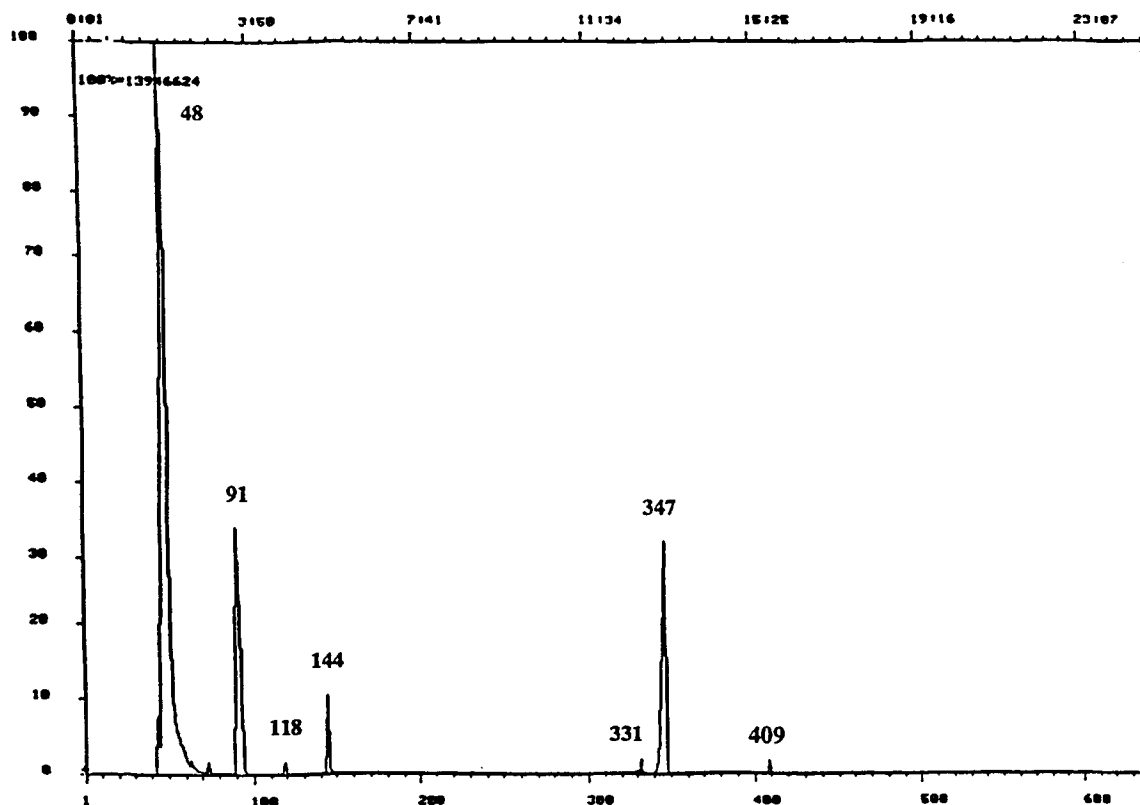


Figure 4 GC (from GC-MS) spectrum of plasma-generated molecular mixture.

Table II Major GC Peaks, Intensity, and Suggested Ion Identities and Chemical Species Trapped From SiCl₄ Plasma With GC-MS Analysis

GC Peak	Major (<i>m/e</i>)	Intensity (%)	Ion Identity	Compound Identity
48	35	58	Cl ⁺	SiCl ₄ ⁺
	63	100	SiCl ⁺	
	98	26	SiCl ₂ ⁺	
	135	100	SiCl ₃ ⁺	
	170	74	SiCl ₄ ⁺	
91	63	15	SiCl ⁺	Cl ₃ Si—O—SiCl ₃ ⁺
	98	5	SiCl ₂ ⁺	
	107	5	—	
	135	28	SiCl ₃ ⁺	
	179	13	—	
	214	3	—	
	249	100	Si ₂ Cl ₅ O ⁺	
	284	3	Si ₂ Cl ₆ O ⁺	
	331	28	15	
32		100	O ₂	
36		28	Cl	
117		3	?	
347	63	43	SiCl ⁺	$\begin{array}{c} \text{Cl} \\ \\ \text{Cl}_3\text{SiOSiOSiCl}_3^+ \\ \\ \text{Cl} \\ \text{(or fragment)} \end{array}$
	98	17	SiCl ₂ ⁺	
	135	58	SiCl ₃ ⁺	
	177	6	—	
	193	8	Cl ₃	
	249	9	Si ₂ Cl ₅ O ⁺	
	293	6	—	
	365	100	Si ₃ Cl ₇ O ₂ ⁺	
409	63	6	SiCl ⁺	$\begin{array}{c} \text{Cl}_2\text{Si—O—SiCl}_2^+ \\ \quad \quad \\ \text{O} \quad \quad \text{O} \\ \quad \quad \\ \text{Cl}_2\text{Si—O—SiCl}_2 \\ \text{(or fragment)} \end{array}$
	135	11	SiCl ₃ ⁺	
	195	3	—	
	253	4	—	
	309	20	Si ₃ Cl ₅ O ₃ ⁺	
	353	12	Si ₃ Cl ₃ O ₃ ⁺	
	425	100	Si ₄ Cl ₇ O ₄ ⁺	

15°C/min, electron energy 38 eV) and high-resolution mass spectrometer (HR-MS, Kratos MS × 80, electron energy 50 eV). Both instruments are double-focusing mass spectrometers (electrostatic analyzer and magnet). It is noteworthy that the dimensions of connecting tubings (8, 14) match the ID of the HR-MS gas-feeding line, permitting a vacuum-tight connection of the trap and evacuation of the feed-in line before sampling. The plasma-induced molecular fragmentation of SiCl₄ was simulated by performing MS with electron energies of 30, 50, and 70 eV.

Plasma Reactions

The SiCl₄ plasma reactions and plasma treatments of substrates were carried out in a multifunctional capacitively coupled parallel plate stainless steel cylindrical reactor, described earlier.^{14,15} The two-vac-

uum-line system of the reactor allows the easy evacuation of the reactor, maintenance of a steady-state working condition, and the efficient trapping of plasma-generated species. It is noteworthy that the trapping vacuum line is provided with an additional liquid nitrogen trap to avoid pump oil flashback contamination of the analytical trap. Each experiment was preceded by a cleaning operation (CF₄ plasma, pressure 300 mT, power 200 W, flow rate 10 sccm, treatment period 5 min, followed by an argon plasma under similar conditions) in the absence of substrates in order to remove possible contaminants from earlier runs. SiCl₄ was degassed by freezing it at liquid nitrogen temperature, followed by evacuation to base pressure level and isolation by closing the proper valves. During the plasma treatments, the SiCl₄ reservoir was kept at room temperature.

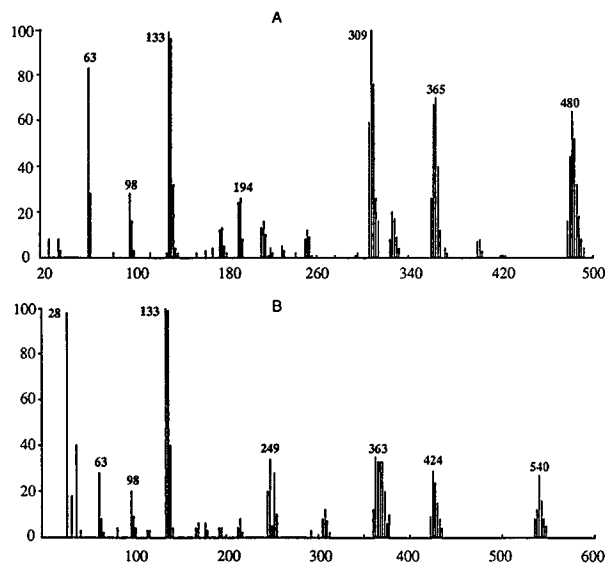


Figure 6 MS patterns of higher molecular weight compounds of the plasma-generated molecular mixture.

In a typical experiment, the reactor was closed and the system was evacuated with the aid of a high-capacity vacuum pump to ground pressure level. The second vacuum system was also operated, but the whole line was isolated from the reactor. Both traps were then cooled down to liquid nitrogen temperature, and the connecting stainless steel tubing between the SiCl_4 reservoir and the gas-mixing chamber of the plasma reactor was evacuated. Then the flow-meter valve was closed and the SiCl_4 valve was opened. By adjusting the open valves and flow meter, the preselected flow rate and pressure of SiCl_4 were established at a steady-state rate. At the plasma ignition moment, trapping was started for the plasma-generated species and the discharge was sustained for the required time period. At the end of the reaction, the vacuum trap was isolated from the system, and the trap was removed and stored for analytical purposes.

The plasma treatment of polymeric surfaces was carried out under similar conditions, with the substrates located on the lower electrode. During the surface modification of polymeric materials, the vacuum trap line was closed.

The experimental conditions used during the plasma treatments were as follows:

- Plasma medium: SiCl_4
- RF power: 100 W
- Ground pressure: 20 mT
- Pressure in the absence of plasma: 150 mT
- Pressure in the presence of plasma: 160 mT

- Flow rate of SiCl_4 : 8 sccm
- Temperature of electrode and reactor: room temperature
- Trapping period: 30 min
- Treatment time for polymeric substrates: 1 and 5 min

RESULTS AND DISCUSSIONS

Analysis of Reaction Products

The MS simulation of molecular fragmentation of SiCl_4^+ at different electron energy levels is shown in Figure 2. One can notice that, regardless of the electron energy levels, the most predominant fragment is SiCl_3^+ ($m/z = 135$), and that the SiCl_4^+ molecular ion constitutes a significant percentage (40%) of the ionic mixture at the lowest electron energy level (30 eV). The presence of SiCl_2^+ and SiCl^+ cations can also be noted. These data suggest that hexachlorodisilane and higher molecular weight halo silanes could be formed and collected from the recombination of these molecular fragments of SiCl_4 in the trap.

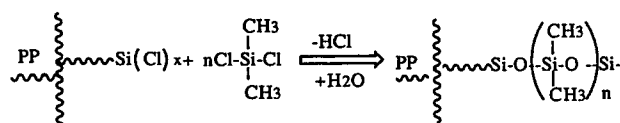
Table I and Figure 3 exhibit high-resolution MS data collected for SiCl_4 and Si_2Cl_6 model compounds and their mixture, and from the resulting molecular mixture in the trap from the recombination of plasma-generated active species. The m/z values and the corresponding isotopic ratios clearly indicate the presence of SiCl_4^+ and SiCl_3^+ in all of the cases except hexachlorodisilane, in which SiCl_4^+ is not generated. Comparison of relative ratios of these charged species for the model and plasma-generated samples clearly indicates the existence of hexachlorodisilane in the plasma-generated mixture. It is noteworthy that apart from unreacted tetrachlorosilane and hexachlorodisilane, only the presence of a minute quantity of hexachlorodisiloxane was evidenced.

GC-MS data from the ex situ plasma-generated mixture provide additional information. The GC diagram exhibits eight distinctive peaks (Fig. 4), and the corresponding MS patterns and assignments for two of them (118 and 144) are presented in Figure 5(A,B). Table II shows the suggested structures for the rest of the GC peaks. One can notice the presence of unreacted SiCl_4 and relatively high molecular weight linear and cyclic halosiloxane structures as well as a small quantity of Si_2Cl_6 . Due to the weakness of Si—Si (78 kcal/mol) and Si—Cl (96 kcal/mol) bonds in comparison to Si—O linkages (191 kcal/mol) and the sensitivity of the two former bonds under open laboratory conditions (in the

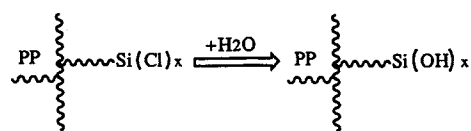
presence of oxygen and moisture), the polyhalosilanes from the recombination of the SiCl_x active fragments will be instantly converted into siloxane-type derivatives upon open laboratory exposure. The almost total absence of halosiloxanes in the unexposed samples (HR-MS) in comparison to those analyzed by using the syringe technique (GC-MS) verifies the effect of oxygen and moisture exposure. It is important to note that by injecting larger sample quantities even higher molecular weight halosiloxane-type structures are formed [Figure 6(A,B)]. This novel approach to synthesis of polyhalosilanes and polyhalosiloxanes with the aid of RF plasma opens up new possibilities for creating cyclic halosiloxane-nucleated starlike polyorganosiloxanes and for synthesis of ceramic-type polymeric structures.

Plasma Modification of Substrates

The extremely high reactivity of silylium ions and radicals allows the surface functionalization under plasma conditions of even the most inert polymeric substrates. Surface implanted SiCl_x functionalities allow additional means for grafting or for increasing surface polarity through hydrolysis or condensation reactions (Scheme 1).



(PDMS Grafted PP)



Scheme 1

PP, CP, PET, and PTFE substrates were exposed to SiCl_4 RF plasma conditions, and the relative surface atomic compositions were analyzed by ESCA. Figures 7(A-D) show the ESCA survey spectra of untreated, 1 min, and 5 min plasma-modified PP, PET, CP, and PTFE substrates and the corresponding surface atomic compositions. One can notice that besides the C1s (285 eV, in all of the cases), O1s (533 eV, for PET and CP), and F1s (690 eV, for PTFE) original signals of the virgin substrates, intense Si2p (103 and 155 eV) and O1s peaks and relatively weak Cl2p (201 eV) signals can be seen for all of the plasma-treated samples.

Longer treatment times reduce almost totally the surface fluorine and chlorine contents and lead to a saturation Si2p value (around 20%). These data clearly indicate a very high reactivity of plasma-generated halo-silicon cations and radical species, which permit the easy replacement of even the fluorine and chlorine atoms from C—F and C—Cl linkages.

High-resolution C1s ESCA data (Fig 8) provide even more information on the nature of SiCl_4 plasma induced chemical changes of polymeric substrates (untreated, 1 min, and 5 min treated PP, PET, CP, and PTFE).

One can observe that the symmetrical C1s peak of untreated PP is replaced by a trimodal pattern, indicating both the presence of C—O (286–286.5 eV) and an unidentified (289.5 eV) group on the surface of the plasma-modified substrate. Due to the close binding energy values of Si—C (284.6 eV) and C—C (285 eV) bonds, they do not appear distinctively on the diagram.

The characteristic trimodal high-resolution binding energy pattern of PET is also significantly altered by the plasma treatment. A higher oxygen content (more intense C—O, 286.5 and O—C=O, 288.8 eV peaks) and the presence of a 289.5-eV peak corresponding to an unknown nonequivalent carbon linkage can be observed.

The C1s region of unmodified cellulose samples (CP) clearly shows the contamination origin carbon-carbon (285 eV) and both C—OH (286.6 eV) and C—O (288 eV) ether-type binding energy peaks. For the plasma-treated cellulose samples, there was a gradual treatment-time-dependent diminution of both the 286.6 eV and 288 eV peak areas, which suggests that the plasma-induced chemistry probably alters both the C—OH, C(OH)—C(OH), and C—O—C linkages. A magnesium ion induced pyranosic ring opening mechanism at C2—C3 has also been suggested by Ranby with cellulose grafting reaction.¹⁶

Teflon surfaces can also be efficiently functionalized under SiCl_4 plasma conditions. High-resolution ESCA data from 1-min treatment time clearly indicate significant diminution of the CF_2 peak (292.5 eV) and the appearance of intense CF (291 eV) and C—O (286.5) signals. The presence of the specific unidentified peak (289.5) can also be observed. Longer treatment times (5 min) show the total absence of fluorine-containing groups and the presence of C—C and Si—C related (large, 284.5–285 eV area) linkages. It can be concluded that halosilicon active species can replace the fluorine atoms on the surface layers of Teflon substrates and create unsaturated structures (e.g., free radical sites) ca-

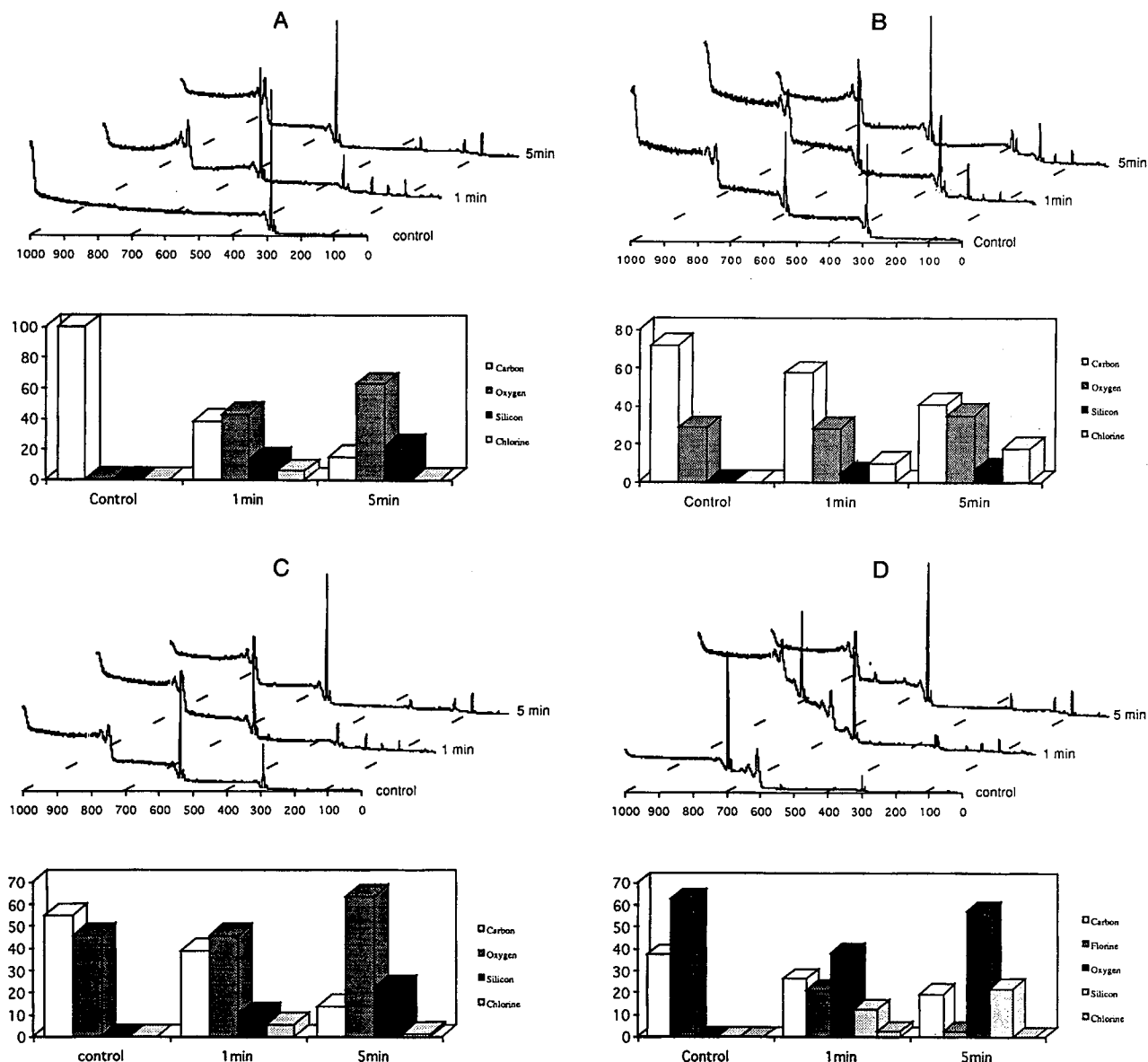


Figure 7 ESCA survey spectra and the corresponding relative surface atomic compositions of SiCl₄ plasma-treated (A) PP, (B) PET, (C) CP, and (D) PTFE substrates.

pable of oxidation reactions. Plasma-induced surface unsaturation and free radical formation reactions are most likely responsible for oxygen uptake under open laboratory conditions, regardless of the chemical nature of the substrate. The increased 285-eV peak surface areas in the cases of all SiCl₄ plasma-treated samples indicated the presence of Si—C linkages. The existence of 298.5-eV peaks in the ESCA spectra of all modified substrates and their increased intensity associated with longer treatment times suggest the formation of a specific (unidentified) nonequivalent carbon bond under the action of plasma species.

CONCLUSIONS

GC-MS and HR-MS measurements indicate that RF plasma induced fragmentation of SiCl₄ results predominantly in SiCl₃⁺ cations. These cations are extremely reactive and capable of interacting even with the most inert polymeric surfaces. Surface survey and high-resolution ESCA data collected from SiCl₄ plasma-treated PP, PET, CP, and PTFE indicate efficient implantation of SiCl_x functionality regardless of the nature of the substrate. The silicon-based molecular fragment implantations are accompanied by defluorination, dehydrogenation, and

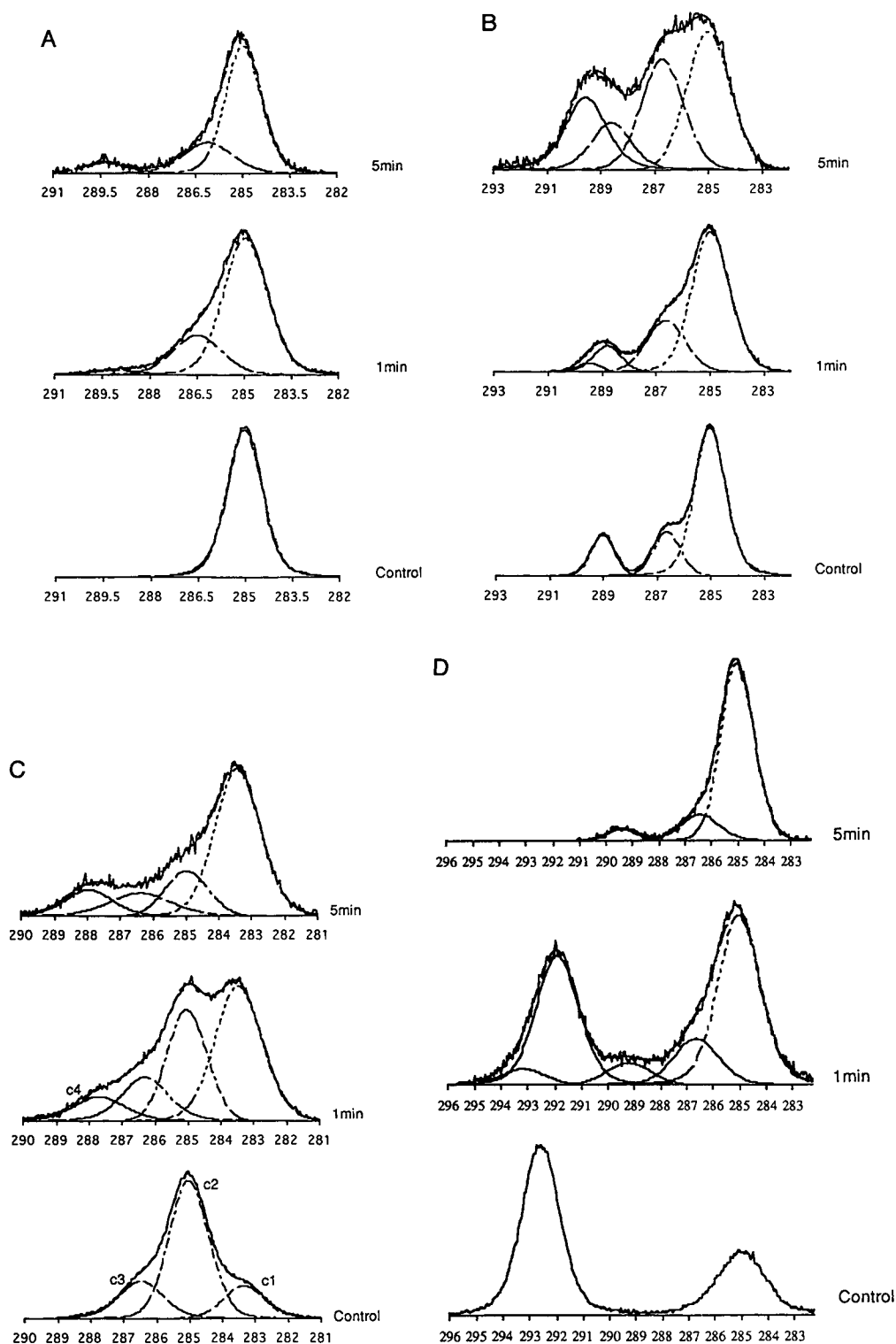


Figure 8 Deconvoluted high-resolution (C1s) ESCA spectra of untreated, 1 min, and 5 min treated (A) PP, (B) PET, (C) CP, and (D) PTFE substrates.

other reactions, leading to surface unsaturation and free radical formation. These processes are probably responsible for the post plasma oxidation reactions.

The RF plasma induced generation of SiCl_x ($x < 4$) also demonstrates new routes for the synthesis of polyhalosilanes and polyhalosiloxanes.

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