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High structural retention during pulsed plasma polymerization of 1H,1H,2H-perfluorododecene: an NMR and TOF-SIMS study

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Abstract

A combined NMR and TOF-SIMS study has been carried out on 1H,1H,2H-perfluorododecene plasma polymers. Pulsed plasma polymerization is found to give rise to a high level of structural retention for the perfluoroalkyl groups, whereas continuous wave conditions lead to monomer fragmentation and cross linking. This investigation provides unequivocal proof that pulsed plasma deposition is a simple and highly effective method for functionalising solid surfaces.

Keywords: Fluoropolymer; Coating; Plasma

1. Introduction

Liquid repellent surfaces play an important role in many everyday applications [1–4]. For example, long chain perfluoroalkyl groups give rise to low energy surfaces due to the nonpolarizing nature of nonbonding electron pairs on the fluorine atoms hindering hydrogen bonding and dispersion interactions with polar and nonpolar liquids, respectively [5]. The degree of fluorination at the carbon centres (i.e. $CF_3 > CF_2 > CF$) and the overall length of the perfluoroalkyl chain (greater electron density withdrawal from the terminal CF_3 group) helps to minimise the surface energy at the air-solid interface.

Such highly repellent surfaces can be made by pulsed plasma polymerization of gaseous precursors containing long fluorocarbon chains and unsaturated carbon–carbon bonds [6,7]. This entails modulating the electrical discharge on the millisecond–microsecond timescale in order to impart minimal damage of the growing film during the duty cycle on-period, whilst enabling conventional polymerization to proceed during the off-period [8]. Previous experimental investigations based on X-ray photoelectron spectroscopy (XPS), infrared spectroscopy, atomic force microscopy (AFM), and surface energy measurements have demonstrated that the perfluoroalkyl chains do indeed remain intact during low duty cycle pulsed plasma deposition conditions to yield highly liquid repellent films [6,7].

In this study, a more detailed insight into the mechanistic pathways governing the pulsed plasma polymerization of 1H,1H,2H-perfluorododecene ($CF_3(CF_2)_9CH{=}CH_2$) has been undertaken by employing solid state ^{19}F NMR and time-of-flight secondary ion mass spectrometry (TOF-SIMS).

In particular, the former technique provides a detailed structural analysis of the fluorinated polymeric film [9–14], whilst the latter is able to distinguish regular repeat units contained in the polymer structure [15–21].

2. Experimental section

Plasma polymer depositions were carried out in a cylindrical glass reactor (5 cm diameter, 470 cm^3 volume, 2×10^{-3} mbar base pressure, and a leak rate better than 6×10^{-9} mol s^{-1}). This was connected to a two-stage Edwards rotary pump via a liquid nitrogen cold trap, a thermocouple pressure gauge, and a monomer tube containing 1H,1H,2H-perfluorododecene (Fluorochem, +98% purity, further

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purified using multiple freeze-thaw cycles). All connections were grease-free. An L–C matching unit was used to minimize the standing wave ratio (SWR) of the transmitted power between a 13.56 MHz radio frequency (RF) generator and a copper coil externally wound around the glass chamber. In the case of pulsed plasma deposition experiments, the RF source was triggered by a signal generator and the pulse width and amplitude were monitored by an oscilloscope. Plasma polymers were deposited either using continuous wave (5 W) or pulsed (70 W peak power, 20 µs on-time, 2 ms off-time) electrical discharge conditions.

^{19}F NMR spectroscopy was carried out on a Varian UNITY plus spectrometer equipped with a 5 mm outer diameter rotor Doty Scientific XC probe. Plasma polymer material was deposited onto glass microscope slides which were then ground up to fill the rotor.

TOF-SIMS analysis of the deposited plasma polymer surfaces was carried out using a Physical Electronics 7200 instrument. The primary ion beam (8 keV Cs^+) was focused to a spot size of ~50 µm and rastered over 100×100 µm^2 area whilst keeping the total dose well under 10^{13} ions cm^{-2} (static conditions).

3. Results

3.1. ^{19}F NMR

Solution state ^{19}F NMR spectroscopy of 1H,1H,2H-perfluorododecene monomer produced seven sharp peaks, Table 1: $CF_3CF_2CF_2$– (−81 δ_F), CF_2 fluorine environments located at different distances from the terminal CF_3– group (five signals around −122 to −127 δ_F, where the CF_2 groups closest to the terminal CF_3– group are the most deshielded, and each additional perfluoromethylene group separated from the CF_3– leads to a more shielded fluorine environment), and finally the CF_2 functionality adjacent to the alkene –CH=CH$_2$ hydrocarbon segment contained in the monomer (−114 δ_F). All of these features are well resolved due to high molecule mobility in solution phase.

The solid state ^{19}F NMR spectrum obtained from continuous wave deposited 1H,1H,2H-perfluorododecene plasma polymer displayed three major well-resolved peaks, Table 1 and Fig. 1 $CF_3CF_2CF_2$– (−81 δ_F), mid-chain CF_2s, i.e. –$CF_2CF_2CF_2$– (−123 δ_F) and $CF_2CF_2CF_3$ (−127 δ_F). In addition there is a weak signal associated with CF_3 groups (−64 δ_F). The −72 δ_F and −172 δ_F peaks are sidebands belonging to the −123 δ_F peak. The overall peak broadness and presence of sidebands can be attributed to reduced molecular mobility [22] in the plasma polymer film due to the occurrence of extensive cross linking under these highly energetic deposition conditions. Furthermore, the identification of new CF_3 environments (not predicted in the case of 1H,1H,2H-perfluorododecene undergoing clean polymerization), provides further evidence for structural rearrangement and cross-linking during continuous wave plasma polymerization. The signal due to $CF_2CH{=}CH_2$ in the monomer is not present, consistent with polymerization and rearrangement of the monomer.

In contrast, the solid state ^{19}F NMR spectrum obtained under pulsed plasma deposition conditions exhibits predominantly four well-resolved sharp lines: $CF_3CF_2CF_2$– (−83 δ_F), mid chain –$CF_2CF_2CF_2$– (−123 δ_F), –$CF_2CF_2CF_3$ (−124 δ_F), and –$CF_2CF_2CF_3$ (−127 δ_F) environments. These signals verify the existence of predominantly perfluoroalkyl ($CF_3(CF_2)_n$–) chains in the pulsed plasma polymer structure. The narrow peak widths, lack of cross-linked environments, and attenuated sideband intensity relative to the continuous wave film is consistent with high structural retention of perfluoroalkyl groups belonging to the monomer during pulsed plasma polymerization. The feature corresponding to a CF_2 group adjacent to the alkene hydrocarbon (–CH=CH$_2$) segment in the monomer (−114 δ_F) is absent, thereby confirming that the double bond preferentially undergoes polymerization.

3.2. Negative ion TOF–SIMS

The negative ion TOF–SIMS spectrum of the 1H,1H,2H-perfluorododecene pulsed plasma polymer film is indicative of a hydrocarbon polymer backbone with fluorocarbon side

Table 1
^{19}F NMR assignments

ppm shift	Environment	Present in			Ref
		Monomer	Pulsed	CW	
−64	$(CF_3)_3C$	No	No	Yes (broad)	[29]
−72	Sideband	No	Yes (minor)	Yes (broad)	
−81	CF_3CF_2	Yes(v. sharp)	No	No	[30]
−83	CF_3CF_2	No	Yes	Yes	[22]
−114	$CF_2CH{=}CH_2$	Yes (v. sharp)	No	No	
−122	$CF_3CF_2CF_2$ CF_2CF_2	Yes (double peak, v. sharp)	No	No	[30]
−123	$CF_2CF_2CF_2$	Yes (v. sharp)	Yes (sharp)	Yes (broad)	[22,30]
−124	$CF_3CF_2CF_2$	Yes (v. sharp)	Yes (sharp)	No	[30]
−127	CF_2CF_3	Yes (v. sharp)	Yes (sharp)	Yes (broad)	[22,30]
−172–−173	Sideband	No	Yes (minor, broad)	Yes (broad)	

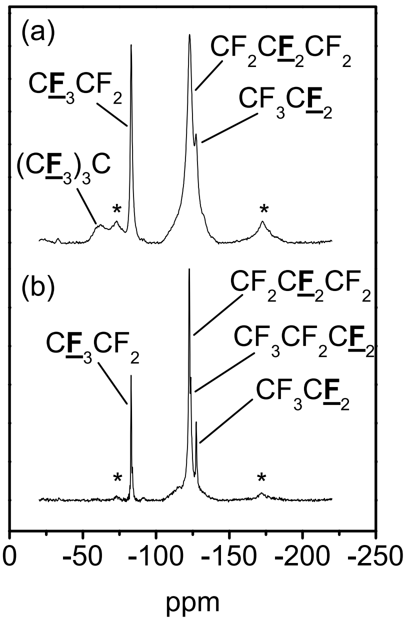

Fig. 1. Solid State ^{19}F NMR spectra of 1H,1H,2H-perfluorododecene ($CF_3(CF_2)_9CH{=}CH_2$) plasma polymers: (a) 5W CW; and (b) pulsed (70 W peak power, 20 μs on, 20,000 μs off). * denotes sidebands.

chains, Fig. 2. During TOF-SIMS analysis, the plasma polymer is most likely to fragment at the CH–CH linkages to yield fluorocarbon chain fragments [23,24]. The mass range below that of a single monomer repeat unit (546 amu for 1H,1H,2H-perfluorododecene) is dominated by mass clusters regularly separated by 50 amu. These correspond to $(CF_2)_n$ chains with various terminating groups, extending up to the intact perfluoroalkyl chain length, Tables 2–4. For example, in Fig. 2(a) the mass at 493 amu represented by Y_9, corresponds to the fragment $CF_3(CF_2)_8C_2$. The presence of this type of fragment is consistent with the perfluoroalkyl side chains remaining intact during pulsed plasma polymerization (and then subsequently being broken up under TOF-SIMS conditions).

Beyond the monomer parent mass (546 amu), the spectrum displays featureless, low intensity regions interdispersed between 'humps' of higher intensity. These fragment groupings correspond to very similar structures, differing only by a single fluorine or carbon atom. For example, the fragments at 2025, 2043 and 2063 amu contain a hydrocarbon backbone with four fluorocarbon side chains intact, but each fragment in the series contains an extra fluorine atom, whilst the adjacent peaks of lower intensity are associated with retention or loss of hydrogens. These mass groupings occur at approximately 546 amu intervals, thereby indicating the incorporation of additional monomer units into the detected fragment. Some examples of this progression are the masses at 1029, 1537, 2043 and 2550 amu which bear a strong structural resemblance apart from an incremental addition of one monomer unit. This trend continues up to 2550 amu, which is a signature fragment of a hydrocarbon backbone with five intact fluorocarbon side chains.

In contrast, negative ion TOF-SIMS analysis of the continuous wave 1H,1H,2H-perfluorododecene plasma polymer presents a very different picture, Fig. 3 and Table 4. The spectrum displays $(CF_2)_n$ chains with a variety of terminating

Table 2
TOF-SIMS fragment key

Fragment formula	Fragment symbol	Mass (amu)
$[CF_2]_nCF$	Z_n	$31+(50\times n)$
$[CF_2]_nC_2F$	Y_n	$43+(50\times n)$
$[CF_2]_nC_3F$	X_n	$55+(50\times n)$
$[CF_2]_nC_4F$	W_n	$67+(50\times n)$
$[(CF_2)_9C_2F]_n$ [a]	V_n	493
$[(CF_2)_9C_3F]_n$ [b]	T_n	505
$[(CF_2)_{10}CHCH]_m$	S_m	526
$[CF_3(CF_2)_9CHCH]_n$	R_n	545
$[CF_3(CF_2)_7(CH_2)_2OCOCHCH]_n$	Q_n	517
$[(CF_2)_7(CH_2)_2OCOCHCH]_n$	P_n	448
$[CF_3(CF_2)_7(CH_2)_2OCOCH]_n$	N_n	504
$CF_3(CF_2)_9CH{=}CH_2$	1H,1H,2H-perfluorododecene	546

[a] In the case of $V_{n=1}$, this is equivalent to $Y_{n=9}$.
[b] In the case of $T_{n=1}$, this is equivalent to $X_{n=9}$.

Table 3
Negative ion TOF-SIMS fragment summary

Fragment	Symbol	Mass (amu)	Values of n	
			Pulsed	CW
$[CF_2]_nC_2F$	Y_n	$(50\times n)+43$	0, 1, 2, 3, 4, 5, 6, 7, 8, 9	0, 1, 2, 3, 4, 5, 6, 7, 8
$[CF_2]_nC_3F$	X_n	$(50\times n)+55$	1, 2, 3, 4, 5, 6, 9	0, 1, 2, 3, 4, 5, 6, 7, 8
$[CF_2]_nC_4F$	W_n	$(50\times n)+67$	1, 2, 3, 4, 5, 6, 7, 8	0, 1, 2, 3, 4, 5, 6, 7, 8

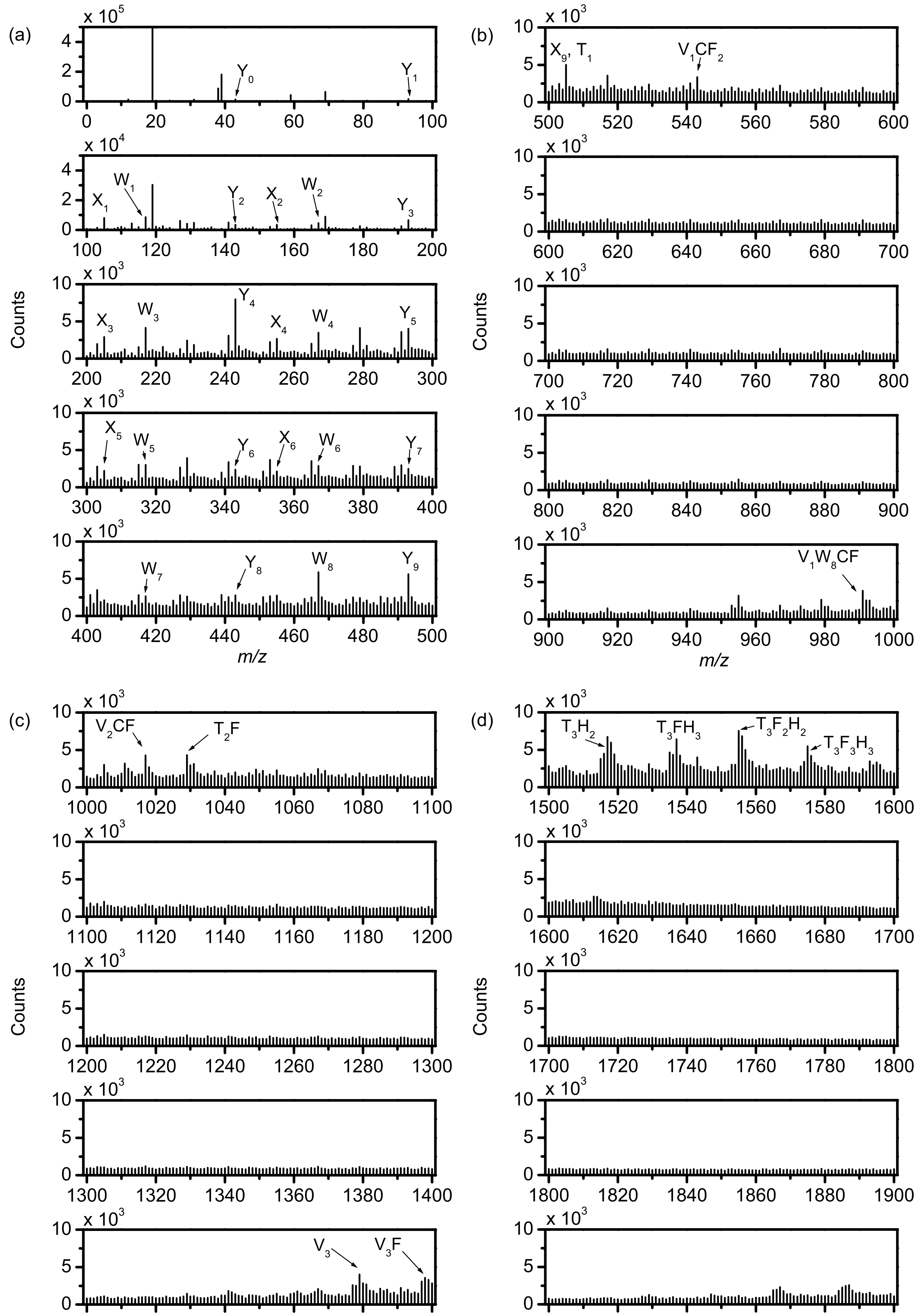

Fig. 2. Negative ion TOF-SIMS spectra of 1H,1H,2H-perfluorododecene pulsed plasma polymer: (a) 0–500 amu; (b) 500–1000 amu; (c) 1000–1500 amu; (d) 1500–2000 amu; (e) 2000–2500 amu; and (f) 2500–3000 amu (NB the fluorine peak at mass 19 is off-scale).

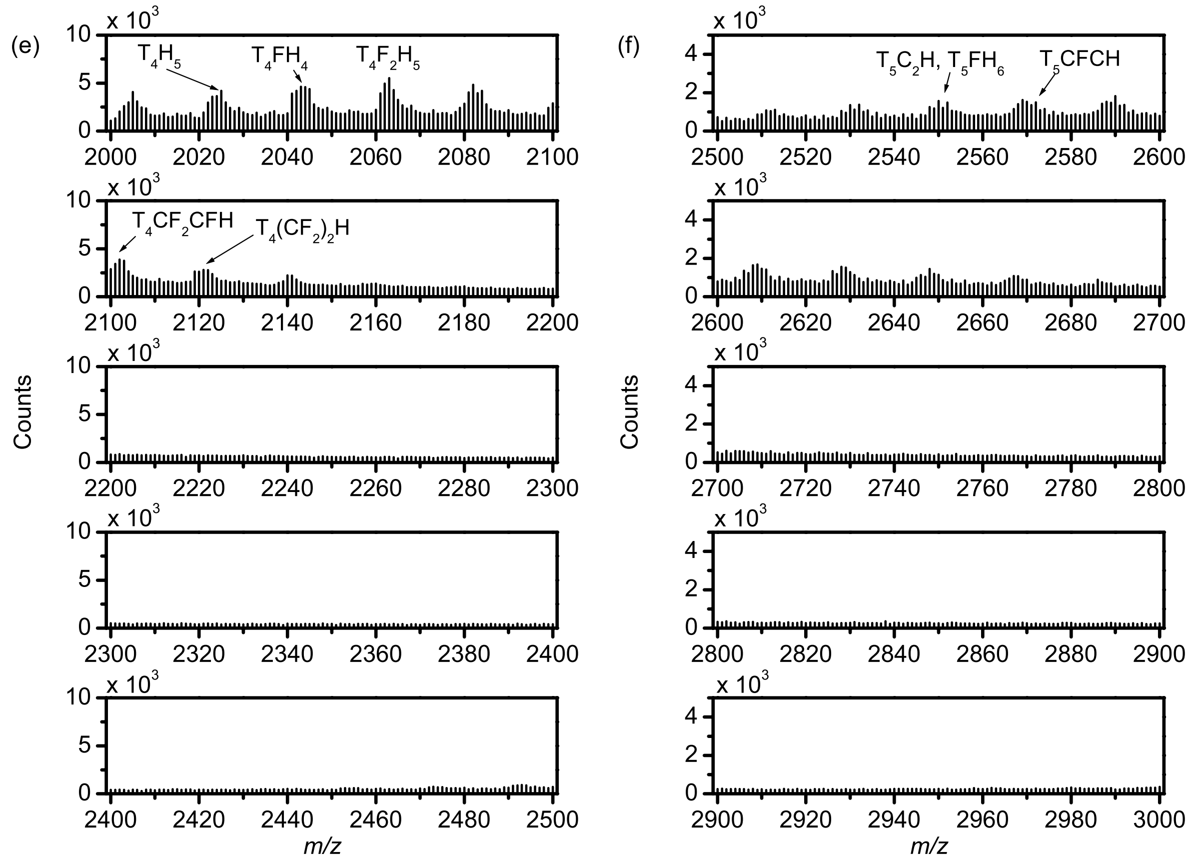

Fig. 2 (*continued*)

groups up to the parent monomer mass (546 amu). Furthermore, regular repeat units are absent in the higher mass range, thereby indicating poor structural retention.

3.3. Positive ion TOF-SIMS

The overall positive ion TOF-SIMS spectra of 1H,1H,2H-perfluorododecene pulsed plasma polymer film display similar trends to those previously seen for negative ion TOF-SIMS, Tables 5 and 6. Fragments corresponding to a hydrocarbon polymer backbone with fluorocarbon side chains begin at approximately 500 amu, (starting with the molecular mass of the monomer). Below this mass, $(CF_2)_nCF$ groups up to the length of the initial fluorocarbon backbone confirm structural retention of the perfluoroalkyl side chain. Higher mass oligomers were identified at 1599, 1617 and 1635 amu. These SIMS fragments correspond to a hydrocarbon backbone containing three intact fluorocarbon side chains.

Positive TOF-SIMS analysis of the continuous wave 1H,1H,2H-perfluorododecene plasma polymer film also gave a very different picture. Below 300 amu, $(CF_2)_nCF$ chain fragments corresponding to a maximum carbon chain length of seven carbons are seen, Tables 5 and 6. A variety of masses are present above 300 amu, with no well defined fragment intensities. Once again, this confirms that the long perfluoroalkyl side chain contained in the monomer does not survive the continuous wave conditions intact.

Table 4
Negative ion TOF-SIMS highest mass fragment summary

Fragment type	Pulsed plasma			Continuous wave plasma		
	Highest mass	Formula	Chain length ($n+m$)	Highest mass	Formula	Chain length ($n+m$)
Y_n	493	Y_9	N/A	443	Y_8	N/A
X_n	505	X_9	N/A	N/A	X_8	N/A
W_n	467	W_8	N/A	N/A	W_8	N/A
V_n	1498	V_3F	3	N/A	N/A	0
T_n	2569	T_5CFCH	5	N/A	N/A	0

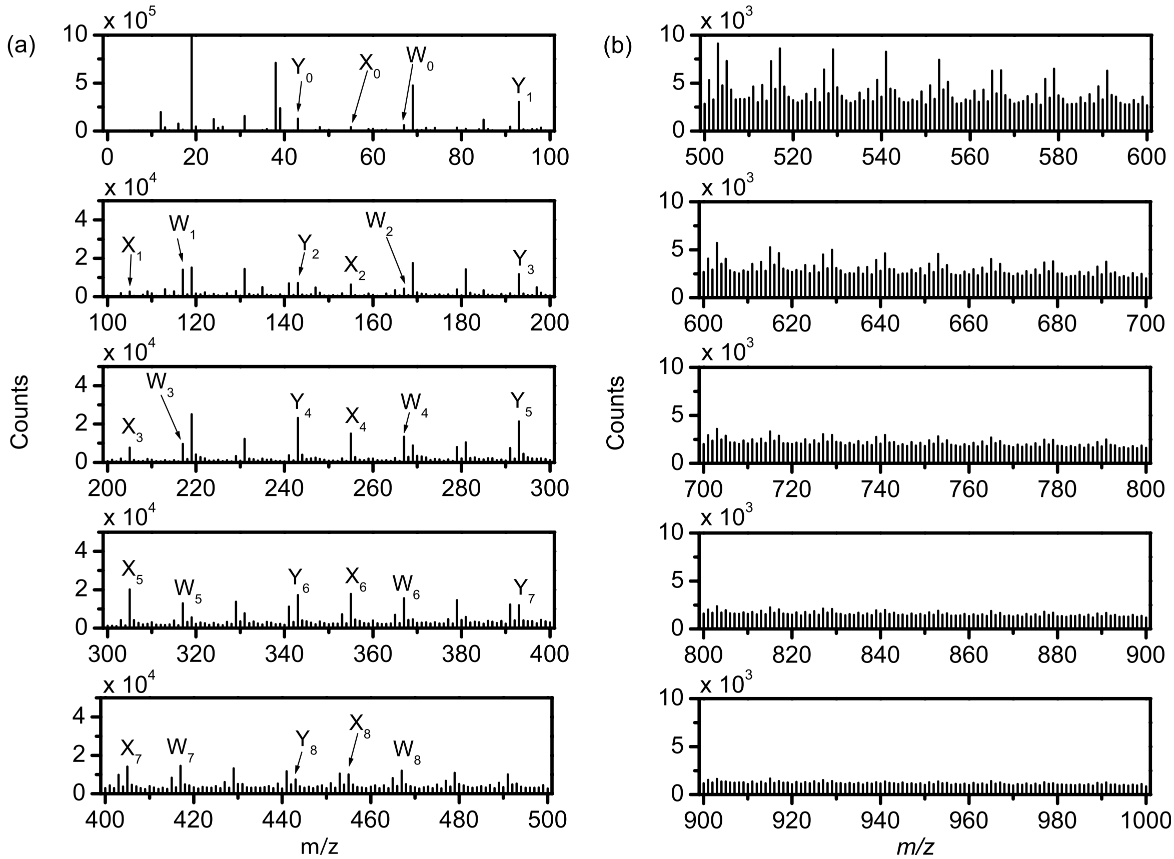

Fig. 3. Negative ion TOF-SIMS spectra of 1H,1H,2H-perfluorododecene continuous wave plasma polymer: (a) 0–500 amu; and (b) 500–1000 amu (NB the fluorine peak at mass 19 is off-scale).

Table 5
Positive ion TOF-SIMS fragment summary

Fragment	Symbol	Mass (amu)	Values of $n+m$	
			Pulsed	CW
$[CF_2]_nCF$	Z_n	$(50\times n)+31$	0, 1, 2, 3, 4, 5, 6, 7, 8, 9	0, 1, 2, 3, 4
$[(CF_2)_{10}CHCH]_m$	S_m	526	1, 2, 3	0
$[CF_3(CF_2)_9CHCH]_n$	R_n	545	1, 2, 3	0
$[CF_3(CF_2)_9CHCH]_n[(CF_2)_{10}CHCH]_m$	R_nS_m		2, 3	0

Table 6
Positive ion TOF-SIMS highest mass fragment summary

Fragment type	Pulsed plasma conditions			Continuous wave plasma conditions		
	Highest mass	Formula	Chain length ($n+m$)	Highest mass	Formula	Chain length ($n+m$)
Z_n	481	Z_9	N/A	281	Z_5	N/A
S_m	1599	S_3H	3	N/A	N/A	0
R_nS_m	1617	R_2S_1H	3	N/A	N/A	0
R_n	1635	R_3	3	N/A	N/A	0

4. Discussion

Previous XPS and infrared spectroscopy studies related to plasma polymerization of 1H,1H,2H-perfluorododecene [6] indicated greater structural retention of perfluoroalkyl groups during electrically pulsed compared to continuous wave conditions at the same average power. This stems from less fragmentation and damage of the fluorinated side chain during oligomerization as a consequence of milder ion bombardment of the growing film [25] and less VUV surface damage during the plasma on-period [26]. ^{19}F NMR and TOF-SIMS analysis in the present investigation have confirmed these conclusions. This is evident from the narrower line widths and lack of cross-linked environments in the ^{19}F NMR spectra for the pulsed plasma deposited film. The selective loss of characteristic alkene features (disappearance of the characteristic ^{19}F signal from fluorine atoms neighbouring the alkene bond seen for the monomer) is consistent with previous infrared spectroscopy studies [6]. Similar conclusions have been made in the case of ^{19}F NMR structural studies of pulsed plasma polymer films made from short chain fluorocarbon monomers [9,11–14]. Long range structural order within the pulsed plasma deposited material has been verified by the high mass regions of the TOF-SIMS spectra. These conclusions are consistent with previous SIMS characterisation studies undertaken on plasma polymers produced from smaller molecules, where high levels of functionality have been observed for low duty cycle pulsed plasma deposition (hexafluoropropylene oxide [15] and glycidyl methacrylate [21]) and can be contrasted with poor structural retention during continuous wave conditions (benzene [17], perfluorobenzene [17], acrylic acid [27], and hexamethyldisiloxane [28]).

5. Conclusions

Pulsed plasma polymerization of 1H,1H,2H-perfluorododecene produces structurally well-defined polymer films with perfluoroalkyl side chains. This is consistent with the alkene bond undergoing conventional polymerization reactions during the pulsed plasma duty cycle off-period.

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