The characterization of plasma polymers by X.p.s. and static s.i.m.s.

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X-ray photoelectron spectroscopy and static secondary ion mass spectrometry (s.i.m.s.) have been used to characterize plasma polymers of perfluorobenzene (PFB), perfluorotoluene (PFT), perfluorocyclohexene, perfluorocyclohexane and benzene. The plasma polymers of PFB and PFT appear to be based on a perfluoroalkylbenzene-type structure, with lesser amounts of other ring systems and very few aliphatic chains. The polymers derived from perfluorocyclohexene and perfluorocyclohexane were found to be much more aliphatic in nature, with fewer aromatic and other ring systems. The s.i.m.s. analysis of plasma-polymerized benzene was almost identical to that of polystyrene, but this probably does not reflect the true nature of the plasma polymer.

INTRODUCTION

Plasma polymers are generally prepared as thin films (less than 2000 Å thick) which, with their general inherent intractability, presents problems for their characterization by solution and bulk solid state methods. X-ray photoelectron spectroscopy (X.p.s.) has been shown to be a valuable technique for the characterization of polymer surfaces, providing elemental analysis and some functional group analysis, and has also been successfully applied to the study of plasma polymers[1,2]. In the case of fluorinated plasma polymers[2-5] the wide range of chemical shifts in the C_{1s} core-level spectra for carbon atoms bonded to 1, 2 and 3 fluorine atoms has provided a considerable amount of quantitative information with respect to the nature of the bonding in the plasma polymer. Although the carbon–fluorine chemical shifts are large, it is not possible to distinguish, for example in a plasma that may contain aliphatic and aromatic moieties, between CF_2 groups bonded to an aromatic ring and those in an aliphatic chain. Consequently it is difficult to propose a structure from the X.p.s. data alone.

More recently, static secondary ion mass spectrometry (s.i.m.s.) has also been shown to be a viable technique for the characterization of polymer surfaces[6]. The detection of elemental and molecular ions, which are representative of the structures present in the surface, has been well demonstrated for a wide range of conventional polymers[6] and hence s.i.m.s. can be used to provide molecular information regarding the composition of the surface which may be considered complementary to that obtained by X.p.s.

In this paper we report the combined use of X.p.s. and s.i.m.s. in the characterization of plasma polymers derived from perfluorobenzene (PFB), perfluorotoluene (PFT), perfluorocyclohexene, perfluorocyclohexane and benzene. These can all be regarded as unknowns with respect to their structures.

EXPERIMENTAL

All monomers were supplied by Aldrich and were degassed before use by a series of freeze–thaw cycles. Plasma polymerization was carried out in a tubular reactor, similar to that described previously[5], inductively coupled via a nine-turn copper coil to a 13.56 MHz r.f. generator. The r.f. power was kept constant at 15 W for all the polymerizations, and monomer flow-rates of between 0.3 and 1.8 cm³(stp) min⁻¹ were used. Plasma polymers for analysis were collected from the coil region of the reactor by deposition onto aluminium foil substrates.

X.p.s. spectra were recorded on a Kratos ES 300 spectrometer (base pressure of 5×10^{-9} torr) in the fixed retardation mode employing $MgK\alpha$ X-rays and a 35° electron take-off angle. The C–H component at a binding energy of 285.0 eV was used for energy calibration.

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The component analysis of the C_{1s} spectrum was accomplished on a Kratos DS 300 data system by fitting Gaussian peaks of constant full width at half maximum at known binding energies[3-5].

S.i.m.s. spectra were obtained on a modified VG SIMSLAB spectrometer[7], run in the static mode with a quadrupole analyser, employing 2 keV argon atoms with a total ion dose of 2×10^{-12} per sample. Time of flight (TOF) s.i.m.s. spectra were run on a Kratos TOF s.i.m.s. spectrometer using a gallium liquid metal ion gun giving 10 kV ions with an ion current of 200 pA.

RESULTS AND DISCUSSION

Perfluorobenzene and perfluorotoluene plasma polymers

The X.p.s. C_{1s} core-level spectrum of a typical PFB plasma polymer, shown in *Figure 1*, is similar to those previously reported for plasma-polymerized PFB[8]. It is broad and complex due to the variety of carbon–fluorine environments present. On peak fitting, components due to C–H (5%), C–CF(23%), CF(41%), $\underline{C}F$–CF_n (12%), CF_2 (13%), CF_3 (5%) and a π–π* shake-up satellite (1%) become apparent at binding energies of 285.0, 286.6, 288.4, 289.5, 291.2, 293.3 and 295.2 eV respectively. The hydrocarbon component is present as a surface contamination arising mainly from the storage of the sample prior to analysis. The shake-up satellite is indicative of some unsaturation in the plasma polymer. The predicted F/C atomic ratio from the C_{1s} components (excluding hydrocarbon) is 0.99:1 and is in good agreement with the value of 0.93:1 determined from the F_{1s}/C_{1s} core-level area ratio. A small O_{1s} signal was also observed, corresponding to an O/C ratio of 0.02:1. The X.p.s. data show that the overall stoichiometry of the starting vapour is retained in the plasma polymer, but that the reactions in the plasma lead to substantial rearrangement.

Plasma polymers of PFB produced at different flow-rates, using a constant power of 15 W, showed some variation when analysed by X.p.s., as shown in *Figure 2*. As the flow-rate was increased the amount of CF_2 decreased while the amount of C–CF, which is likely to represent linked or substituted aromatic rings, increased. This means that at high flow-rate, when the power to flow-rate ratio is low, the polymer structure is less altered from that of the monomer, while at low flow-rate, when the power available per unit monomer is greater, the structure is changed to a greater extent with the introduction of more CF_2 groups.

Plasma polymers derived from PFT were shown by X.p.s. to be basically similar to those of PFB, but generally contained slightly fewer CF and more CF_3 groups, as
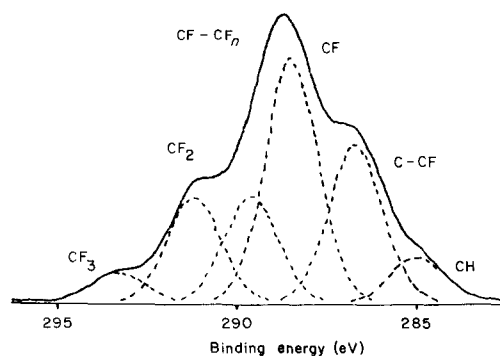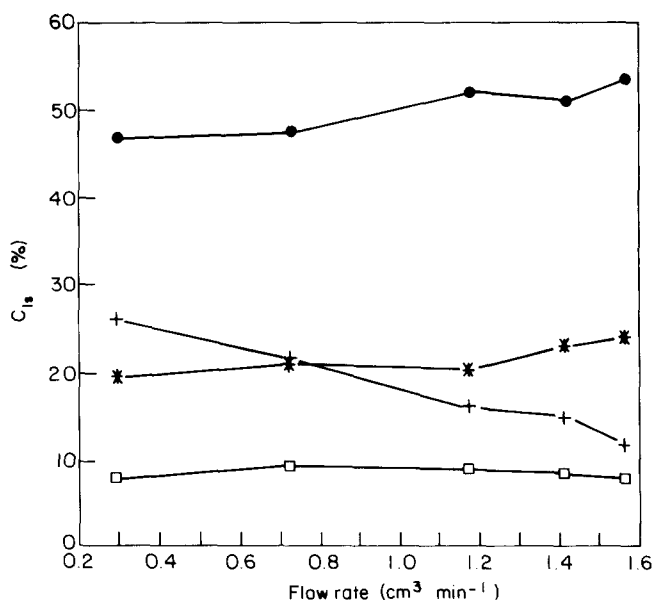

Figure 2 Variation in composition of PFB plasma polymers with flow rate at constant power: ●, CF; +, CF_2; *, C–CF; □, CF_3
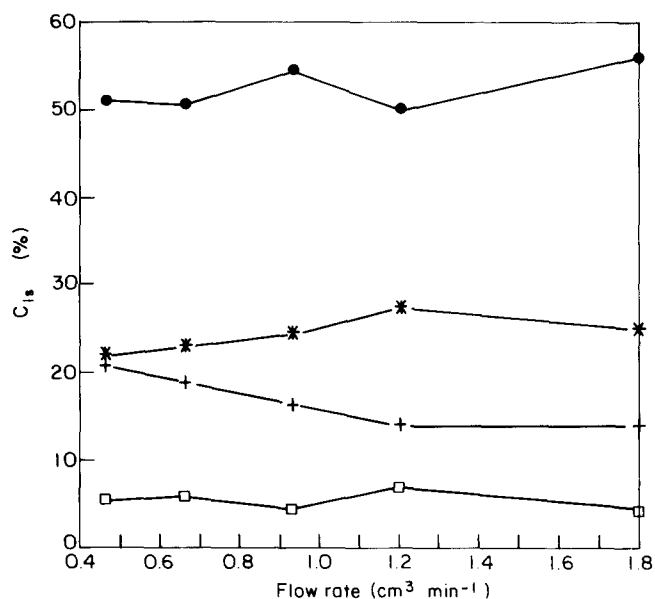

Figure 3 Variation in composition of PFT plasma polymers with flow rate at constant power: ●, CF; +, CF_2; *, C–CF; □, CF_3

might be expected from the monomer structures. The PFT plasma polymers also showed a similar variation with flow-rate as the PFB plasma polymers, although the variations were slightly more pronounced (*Figure 3*).

The positive-ion static s.i.m.s. spectrum of a PFB plasma polymer is shown in *Figure 4*. Like the X.p.s., the positive-ion s.i.m.s. shows evidence of hydrocarbon contamination. This can be observed in the peak at 15 amu (CH_3^+), and in the clusters of peaks at 27–29 ($C_2H_{3-5}^+$), 39–43 ($C_3H_{3-7}^+$) and 53–57 ($C_4H_{5-9}^+$).

The main fluorocarbon peaks below 220 amu are listed in *Table 1*. The assignment of structural features from which the observed ions might originate has been accomplished by comparison with the electron-impact mass spectra of fluorocarbons[9]. Although there may well be differences in the fragmentation mechanisms between the electron impact and the ion impact of s.i.m.s. on the solid, this may serve as a reasonable guide to the

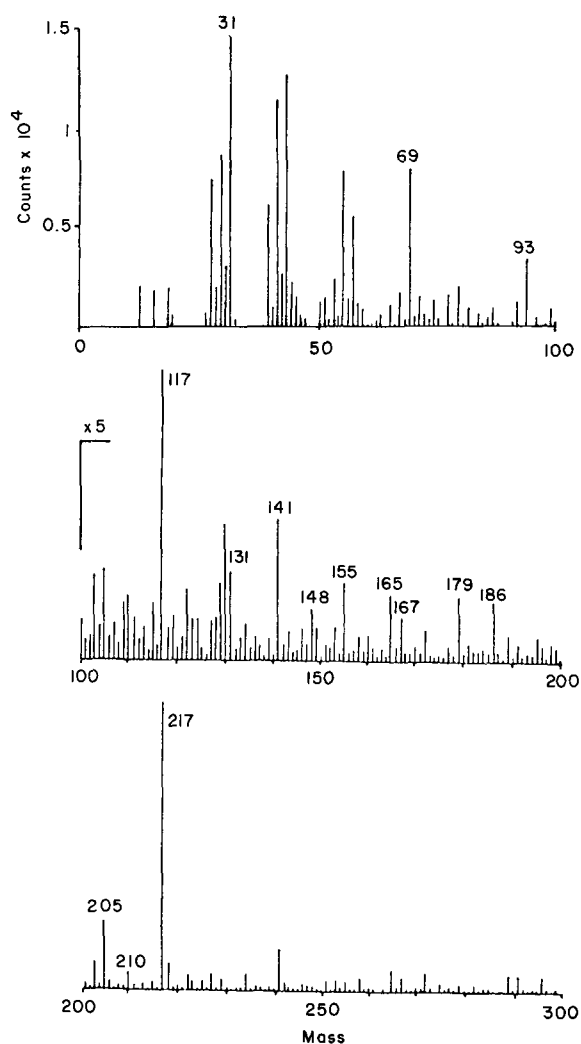Figure 1 X.p.s. C_{1s} spectrum of a PFB plasma polymer

Figure 4 Positive-ion static s.i.m.s. spectrum of a PFB plasma polymer

Table 1 Assignment of peaks in the positive-ion s.i.m.s. spectrum of plasma-polymerized PFB

Peak (amu)	Assignment	Peak (amu)	Assignment
217	$C_7F_7^+$	148	$C_6F_4^+$
210	$C_8F_6^+$	141	$C_7F_3^+$
205	$C_6F_7^+$	131	$C_3F_5^+$
186	$C_6F_6^+$	117	$C_5F_3^+$
179	$C_7F_5^+$	93	$C_3F_3^+$
167	$C_6F_5^+$	69	CF_3^+
165	$C_9F_3^+$	31	CF^+
155	$C_5F_5^+$		

fluorocarbon groups present. The positive-ion s.i.m.s. spectrum of Teflon[10] is basically similar to the electron-impact mass spectra of linear perfluoroalkanes, although it may also contain some extra peaks of low intensity. It is difficult to obtain any quantitative information from the relative heights of individual peaks in the s.i.m.s. spectrum, as factors such as the position of the energy acceptance window of the quadrupole and the efficiency of charge neutralization can have a large influence on the peak intensities obtained, although there have been some attempts to obtain quantitative s.i.m.s. data, for example in a range of copolymer systems[11].

The peaks at 31, 69, and 93 amu correspond to the ions CF^+, CF_3^+ and $C_3F_3^+$, which are present in the mass

spectra of all perfluorocarbons. The peaks at 186 (which would correspond to the molecular ion of PFB), 167, 155 and 117 amu are all present in the electron-impact mass spectrum of PFB. Peaks at 217 (which is particularly intense), 179, 148 and 141 amu are not present in the mass spectrum of PFB, but are found in the spectra of perfluorinated alkyl benzenes and styrene. The peak at 210 amu is present in the spectrum of perfluorostyrene, that at 205 in perfluorocyclohexadiene and that at 165 from perfluoronaphthalene, while the peak at 131 amu could be derived from perfluoroalkanes or perfluoroalkenes. The lack of any significant peaks at 119, 169, 181 and 219 amu (all prominent in the spectrum of Teflon) suggests that there is little or no aliphatic structure in the plasma polymer.

There are a number of low-intensity peaks at masses of greater than 220 amu, corresponding to larger fragments from the polymer. These are more difficult to assign to any particular structure, although the peaks at 272, 253, 241 and 203 amu ($C_{10}F_8^+$, $C_{10}F_7^+$, $C_9F_7^+$ and $C_9F_5^+$) could derive from a perfluoronaphthalene-type structure, while the peak at 267 amu ($C_8F_9^+$) is also present in the mass spectra of perfluoroalkylbenzenes.

The negative-ion s.i.m.s. spectrum of the PFB plasma polymer was dominated by the peak at 19 amu due to F^-. A series of peaks of diminishing intensity corresponding to C_n^- at 12, 24, 36, 48, 60 and 72 amu for $n = 1-6$ and C_nF^- for $n = 1-6$ at 31, 43, 55, 67, 79 and 91 amu were also observed. The lack of any peaks at higher molecular mass makes the negative-ion data much less informative than that from the positive ions.

From the positive-ion s.i.m.s. data it can be proposed that the PFB plasma polymer is mainly composed of aromatic ring structures with some cyclohexadiene and naphthalene, linked by short perfluoroalkene or perfluoroaliphatic chains (probably no more than one carbon atom long in the case of most of the aliphatic groups), or directly bonded to one another. This is fairly similar to the structure proposed by Kaplan and Dilks for plasma-polymerized toluene[12], when perfluorinated, although that structure did not include any naphthalene groups.

TOF s.i.m.s. analysis of a PFB plasma polymer showed no peaks at higher mass than had been found in the spectra obtained using a quadrupole analyser. This lack of high-mass fragments might be due to extensive cross-linking in the polymer, although this is very uncertain.

A series of five PFB plasma polymers made using a power of 15 W and flow-rates varying from 0.45 to 1.8 cm³(stp) min⁻¹ (the same sets of conditions as used in producing the polymers examined by X.p.s.), were analysed using static s.i.m.s. All gave very similar spectra with only minor variations in individual peak intensities. It can therefore be concluded that the basic structural features of plasma-polymerized PFB are the same, no matter what flow-rate conditions are used in the plasma. Differences in the relative abundances of the various fluorocarbon species are more clearly seen by X.p.s. than by s.i.m.s.

A similar series of PFT plasma polymers formed at 15 W and with flow-rates ranging from 0.3 to 1.55 cm³(stp) min⁻¹ were also analysed by s.i.m.s. As for the PFB plasma polymers, few changes were observed in the s.i.m.s. spectra between these samples, despite differences in the corresponding X.p.s. spectra. In fact the

s.i.m.s. spectra of the PFT plasma polymers were very similar to those of the PFB polymers, suggesting that plasma polymers of PFB and PFT are essentially the same material, with only minor differences in the abundances of various components as seen by X.p.s. The mechanism for the formation of the polymer is therefore probably the same in each case — with the CF_3 group not playing a major role — and may be a general mechanism for the plasma polymerization of perfluoroaromatic compounds.

Perfluorocyclohexane and perfluorocyclohexene plasma polymers

The X.p.s. C_{1s} core-level spectra of these two plasma polymers (prepared using monomer flow-rates of $0.6 \, cm^3(stp) \, min^{-1}$) are shown in *Figure 5*. It can be seen that the two are broadly similar to each other, but significantly different from the spectrum of the PFB polymer formed under similar conditions, shown in *Figure 1*. Comparisons between the X.p.s. spectra of these polymers and that of PFB are presented in *Table 2*.

As might be expected from the composition of the monomers, the plasma polymers of perfluorocyclohexane and perfluorocyclohexene contain a considerably higher ratio of fluorine to carbon than does plasma-polymerized PFB. This is manifested in the C_{1s} core-level spectra in the form of larger peaks corresponding to CF_2 and CF_3 groups, which suggests that there is more aliphatic character in these plasma polymers. The CF peak (which includes aromatic CF groups) and the C–CF peak are considerably smaller in both cases than for the PFB polymer, again suggesting less aromatic nature. The perfluorocyclohexane plasma polymer is generally slightly more aliphatic in nature than that of perfluorocyclohexene, as would be expected from the
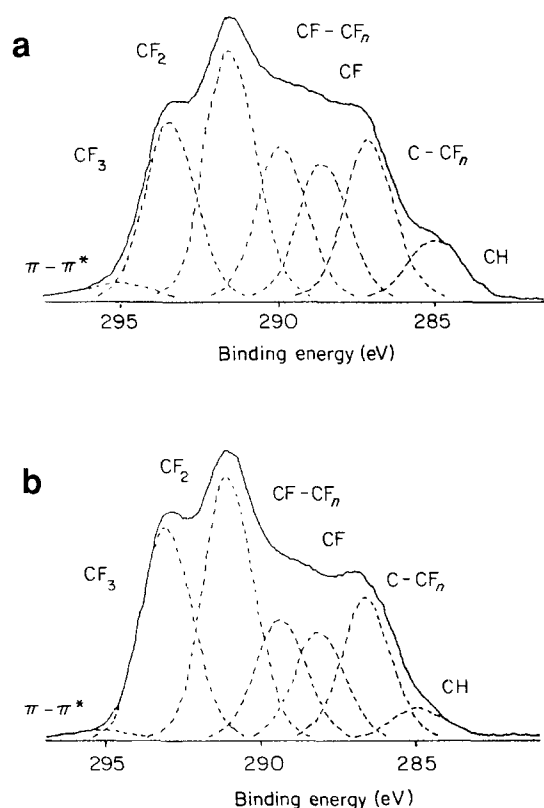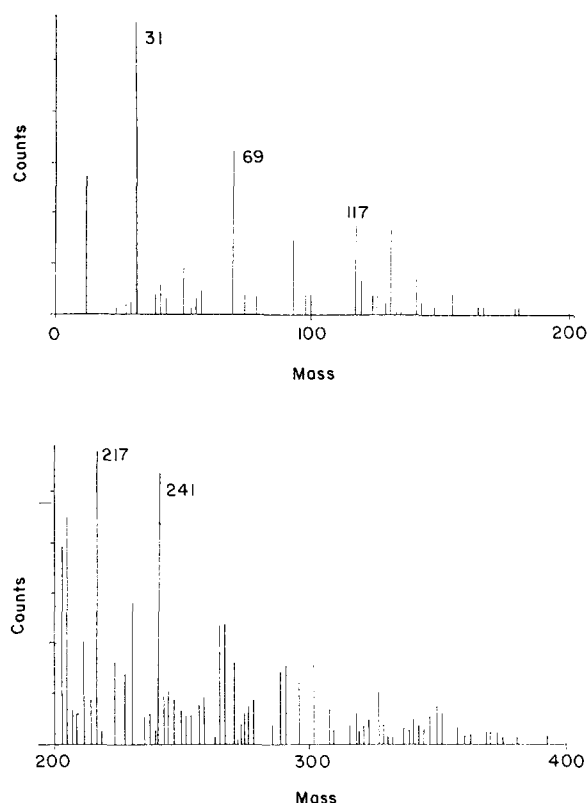

Figure 6 Positive-ion static s.i.m.s. spectrum of plasma-polymerized perfluorocyclohexane

Table 2 Comparison of X.p.s. analyses of plasma polymers of PFB, perfluorocyclohexene and perfluorocyclohexane, as percentage of groups present

	PFB $F:C = 0.92$	Perfluorocyclohexene $F:C = 1.40$	Perfluorocyclohexane $F:C = 1.60$
C_{1s}			
CH	6	6	3
C–CF	25	17	17
CF	35	14	13
CF–CF_n	15	16	14
CF_2	15	26	31
CF_3	4	19	25
$\pi-\pi^*$ shake up	2	2	1

structures of the monomers. All these plasma polymers are basically similar to those reported by Clark and Shuttleworth[8,13].

The positive-ion static s.i.m.s. spectrum of the plasma polymer of perfluorocyclohexane is shown in *Figure 6*. It is fairly similar to the spectrum of the PFB plasma polymer shown in *Figure 4*, but there are some differences. The most obvious one is the presence of more high-mass fragments than in the PFB spectrum. This may indicate less cross-linking in the perfluorocyclohexane polymer, but it could also be caused by differences in the operating conditions used in the s.i.m.s. experiment. There is no peak at 186 amu corresponding to perfluorobenzene, and the intensities of the peaks at 217, 179 and 167 amu, arising from perfluoroalkylbenzene-type structures, are low compared to the spectrum from the PFB plasma polymer, suggesting less aromatic character. A new peak is present at 231 amu ($C_5F_9^+$), likely to be derived from aliphatic or olefinic fluorocarbon. The peaks at 203 and

Figure 5 X.p.s. C_{1s} spectra of plasma polymers of (a) perfluorocyclohexene and (b) perfluorocyclohexane
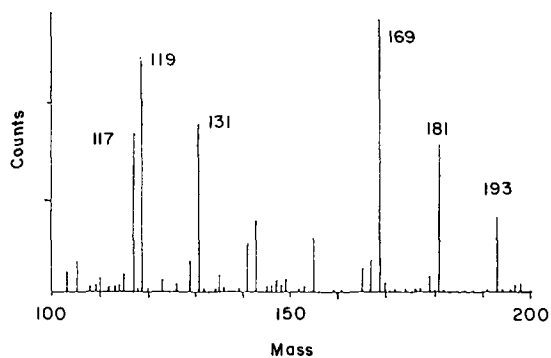
Figure 7 Negative-ion static s.i.m.s. spectrum of plasma-polymerized perfluorocyclohexane

Table 3 Assignment of peaks in the negative-ion s.i.m.s. spectrum of plasma-polymerized perfluorocyclohexane

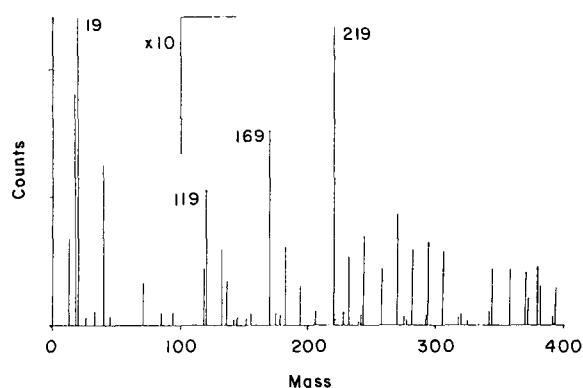| Peak (amu)	Assignment	Peak (amu)	Assignment
193	$C_5F_7^-$	141	$C_7F_3^-$
181	$C_4F_7^-$	131	$C_3F_5^-$
169	$C_3F_7^-$	119	$C_2F_5^-$
155	$C_5F_5^-$	117	$C_5F_3^-$
143	$C_4F_5^-$		

Figure 8 Negative-ion TOF s.i.m.s. spectrum of plasma-polymerized perfluorocyclohexane

241 amu, probably derived from a naphthalene-type structure, are also present with comparatively high intensities.

The negative-ion s.i.m.s. spectrum was dominated by the F^- peak at 19 amu, but unlike the spectrum of the PFB plasma polymer there were also a number of peaks in the range 100–200 amu (*Figure 7*) which could yield some structural information. The major peaks, tabulated in *Table 3*, are all present in the negative-ion s.i.m.s. spectrum of Teflon[10], although the peaks at 117, 141, 143 and 145 amu are present in considerably higher relative intensities. These are the peaks containing the higher ratios of carbon to fluorine, so their increased intensities probably represent the presence of unsaturated structural features. Peaks at 119, 131, 169, 181 and 193 amu are all intense in the spectrum of Teflon and represent saturated aliphatic fluorocarbon. The negative-ion s.i.m.s. spectrum obtained using a TOF analyser (*Figure 8*) showed that the spectrum continued up to masses greater than 800 amu and continued to be similar to that of Teflon at high mass.

It can therefore be proposed that the plasma polymer of perfluorocyclohexane contains the same sort of aromatic, cyclohexadiene and naphthalene structures as that of PFB, but also contains a considerable amount of aliphatic fluorocarbon. It appears that the negative s.i.m.s. is more sensitive to the aliphatic fluorocarbon, while the positive-ion spectrum contains more information about the more unsaturated structures.

The positive- and negative-ion s.i.m.s. spectra of plasma-polymerized perfluorocyclohexene were very similar to those of the perfluorocyclohexane plasma polymer described above, with only small differences in the intensities of a few peaks. The structures of the two polymers are probably therefore much the same.

Benzene plasma polymer

Little information can be gained from the X.p.s. analysis of plasma-polymerized benzene, as the different hydrocarbon groups do not induce a chemical shift in the C_{1s} core-level spectrum. A single peak was observed at 285.0 eV, corresponding to hydrocarbon, and a $\pi-\pi^*$ shake-up satellite indicating the presence of aromaticity. A small oxygen signal was also observed.

The positive-ion static s.i.m.s. spectrum (obtained using a quadrupole analyser) of a benzene plasma polymer formed using a monomer flow-rate of 1.5 cm^3(stp) min^{-1} is shown in *Figure 9*. *Figure 10* shows a positive-ion s.i.m.s. spectrum of polystyrene, and a comparison of this with the spectrum of the plasma polymer shows they are virtually identical. There is a small difference, however, in that the clusters of peaks around masses 178 and 191 amu are centred at slightly lower mass in the spectrum of the plasma polymer, indicating a slightly lower hydrogen to carbon ratio and hence a higher degree of
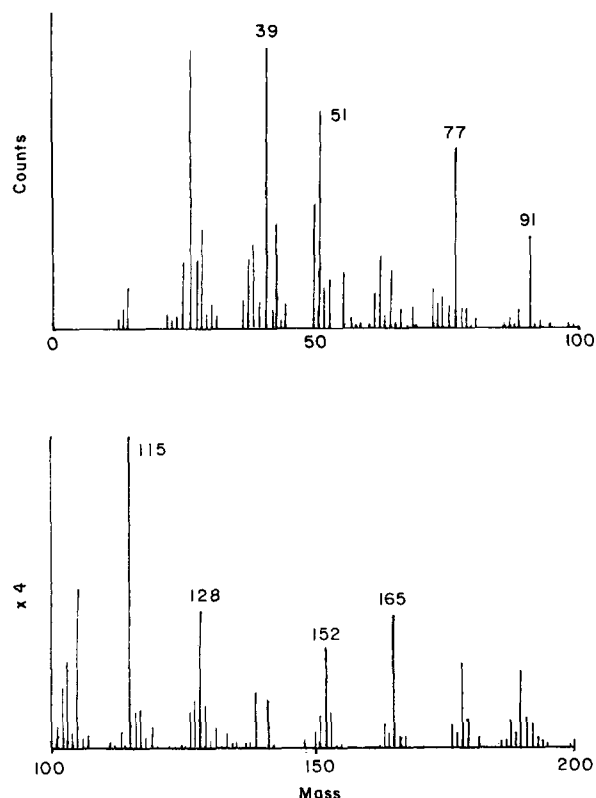

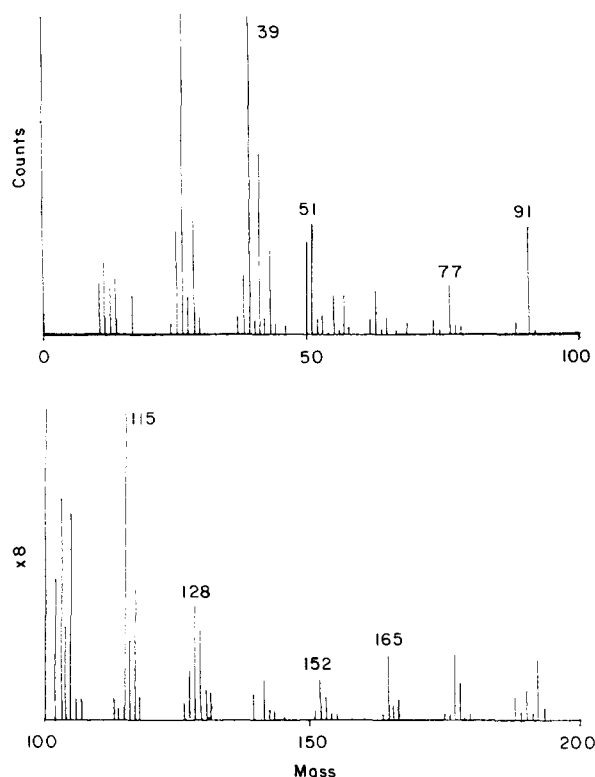**Figure 9** Positive-ion s.i.m.s. spectrum of plasma-polymerized benzene

Figure 10 Positive-ion s.i.m.s. spectrum of polystyrene

The basic structure of plasma polymers formed at different flow-rates is the same, but the percentages of aromatic- and aliphatic-type structures may change. Plasma polymers of perfluorocyclohexane and perfluorocyclohexene contain similar structures, but much of the polymer is made up of aliphatic fluorocarbon. The plasma polymer of perfluorocyclohexene is shown by X.p.s. to contain a slightly lower percentage of aliphatic structure than that of perfluorocyclohexane. The s.i.m.s. analysis of plasma-polymerized benzene suggests that it has a structure similar to polystyrene, but it is, in fact, probably a much less ordered structure, more like the PFB plasma polymer.

S.i.m.s. and X.p.s. are complementary techniques and the combination of the two can provide a useful insight into the structure of plasma polymers. The interpretation of the s.i.m.s. data from unknown materials such as plasma polymers presents some difficulty, however, and the structural information about plasma polymers determined in this paper, although probably correct, cannot be taken as absolutely certain. As an increasing number of standard spectra of polymeric materials are collected, interpretation should become easier and static s.i.m.s. may become increasingly important in the structural analysis of plasma polymers. X.p.s. will still be required, however, as s.i.m.s. cannot provide quantitative data and does not show some of the differences between different materials observed by X.p.s.

unsaturation. It is unlikely that the structure of the plasma polymer is the same as that of polystyrene, as plasma polymers generally have a random, highly cross-linked structure, unlike the regular repeat units found in conventional polymers. The most likely structure for plasma-polymerized benzene consists of aromatic rings joined randomly by short alkyl chains in a cross-linked three-dimensional network, i.e. similar to the structure proposed for PFB and PFT plasma polymers, although no evidence was seen for naphthalene or cyclohexadiene rings. The s.i.m.s. spectrum is probably typical of polymers with an alkylbenzene-type structure, and demonstrates that s.i.m.s. cannot necessarily be relied upon to give unique 'fingerprint' spectra for all materials.

SUMMARY

Plasma polymers of PFB and PFT are composed mainly of a perfluorinated alkyl benzene-type structure, with benzene rings linked together by very short alkyl chains. The polymers also contain perfluoronaphthalene and cyclohexadiene rings in a highly cross-linked network.

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