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Plasma Polymerization of Ethylene and the Series of Fluoroethylenes: Plasma Effluent Mass Spectrometry and ESCA Studies

A. Dilks

Chemistry Department, University of Durham, Durham DH1 3LE, England

E. Kay*

IBM Research Laboratory, San Jose, California 95193.

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ABSTRACT: The plasma polymerization of ethylene and the series of fluorinated ethylenes has been investigated in a capacitively coupled, low-pressure radio-frequency system. ESCA analysis of the polymer films allowed the relative concentrations of CF_3, CF_2, CF, and carbon not directly attached to fluorine to be determined. The structures and stoichiometries of the films were found to exhibit distinct trends depending on the injected material. The neutral species in the effluents of the plasmas were analyzed by mass spectrometry and this data coupled with the ESCA data allowed the primary precursors to polymerization to be identified. In going along the series from ethylene to tetrafluoroethylene the relative importance of acetylene in the plasma steadily decreases while that of difluoroacetylene increases. The relative importance of fluoroacetylene exhibits a maximum at the isomeric difluoroethylenes. Methylene plays an important role in the ethylene plasma while the relative importance of difluorocarbene increases along the series until for tetrafluoroethylene the plasma reactions are dominated by $:CF_2$ and CF_2CF_2 itself. We believe that plasma polymerization proceeds via a plasma-induced mechanism involving the unchanged injected material and a second mechanism involving the initial formation of these other precursors in the plasma.

Introduction

In previous papers[1,2] we have shown how the ESCA investigation of plasma-polymerized films, coupled with direct mass spectrometric sampling of the low molecular weight neutral products in the plasma effluent, provides a new dimension to the investigation of structure and polymerization mechanism for plasma-polymerized materials. In those investigations[1,2] involving the synthesis of metal-containing plasma-polymerized fluoro polymers, detailed information was derived concerning both the state of the metal and the structure of the polymer matrix. The mass spectrometric studies allowed the primary precursors of the polymerization to be identified.

In this paper we present a study of the plasma polymerization of ethylene and the series of fluorinated ethylenes: fluoroethylene, 1,1-difluoroethylene, *cis*- and *trans*-1,2-difluoroethylenes, trifluoroethylene, and tetrafluoroethylene. For comparison purposes we also include the results from an experiment involving the formation of a plasma-polymerized film produced by argon plasma sputtering of a poly(tetrafluoroethylene)-coated excitation electrode and subsequent condensation of the sputtered species on a substrate after they have traversed the plasma. The motivation for this investigation lies in the increasing interest in fluorinated plasma polymers and how fluorocarbon systems differ from hydrocarbon and fluorohydrocarbon plasmas. In addition, this work has provided valuable background data for our investigations of simultaneous etching and polymerization in plasmas excited in mixtures of fluorocarbons and hydrogen.[2]

In a previous publication,[3] Kay and co-workers have shown how a definite correlation exists between the polymer deposition rate and the sum of the partial pressures of all unsaturated neutral species in a tetrafluoroethylene plasma as the mass flow rate is increased at constant pressure. A similar correlation for the saturated species in the plasma did not exist.[4] We have described similar observations in our work on metal-containing fluorocarbon films produced by simultaneous plasma etching and polymerization.[1] Thus, for plasmas excited in the series of perfluorinated alkanes in a diode reactor configuration, employing a variety of electrode materials, the polymer deposition rate is directly related to the total partial pressure of unsaturated species in the plasma. Addition of hydrogen to a fluorocarbon plasma greatly enhances the polymer deposition rate and we have shown this to be via the formation of unsaturated species in the gas phase.[2] Throughout this work, therefore, we have made the starting assumption that plasma polymerization of the fluorinated ethylenes will proceed via unsaturated precursors. We might expect polymerization to occur by a mechanism which is analogous to conventional chain-growth polymerization. This may occur either in the gas phase[1] or at a surface. However, the relatively large concentration of available initiators and chain terminators in the plasma, as well as the low pressure of the system, will ensure that the chain lengths of these initial polymer products are relatively short. This process is almost certainly accompanied by a concomitant process involving the interaction of photons, ions, radicals, and metastables with the forming polymer to cause C–H, C–F, or C–C bond cleavage and molecular rearrangements. This latter process results in the formation of cross-links, unsaturation, and free radicals in the polymer. The unsaturated structures and free radicals may further react with other species in the plasma, and this may initiate other chain-growth reactions.

The present investigation, therefore, has the limited objective to identify the unsaturated primary precursors to the polymerization rather than to attempt to give a detailed account of all the processes involved in the plasma chemistry.

Experimental Section

A. Plasma Apparatus and Operating Conditions. The reactor used in this investigation has been discussed in detail elsewhere.[1] It is based on a ~30-cm-diameter × ~30-cm-deep cylinder, containing the excitation electrode (a 10-cm-diameter copper disk) and grounded electrode (a 15-cm-diameter aluminum disk), mounted 6 cm apart at the center. In this arrangement the plasma is largely confined to a volume of ~1 L. Radio-frequency power is delivered to the excitation electrode by a Heathkit Model DX-60B radio-frequency generator (frequency 13.56 MHz) via a National Radio Co., Inc., Model NCL-2000 power amplifier and a Bendix Corp. Model 263 power meter. This system can deliver 0–300 W of radio-frequency power maintained at a constant level by a power level control unit. The output of the radio-frequency power unit is impedence matched to the excitation electrode by an *LC* matching network.

The gases used in this investigation were obtained from PCR Research Chemicals, Inc., and were used without further purification. They were metered into the reactor by a flow rate controller mechanism which is able to maintain constant flow rates in the range 0–100 $cm^3 min^{-1}$ (at STP). The pressure in the system was monitored by a Datametrics Baracel electronic capacitance manometer.

In all of the experiments described in this paper involving injected organic materials the operating parameters were as follows: pressure 0.015 torr; flow rate of injected material, 5 $cm^3 min^{-1}$ (at STP); radio-frequency power, 20 W. For the film preparation by argon sputtering of a poly(tetrafluoroethylene)-covered excitation electrode a pressure of 0.015 torr of argon was employed at a power of 100 W. The polymer films were collected on clean gold substrates, ~1 cm^2 in area, mounted in the grounded electrode plane but electrically isolated from it. The substrates and grounded electrode were, however, maintained in good thermal contact and water cooled. Their temperature during deposition was monitored by means of a thermocouple and was typically ~16 °C. Depositions were carried out in all cases for 50 min and rates of deposition determined by gravimetry. The full experimental procedure is the same as that discussed elsewhere.[1]

B. Plasma Effluent Analysis. The neutral gas-phase products in the plasma effluent were monitored by means of a UTI Type 100C quadrupole mass spectrometer positioned ~30 cm from the center of the plasma region. It is separated from the reactor by a gate valve and a 0.003-in-diameter × 0.010-in-long orifice and is differentially pumped.[1] The average electron energy in the ionizer region was fixed in this study at ~15 eV. Ions with an appearance potential >15 eV are therefore not observed, which, as far as this present investigation is concerned, only precludes the detection of HF and CF_4.[5] At this low ionization energy unsaturated molecules undergo relatively little fragmentation (i.e., typically >95% of the detected signal is at the mass corresponding to the parent ion). The saturated species, on the other hand, fragment to a greater extent, although their signal intensities are generally lower.[1] In the discussions to follow, a common occurrence is the increase in intensity of signals, or the appearance of new signals, at positions in the mass spectrum corresponding to unsaturated ions (e.g., $C_2H_2^+$, C_2HF^+, $C_2HF_3^+$). In every case where this increase in signal intensity is large we have attributed it to an increase in partial pressure of the corresponding neutral species (e.g., C_2H_2, C_2HF, C_2HF_3) in the plasma reactor; i.e., the increase in signal intensity is too large to be associated with saturated species or higher molecular weight unsaturated species. Furthermore, a saturated molecule would also give rise to a full fragmentation pattern of comparable intensity and this was not observed in any of the data.

The overall detection efficiency of the quadrupole mass spectrometer decreases with increasing mass such that at 150 amu the efficiency is ~10% that at 18 amu. This has been taken into account in the following discussions when comparing signal intensities in the mass spectrometric measurements.

C. Structural Analysis of Polymers. The analytical techniques available for the investigation of structure and bonding of plasma-polymerized fluoro polymers are strictly limited. The most powerful tool available at present for such studies is X-ray photoelectron spectroscopy (XPS or ESCA) and we have employed this technique in this work. ESCA spectra of the deposited plasma-polymerized films were recorded on a Hewlett-Packard 5950B spectrometer employing monochromatic Al $K\alpha_{1,2}$ exciting radiation. In this system the angle between the X-ray source and analyzer is fixed, as is the angle of the sample with respect to the analyzer. Under the conditions used in this investigation the full width at half-maximum (fwhm) of the $Au_{4f_{7/2}}$ core level of a clean gold sample at a binding energy of 84.0 eV, used for calibration, was 0.85 eV. The effects of sample charging were alleviated by preparing the samples sufficiently thin (i.e., <1 μm) such that the incident X-rays could penetrate the polymer film to the substrate, maintained in electrical contact with the ESCA spectrometer, and thus create sufficient charge carriers in the sample to effectively neutralize the surface. Energy referencing was achieved by monitoring the signal at 285.0-eV binding energy arising from extraneous hydrocarbon contamination, which built up on the sample to detectable levels after it had remained in the spectrometer overnight. Analysis of the samples by ESCA was carried out after air exposure.

Integration and curve resolution of complex line shapes was carried out with a Du Pont 310 analog curve resolver within the framework of an extensive volume of background data for binding energies in fluorinated systems.[6] In general, the procedure involves grouping similar structural features under a broadened Gaussian envelope representing a range of chemically different environments. For example, the binding energy of the C_{1s} levels in CF structural features will increase with an increasing number of β-fluorine substituents (i.e., fluorine on the next carbon atom in the chain). Where the binding energies of a given structural feature span a large range, two Gaussian envelopes have been fitted (i.e., in systems containing significant quantities of a given feature in both largely hydrocarbon and highly fluorinated environments, the latter being at a somewhat higher binding energy). This type of analysis has often proved successful in ESCA in-

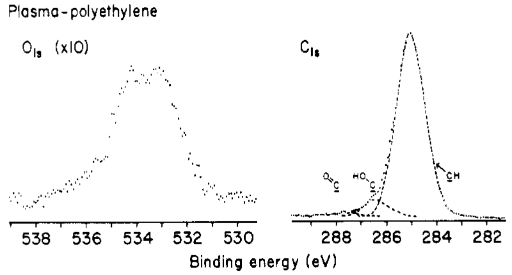


Figure 1. ESCA spectra of plasma polyethylene. The dashed curves represent the components of the line shape analysis.

vestigations of polymers,[7,8] and the overall consistency of the data in this invesigation will become apparent.

It is important at this point, however, to provide some estimate of the errors involved in this type of analysis and to indicate how they relate to the discussions of the data. Throughout this work two independent sources of intensity data have been exploited to provide information regarding the structure of the polymer films, namely, the total F_{1s}/C_{1s} signal intensity ratio and the relative intensities of the components fitted to the C_{1s} envelope.

The ratio of the total intensities of the F_{1s} and C_{1s} core level signals provides a direct quantitative measure of the F:C stoichiometry of the film. We can measure the F_{1s}/C_{1s} intensity ratio by three independent methods: (i) using the digital integration facility of the Hewlett-Packard 5950B ESCA spectrometer's computer system, (ii) using the Du Pont 310 curve resolver, and (iii) cutting out and weighing photocopies of the spectra. In all cases these methods were in excellent agreement for a given sample and although we have not conducted a complete error analysis, ±5% is almost certainly an upper limit on the error of the total F_{1s}/C_{1s} ratio. The stoichiometry of the film is derived from this figure by correcting it by a relative sensitivity factor (i.e., $F_{1s}/C_{1s} = 4.9 \pm 0.1$ for unit stoichiometry), derived from a number of standard homogeneous fluorocarbon samples.[6]

A discussion of the C_{1s} band profiles of the plasma-polymerized films in this work is made possible by the curve resolution procedure involving the Du Pont 310 system. The errors involved in the determination of the C_{1s} component intensities are somewhat greater than for total intensity ratios. However, since the chemistry of the system is a primary consideration, the number of curves under the spectral envelope and number of possible fits are strictly limited.[6] Also, in a series of related systems the requirement of smooth trends in the data often allows only one reasonable fit for each C_{1s} envelope. This was found to be the case for the series of plasma polymers described in this work. The estimates on the reproducibility of the component intensities for a given sample range from ±5% for the CF_3 component to ±15% for the components associated with carbon atoms not attached to fluorine in samples where this region of the spectrum is poorly resolved. (This arises from the fact that as the number of α-fluorine substituents decreases, the number of possible β-fluorine substituent patterns increases. Thus, the span in possible binding energies of a given structural type increases in going from $CF_3 \rightarrow CF_2 \rightarrow CF \rightarrow C$.) The F:C stoichiometry of a given film derived from the C_{1s} data alone is given by $(3CF_3 + 2CF_2 + CF)/(\text{total } C_{1s})$ and we estimate an error of the order of ±10% in this value. In general, our discussions relating to the components of the C_{1s} band profiles are qualitative in nature. For a given injected material material under a given set of operating parameters the structure of the deposited film as determined by ESCA is extremely reproducible.

Previous work has demonstrated that the structure of plasma polymers derived from ESCA analysis is representative of the bulk material.[7,8] Since our prime motivation is to produce thin film materials (<1-μm thick), under the conditions used to synthesize the plasma polymers discussed in this work, the deposition rates are very low (typically 10^{-6} g cm^{-2} (fw)$^{-1}$ s^{-1}). Preparation of sufficient material for bulk analysis would therefore be extremely time consuming and we have relied entirely on ESCA for structural analysis of the polymers.

Results and Discussion

A. Ethylene. Figure 1 shows the C_{1s} and O_{1s} core level spectra of the polymer film formed in an ethylene plasma. The most intense component in the C_{1s} spectrum centered at ~285.0-eV binding energy can be attributed to all carbon atoms attached only to hydrogen and other carbon atoms. It is clear, however, from Figure 1 that the C_{1s} spectrum for plasma polyethylene also contains significant contributions from higher binding energy levels. These can be attributed to C—OH at ~286.6 eV and C=O at ~287.9 eV by comparison with previous data compiled in relation to the plasma oxidation of hydrocarbon polymers.[9] The presence of alcohol- and ketone-type functionalities in plasma polyethylene is now well documented in the literature and is attributable to the interaction of free radical sites remaining in the polymer with atmospheric oxygen.[10] However, the relatively high concentration in the outermost layers of the material as determined from both the C_{1s} and O_{1s} core level spectra in Figure 1 will almost certainly be reduced further into the bulk sample, due to the diffusion-controlled nature of the reaction producing these features.

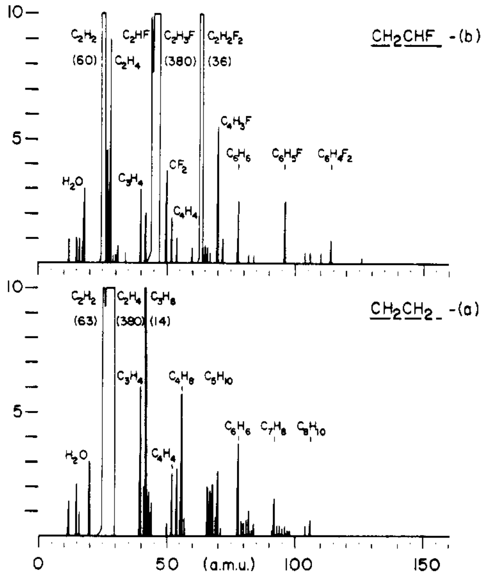


Figure 2. Mass spectra taken with an ionization energy of ~15 eV for the neutral gas-phase products of plasmas excited in (a) ethylene and (b) fluoroethylene.

Figure 2a shows the plasma effluent neutrals' mass spectrum for the plasma excited in ethylene. The major peaks in the spectrum obtained from the system with the discharge turned off are C_2H_4 and C_2H_2, of intensity 400 and 32 arbitrary units, respectively. Under the conditions and resolution used in these experiments, H_2 is not detectable. Signals at 18 and 28 amu are present due to the extraneous background atmosphere in the spectrometer. These signals increase typically by 20–30% on initiating the plasma, which we can attribute to H_2O and CO being desorbed from the reactor walls, particularly in and around the mass spectrometer orifice. This situation exists in all of the experiments described here.

On turning on the plasma the C_2H_4 signal intensity decreases slightly while the C_2H_2 signal increases by a factor of ~2. In addition, a wide range of higher molecular weight oligomers are observed, the most notable of which are in the series (i) C_2H_4, C_3H_6, C_4H_8, and C_5N_{10} and (ii) C_6H_6, C_7H_8, and C_8H_{10}. Also present are many peaks of lower intensity which may be derived from either neutral species in the plasma or fragmentation patterns of the aforementioned species. Our discussion here and throughout this paper, however, will be restricted to the major components and their products rather than to at-

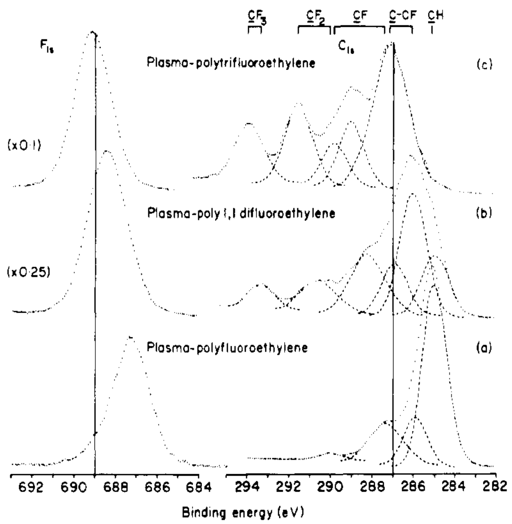


Figure 3. ESCA spectra of (a) plasma poly(fluoroethylene), (b) plasma poly(1,1-difluoroethylene), and (c) plasma poly(trifluoroethylene). The dashed curves represent the components of the line shape analyses. (Refer to text for assignments.)

tempt a chemical account of all the minor peaks observed.

The most striking difference between the spectrum shown in Figure 2 and previously reported data for this system[11,12] is the presence of a significant amount of material of molecular weight >28. In fact, more than 50% of the mass spectrometric intensity due to the products in the plasma is above mass number 28. At this relatively low pressure, i.e., 0.015 torr, therefore, there is more gas-phase chemistry involved in the plasma polymerization of ethylene than had previously been inferred.[11,12] The dominance of C_2H_2 as the major unsaturated species apart from C_2H_4 itself is clear from the figure. The ability of C_2H_2 to polymerize under these conditions is indicated by the presence of benzene (C_6H_6) in the gas phase. It is interesting to note, however, that the two series mentioned above, i and ii, starting with C_2H_4 and C_6H_6, respectively, are both incremented by [CH_2]. This suggests that methylene also plays a role in the plasma chemistry of ethylene. The most likely precursors to polymerization in the ethylene plasma in addition to ethylene itself are therefore acetylene and methylene formed in the following reactions:

$$CH_2{=}CH_2 \rightarrow CH{\equiv}CH + H_2 \qquad (1)$$

$$CH_2{=}CH_2 \rightarrow 2{:}CH_2 \qquad (2)$$

B. Fluoroethylene. In fluoroethylene we have one of the hydrogen atoms of ethylene substituted by fluorine. The ESCA spectrum in Figure 3a confirms that fluorine is also incorporated into the plasma polymer derived from this material. Thus, a F_{1s} signal is observed at ~687.3 eV and components are present in the C_{1s} spectrum at ~287.4 and ~290.0 eV, where we would expect to find CF and CF_2 structural features, respectively, in largely hydrocarbon environments. The signal centered at ~285.9 eV is due to carbon atoms having only hydrogen and carbon nearest neighbors but having fluorine in a β position. The largest component in the C_{1s} spectrum at ~285.0 eV can be assigned to carbon atoms in a completely hydrocarbon environment, i.e., no α- or β-fluorine substituents.

The F:C stoichiometry of this plasma poly(fluoroethylene) derived from the F_{1s}/C_{1s} intensity ratio is $\sim C_2F_{0.28}$. Clearly, it is severely fluorine deficient when compared to the injected material, CH_2CHF. We can also obtain an estimate of the F:C stoichiometry from the intensities of the C_{1s} components. As has been pointed out by Clark and Shuttleworth,[7] this value will contain an error if $\pi \rightarrow \pi^*$ shake-up satellites associated with photoionization of vinylic CH features are present. These are shifted higher on the binding energy scale than the CH signals and therefore add a few percent to the measured intensity of the CF_2 and CF_3 components. Where this is the case, we obtain a high estimate of the F:C stoichiometry. Indeed, for plasma poly(fluoroethylene) the estimated stoichiometry derived from the C_{1s} components is higher than the actual value derived from the F_{1s}/C_{1s} intensity ratio by a factor of ~1.9. This would suggest that the component assigned as CF_2 structural features in Figure 3a is, in fact, almost entirely due to shake-up satellites associated with vinylic CH. If we also subtract a few percent from the CF component as being due to carbon attached to oxygen (cf. Figure 1) since oxygen is also observed for this material, then the stoichiometry derived from the C_{1s} components can be adjusted to agree with the actual stoichiometry (i.e., ~4% subtracted from CF).

The conclusions drawn from the ESCA data are therefore that the stoichiometry of the plasma poly(fluoroethylene) film is $\sim C_2F_{0.28}$, the fluorine is predominantly present as CF structural features, and the film contains a significant amount of vinylic CH.

Now turning to the plasma effluent mass spectrum for this system in Figure 2b, we can draw conclusions which are consistent with the ESCA data. With the discharge off, the spectrum of CH_2CHF shows only CH_2CHF and C_2H_2 of intensities 400 and 30 arbitrary units, respectively. The most prominent unsaturated species observed when the plasma is turned on, apart from fluoroethylene itself, are C_2H_2 and $C_2H_2F_2$. A comparison with the data for ethylene (Figure 2a), for which the C_2H_2 signal is of comparable intensity, allows the peak at 78 amu to be assigned to the trimer C_6H_6 (rather than $C_3H_4F_2$). This then suggests that the peaks at 96 and 114 amu are C_6H_5F and $C_6H_4F_2$, respectively, formed by the involvement of C_2HF (fluoroacetylene), which can be seen at 44 amu. Also present in the mass spectrum are the acetylene dimers C_4H_4 and C_4H_3F.

The most likely primary precursors to plasma polymerization in this system appear to be, in addition to fluoroethylene itself, the unsaturated species formed in the following reactions:

$$CH_2{=}CHF \rightarrow CH{\equiv}CH + HF \qquad (3)$$

$$CH_2{=}CHF \rightarrow CH{\equiv}CF + H_2 \qquad (4)$$

$$CH_2{=}CHF + [F] \rightarrow C_2H_2F_2 + [H] \qquad (5)$$

Such a hypothesis accounts for most of the conclusions drawn from the ESCA data.

C. 1,1-Difluoroethylene. The ESCA data for the polymer derived from 1,1-difluoroethylene (Figure 3b) immediately affirm that the polymer structure is drastically altered when a second hydrogen atom of the C_1 atom of the injected material is replaced by fluorine. Although the total number of carbon atoms not attached to fluorine only decreases by ~20% compared to plasma poly(fluoroethylene), their binding energy distribution is very different. For plasma poly(1,1-difluoroethylene) a greater proportion of the carbon atoms not attached to fluorine have fluorine in a β position. Furthermore, a new C_{1s} component, at ~287.0 eV, which can be associated with carbon atoms not attached to fluorine but in a highly fluorinated environment, is necessary to complete the fit. While the intensity of the CF signal (~288.2 eV) is similar to that in plasma poly(fluoroethylene), the CF_2 signal (~290.6 eV) is larger and a moderately strong component is apparent due to CF_3 structural features at ~293.4 eV.

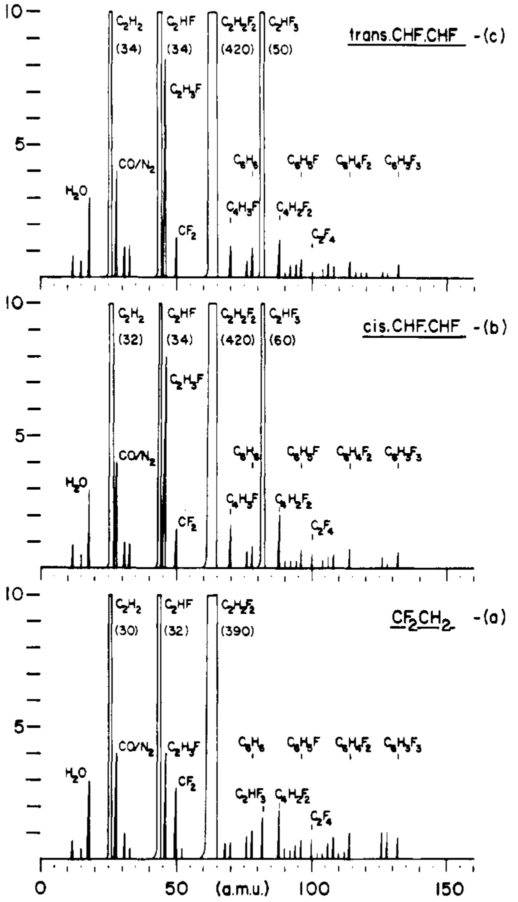


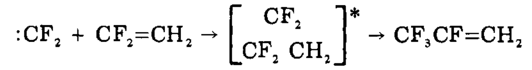
Figure 4. Mass spectra taken with an ionization energy of ~15 eV for the neutral gas-phase products of plasmas excited in (a) 1,1-difluoroethylene, (b) *cis*-1,2-difluoroethylene, and (c) *trans*-1,2-difluoroethylene.

The greatly increased content of fluorine is reflected by the larger F_{1s} intensity and the increased mean binding energy, by ~1 eV, of the F_{1s} envelope is indicative of the fluorine atoms being in more fluorinated environments. This trend is also seen in the C_{1s} levels.

The stoichiometry derived from the F_{1s}/C_{1s} intensity ratio is $\sim C_2F_{1.02}$, which again is severely fluorine deficient when compared to the injected material, CF_2CH_2. The estimated stoichiometry derived from the C_{1s} components is higher by a factor of ~1,2 than the actual value, which suggests the presence of some vinylic CH but less than that found earlier for plasma poly(fluoroethylene).

The mass spectrum obtained for 1,1-difluoroethylene with the discharge off shows a dominant parent peak at 64 amu (intensity 410 arbitrary units). Relatively minor signals are also seen at 26 and 44 amu due to C_2H_2 and C_2HF, respectively (intensities 2 and 3 arbitrary units, respectively). On turning on the discharge (Figure 4a), the $C_2H_2F_2$ peak is reduced in intensity and the acetylenic species C_2H_2 and C_2HF become very much more prominent. In comparing the CH_2CH_2 system with that of CH_2CHF in Figure 2b, it can be seen that the C_2H_2 signal is reduced to ~0.5 that found in the CH_2CHF plasma spectrum, while the C_2HF signal is increased by a factor of ~3. The signals at 78, 96, 114, and 132 amu are again likely to be benzene and mono-, di-, and trisubstituted fluorobenzenes, i.e., the acetylene trimers. The most notable addition in the spectrum of the 1,1-difluoroethylene plasma is C_2F_4 at 100 amu, which suggests that although the predominant reactions involve the acetylenic species, $:CF_2$ may also play a role in the gas-phase chemistry,[1] and indeed $:CF_2$ itself is observed at 50 amu.

In comparing the mass spectrometric data with the ESCA data, we obtain several consistent observations. The ESCA data have shown vinylic CH to be present in the plasma poly(1,1-difluoroethylene) film but in an amount less than found for plasma poly(fluoroethylene). This is consistent with a switch from acetylene to fluoroacetylene being the predominant acetylenic precursor as found in the gas-phase analysis. In contrast to the situation found for plasma poly(fluoroethylene), however, the plasma poly(1,1-difluoroethylene) film structure cannot be accounted for by the injected material and acetylenic precursors alone. This arises from the observation of CF_3 structural features by ESCA for which it would be difficult to describe a route to formation based on the injected material and acetylenic precursors even when invoking ion, metastable, and/or photon bombardment enhanced surface reactions. The involvement of difluorocarbene, however, may account for these structural features in the polymer as follows:



$$:CF_2 + CF_2{=}CH_2 \rightarrow \left[\begin{matrix} & CF_2 & \\ CF_2 & & CH_2 \end{matrix}\right]^{*} \rightarrow CF_3CF{=}CH_2 \qquad (6)$$

where $:CF_2$ and $CF_3CF{=}CH_2$ are also precursors to polymerization. The peak at 114 amu in the mass spectrum (Figure 4a), therefore, also contains a contribution from this latter species.

In addition to 1,1-difluoroethylene itself, the primary precursors to plasma polymerization in this system appear to be the unsaturated products of the following reactions:

$$CH_2{=}CF_2 \rightarrow CH{\equiv}CF + HF \qquad (7)$$

$$CH_2{=}CF_2 \rightarrow CH{\equiv}CH + 2F \qquad (8)$$

$$CH_2{=}CF_2 \rightarrow :CH_2 + :CF_2 \qquad (9)$$

Equation 9 obviously points out that $:CH_2$ can be an important precursor to plasma polymerization. Unfortunately, our approach involving compositional analysis of the polymer products by ESCA and its correlation to gas-phase precursors by mass spectroscopy was not possible for hydrocarbons since the chemical shifts in ESCA for different carbon environments are insufficient to be useful.

It is interesting at this point in the discussion to compare this investigation of 1,1-difluoroethylene with the ESCA analysis of the plasma-polymerized film undertaken recently by Clark and Shuttleworth.[7] In the latter work an inductively coupled radio-frequency system was employed, with a higher pressure of "monomer" (~0.2 torr) than used in this investigation. The curve resolution of the C_{1s} envelope in both cases led to a close correspondence in terms of the positions of the centroids of the components on the binding energy scale. The components at ~285.0 and ~286.0 eV were combined by Clark and Shuttleworth,[7] and this was made possible since the signal at ~285.0 eV was more intense and the signal at ~286.0 eV much less intense in the plasma polymer produced at the higher pressure in the inductive system. This suggests that at the higher pressure CHCH is of relatively greater importance.

D. Isomeric 1,2-Difluoroethylenes. The ESCA spectra of the polymers derived from *cis*- and *trans*-difluoroethylenes are very similar in all respects. In comparing the plasma polymer derived from the 1,2 isomers with that derived from the 1,1 isomer discussed in the previous section, the number of CF_3 features is decreased by ~50%, the number of CF_2 features is similar, and the number of CF features is increased by ~20%. The F_{1s} levels show a decrease in total fluorine content of ~20% and the overall shift from CF_3 to CF results in a decrease in the mean F_{1s} binding energy by ~0.9 eV. The CF_3 and

CF_2 binding energies decrease by ~0.6 eV and the CF binding energy decreases by ~0.4 eV. The total number of fluorinated vs. nonfluorinated sites, however, remains approximately constant. These conclusions are in overall agreement with previously published data pertaining to the plasma polymerization of the isomeric difluoroethylenes in an inductively coupled system.[7]

The major signals in the mass spectra taken before initiating the discharge for the *cis*- and *trans*-1,2-difluoroethylenes are due to $C_2H_2F_2$ (intensity 450 arbitrary units), C_2HF (cis 7 and trans 9 arbitrary units, respectively), and C_2H_2 (cis 7 and trans 8 arbitrary units, respectively). Striking the discharge has the effect of decreasing the $C_2H_2F_2$ signal and increasing the C_2HF and C_2H_2 signals. The full spectra are displayed in Figure 4b,c. The plasma effluent mass spectrometric data alone would suggest that the plasma polymers derived from the 1,2 isomers would be very similar in structure, while that derived from the 1,1 isomer would be different. The most striking difference between the spectra in Figure 4b,c and that in Figure 4a is the large increase in the signal at 82 amu for the 1,2 isomers, which can be assigned to C_2HF_3. Indeed, 1,1-difluoroethylene is unique in this series of fluorohydrocarbon plasmas studied here in that it is the only one which does not show a pronounced peak corresponding to an overall substitution of hydrogen by fluorine in the injected material. It is also the only one not having a CHF functionality. The spectra in Figure 4 are all very similar in all other respects and the acetylene dimers and trimers are pronounced.

Since the 1,2-difluoroethylenes are symmetric about the carbon–carbon double bond, only one type of diradical species is formed on cleavage of this bond, i.e., :CHF. It is interesting then to compare these systems with CH_2CH_2 and CF_2CF_2, which also only form one type of diradical, i.e., $:CH_2$ and $:CF_2$, respectively. We have already seen that in the CH_2CH_2 discharge, $:CH_2$ is formed and the product of cycloaddition of this to the injected material is pronounced in the mass spectrum at 42 amu (Figure 2a). We shall see in the discussion of the CF_2CF_2 plasma that an analogous situation is evident for this system and the product of cycloaddition of $:CF_2$ to CF_2CF_2 is pronounced in the mass spectrum at 150 amu (Figure 5b). In contrast, however, only a small signal is observed at 96 amu in Figure 4 for the isomeric 1,2-difluoroethylene plasmas, where we would expect to observe the cycloaddition product of :CHF and CHFCHF. Indeed, part of the signals at 96 amu in Figure 4b,c has already been attributed to C_6H_5F. It appears, therefore, that reactions of :CHF are less important than reactions of $:CH_2$ and $:CF_2$ in these plasmas.

As was the case for CF_2CH_2, signals are observed in the plasma effluent mass spectra for the 1,2 isomers (Figure 4) at 50 and 100 amu, indicating the formation of difluorocarbene in these plasmas. The intensities of these signals, however, are somewhat smaller in the case of the 1,2 isomers (by ~50%) and this goes some way to account for the decrease in CF_3 content as observed by ESCA (i.e., reactions analogous to reactions 5 and 6 above). The stoichiometry derived from ESCA for both cis and trans isomers is $\sim C_2F_{0.80}$, the estimate from the C_{1s} components being higher by a factor of ~1.3. The lower fluorine content compared to that for plasma poly(1,1-difluoroethylene) and greater vinylic CH content would therefore suggest a greater involvement of CHCH in the plasma polymerization of the 1,2 isomers.

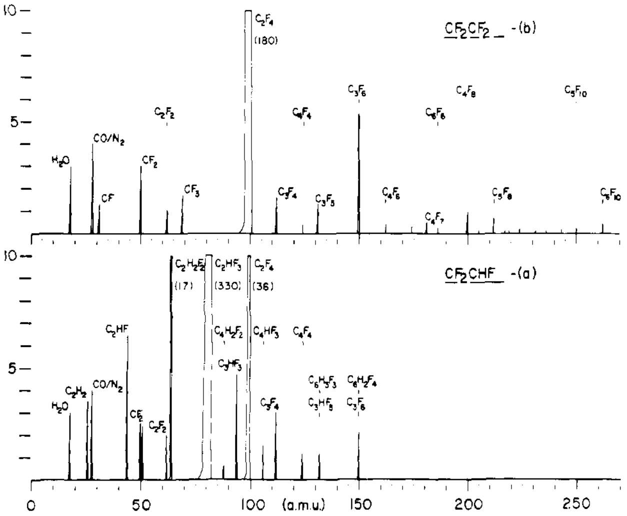


Figure 5. Mass spectra taken with an ionization energy ~15 eV for the neutral gas-phase products of plasmas excited in (a) trifluoroethylene and (b) tetrafluoroethylene.

In addition to the 1,2-difluoroethylenes themselves, the primary precursors to polymerization in these systems appear to be the unsaturated products of the following equations:

$$CHF{=}CHF \rightarrow CH{\equiv}CH + 2\dot{F} \qquad (10)$$

$$CHF{=}CHF \rightarrow CH{\equiv}CF + HF \qquad (11)$$

$$CHF{=}CHF + [F] \rightarrow CHF{=}CF_2 + [H] \qquad (12)$$

$$CHF{=}CF_2 \rightarrow :CF_2 + [:CHF] \qquad (13)$$

E. Trifluoroethylene. The ESCA spectrum of the plasma polymer formed from the discharge excited in trifluoroethylene is shown in Figure 3c. The trends in going from fluoroethylene (Figure 3a) to 1,1-difluoroethylene (Figure 3b) are continued in going to trifluoroethylene. Both the CF_3 and CF_2 components (at ~294.0 and ~291.6 eV, respectively) increase in intensity, the CF component stays virtually constant, and the C component decreases in intensity. The CF signal is fitted with two overlapping curves (~289.9 and ~289.0 eV) in the curve resolution procedure for this material, due to the increased number of CF features in a highly fluorinated environment. The F_{1s} signal intensity has increased and moved to a higher mean binding energy of ~689.1 eV, and the total intensity due to carbon atoms not directly attached to fluorine has shifted to a position (~287.2 eV) corresponding to a highly fluorinated environment. The stoichiometry of this plasma poly(trifluoroethylene) film is determined to be $\sim C_2F_{2.00}$ from both the F_{1s}/C_{1s} intensity and the C_{1s} components. Vinylic CH features are therefore absent from this material.

The mass spectrum recorded in the absence of a discharge for trifluoroethylene is dominated by the parent ion at 82 amu (intensity 450 arbitrary units), with a minor signal due to the CHF_2^+ fragment (intensity 4 arbitrary units). The plasma effluent mass spectrum (Figure 5a) shows many additional signals, the most important of which are those due to $C_2H_2F_2$, C_2F_4, smaller signals due to the acetylenes (C_2H_2, C_2HF, and C_2F_2), and $:CF_2$. The peaks at 88, 106, and 124 amu represent the dimers $C_4H_2F_2$, C_4HF_3, and C_4F_4, suggesting an involvement of the acetylenes C_2HF and C_2F_2 in the plasma chemistry. At least part of the signals at 132 and 150 amu will be therefore attributable to the trimers $C_6H_3F_3$ and $C_6H_2F_4$. However, the major contributions to these signals at 132 and 150 amu will undoubtedly be the species formed by cycloaddition of $:CF_2$ to CF_2CHF and CF_2CF_2, respectively (i.e., C_3HF_5 and C_3F_6). Equations 14 and 15 then account

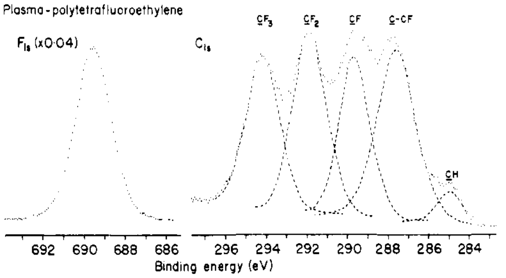


Figure 6. ESCA spectra of plasma poly(tetrafluoroethylene). The dashed curves represent the components of the line shape analysis.

for the formation of precursors which lead to the relatively large number of CF_3 features found in the polymer by ESCA. The signals at 94 and 112 amu may well be due to a net addition of $:CF_2$ to C_2HF and C_2F_2, respectively.

$$:CF_2 + CF_2{=}CHF \rightarrow \begin{bmatrix} & CF_2 & \\ CF_2 & & CHF \end{bmatrix}^* \rightarrow CF_3CF{=}CHF \quad (14)$$

$$:CF_2 + CF_2{=}CF_2 \rightarrow \begin{bmatrix} & CF_2 & \\ CF_2 & & CF_2 \end{bmatrix}^* \rightarrow CF_3CF{=}CF_2 \quad (15)$$

The absence of vinylic CH in the polymer suggests that the primary acetylenic precursor is CFCF, although the gas-phase chemistry suggests also some involvement of CHCF. We can summarize the primary precursor-forming reactions as follows:

$$CF_2{=}CHF \rightarrow CH{\equiv}CF + HF \quad (16)$$

$$CF_2{=}CHF \rightarrow CH{\equiv}CF + 2\dot{F} \quad (17)$$

$$CF_2{=}CHF \rightarrow :CF_2 + [:CHF] \quad (18)$$

$$CF_2{=}CHF + [F] \rightarrow CF_2{=}CF_2 + [H] \quad (19)$$

$$2:CF_2 \rightarrow CF_2{=}CF_2 \quad (20)$$

These reactions can account for all of the features in the polymer observed by ESCA.

F. Tetrafluoroethylene. Tetrafluoroethylene is perhaps the most widely studied fluorocarbon for plasma polymer formation[13,14] and in this investigation represents a system which contains carbon and fluorine only. The ESCA spectrum of plasma poly(tetrafluoroethylene) is shown in Figure 6. The trends discussed in relation to Figure 3 are continued through to Figure 6 in that the CF component (~289.7 eV) again accounts for ~21% of the intensity in the C_{1s} spectrum while the CF_2 and CF_3 components (~291.9 and 294.1 eV, respectively) have increased to ~26% and ~20%, respectively. The total number of carbon atoms not attached to fluorine (C at ~287.6 eV) is considerably reduced. The very high fluorine content of the polymer is further emphasized by the intense F_{1s} signal and a general shift of the centroids of the spectral components to higher binding energy. For example, the mean F_{1s} binding energy increases by ~2 eV in going form plasma poly(fluoroethylene) to plasma poly(tetrafluoroethylene).

The ESCA spectrum in Figure 6 is quite similar to the spectra of tetrafluoroethylene polymerized in a variety of plasma configurations by other workers but differs from polymers produced in nonglow regions.[13] Furthermore, it also compares extremely favorably to the corresponding data obtained in our previous study of metal-containing plasma polymers derived from perfluoropropane.[1]

Under the conditions employed in this present investigation the mass spectrum of the tetrafluoroethylene in the absence of a discharge is dominated by the parent ion at 100 amu (intensity 340 arbitrary units), with smaller signals at 69 and 31 amu due to the CF_3^+ and CF^+ fragments (intensities 2 and 1 arbitrary units, respectively). The mass spectrum of the neutral species in the plasma effluent is displayed in Figure 5b. In situ mass spectrometric sampling in similar systems has previously been reported by Kay and co-workers[3] (sampling through an orifice in the grounded electrode) and Vasile and Smolinsky[15] (sampling radially, very close to the plasma). Since the ionizing energy in the mass spectrometer ionization chamber is somewhat larger in these previous studies (~20 eV) than employed here and since the discharge parameters also differed, it is inappropriate to compare the results in any great detail. However, they are in generally good agreement in terms of the observed species. Kay and co-workers[3] have correlated the quantity of unsaturated species observed in the mass spectrum with the polymer deposition rate. Vasile and Smolinsky[15] have presented an account of the likely neutral and ion chemistry occurring in the plasma which produce the low molecular weight products in the gas phase. We have extended this discussion in a speculation of the likely route to polymer formation involving a plasma polymerization mechanism via primary precursors of general formula $(CF_2)_n$ formed by the reaction scheme presented in previous work.[1,15] These precursors included difluorocarbene as well as perfluorinated monoolefins (e.g., CF_2CF_2, CF_3CFCF_2, and $(CF_3)_2CCF_2$), which can be readily identified in Figure 5b by comparison with our previous work on perfluorinated systems.[1,16] In addition, however, Figure 5b also shows low-intensity signals corresponding to C_2F_2,C_4F_4, and C_6F_6, and it is likely, therefore, that difluoroacetylene also plays a role in the gas-phase chemistry for tetrafluoroethylene.

The stoichiometry of the plasma poly(tetrafluoroethylene) films formed under the conditions used in this investigation derived from the F_{1s}/C_{1s} intensity ratio is $\sim C_2F_{2.66}$ and, as might be anticipated, the value derived from the C_{1s} components is the same. As had been generally found to be the case throughout this work, the plasma polymer is fluorine deficient with respect to the injected material.

G. Sputtered Films. The ESCA spectrum of the fluorocarbon film produced at the grounded electrode in a system having a poly(tetrafluoroethylene) (conventional Teflon) coated excitation electrode is almost identical with that of plasma poly(tetrafluoroethylene) shown in Figure 6. This strongly suggests that the same primary precursors to polymerization are involved in these two systems. Very little can be derived from the plasma effluent mass spectrometry since the spectrum is dominanted by Ar^+ at 40 amu, with little evidence for the very low partial pressure of fluorinated species.

It is interesting that we have produced essentially the same plasma polymer in three different systems, namely, (i) plasma in tetrafluoroethylene, (ii) plasma in argon plus poly(tetrafluoroethylene)-coated excitation electrode, and (iii) plasma in perfluoropropane plus a variety of excitation electrode materials.[1] Although the primary precursors to polymerization are likely to be the same in these systems (e.g., $(CF_2)_n$), the bulk properties of the plasma, in terms of average electron energy, electron density, reactive species present, UV and vacuum-UV emission, etc., will be very different. This would suggest that the surface reactions induced by the interaction of the plasma as a whole with the forming polymer are relatively insensitive to the exact nature of the plasma for these systems.

Summary and Conclusions

We have previously noted the trends in the signal intensities in the ESCA spectra of the individual plasma-polymerized materials synthesized in this study. Further inspection of the data (Figures 1, 3, and 6) also reveals distinct trends in the mean core binding energies in that for a given structural type, they tend to increase with increasing fluorine content of the polymer. This is entirely consistent with previous studies on fluorine-containing systems.[8,17] The smooth nature of the trends in both signal intensity and mean binding energy demonstrates the internal consistency of the curve analysis procedure adopted in this investigation. All of the ESCA data as well as the mass spectrometry data clearly show that substantial molecular rearrangement occurs in the plasma and that a variety of reactions may occur in the gas phase prior to polymerization.

As has been discussed in the literature,[18,19] plasma polymerization of ethylenic compounds injected into the plasma is likely to proceed via two major routes. The first involves the formation of polymer directly from the injected material via a mechanism analogous to conventional chain-growth polymerization. This route has been termed "plasma-induced polymerization".[18,19] The second route involves the formation of species, other than the injected material, in the gas phase, which may then undergo polymerization. The mechanism of this second route has largely remained unaddressed, although it is clear from our work that the term "atomic polymerization" used to describe these processes[18] is misleading.

From the preceding discussions it is clear that a variety of unsaturated species are formed under plasma conditions from a given injected material. Under the experimental arrangement used in this work,[1] where the mass spectrometer entrance is ~30 cm from the center of the plasma region, a large contribution arises in the mass spectrum due to unreacted starting material, a significant proportion of which has not passed through the plasma region. Bearing this in mind, an inspection of Figures 2, 4, and 5 reveals that these plasmas must contain a substantial partial pressure of unsaturated species other than the injected material. Furthermore, many of these species are likely to be more susceptible to polymerization under plasma conditions than the injected material itself (e.g., polymer formation in an acetylene plasma is much more rapid than in an ethylene plasma[18]). We feel that the polymerization of these precursors, by a mechanism analogous to conventional chain-growth polymerization, constitutes the second major route to plasma polymerization for these systems.

Throughout the previous discussions it was apparent that acetylenic species play an important role in the plasma polymerization of the series of fluorinated ethylenes. In going along the series from ethylene itself to tetrafluoroethylene the relative importance of CHCH steadily decreases while that of CFCF increases. The relative importance of CHCF exhibits a maximum at $C_2H_2F_2$, the isomeric difluoroethylenes. These trends are evident both from the intensities of these species in the mass spectra of the plasma effluents and from the vinylic CH content of the polymers as determined by ESCA.

We have seen that methylene plays an important role in the ethylene plasma while the relative importance of difluorocarbene increases along the series until for tetrafluoroethylene the plasma reactions are dominated by $:CF_2$ and CF_2CF_2 itself, whose reactions produce the higher precursors to polymerization. These conclusions are again drawn from the mass spectrometric data and the ESCA data, where we have proposed that a route to the inclusion of CF_3 structural features in the polymers is via reactions of $:CF_2$, such as eq 6, 14, and 15, to produce fluorinated propene precursors containing CF_3.

At the pressure of 0.015 torr used in the plasma reactor, all of the ethylenes investigated here fortuitously give similar intensities by mass spectrometry in the absence of a discharge. We can therefore compare the intensities of their signals in the plasma effluent mass spectra directly to obtain qualitative information on their relative partial pressures in the plasmas. For each plasma into which a partially fluorinated ethylene is injected, we see a signal corresponding to the ethylene formed by substitution of fluorine by hydrogen. With the exception of 1,1-difluoroethylene, however, this reaction is of less importance than substitution of hydrogen by fluorine in the injected material.

In this series of ethylene and fluorinated ethylenes we have shown that a complex mixture of likely precursors to polymerization exists in the plasma gas phase. We have gone some way to identifying the primary precursors for each system studied and, in general, the conclusions drawn from the mass spectrometric investigation of the neutral species in the plasma effluents and ESCA investigation of the plasma polymer structures are in good agreement.

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