Plasma Polymerization of Trifluoromethyl-Substituted Perfluorocyclohexane Monomers

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Received May 15, 1995; Revised Manuscript Received October 6, 1995[⊗]

ABSTRACT: The plasma polymerization of a variety of substituted perfluorocyclohexane monomers (perfluorocyclohexane, perfluoromethylcyclohexane, perfluoro-1,2-dimethylcyclohexane, perfluoro-1,3-dimethylcyclohexane, and perfluoro-1,3,5-trimethylcyclohexane) is systematically compared under identical experimental conditions. The relative abundance of the various CF_n ($n = 0-3$) functionalities found in the respective plasma polymers is shown to be strongly influenced by the electrical discharge power and the structural nature of the fluorocarbon precursor.

Introduction

Plasma polymerization can be used to deposit organic coatings at ambient temperatures from a wide range of precursors onto almost any surface. Polymerization occurs via activation and reaction of the precursor molecules.[1] Ions, radicals, and excited molecules polymerize in the gas phase and react with the growing polymeric film.[2] Conventional polymer synthesis tends to produce structures containing repeat units which bear a strong resemblance to the monomer species, whereas the plasma polymer network can be extremely complex. Plasma polymerization is recognized as being a clean, dry technique that generates little waste compared to conventional wet chemical methods. However, it does have some limitations, in that the stoichiometry and physical characteristics of the plasma polymer product are strongly influenced by process parameters (e.g., gas composition and flow rate,[3,4] substrate temperature,[5] position of the substrate relative to the glow discharge,[6] type of substrate,[25] discharge power,[7] etc.). Low-temperature glow discharge polymerization of perfluorocarbons can yield low surface energy films[13] which find application as hydrophobic,[8,9] protective,[10,11] and biocompatible coatings.[12,13] Cyclic fluorocarbons are reported to undergo plasma polymerization much more readily than their acyclic counterparts.[14] In this article we evaluate the plasma polymerization of a range of substituted cyclic fluorocarbons: perfluorocyclohexane (PFCH), perfluoromethylcyclohexane (MCH), perfluoro-1,2-dimethylcyclohexane (12DM), perfluoro-1,3-dimethylcyclohexane (13DM), and perfluoro-1,3,5-trimethylcyclohexane (TMCH). All of these molecules contain an equivalent fluorine to carbon ratio (F/C = 2). The relative abundance of different CF_n ($n = 0-3$) functionalities found in the corresponding plasma polymers has been determined using X-ray photoelectron spectroscopy (XPS).

Experimental Section

Monomers were purchased from Fluorochem Ltd. and further purified via freeze−thaw cycles. Plasma polymerization experiments were carried out in an electrodeless cylindrical glass reactor (internal diameter = 5 cm, volume = 490 cm^3) enclosed in a Faraday cage[15] (Figure 1). This was continuously pumped by a 33 $dm^3\ hr^{-1}$ Edwards E2M2 mechanical rotary pump via a liquid nitrogen cold trap yielding a base pressure of 2×10^{-3} mbar and a leak rate of better than 2.3×10^{-12} kg s^{-1} (calculated assuming ideal gas behavior).[16] This ensured that at an operating pressure of 0.2 mbar over 99% of the reactor contents were fluorocarbon monomer. A 13.56 MHz rf generator was inductively coupled to the gas via an LC matching circuit and a copper coil (0.5 cm diameter, 10 turns) was wound externally around the reaction chamber spanning 8−16 cm from the gas inlet. Prior to each experiment, the reaction vessel was scrubbed with detergent, rinsed with isopropyl alcohol, oven-dried, and then cleaned with a 50 W air plasma at a pressure of 0.2 mbar for 30 min. A glass slide, which had been washed in detergent and rinsed in isopropyl alcohol, was positioned in the center of the copper coils. The reactor was purged with monomer at 0.2 mbar for 2 min prior to igniting the glow discharge. Plasma polymerization was carried out for 10 min. Upon termination, the reaction zone was flushed with monomer for a further 2 min, and then vented to air.

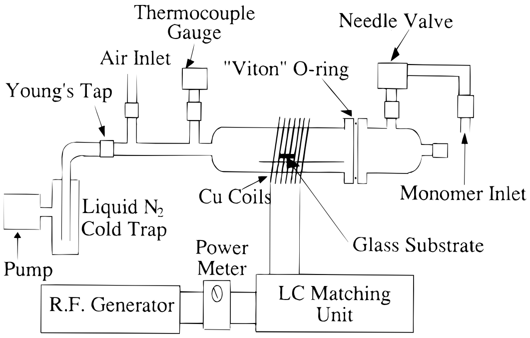

Figure 1. Experimental apparatus used for plasma polymerization.

A Kratos ES200 X-ray photoelectron spectrometer with an unmonochromated X-ray source (Mg $K\alpha_{1,2}$ = 1253.6 eV) was used for chemical characterization of the deposited fluorocarbon films. Emitted core level electrons were collected at a take-off angle of 30° from the substrate normal with a cylindrical hemispherical analyzer (CHA) operating in fixed retardation ratio mode (FRR = 22:1). The spectrometer was calibrated with respect to the gold $4f_{7/2}$ peak at 83.8 eV, (FWHM = 1.2 eV).[17] Instrumentally determined sensitivity factors for unit stoichiometry were taken as C(1s):F(1s):O(1s):N(1s):Si(2p) = 1.00:0.53:0.55:0.74:1.05. The absence of any Si(2p) XPS feature following plasma polymerization was taken as being indicative of complete coverage of the glass substrate.

Results

A Marquardt minimization computer program which assumed a Gaussian peak shape with a fixed relative

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[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1995.

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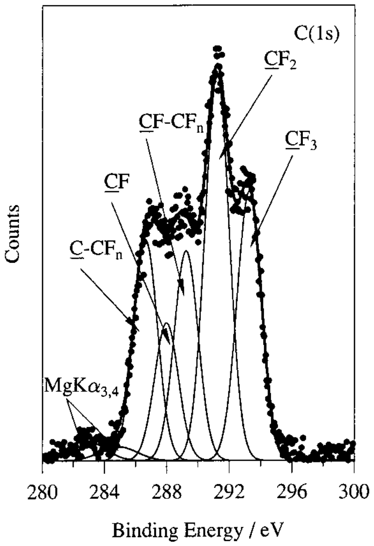

Figure 2. C(1s) XPS peak fit for a 5 W PFCH plasma polymer.

full width at half-maximum (FWHM) was used to fit the C(1s) envelope for each plasma polymer with five different carbon functionalities:[18] C-CF$_n$ (286.6 eV), CF (287.8 eV), CF-CF$_n$ (289.3 eV), CF$_2$ (291.2 eV), and CF$_3$ (293.3 eV). The CF$_3$ and CF$_2$ components could be assigned unambiguously, and so the dominant CF$_2$ feature at 291.2 eV was used as a reference offset. Mg K$\alpha_{3,4}$ satellite peaks at lower binding energies with different FWHM were also taken into account.[18] Figure 2 shows a typical C(1s) peak fit for a 5 W PFCH plasma polymer. The relative concentration of each carbon functionality was calculated by dividing the corresponding peak area by the total C(1s) area. The elemental F/C ratio for each film was calculated from the F(1s) and C(1s) peak areas taking into account the appropriate sensitivity factors.

Experiments were carried out employing discharge powers in the 1.5−40 W range, Figures 3 and 4. The composition of plasma polymers produced using powers greater than 7 W was found to be independent of discharge power and the degree of substitution of the perfluorocyclohexane precursor molecule, yielding an F/C ratio of 1.5 ± 0.03 together with 17% ± 0.5% C-CF$_n$, 31% ± 0.4% CF (total), 30% ± 0.5% CF$_2$, and 22% ± 0.5% CF$_3$. At glow discharge powers lower than 7 W, a strong variation in the relative concentration of CF$_n$ functionalities was found which depended upon the power used and the structure of the fluorocarbon monomer. In the case of PFCH the contribution of the C-CF$_n$ peak to the overall C(1s) envelope drops from 19% ± 0.7% at 7 W to 13% ± 0.7% at 1.5 W, which coincides with an increase in the CF$_2$ content from 30% ± 0.5% to 40% ± 0.5% respectively, Figure 3. In comparison, for TMCH the C-CF$_n$ content drops from 19% ± 0.7% at 7 W to 12% ± 0.7% at 1.5 W, and the CF$_2$ rises slightly from 29% ± 0.5% at 7 W to 33% ± 0.5% at 1.5W, Figure 4. The CF$_3$ contribution for PFCH remains approximately constant at 22% ± 0.5% irrespective of power, whereas for TMCH it rises from 23% ± 0.5% at 7 W to 28% ± 0.5% at 1.5 W. The chemical compositions of plasma polymers formed from monosubstituted MCH and disubstituted 12DM and 13DM at low powers fall between the values reported for the unsubstituted (PFCH) and trisubstituted (TMCH) plasma polymers. It is of interest to note that the structural isomers perfluoro-1,2-dimethylcyclohexane (12DM) and perfluoro-1,3-dimethylcyclohexane (13DM) yield identical plasma polymers at any given power. For all of the substituted perfluorocyclohexane precursors, the F/C ratios found in the plasma polymer deposits decrease with increasing electrical discharge power.

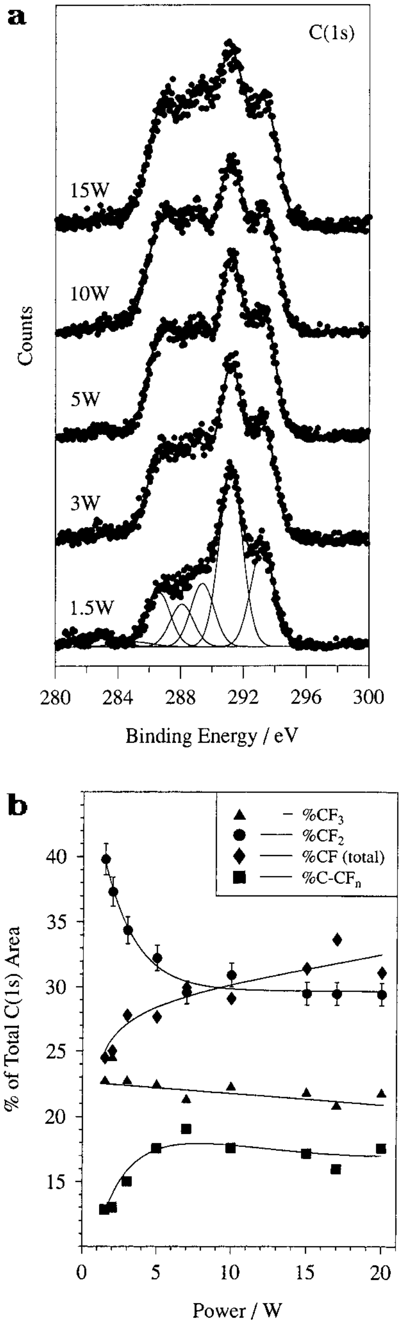

Figure 3. (a) C(1s) XPS spectra of PFCH plasma polymers deposited as a function of input power. (b) Variation in the relative CF$_n$ concentrations as a function of input power for PFCH plasma polymers.

Discussion

Plasma polymerization of cyclic fluorocarbons is an effective way of producing polymeric layers at a high deposition rate and with a high F/C ratio.[19] The effect of altering the discharge power upon the composition of plasma polymers depends not only on the geometry of the reactor, the position of the substrate, and the powers used, but also to varying degrees on the structural nature of the precursors.[3,20−24] In the present plasma polymerization study, where the only difference between the monomers is the number of trifluoromethyl

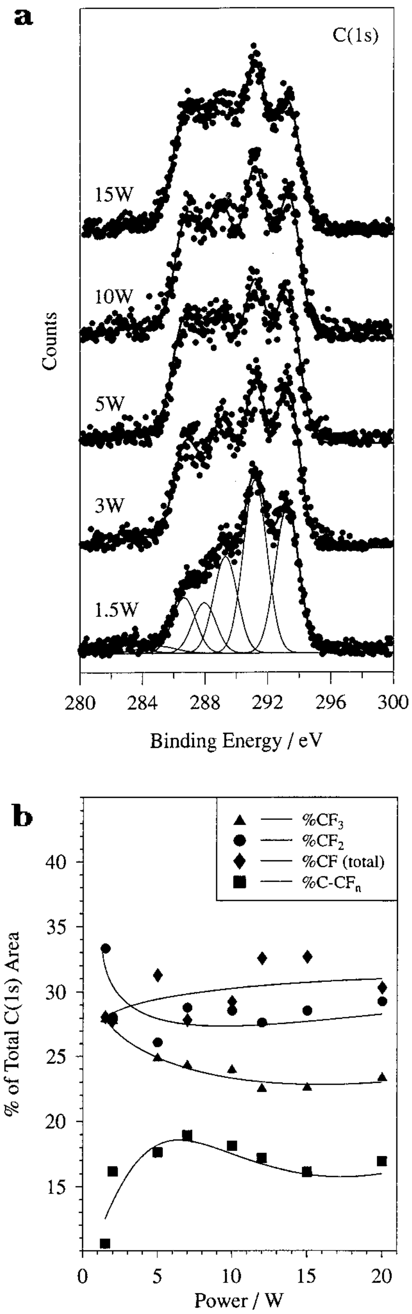

Figure 4. (a) C(1s) XPS spectra of TMCH plasma polymers deposited as a function of input power. (b) Variation in the relative CF_n concentrations as a function of input power for TMCH plasma polymers.

groups on the perfluorocyclohexane ring (ranging from 0 to 3), the relative incorporation of CF_n functional groups into the plasma polymer matrix is dependent upon the discharge power used. At discharge powers greater than approximately 7 W, the chemical composition becomes independent of monomer structure and power. This may be attributed to extensive fragmentation of the precursor molecules to yield effectively the same chemical species in the plasma phase since all of the fluorocarbon monomer structures under investigation possess the same F/C elemental ratio. However, at powers below 7 W, the structure of the deposited polymer is influenced by discharge power and also the chemical nature of the perfluoromonomer, Figure 5. For very low discharge powers the amount of CF_2/CF_3 in the plasma polymer reflects the amount of CF_2/CF_3 in the precursor molecule, Figure 5; the observed increase in

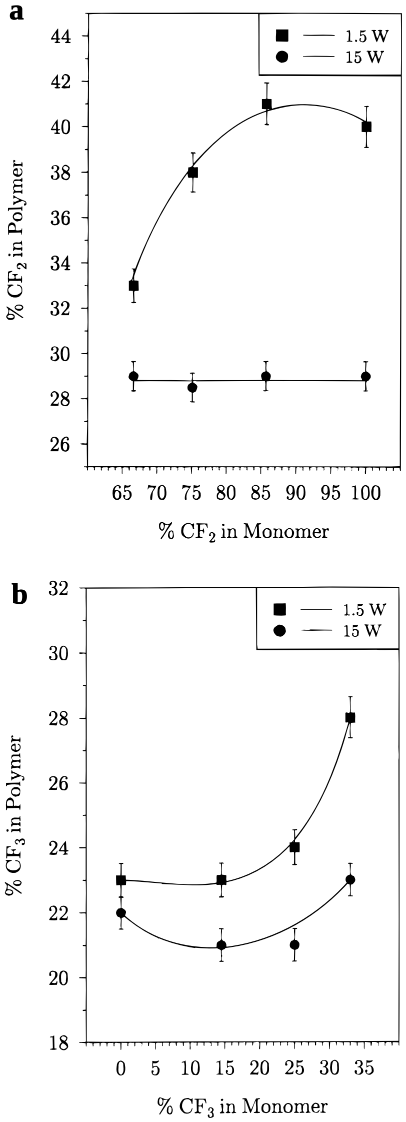

Figure 5. (a) Comparison of $\%CF_2$ found in plasma polymer as a function of $\%CF_2$ contained in the fluorocarbon precursor molecule. (b) Comparison of $\%CF_3$ found in plasma polymer as a function of $\%CF_3$ contained in the fluorocarbon precursor molecule.

CF_2 and CF_3 content is accompanied by a reduction in cross-linking. This can be attributed to less fragmentation of precursor molecules in the gas phase and/or lower ion bombardment within the growing film. The average electron energy in low-pressure glow discharges is typically only a few electron volts.[2] This is well below the energy needed for the dissociative ionization of a fluorocarbon, ~13 eV.[3] Since electrons within a plasma have a range of energies, only electrons from the high-energy tail of the distribution that will possess sufficient energy to cause dissociative ionization. A decrease in the discharge power will cause a drop in the electron population of the high-energy tail, leading to a greater number of nonfragmented precursor molecules impinging onto the growing plasma polymer surface. Increased incorporation of these nonfragmented molecules in the plasma polymer would result in the composition of the final plasma polymer bearing more of a resemblance to the starting material. Such a drop in electron energies at lower powers will also reduce the plasma potential (the substrate is at a floating potential) which will produce less ion and electron bombardment of the growing polymeric film and hence less cross-linking.[25]

A drop in the number of excited species present within the plasma at lower powers will also cause an attenuation in the VUV irradiation of the growing polymer. VUV irradiation of polymers is known to cause C−C bond scission which can lead to cross-linking.[26]

Conclusions

Plasma polymerization of perfluorocyclohexane (PFCH), perfluoromethylcyclohexane (MCH), perfluoro-1,2-dimethylcyclohexane (12DM), perfluoro-1,3-dimethylcyclohexane (13DM), and perfluoro-1,3,5-trimethylcyclohexane (TMCH) produces polymeric fluorocarbon coatings. At electrical discharge powers above 7 W, the chemical nature of the plasma polymer becomes independent of power level and monomer structure. At powers below 7 W, the structural differences between the various precursor molecules are reflected in the composition of the final plasma polymers.

Acknowledgment. A.M.H. and M.J.S. thank the CEC and Du Pont, respectively, for financial support during the course of this work.

References and Notes

(1) Yasuda, H. *Plasma Polymerization*; Academic Press: Orlando, 1985.
(2) Grill, A. *Cold Plasmas in Materials Technology*; IEEE Press: Piscataway, NJ, 1994.
(3) Clark, D. T.; Shuttleworth, D. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 27.
(4) d'Agostino, R.; Cramarossa, F.; Illuzzi, F. *J. Appl. Phys.* **1987**, *61*, 2754.
(5) Ratner, B. D.; Lopez, G. P. *J. Polym. Sci., Polym. Chem. Ed.* **1992**, *30*, 2415.
(6) Shard, A. G.; Munro, H. S.; Badyal, J. P. S. *Polym. Chem.* **1991**, *32*, 152.
(7) d'Agostino, R. D.; Favia, P.; Fracassi, F. *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 3387.
(8) Kohoma, M.; Okazaki, S.; Uchama, H. JP 06 41755, Feb 1994.
(9) Iriyama, Y.; Yasuda, T.; Cho, D. L.; Yasuda, H. *J. Appl. Polym. Sci.* **1990,** *39*, 249.
(10) O'Kane, D. F.; Rice, D. W. *J. Macromol. Sci., Chem.* **1976**, *A10*, 567.
(11) Sato, K.; Omae, S.; Kojima, K.; Hashimoto, T.; Koinuma, H. *Jpn. J. Appl. Phys.* **1988**, *27*, L2088.
(12) Clarotti, G.; Schue, F.; Sledz, J.; Geckeler, K. E.; Göpel, W.; Orsetti, A. *J. Membr. Sci.* **1991**, *61*, 289.
(13) Clarotti, G.; Aoumar, A. A. B.; Schué, F.; Sledz, J.; Geckeler, K. E.; Flösch, D.; Orsetti, A. *Makromol. Chem.* **1991**, *192*, 2581.
(14) Yasuda, H.; Hsu, T. S. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2411.
(15) Shard, A. G.; Munro, H. S.; Badyal, J. P. S. *Polym. Chem.* **1991**, *32*, 152.
(16) Ehrlich, C. D.; Basford, J. A. *J. Vac. Sci. Technol.* **1992**, *A10*, 1.
(17) Wagner, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, J. F.; Muilenberg, G. E. *Handbook of X-Ray Photoelectron Spectroscopy*; Perkin-Elmer Corporation: Eden Prairie, MN, 1978.
(18) Wells, R. K.; Ryan, M. E.; Badyal, J. P. S. *J. Phys. Chem.* **1993**, *97*, 12879.
(19) Clark, D. T.; Shuttleworth, D. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 27.
(20) Clark, D. T.; Shuttleworth, D. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 407.
(21) Clark, D. T.; Abrahman, M. Z. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 2129.
(22) Clark, D. T.; Abrahman, M. Z. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 2689.
(23) Clark, D. T.; Abrahman, M. Z. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 691.
(24) Clark, D. T.; Abu-Shbak, M. M. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2907.
(25) O'Keefe, M. J.; Rigsbee, J. M. *J. Appl. Polym. Sci.* **1994**, *53*, 1631.
(26) Hudis, M.; Prescot, L. E. *Polym. Lett.* **1972**, *10*, 179.

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