potential ($\sim 10^{-2}\ \Omega^{-1}\ \mathrm{cm}^{-1}$) is still much greater than that of the neutral film ($<10^{-6}\ \Omega^{-1}\ \mathrm{cm}^{-1}$).

Parts of c and d of Figure 1 show the cyclic voltammogram and the I_D–V_G characteristic, respectively, of polyacetylene in tetrahydrofuran/0.1 M [(n-Bu)$_4$N]AsF$_6$. The I_D–V_G curve shows that polyacetylene also has a finite potential window of high conductivity (~0.9 V wide) when it is reduced. A maximum in conductivity as a function of potential for electrochemically reduced polyacetylene has been reported previously.[21] Integration of the voltammogram in Figure 1c indicates that at the potential of maximum conductivity, polyacetylene is reduced to the extent of ~0.05 electron/double bond, while at the negative potential limit shown, the polymer is reduced by ~0.1 electron/double bond. Figure 1d shows a ~100-fold difference in conductivity for the reduced and oxidized polyacetylene film. A similar finding has been reported for reduced vs oxidized polythiophenes.[3] The conductivity of reduced polyacetylene has been reported to be quite sensitive to the size of the intercalating cation.[22] However, we obtain similar conductivities using either [(n-Bu)$_4$N]AsF$_6$ or NaAsF$_6$ as the electrolyte. Unoriented Durham polyacetylene has been reported to be substantially less crystalline than polyacetylene prepared by other methods,[17] and this may explain why the maximum conductivity does not show a cation dependence. The highest conductivities reported to date for oxidized polyacetylene[19] are significantly larger than any high conductivities reported for reduced polyacetylene;[23] however, this is the first time that conductivities of oxidized and reduced polyacetylene have been compared in a single experiment on the same sample. These results establish that the intrinsic conductivity of reduced polyacetylene is significantly lower than that of oxidized polyacetylene, as is indicated by published data.[19,21,23,24] They are also in agreement with calculations predicting higher conductivity for polyacetylene when it is oxidized than when it is reduced,[25] which, in turn, are based on calculations that anions are more localized on polyacetylene chains than are cations.[5]

The observation of a finite potential window of high conductivity for polyacetylene is consistent with theoretical expectations and establishes that this effect is general for conducting polymers. It appears that polyacetylene, the most highly conducting of these polymers, also has the widest potential window of high conductivity upon oxidation and that it is more conducting when oxidized than when reduced. We are currently making use of our ability to synthesize highly monodisperse polyacetylene and polyene oligomers[8,9] in order to study the dependence of conductivity upon chain length.

Acknowledgment. We thank the Office of Naval Research, the Department of Energy, the Defense Advanced Research Projects Agency, and the National Science Foundation through the M.I.T. Materials Research Laboratory for partial suppot of this research.

---

(21) Shacklette, L. W.; Toth, J. E. *Phys. Rev. B* **1985**, *32*, 5892.

(22) Ignatious, F.; François, B.; Mathis, C. *Synth. Met.* **1989**, *32*, 283.

(23) Mathis, C.; Francois, B. *Makromol. Chem. Rapid Commun.* **1984**, *5*, 359.

(24) (a) MacDiarmid, A. G.; Heeger, A. J. *Synth. Met.* **1980**, *1*, 101. (b) MacDiarmid, A. G.; Kaner, R. B. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Chapter 20. (c) Pekker, S.; Jánossy, A. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Chapter 2. (d) Chien, J. C. W. *Polyacetylene: Chemistry, Physics and Materials Science*; Academic Press: London, 1984.

(25) Phillips, P.; Wu, H., submitted for publication.

Molecular Control of Surface Film Compositions via Pulsed Radio-Frequency Plasma Deposition of Perfluoropropylene Oxide

Charles R. Savage and Richard B. Timmons*

Department of Chemistry, Box 19065
The University of Texas at Arlington
Arlington, Texas 76019-0065

Jacob W. Lin

Polytronix Inc., 805 Alpha Drive
Richardson, Texas 75081

Received February 28, 1991
May 13, 1991

Surface modifications employing plasma polymerizations represent a very active research area at the present time.[1] Examples of improved surface properties obtained via this approach have been demonstrated with materials employed in biocompatibility studies,[2] inert coatings to reduce oxidative degradation,[3] and membrane permselectivity[4] to mention but a few of the many applications under current development. To date, the overwhelming majority of these plasma polymerization studies have been carried out using continuous wave (CW) systems with an emphasis on adjusting plasma variables (e.g., reactant pressure and flow rate, absorbed radio-frequency (rf) power) to produce uniform films on targeted substrates.

The purpose of the present communication is to illustrate that the use of a pulsed rf plasma, in lieu of the CW mode, can provide an important added dimension in plasma-induced surface modifications. Specifically, we wish to report a level of control over the molecular composition of the surface modifications achieved as a function of the rf duty cycle employed. This surface modification controllability is demonstrated in the present case by the pulsed rf plasma deposition of hexafluoropropylene oxide (C_3F_6O) in which marked changes in film composition are noted as a function of the rf duty cycles employed. The variation in molecular composition of the surface depositions is established by both XPS and FT-IR analyses of the resultant films.

The pulsed rf plasma polymerizations were carried out in a cylindrical Pyrex glass reactor 10 cm wide and 30 cm in length. Rf power was provided to the reactor through two concentric rings located around the exterior of the reactor. The rf circuitry included function and pulse generators, rf amplifier, frequency counter, and matching network (with wattmeter) to minimize reflected power. An oscilloscope was employed in tuning the rf circuit under pulsing conditions. All reactor variables such as rf frequency (13.56 MHz), monomer pressure (0.43 torr), flow velocity (9.6 cm^3 min^{-1}), rf power (300 W), and positioning of the substrate samples in the reactor were held constant. In this way, the influence of the variable rf duty cycle on molecular composition of the films obtained was isolated. Substrates employed were mainly polished silicon and KCl

---

(1) See: Symposium on Plasma Polymerization and Plasma Interactions with Polymeric Materials; Division of Polymeric Materials: Science and Engineering, ACS National Meeting, Spring 1990, Boston, MA.

(2) Hoffman, A. S. *J. Appl. Polym. Sci.; Appl. Polym. Symp.* **1988**, *42*, 251.

(3) Wydeven, T.; Golub, M. A.; Lerner, N. R. *J. Appl. Polym. Sci.* **1989**, *37*, 3343.

(4) Inagaki, N.,; Kawai, H. *J. Polym. Sci.: Part A, Polym. Chem.* **1986**, *24*, 3381.

0897-4756/91/2803-0575$02.50/0

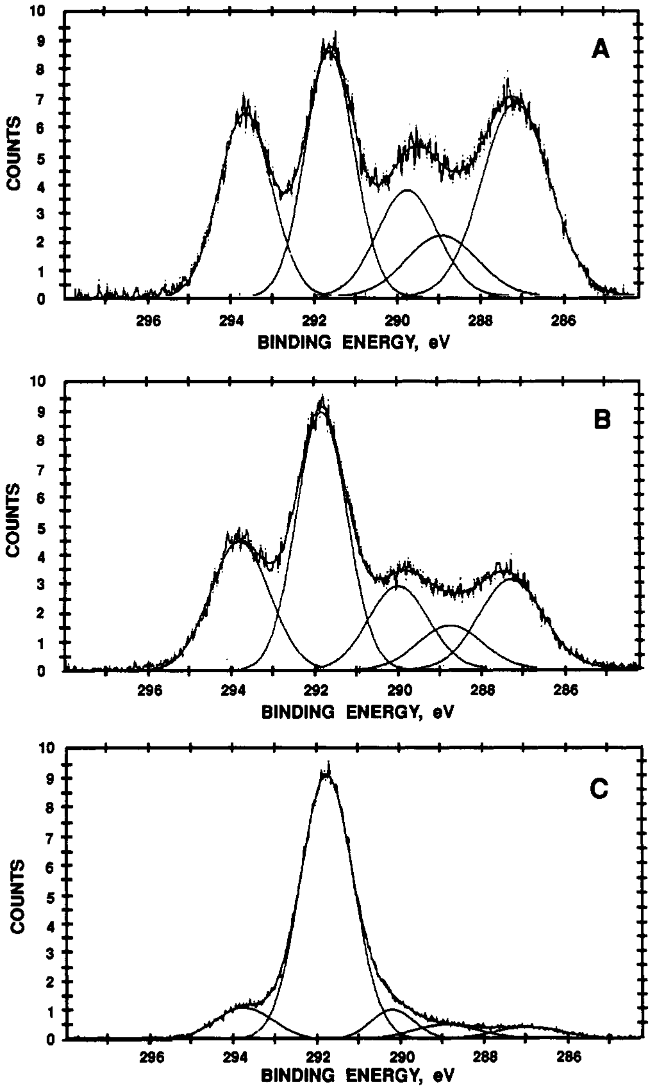

Figure 1. C(1s) X-ray photoelectron spectra obtained for plasma depositions of C_3F_6O on a silicon substrate as a function of rf duty cycle. Duty cycles expressed as ratio of on:off times (in ms): (A) 10/60, (B) 10/100, and (C) 10/200.

disks. Substrates were treated with a CW argon plasma at 0.7 Torr for 10 min prior to the plasma polymerization step. The pulsed rf plasma depositions were carried out using a constant "on" time followed by an "off" period that was varied systematically in duration. The on/off duty cycle times employed (in ms) were 10/20, 10/60, 10/100, 10/200, 10/400, 10/600, and 10/1000. In general, plasma depositions were carried out for a total elapsed time (on + off) of 30 min per run. CW experiments carried out with the C_3F_6O monomer under reaction conditions identical with those described above resulted in virtually no substrate film formation.

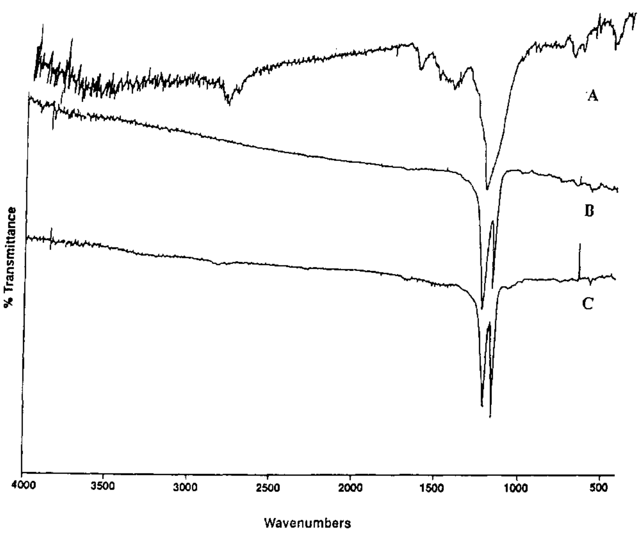

Figure 2. FT-IR absorption spectra of plasma deposited films of C_3F_6O on a KCl disk as a function of rf duty cycle. Duty cycles expressed as a ratio of on:off times (in ms): (A) 10/20, (B) 10/200, and (C) 10/400.

Table I. Atomic Ratios of Films Deposited in the Pulsed Rf Plasma Polymerization of C_3F_6O As Obtained by XPS Analysis

rf duty cycle on/off, ms	% F	% C	% O	% Si	F/C
10/60	56.1	39.2	3.7	1.0	1.4
10/100	60.9	38.5	0.6	0	1.6
10/200	66.1	33.9	0	0	1.9
10/1000	67.5	32.5	0	0	2.1

The variations in surface molecular compositions as a function of rf duty cycle are documented by spectroscopic analysis of the plasma deposited films. Figure 1 shows high-resolution C(1s) XPS spectra obtained for films produced at on/off duty cycles of 10/60, 10/100, and 10/200. These spectra, resolved into Gaussian subpeaks as shown, can be used to identify and quantify the types of carbon atoms positioned in various chemical bonding environments. The curve-fitting procedure involving only five separate C(1s) functionalities provides a good fit of the experimental XPS peaks, as shown in Figure 1. This curve-fitting procedure results in C(1s) binding energy peak maxima at approximately 294, 292, 290, 289, and 287.5 eV. The assignment of high-resolution C(1s) fluorocarbon XPS spectra has been the subject of numerous previous studies of fluorocarbon polymers.[3,5-10] The results from these previous studies suggest the following C(1s) binding energy assignments: 294 eV (CF_3); 292 eV (CF_2); 290 eV (CF–CF_n); 289 eV (CF); 287.5 eV (C–CF_n). There is abundant evidence and consistent agreement among previous workers concerning assignment of the two highest binding energy peaks (i.e., CF_3 and –CF_2–). The remaining assignments, although somewhat less unequivocal, are consistent with both predicted C(1s) binding energy shifts as a function of fluorine atom substitution[6] and with previous assignments in the plasma polymerization of fluorocarbon monomers.[9]

Regardless of the exact functionalities represented by these lower binding energy C(1s) peaks, the significant fact revealed by this XPS analysis is that a well-defined systematic change in the plasma-deposited film composition is noted with variation in the RF duty cycle employed. As revealed in Figure 1, decreasing the rf duty cycle results in progressive and substantial growth of the –CF_2– groups with decreasing rf duty cycle. The shift in molecular composition with varying rf duty cycle is corroborated by elemental composition data obtained by XPS analysis and summarized in Table I. As shown by these data, there is a progressive increase in the observed F/C ratio with decreasing rf duty cycle consistent with that anticipated

---

(5) Clark, D. T.; Feast, W. J.; Ritchie, I.; Musgrave, W. K. R.; Modena, M.; Ragazzini, M. *J. Polym. Sci.* **1974**, *12*, 1049.

(6) Clark, D. T.; Shuttleworth, D. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 27.

(7) Strobel, M.; Corn, S.; Lyons, C. S.; Korba, G. A. *J. Polym. Sci.: Part A, Polym. Chem.* **1987**, *25*, 1295.

(8) Strobel, M.; Thomas, P. A.; Lyons, C. S. *J. Polym. Sci.: Part A, Polym. Chem.* **1987**, *25*, 3343.

(9) Haque, Y.; Ratner, B. D. *J. Appl. Polym. Sci.* **1986**, *32*, 4369.

(10) Wang, D.; Chen, J. *J. Appl. Polym. Sci.* **1991**, *42*, 233.

from the peak assignments in Figure 1. The virtual complete absence of oxygen atom incorporation in the films, despite the presence of oxygen in the starting monomer, is quite unexpected. The F/C ratios obtained at the lowest rf duty cycles represent unusually large values for plasma-polymerized fluorocarbons but they are consistent with the XPS spectral results in Figure 1, revealing mainly CF_3– and –CF_2– groups at the lowest duty cycles. It is clear that a decrease in rf duty cycle results in a progressively less branched polymeric film structure.

The variation in the molecular composition of the plasma-deposited surface films with changing rf duty cycles is further substantiated by IR absorption absorption spectra as shown in Figure 2. The spectra in Figure 2 represent film obtained at rf duty cycles of 10/20, 10/200, and 10/400 (curves A, B, and C, respectively). The absorptions between 1100 and 1300 cm^{-1} are characteristic of C–F stretching vibrations as reported for many fluorocarbon compounds.[11] As shown in Figure 2A, the C–F absorption band obtained at an rf duty cycle of 10/20 is broad and devoid of any significant structure. However, decreasing the rf duty cycle results in a significant change in this absorption band (Figure 2B,C) in that a clear doublet structure is now observed in the C–F stretching region. The presence of this doublet must reflect a more highly ordered structure than that observed at the higher duty cycle. The higher degree of molecular order at low duty cycles observed in the IR spectra is consistent with the molecular structural changes with varying rf duty cycle revealed by XPS analysis. The structured IR band observed at low duty cycles is remarkable for plasma deposited films and can be contrasted with the broad C–F absorption bands reported in previous plasma polymerization of fluorocarbons.[12] It is surprising to note that we do not observe the lower frequency bending and rocking modes (between 500 and 650 cm^{-1}) observed in linear –CF_2– polymers such as Teflon.[13] Apparently, despite the dominant presence of –CF_2– groups in our low rf duty cycle depositions, the resulting polymeric structure inhibits these low-frequency vibrational modes.

Thus, as documented above, the use of a pulsed rf plasma with C_3F_6O results in a dramatic variation in surface composition with varying rf duty cycle. Limited previous work with pulsed plasmas revealed changes in molecular surface compositions[14] as well as in the physical properties of the films obtained.[15] However, the present study, involving a wider range of rf duty cycles, reports a more extensive level of film compositional control than implied by previous workers using the pulsed technique.

Other workers employing techniques such as control of substrate temperatures,[16] variation of absorbed power under CW conditions,[17] and location of substrates at varying distances from the glow discharge region[18,19] have also demonstrated the ability to control substrate surface functionality obtained during plasma depositions. We are currently working to identify the range of surface tailoring available through the use of pulsed rf plasmas via studies with other monomers. In subsequent reports, we plan to contrast and compare the level of surface film compositional control obtainable in pulsed plasmas with those available with variations of other plasma variables such as those cited above.

Acknowledgment. This material is based, in part, upon work supported by the Governor's Energy Management Center—State of Texas Energy Research in Applications Program under Contract No. 003656-005.

Registry No. C_3F_6O (homopolymer), 25038-02-2; C_3F_6O (SRU), 62253-59-2.

---

(11) See: *Aldrich Library of Infrared Spectra*, 2nd ed.; Aldrich Chemical Co., Milwaukee, WI, 1975; p 39.

(12) See: Hasuda, Y. *Plasma Polymerization*; Academic Press: New York, 1986; p 182.

(13) Hummel, D. O. *Infrared Analysis of Polymers, Resins and Additives, An Atlas*; Wiley-Interscience: New York, 1971; p 154.

(14) Nakajima, K.; Bell, A. T. *J. Appl. Polym. Sci.* **1979**, *23*, 2627.

(15) Yasuda, H.; Hsu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 81.

(16) Lopez, G.; Ratner, B. D. *ACS Polym. Mater. Sci. Eng.* **1990**, *62*, 14.

(17) Krishnamurthy, V.; Kamel, I. L.; Wei, Y. *J. Polym. Sci.: Part A, Polym. Chem.* **1989**, *27*, 1211.

(18) O'Kane, D. F.; Rice, D. W. *J. Macromol. Sci., Chem.* **1976**, *A10*(3), 567.

(19) Yasuda, H. *J. Polym. Sci., Macromol. Rev.* **1981**, *16*, 199.