Selective Incorporation of Perfluorinated Phenyl Rings during Pulsed Plasma Polymerization of Perfluoroallylbenzene

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Pulsed plasma polymerization of perfluoroallylbenzene can lead to the deposition of films containing high concentrations of perfluorinated phenyl groups. X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, and deposition rate measurements have shown that low duty cycles give rise to minimal precursor fragmentation accompanied by conventional free radical polymerization during the off-period.

1. Introduction

The very nature of plasma polymerization lends itself to extensive molecular rearrangements during film deposition. Ultraviolet photons, electrons, ions, as well as excited neutrals all possess sufficient energy to dissociate the precursor into many fragments that often bear little or no resemblance to the molecular structure of the original monomer.[1-3] On this basis, any attempts to control the chemical structure of a plasma polymer face inherent difficulties. In spite, or may be even because of this, the quest for retention of precursor functionalities during plasma polymerization has been actively pursued by a number of researchers.[4-12] Ultimately, control over the composition of deposited films offers a completely dry route to chemically tailored surfaces. The approaches taken to achieve structural retention in the final plasma polymer fall into two broad categories: The first involves changing the physical characteristics of the reaction system such as reactor design,[4] power,[5] pressure,[6] flow rate,[7,8] excitation frequency,[9,10] substrate temperature,[11] bias,[12] etc. Alternatively, the chemistry occurring within the reactor can be controlled by a judicious choice of precursor structure,[13] carrier gas,[14] reactant mixtures,[15] and even substrate composition.[16,17] In reality, most investigations involve finding the optimum balance between physical and chemical parameters to yield the desired products. The most successful method to date has been pulsing the electrical discharge on the ms–μs time scales.[18,19] Here, in some cases, structural retention can be attributed to very low average powers, whereas for other monomers, two distinct reaction regimes are present which correspond to the duty cycle on- and off-periods. Plasma polymer films containing high levels of perfluoromethylene,[18,20] trifluoromethyl,[21] hydroxyl,[22] and anhydride[19] groups have been successfully prepared by this technique.

In the past, continuous wave (CW) plasma polymers made from phenyl-containing monomers[23-29] have found application in protective and impermeable coatings,[30-33]

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reverse osmosis membranes,[34] permselective membranes,[35] thin film capacitors,[36,37] semiconductive thin films,[38] dielectric layers,[39] and electroluminescent thin films.[40] In this article, we examine whether pulsed plasma polymerization can lead to a significant enhancement in phenyl center incorporation during deposition. Perfluoroallylbenzene, C_9F_{10}, has been selected as the precursor, because this molecule consists of two potentially reactive functionalities, namely, the perfluorinated phenyl group and the perfluorinated allyl substituent. It is well established that both of these functional groups can undergo CW plasma polymerization.

Perfluoroallylbenzene
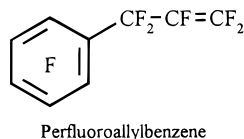
2. Experimental Section

Low-pressure 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.[41] This reactor was continuously pumped by a 33 dm^3 h^{-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 $<2.3 \times 10^{-12}$ kg s^{-1} (calculated assuming ideal gas behavior[42]). A 13.56 MHz radio frequency generator was inductively coupled to the gas via a LC matching circuit and a copper coil (0.5-cm diameter, 10 turns) wound externally around the reaction chamber spanning 8−16 cm from the gas inlet. The substrate was positioned in the center of the glow region. In the case of electrically pulsed plasma polymerization experiments, the rf power source was triggered by a signal generator, and a cathode ray oscilloscope monitored the pulse duration, interval and amplitude. The pulse rise and fall times were measured to be <100 ns. The peak power (P_p) delivered to the copper coil could be altered between 20 and 200 W, and on-times (t_{on}) and off-times (t_{off}) varied between 5 and 8000 μs. The average power ($\langle P \rangle$) delivered during pulsing was calculated using the following expression:[43]

$$\langle P \rangle = P_p \left(\frac{t_{on}}{t_{on} + t_{off}} \right) \quad (1)$$

Prior to each experiment, the reactor and glass substrate slides were scrubbed with detergent, rinsed in isopropyl alcohol, oven dried, and then cleaned with a 50 W air plasma at a pressure of 0.2 mbar for 30 min. Perfluoroallylbenzene (Aldrich) was placed in a Pyrex monomer tube and then deaerated using freeze−thaw cycles. The cleaned reactor was pumped to base pressure, and 0.2 mbar of monomer vapor was introduced at a flow rate of ∼1.45×10^{-7} kg s^{-1}. The electrical discharge was ignited and sustained for 10 min after which the rf power supply was switched off and the system was purged with monomer for a further 2 min prior to venting up to atmosphere.

A Kratos ES300 X-ray photoelectron spectrometer equipped with an unmonochromated magnesium 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 30° takeoff angle from the substrate normal with a concentric hemispherical analyzer (CHA) operating in fixed retardation ratio mode (FRR = 22:1). The spectrometer was calibrated with respect to the Au(4f$_{7/2}$) peak at 83.8 eV [full-width-at-half-maximum (fwhm) = 1.2 eV].[44] High resolution C(1s), O(1s), F(1s), and Si(2p) X-ray photoelectron spectroscopy (XPS) spectra were acquired for all the deposited plasma polymers. Instrumentally determined sensitivity factors for unit stoichiometry were taken as C(1s):O(1s):F(1s):Si(2p) equal to 1:00:0.62:0.53:1.08. Absence of any Si(2p) signal was indicative of complete coverage of the glass substrate.

Transmission infrared (IR) absorption spectra were acquired using a Mattson Polaris Fourier transform IR (FTIR) spectrometer. The liquid monomer was analyzed as a thin film sandwiched between two potassium bromide disks, whereas plasma polymer layers were deposited onto one side of a KBr disk. Typically, 100 scans were collected at a resolution of 4 cm^{-1}.

Deposition rate measurements were made by monitoring the change in mass of a quartz crystal sensor (Kronos QM300) located in the plasma reactor. Careful isolation of the crystal and electronics from the rf power input allowed in situ monitoring of the plasma polymer deposition process.

3. Results and Discussion

For each plasma polymer layer, the C(1s) XPS envelope was fitted with a range of carbon functionalities using a Marquardt minimization computer program:[45] $\underline{C}-CF_n$ (286.6 eV); $\underline{C}F$ (288.4 eV); $\underline{C}F-CF_n$ (289.4 eV); $\underline{C}F_2$ (291.2 eV); and $\underline{C}F_3$ (293.3 eV). The CF$_2$ peak could always be unambiguously assigned and therefore served as the reference offset at 291.2 eV. Gaussian peak shapes assuming a fixed relative fwhm were employed;[46] fwhm values typically varied between 2.0 and 2.6 eV. An additional small component at ∼295 eV (which is too high in energy to be associated with a direct photoionization peak) was taken as corresponding to $\pi-\pi^*$ shake-up satellite transitions associated with the dominant unsaturated $\underline{C}-F$ linkages centered at 288.4 eV.[47] The Mg K$\alpha_{3,4}$ satellite peaks with different fwhm values were also taken into account toward lower binding energies.[44] The relative concentration of each type of carbon functionality was obtained by dividing the corresponding peak area by the total C(1s) envelope area. The accompanying F(1s) peak centered at 688.3 eV had fwhm values ranging between 2.7 and 2.9 eV. The F/C ratios were calculated for each film using the F(1s) and C(1s) peak areas. Oxygen incorporation into the plasma polymer layers was always found to be

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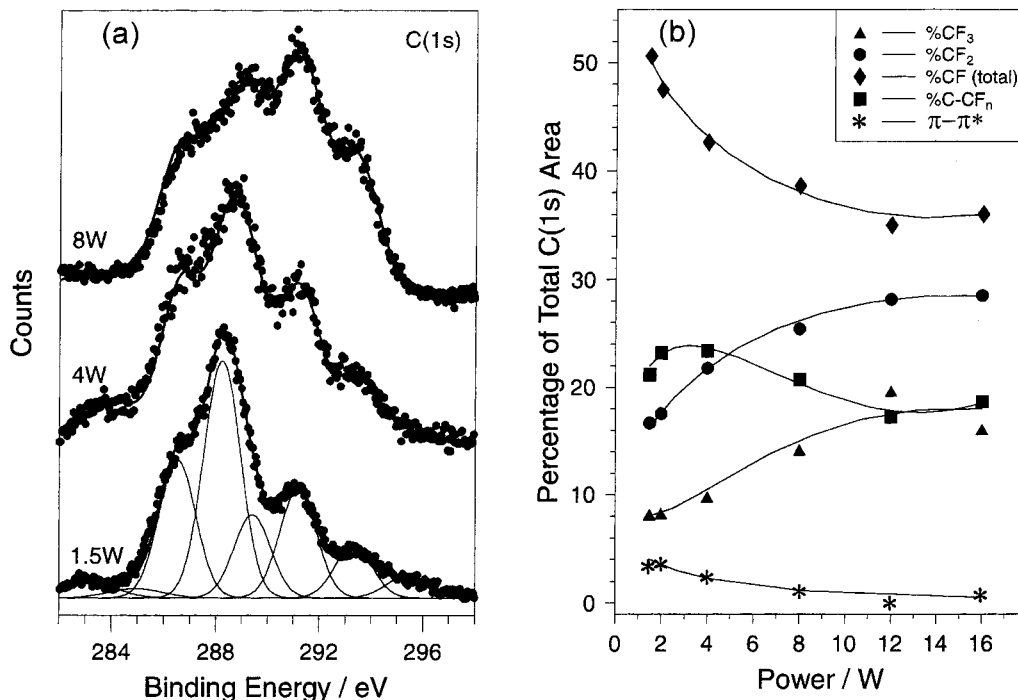(47) Clark, D. T. In *Advances in Polymer Science*, Cantow, H. J., Ed.; Springer-Verlag: Berlin, 1977; Vol. 24, p 125.

Figure 1. Continuous wave plasma polymerization as a function of power: (a) C(1s) XPS spectra; and (b) carbon functionality concentration expressed as a percentage of the total C(1s) peak area.

<1.5% (this small amount is most likely due to reaction of uncapped free radical sites reacting with the atmosphere during sample transfer from the plasma reactor to the XPS spectrometer).

The change in appearance of the overall C(1s) XPS spectra with increasing discharge power during continuous wave plasma polymerization is shown in Figure 1. At low powers, the most intense components correspond to $\underline{C}F$ and $\underline{C}F - CF_n$; that is, $\underline{C}F$(total), which reaches a value of 50% at 1.5 W (compared to 67% in the monomer). The proportion of highly fluorinated carbon centers (i.e., $\underline{C}F_2$ and $\underline{C}F_3$) become more prominent with rising power levels.

The overall power input could also be adjusted by varying the duty cycle parameters during electrical pulsing of the glow discharge. Increasing t_{off} at a fixed t_{on} of 10 μs and 70 W peak power resulted in greater retention of the functionalities associated with the precursor molecule; that is, reaching 58% $\underline{C}F$(total) and a F/C ratio of 0.97 (compared with 67% $\underline{C}F$ and a F/C ratio of 1.11 for perfluoroallylbenzene; Figure 2). Shorter off-times, especially <1000 μs, give rise to incorporation of other functionalities, particularly $\underline{C}F_3$ and $\underline{C}F_2$ at the expense of $\underline{C}F$(total). Comparable behavior was also evident for variable t_{on} experiments (where t_{off} = 6000 μs and peak power = 70 W; Figure 3). Shorter on-times resulted in a plasma polymer structure bearing a greater resemblance to the perfluoroallylbenzene monomer. Again, the $\underline{C}F$(total) concentration approached 58% and the F/C ratio dropped from 1.5 to 0.9 with decreasing average power (i.e., shortening on-times). This trend is consistent with greater incorporation of the carbon-rich perfluoro-phenyl ring into the growing film at lower average powers.

Infrared spectra of perfluoroallylbenzene and all the deposited plasma polymers displayed no absorption peaks above 2000 cm^{-1}, which is typical of most per-

fluoro-compounds.[48] The IR absorption spectrum of the precursor molecule, showed absorption bands at 1788-(s), 1655(m), 1530(s), 1510(s), 1427(w), 1356(s), 1335-(s), 1295(s), 1175(s), 1082(m), 1001(s), 966(s), 812(s), 737(w), and 685(w) cm^{-1}. Spectra of the CW and pulsed plasma polymers are shown in Figure 4. Of most significance is the behavior of the peaks at 1788 and 1655 cm^{-1} and the doublet at 1530/1510 cm^{-1}. The absorption at 1788 cm^{-1} can be assigned to C=C stretching of the double bond contained in the allyl substituent[49-52] whereas the 1655 cm^{-1} peak and 1530/1510 cm^{-1} doublet can be attributed to C−C$_{(aromatic)}$ stretching of the perfluorinated phenyl group.[53] Upon increasing average discharge power during plasma polymerization, all of these peaks gradually disappear, thereby indicating loss of both the allyl and aromatic functionalities. At lower average powers (i.e., low CW powers), long off-times, or short on-times, a corresponding increase in intensity of the C−C$_{(aromatic)}$ stretching peaks (1655 cm^{-1} and 1530/1510 cm^{-1}) is evident. However, the allyl substituent peak at 1788 cm^{-1} is diminished to a far greater extent than what might be expected on the basis of the IR absorption spectrum characteristic of the perfluoroallylbenzene precursor molecule. This result suggests that reaction is occurring preferentially at the allyl group C=C double bond at lower average powers, which is consistent with the allyl group being more susceptible toward activation during

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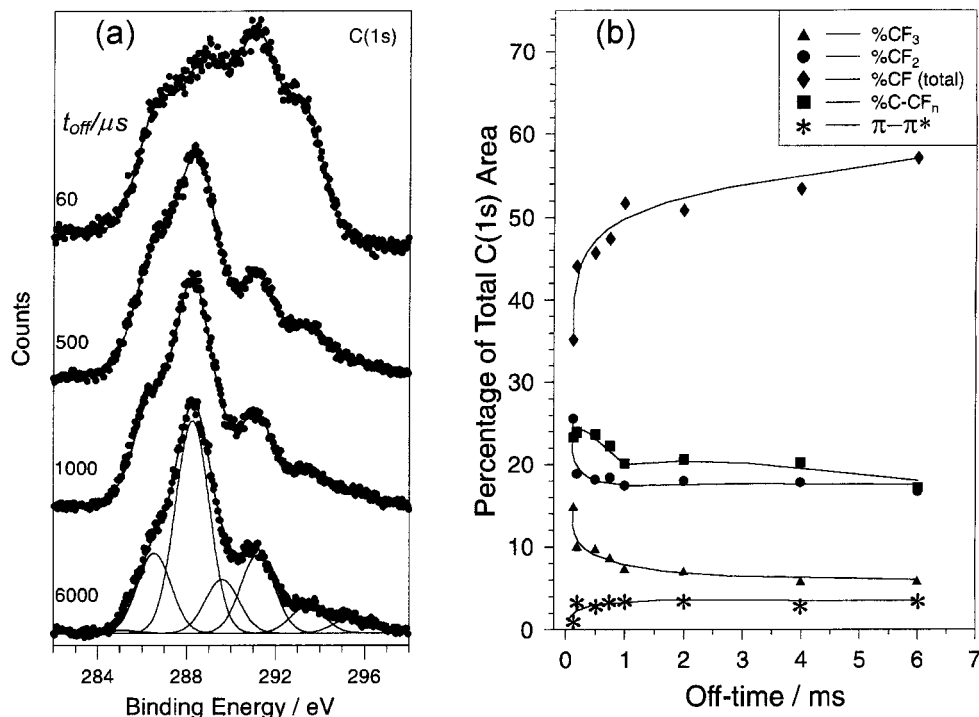
Figure 2. Pulsed plasma polymerization as a function of t_{off} (t_{on} = 10 μs, P_p = 70 W): (a) C(1s) XPS spectra; and (b) carbon functionality concentration expressed as a percentage of the total C(1s) peak area.

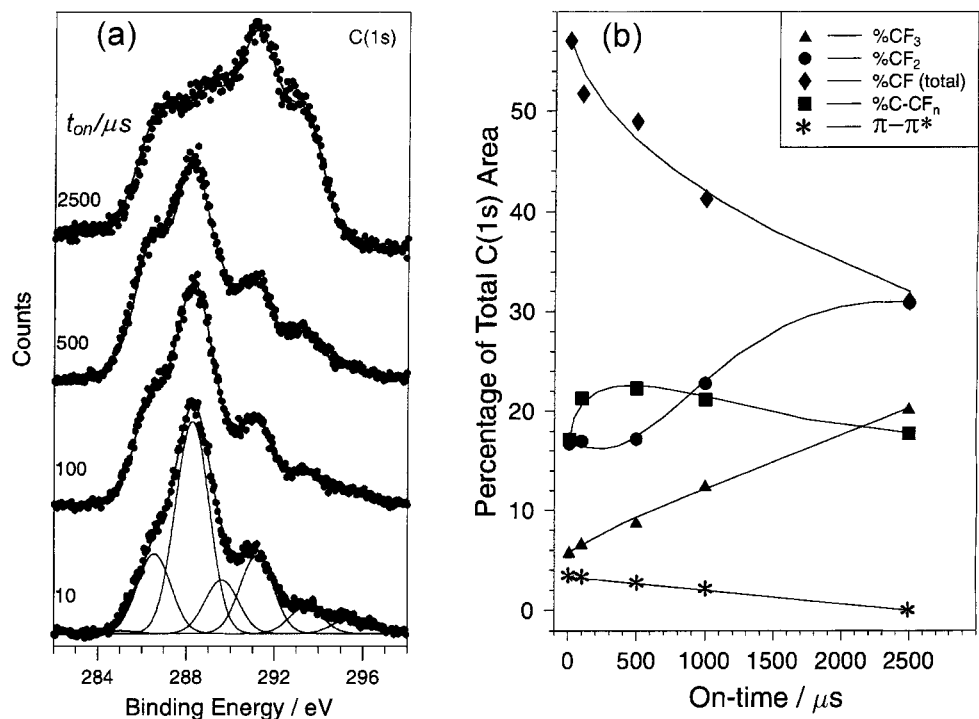**Figure 3.** Pulsed plasma polymerization as a function of t_{on} (t_{off} = 6000 μs, P_p = 70 W): (a) C(1s) XPS spectra; and (b) carbon functionality concentration expressed as a percentage of the total C(1s) peak area.

the on-time of the pulsing cycle, and conventional free radical polymerization reactions[54] within the off-period. By using a fixed duty cycle, peak power, and average power, it can be demonstrated that the observed variation in structural retention is not just simply due to a decreasing average power effect but rather the time scale of pulsing is important (Figure 4d). Peaks in the

1400−1000-cm^{-1} region are difficult to assign unambiguously but are characteristic of C−F stretching vibrations for fluorocompounds.[50,54]

In an attempt to gain further mechanistic understanding concerning the effect of electrical pulsing upon plasma polymerization, deposition rate studies were undertaken using a gold-coated quartz crystal placed into the center of the glow region. The resonant frequency of the crystal is related to the mass of the

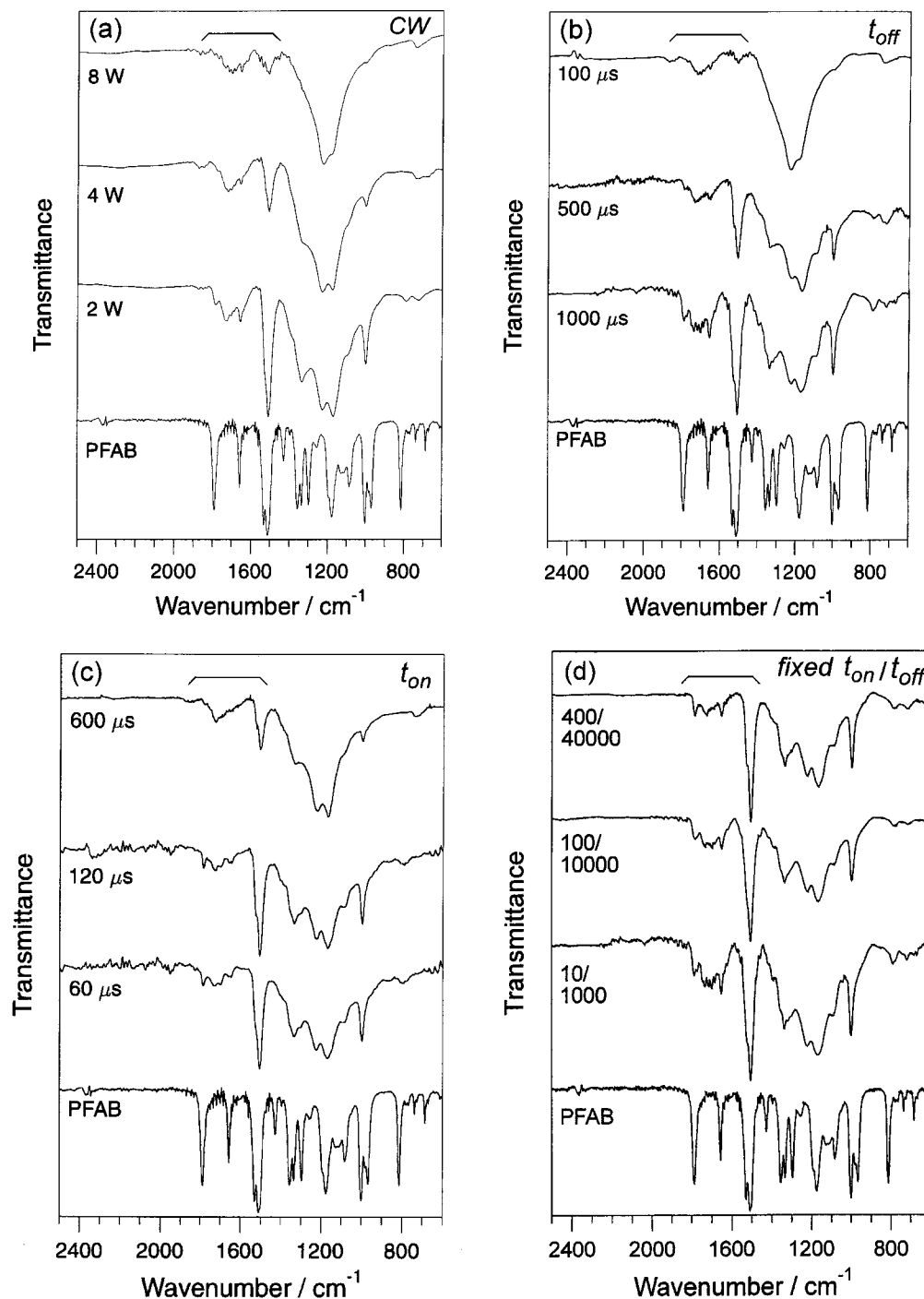(54) Chambers, R. D. *Fluorine in Organic Chemistry*; Wiley & Sons: London, 1973.

Figure 4. Transmission FTIR spectra of plasma polymers: (a) continuous wave; (b) pulsed as a function of t_{off} ($t_{on} = 10\ \mu$s, $P_p = 70$ W); (c) pulsed as a function of t_{on} ($t_{off} = 6000\ \mu$s, $P_p = 70$ W); and (d) pulsed as a function of duty cycle frequency with fixed average power, peak power, and duty cycle ratio ($\langle P \rangle = 0.7$ W, $P_p = 70$ W).

crystal. By monitoring the thickness of film deposited over time, the deposition rate of the plasma polymer was calculated. Figure 5(a) shows the effect of increasing off-time on the film thickness; as expected, this leads to a drop in deposition rate due to the reduced power input into the system. To factor out the effect of variation in average power, the deposition rate per Joule[55] was considered. This rate gives an indication of the amount of polymer formed per unit of energy supplied to the discharge. The deposition efficiency in

Angstroms/Joule was calculated as follows

$$\text{deposition efficiency (Å/J)} = \frac{\text{dep. rate (Å/s)}}{\text{average power (J/s)}} \quad (2)$$

The increase in deposition efficiency observed for longer off-periods can be attributed to conventional free radical polymerization processes occurring during the off-portion of the duty cycle because the species that undergo initiation during the on-time (via UV irradiation, ion or electron bombardment, etc.) have more time to polymerize either in the gas phase or at the gas/substrate interface (Figure 5b). The on-time reactions

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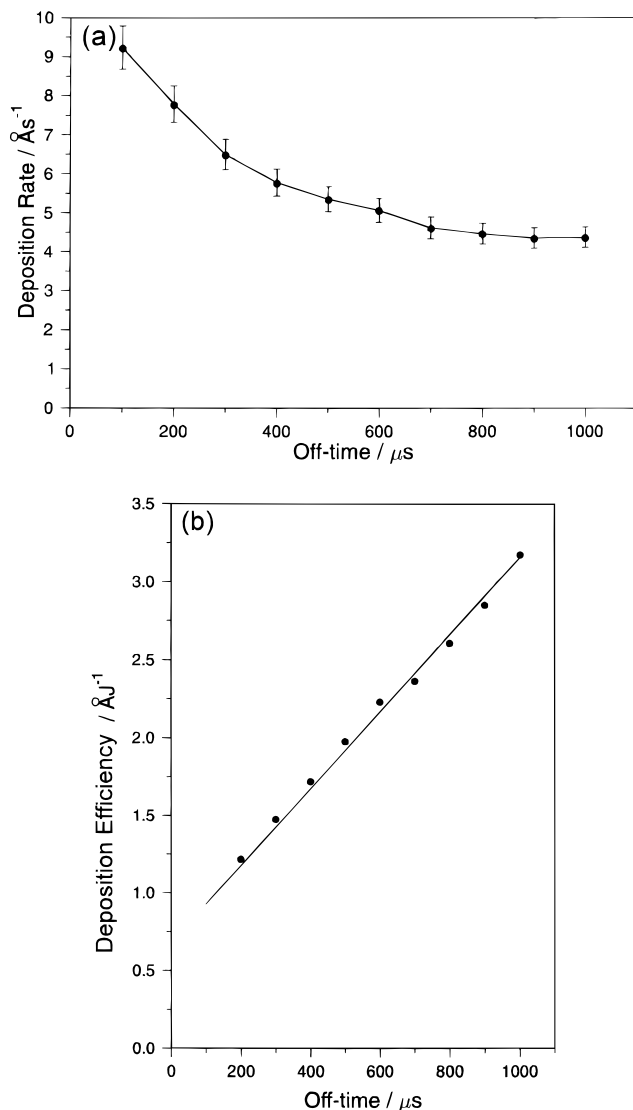
Figure 5. The influence of t_{off} upon deposition during pulsed plasma polymerization of perfluoroallylbenzene ($t_{on} = 20 \ \mu s$, $P_p = 70$ W): (a) deposition rate; and (b) deposition efficiency.

are not significantly different between each duty cycle because a fixed t_{on} value has been employed. Eventu-ally, for very long off-times, the deposition efficiency would be expected to pass through a maximum and fall because there is insufficient energy to effectively initiate sufficient polymerization at such low average powers. A similar enhancement in deposition efficiency was also noted for shorter on-periods at fixed t_{off}, and also at higher duty cycle frequencies where the duty cycle ratio, average power, and peak power were all kept constant. Again, this result highlights the fact that the observed structural retention is not just a manifestation of low average powers.

These plasma polymer films were found to be air stable with respect to aging, as well as insoluble in polar (e.g., water, 2-propanol, acetone) and nonpolar (e.g. alkanes) solvents. Also, the Scotch tape test indicated good adhesion to the substrate.

4. Conclusions

XPS, IR, and deposition rate studies have shown that pulsed plasma polymerization of perfluoroallylbenzene can lead to selective incorporation of perfluorinated phenyl groups into the growing polymeric layer. Lower-ing the duty cycle (either by increasing off-time or decreasing on-time) enhances phenyl ring retention. Two different factors are considered to be important, depending on whether the variable altered is the on-period or the off-period. Shorter on-times reduce frag-mentation of the perfluoroallylbenzene molecules and cause less damage to the growing plasma polymer layer. However, longer off-times improve the likelihood of nonfragmented perfluoroallylbenzene molecules becom-ing incorporated into the growing plasma polymer layer via conventional free radical polymerization before the next pulse cycle. Overall, these experiments have demonstrated that for monomer species containing more than one potentially polymerizable functional site (in this case perfluorinated allyl and phenyl groups), pulsed electrical discharges can facilitate preferential polym-erization at one center.