Surface Molecular Tailoring via Pulsed Plasma-Generated Acryloyl Chloride Polymers: Synthesis and Reactivity

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ABSTRACT: A variable-duty cycle-pulsed radio frequency discharge is shown to provide film chemistry control during plasma polymerization of acryloyl chloride. A nonlinear dependence is observed between the percent retention of acid chloride groups in the deposited films and the average power input during plasma polymerization. Significant C(O)Cl group retention is observed only under conditions of exceptionally low power input, as made available in the pulsed experiments. Additionally, relatively large scale systematic changes in surface morphology and film formation rates are observed with sequential variations in the plasma duty cycle employed during film formation. Specifically, film surface roughness decreases and the film thickness per joule of input energy increases as the plasma duty cycles employed are decreased. The plasma-generated films were employed in subsequent chemical reactions to attach target molecules to the substrate surfaces via facile reactions with the surface acid chloride groups. This concept is illustrated in the present paper with reactions of 1,1,1-trifluoroethanol and allylamine with the plasma-modified surfaces. The results obtained are supportive of the use of the ultralow-energy pulsed plasma technique to introduce reactive surface groups, followed by subsequent covalent coupling of target molecules, as a viable new route to molecular tailoring of surfaces.

Introduction

Surface modification of solid substrates, particularly polymeric materials, represents an exceedingly active research area at the present time. In particular, many of these studies have focused on the introduction of specific chemical groups during the surface modification period. Functional groups so introduced can be employed for subsequent chemical reactions (e.g., binding of biomolecules, catalyst preparation, etc.) and/or for providing desired changes in substrate surface physical properties (e.g., refractive index, dielectric constant, wettability, etc.). A diverse and imaginative range of experimental techniques has been developed to achieve surface modifications. Self-assembled monolayers (SAMs), chemical treatment, radiation and photochemical grafting, ion implantation, and plasma depositions represent but a few of the many techniques currently employed for this purpose.

The present work examines an alternate approach to molecular surface tailoring. Although it is plasma-based, the present study utilizes a pulsed plasma technique in lieu of the traditional continuous wave (CW) operational mode employed in other laboratories. As we have previously demonstrated, the use of a modulated plasma process provides an unusually high level of film chemistry control during gas-phase plasma polymerizations.[1,2] Specifically, progressive variations in the chemical composition of the plasma-generated films are observed as the duty cycles (i.e., the ratio of plasma-on to plasma-off times) are varied in a sequential manner, *all other plasma variables being held constant*. Subsequent studies have demonstrated the general utility of this approach with a wide range of compounds including saturated and unsaturated molecules,[3−9] organometallic monomers,[10] and even mixtures.[11] Dénes has provided a recent comprehensive review of plasma polymerization technology including specific mention of the pulsed plasma approach.[12]

The inherent film chemistry controllability available with the pulsed plasma technique suggests that it may be particularly appropriate as an initial step of a two-step process for molecular level surface modifications. In this approach, the initial plasma polymerization step would be used to introduce controlled concentrations of surface functional groups which would, in turn, be employed to covalently attach targeted substrates to the modified surfaces via direct coupling reactions. Although this concept has been previously employed by others, the distinguishing feature of the present work is to attempt to introduce a significantly more reactive surface functional group [i.e., C(O)Cl] during the initial plasma process than the NH_2 and OH groups employed in earlier studies. Clearly, deposition of more labile reactive groups on a surface would expand the range of possibilities for the subsequent covalent attachment reactions and/or simplify the chemistry of these processes, thus increasing the overall utility of this approach to molecular tailoring.

The present study involves a stringent test of the film chemistry controllability made available via the pulsed plasma polymerization technique by focusing on surface deposition of acid chloride groups. Acyl halides are among the most reactive of all carboxylic acid derivatives.[13] Thus, from the standpoint of subsequent surface derivatization processes, these acid chloride groups would afford a diverse range of coupling reactions, as they react readily with a wide range of molecules via simple nucleophilic processes. However, from the experimental standpoint, retention of the acid chloride group during plasma polymerization represents a major experimental challenge. The high C(O)Cl reactivity, desired for the surface-modified substrate, would also be expected to lead to rapid consumption of these groups under the energetic conditions typically prevailing in a

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plasma polymerization process. Indeed, essentially complete consumption of C(O)Cl groups was observed in the present study for plasma polymerizations of acryloyl chloride carried out under CW conditions. However, as documented below, it is possible to generate polymeric films containing significant concentrations of C(O)Cl groups via the pulsed plasma deposition technique. The C(O)Cl retention is observed only under conditions of exceptionally low average power input corresponding to powers available and useful only under pulsed conditions. Additional, important observations arising from this study pertain to decreased surface roughness and increased film thickness per joule as the average power input (i.e., the radiofrequency (rf) duty cycle) is decreased.

The presence of surface active C(O)Cl groups, retained in the polymers when deposited at low plasma power, was utilized for subsequent coupling reactions of molecules to these modified surfaces. This is illustrated in this paper for reactions of CF_3CH_2OH and allylamine nucleophiles with the acryloyl chloride plasma-modified surfaces.

Experimental Section

The plasma reactor and associated electronics employed in this work have been described previously.[3-5] A 13.56-MHz rf plasma discharge was employed. Silicon, polyethyleneterephthalate (PET), and KCl disks were employed as substrates. The Si and PET samples were cleaned ultrasonically before use. The substrates were located on a glass platform in the center of the reaction chamber, approximately 7.0-cm downstream from the hot electrode. In each run, the system was evacuated to background pressure (~1 mTorr) and samples were then subjected to a brief Ar plasma [Ar pressure = 400 mTorr, flow = 8.9 cm^3/min (STP)] operated at 10-μs on and 50-μs off and 200-W peak power for 5 min to provide additional surface cleaning of the substrates. Following the Ar plasma cleaning, the system was evacuated to background pressure before introduction of the acryloyl chloride monomer. This monomer (Lancaster Corp., 96% purity) was subjected to several freeze−thaw cycles before use. The vapor pressure, from an approximately 20-mL sample of acryloyl chloride at room temperature, was metered to the plasma reactor through a fine control valve. Plasma polymerizations were carried out using a 55-mTorr monomer pressure and a flow rate of 3.5 cm^3/min (STP).

Polymerizations were carried out under both CW and pulsed plasma conditions. Pulsed runs included pulse durations in both milli- and microsecond time scales. A matching network was operated manually to maintain the reflected RF power to less than 5% of the input power at all times. An oscilloscope was employed to monitor the reflected power as well as to adjust pulse times to the desired values. The CW runs were carried out at input powers ranging from 5 to 25 W. Attempts to deposit polymeric films under CW conditions at powers less than 5 W were unsuccessful due to plasma instability, combined with extremely slow film formation rates. The low power limit under CW conditions is dictated by the reactor volume (in this case approximately 2.5 L), the reactor geometry, and other variables such as monomer flow rate and pressure. Pulsed runs were carried out at peak powers ranging from 25 to 200 W. Although the pulsed experiments involved higher peak powers, the average power input in these experiments was usually quite low. The average power employed under pulsed conditions is computed from the equation[14]

$$\langle P \rangle = \frac{\tau_{\rm on}}{\tau_{\rm on} + \tau_{\rm off}} \cdot (\text{peak power}) \qquad (1)$$

where $\tau_{\rm on}$ and $\tau_{\rm off}$ are the plasma-on and -off times employed in a particular run. The average power employed in the majority of the pulsed experiments was below a few watts, extending to a lower limit of 0.25 W. The ability to sustain the plasma polymerization process, with reasonable film formation rates at such low power inputs, is a unique feature of the pulsed plasma technique and, as shown in this study, a pivotal factor in providing the desired enhanced film chemistry controllability during polymerization.

The plasma-generated films were characterized spectroscopically using XPS (Physical Electronics, PHI, Model 5000) and FT-IR (BioRad Model FTS-40) instruments. The XPS analysis utilized monochromatic Al Kα (1486.6 eV) incident radiation and an Al/Be window. The anode was operated at 300 W, 13.0 eV, and 20.5 mA, which gave a 0.60-eV full width maximum at 32 000 counts/s for the Ag($3d_{5/2}$) line at a 367.9-eV binding energy. A pass energy of 89.45 eV was used in obtaining the survey scans. This was reduced to 17.6 eV for the high-resolution scans. An electron flood gun, operated at a 21.5-mA emission current and a 2.5-eV electron energy, was employed to neutralize sample charging on the nonconductive films produced in this work. The majority of the spectra were recorded at a takeoff angle of 70° from the sample surface. However, takeoff angles of 15° and 45° were also used in selected analyses to probe film depth effects on composition. The binding energies were computed relative to assignment of 285.0 eV for the lowest binding energy peak of the C(1s) multiplet.[15] The majority of the XPS studies involved Si substrates. No Si atom XPS signals were detected in any analysis of these samples, consistent with the measured plasma-deposited film thicknesses, which ranged typically from 700 to 2000 Å. FT-IR absorption spectra were acquired using 8-cm^{-1} resolution of films deposited on KCl substrates (Wilmad Corp., Buena, NJ). Films employed in these measurements were generally around 2000-Å thick. Film thicknesses were determined using an Alpha Step 200 (Tencor Instruments) profilometer. Generally, the film thickness across a particular sample was relatively uniform (within ±5%) with the exception of a rapid falloff in thickness at the edges of the substrate.

The surface roughnesses of the plasma-deposited films were examined by AFM (Nanoscope III, Digital Corp.) using the tapping mode method for samples deposited on polished Si substrates. The mean roughness of each film was determined quantitatively as measured by surface vertical height variations relative to the geometric center plane of the AFM image. To obtain statistically meaningful mean roughnesses, 20 randomly selected locations each 3 μm × 3 μm on each polymer film sample (using triplicate samples for each rf duty cycle) were imaged and analyzed.

The reaction of plasma-generated films with CF_3CH_2OH (Aldrich Chemical Corp.) was carried out by immersing coated PET substrates in the neat CF_3CH_2OH liquid. The reactions were permitted to proceed for periods of time ranging from 30 min to 3 h at temperatures ranging from 0 to 37 °C. Temperature regulation was achieved by immersion of the reaction vessel in a constant-temperature (±1 °C) bath. Derivatization of plasma-deposited films by reaction with allylamine (Aldrich) was carried out as a vapor-phase reaction. Coated samples were initially placed in a glass vessel and evacuated to ~1-mTorr pressure. Subsequently the samples were isolated from the vacuum pump and a stopcock was opened to permit allylamine vapor to contact the PET-coated substrates. These vapor-phase reactions were carried out at room temperature.

Results

High-resolution C(1s) XPS spectra of plasma-polymerized films obtained from acryloyl chloride monomer under several different deposition conditions are shown in Figure 1. These spectra are stacked in order of decreasing average input power during plasma deposition, reading bottom to top. Particularly significant is the progressive increase in the peak at 289.4 eV as the rf duty cycle employed during film formation was decreased. By analogy with many other C(1s) high-

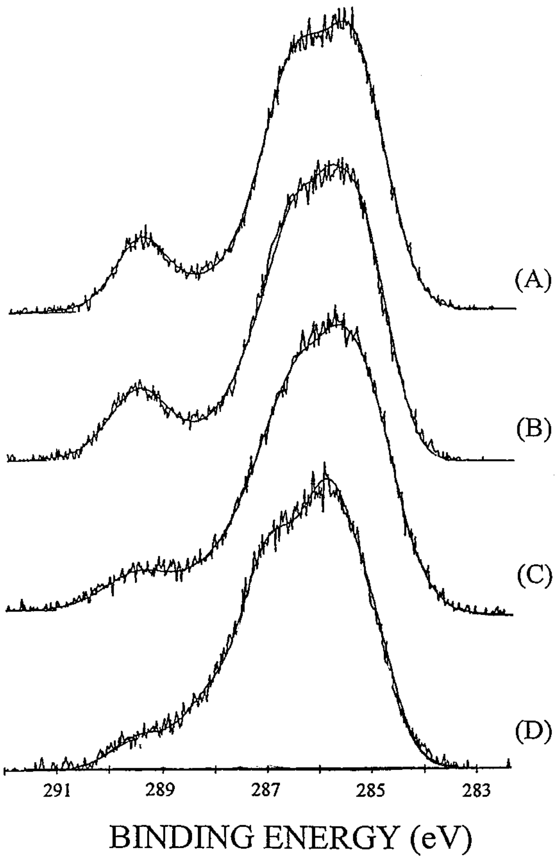


Figure 1. High-resolution C(1s) XPS spectra of films obtained at various pulsed plasma duty cycles and 25-W peak rf power. The plasma on-to-off ratios (in microseconds) were as follows: (A) 10/1000; (B) 10/500; (C) 10/200; (D) 10/50.

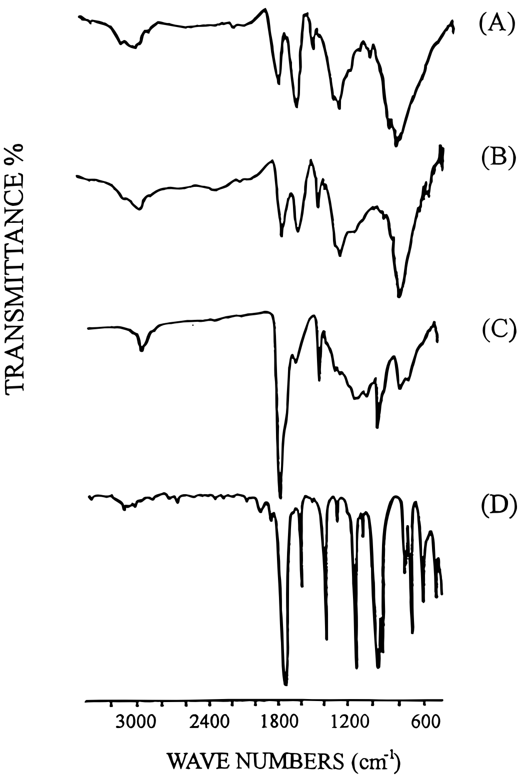


Figure 2. Comparison of FT-IR transmission spectra of plasma-polymerized films with those of neat acryloyl chloride monomer: (A) plasma film obtained under 25-W CW conditions; (B) pulsed plasma film obtained at 10-μs on/50-μs off, 25-W peak power; (C) pulsed plasma film obtained at 10-μs on/1000-μs off, 25-W peak power; (D) acryloyl chloride monomer.

Table 1. Percentage Surface Atom Compositions of Films Obtained from Acryloyl Chloride under CW and Pulsed Plasma Conditions

rf duty cycle on/off times	peak power (W)	average power (W)	atom percent (%)[a]		
			C	Cl	O
		CW Runs			
		5	66.3	29.5	4.2
		25	60.2	37.0	2.8
		50	61.9	34.2	3.9
		100	60.8	35.3	3.9
		Pulsed Runs			
10/1000 μs	25	0.25	62.9	21.4	15.7
10/500 μs	25	0.49	63.3	22.7	14.0
10/200 μs	25	1.19	65.8	22.9	11.3
10/100 μs	25	2.27	67.2	24.9	7.9
10/50 μs	25	4.17	66.4	27.0	6.6
3/150 ms	25	0.49	65.9	22.4	11.7
3/60 ms	25	1.19	65.7	24.5	9.8
3/30 ms	25	2.27	66.7	26.0	7.3
3/5 ms	25	9.37	64.9	31.8	3.3
3/100 ms	50	1.46	67.5	26.5	6.0
3/5 ms	50	18.75	58.7	38.6	2.7
3/100 ms	100	2.91	64.8	31.3	3.9
10/100 μs	200	18.18	59.9	31.6	8.5
10/50 μs	200	33.33	58.9	36.4	4.7
10/30 μs	200	50.00	58.2	36.8	5.0
10/50 ms	200	33.33	61.5	36.5	2.0
10/30 ms	200	50.00	62.9	34.8	2.3

[a] These values compare to the 60:20:20 C/Cl/O atom ratio in the starting acryloyl chloride monomer.

resolution spectra, this high-binding-energy peak can confidently be assigned to carbon atoms in acid chloride [i.e., *C*(O)Cl] groups. For example, the 4.4-eV binding energy chemical shift observed between C(1s) electrons from carbon atoms in acid chloride groups and those from unsubstituted C atoms is very similar to the average 4.0-eV chemical shift observed for C(1s) electrons from C atoms involved in ester groups [i.e., COC(O)].[15] The presence of the acid chloride group in films deposited at low plasma duty cycles is further confirmed by FT-IR analysis, as shown in Figure 2. The stacked IR transmission spectra shown in this figure represent films deposited at 25 W CW; 10-μs on/50-μs off, 25 W; 10-μs on/1000-μs off, 25 W; and neat acryloyl chloride monomer, reading top to bottom. Of particular significance is the sharp increase in the absorption band at 1760 cm^{-1} as the average power employed during plasma polymerization is reduced. This peak is attributed to the presence of increasing C(O)Cl groups, as shown by comparison of the IR spectra of the plasma-generated films to those of the neat acryloyl chloride monomer. Assignment of the 289.4-eV XPS C(1s) peak to C(O)Cl, as opposed to ester or carboxylic acid groups, is also consistent with the absence of IR absorptions attributable to these groups. For example, there are no broad absorptions between 3500 and 3000 cm^{-1} characteristic of OH groups in carboxylic acids. Additionally, the relative atom content of these films would argue against the significant presence of ester or carboxylic acid functionalities. As shown in Table 1, the oxygen atom content in the films is generally low relative to the carbon and chlorine atom percentages. In fact, an interesting aspect of the plasma polymerization of the acryloyl chloride monomer is the selective loss of oxygen atom content in the films relative to C and Cl content, as observed in runs at higher average powers.

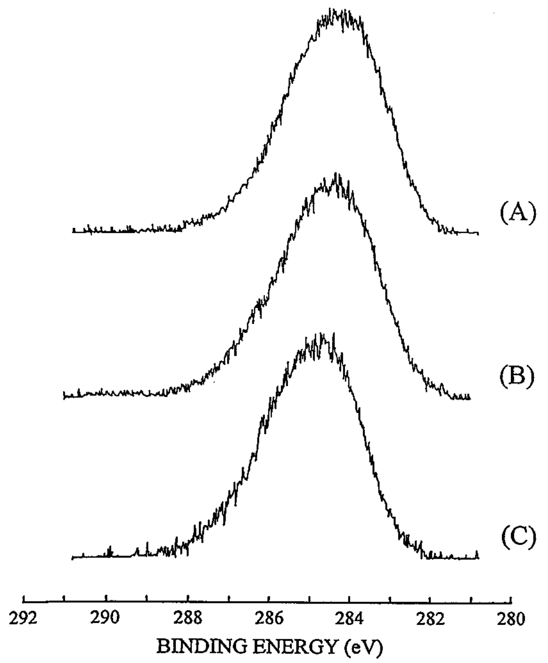


Figure 3. High-resolution C(1s) XPS spectra of films plasma-polymerized under CW conditions at different powers: (A) 50 W; (B) 25 W; (C) 5 W.

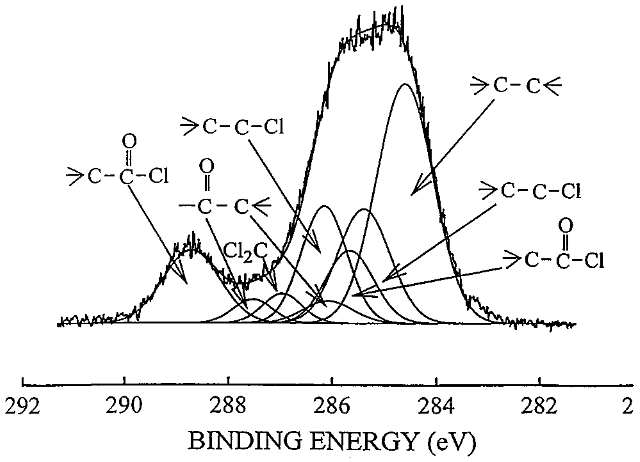


Figure 4. Resolved high-resolution C(1s) XPS peak of the pulsed plasma-polymerized film obtained at a rf duty cycle of 10-μs on/1000-μs off. Functional groups employed in the deconvolution process are as indicated.

High-resolution C(1s) XPS spectra of films deposited at rf powers from 5 to 50 W under CW conditions are shown in Figure 3. In contrast with the case of the pulsed plasma-generated films, there is relatively little change in the C(1s) spectra and, in particular, there is no significant contribution of high-binding-energy electrons (i.e., 289.4 eV) in these films. This includes films obtained at the 5-W power input, the lowest power CW accessible under our conditions capable of maintaining a continuous discharge and film deposition.

Assignment of the resolved high-resolution C(1s) XPS peaks into individual contributions of different carbon atoms was carried out, as shown in Figure 4. This assignment must be considered as being only approximate in that an unusually wide range of C atom functionalities must be considered. In fact, the fitting procedure employed undoubtedly represents an oversimplification of the various carbon atom groups present in these films. The various functional groups employed, along with assigned binding energies, are indicated in Figure 4. Where possible, the assignments are based on recommended values from Cl- and O-containing polymers.[15] Despite the overall compositional complexity, the relative C, O, and Cl film contents based on the C(1s) multiplet assignments shown in Figure 4 are in good agreement with the atom compositions obtained directly from integration of XPS signal intensities of the individual C(1s), O(1s), and Cl(2p) peaks. For example, assignments shown in Figure 4 for the integrated peaks at 289.4 [C(O)Cl], 287.8 (C=O), 287.6 (CCl_2), and 286.6 (CCl) eV for the Cl- and O-containing groups (including the stoichiometric factor of 2 for the CCl_2 peak) relative to the total area of the C(1s) peak yield a C/Cl/O ratio of 64.5/21.3/14.7, respectively. In this computation, the contributions from the β-C peaks [i.e., *C*CCl (285.5 eV); *C*C(O)Cl (285.8 eV); and C(O)*C* (286.1 eV)] are, of course, not included in obtaining the Cl and O content, as these contributions are included in the areas of the α-*C* peaks of the same groups. The above C/Cl/O ratios computed from the deconvoluted C(1s) spectrum can be compared with ratios of 63.2/22.8/15.0 obtained directly from the integrated C, Cl, and O XPS signals. This assignment is an oversimplification in that it does not include possible contributions from groups such as C(O)O, COC, and COCl. However, in view of the reasonably good agreement between the atom percentages obtained from the C(1s) multiplet assignments and the directly measured C, Cl, and O atom XPS signals, it is felt that a more detailed analysis of C(1s) multiplets is not justified at this time.

AFM measurements of pulse plasma-polymerized acryloyl chloride films reveal dramatic decreases in average surface roughness of the films with decreasing rf duty cycles employed during deposition. This result is shown in Figure 5 in terms of AFM roughness measurements of film line segments obtained at different rf duty cycles. Note particularly the variation in the vertical scale (i.e., ordinate) employed in presenting these data. The average surface roughness values are indicated in Figure 5. As these numbers reveal, the plasma-generated films span a range of values from 6.7 to 0.24 nm, with the average roughness of films deposited at ultralow average powers approaching that of the uncoated, polished Si substrate. The dramatic variations in surface morphology with plasma duty cycle are further illustrated with the full-field 3-D AFM images shown in Figure 6. Again, note that it is necessary to vary the *Z*-scale dimension in order to illustrate this comparison within reasonable spatial considerations.

Measurement of film deposition rates obtained during polymerization of acryloyl chloride reveals large increases in film thickness per joule of input energy as the duty cycle employed during deposition is decreased. An example of this enhanced deposition with decreasing rf average power input is shown in Figure 7 for a series of runs all carried out at plasma-on periods of 10 μs and 25-W peak power but plasma-off times ranging from 50 to 1000 μs. The data point at zero off-time represents a CW run at 25-W power. The marked increases in film thickness per joule with decreasing rf duty cycle observed with acryloyl chloride are similar to those observed with other monomers under pulsed plasma conditions.[3,5,8,16] We believe the increased film thickness per joule with increasing plasma-off time provides clear evidence for significant film formation during

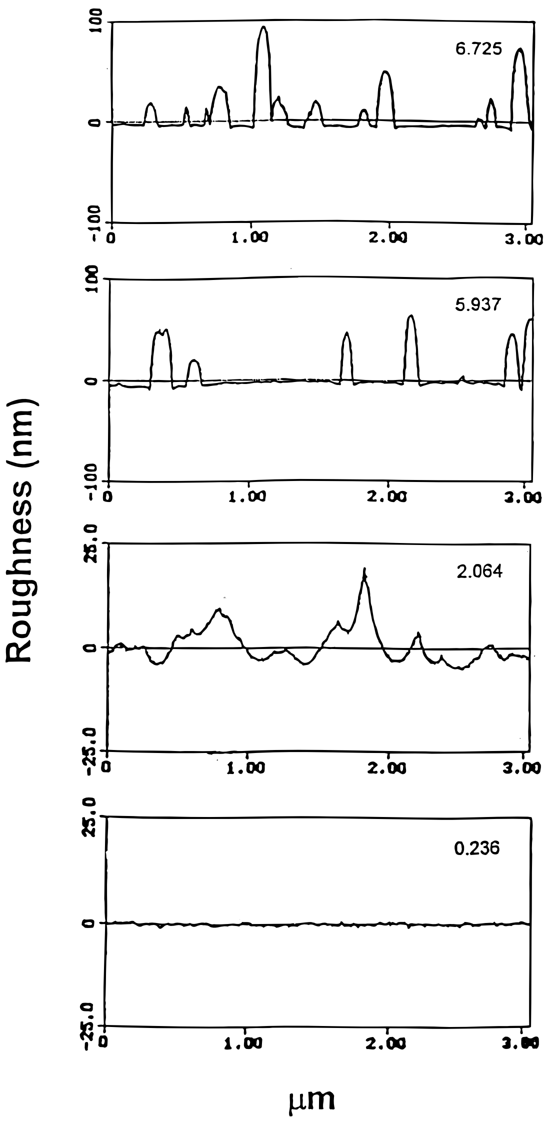


Figure 5. Roughness of pulsed plasma films polymerized at various rf duty cycles. The mean roughness (nm) of each film is shown on each graph. Plasma duty cycles (on/off times in microseconds) and peak rf powers employed during film formation were as follows: (A) 10/50, 200 W; (B) 10/50, 25 W; (C) 10/1000, 200 W; (D) 10/1000, 25 W.

plasma-off periods. The implications of these deposition rates with respect to film chemistry control are discussed below.

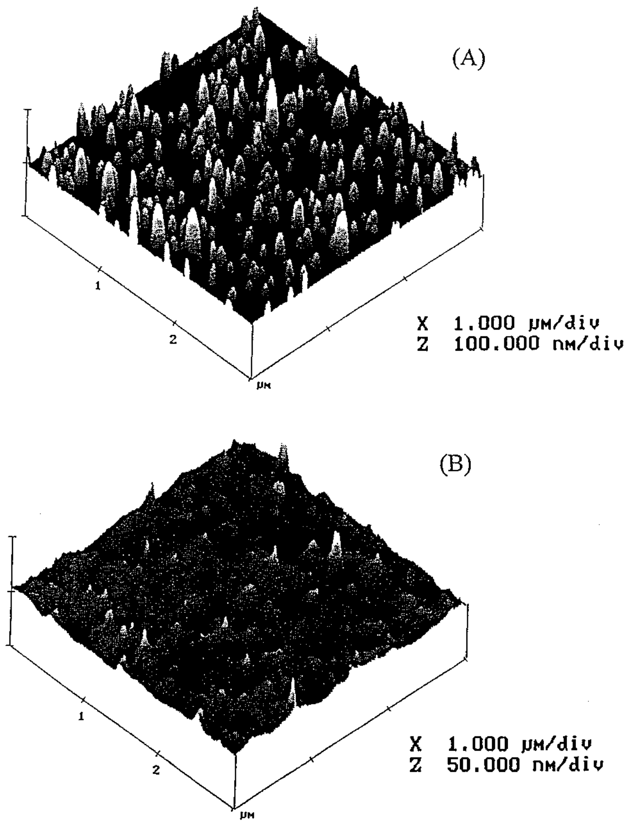


Figure 6. Surface morphology of films obtained at two different pulsed plasma duty cycles but constant peak power: (A) 10/50 μs, 200 W; (B) 10/1000 μs, 200 W. Note the change in vertical (i.e., Z scale) resolution employed.

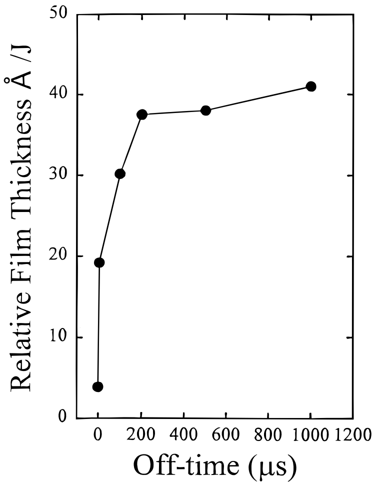


Figure 7. Variation in the relative thickness per joule of input energy as a function of the plasma-on time. All pulsed runs were carried out at 10-μs on time and 25-W peak power. The zero on-time data point is from a CW run at 25 W.

Finally, we describe two experiments in which the reactive acid chloride groups retained in the plasma-deposited films were subsequently employed to attach target molecules to the surface. In one series of reactions, plasma films deposited on PET were reacted with CF_3CH_2OH by simple immersion of the coated substrates in liquid CF_3CH_2OH. These reactions were carried out at temperatures of 0, 25, and 37 °C for times ranging from 30 to 180 min. After removal from the CF_3CH_2OH, the coated substrates were repeatedly rinsed with 1% sodium dodecyl sulfate (SDS) solution and then vacuum oven dried before being subjected to XPS analysis. Figure 8 shows a typical high-resolution C(1s) XPS spectrum of the derivatized films. Of particular significance is the presence of the high-binding-energy peak at 294 eV, providing clear evidence for incorporation of CF_3 surface groups[15] during the derivatization process. Essentially no change in the 289.2-eV peak is noted during this reaction. This latter result is as expected considering that the acid chloride is converted to an ester group. XPS analysis cannot distinguish between *C*(O)Cl and *C*(O)O carbons in terms of binding energies under the conditions of this experiment. The extent of F atom incorporation in the films, as obtained from XPS analysis, is shown in Figure 9 as a function of the time and temperature of the CF_3CH_2OH coupling reactions. Clearly F atom incorporation in these films is increased by higher temperature and longer reaction times. Control experiments in which uncoated PET samples were exposed to trifluoroethanol

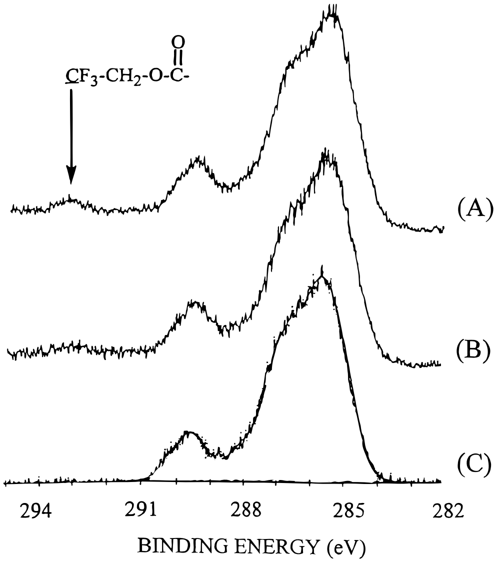


Figure 8. Comparison of high-resolution C(1s) XPS spectra of pulsed plasma polymerized acryloyl chloride films before and after reaction with CF_3CH_2OH at 0 °C: (A) after 180 min of reaction; (B) after 30 min of reaction; (C) no reaction. The film was synthesized using a 10/1000-μs duty cycle and 25-W peak power.

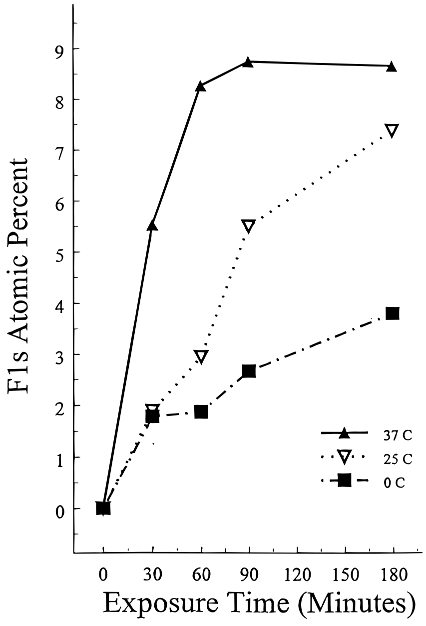


Figure 9. Variation in the surface fluorine atom percent after reaction of the plasma-polymerized films with CF_3CH_2OH at temperatures of 0, 25, and 37 °C, as shown, as a function of reaction time. Plasma conditions employed in film synthesis were the same as those shown in Figure 7.

and subsequently rinsed revealed no surface F atoms, as shown by XPS.

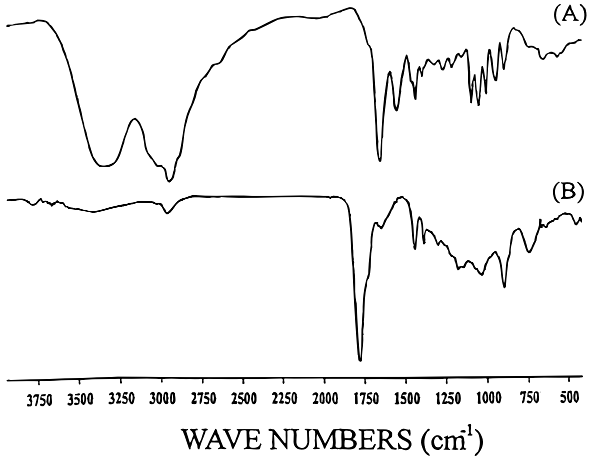


Figure 10. Comparison of FT-IR absorption spectra of pulsed plasma-polymerized acryloyl chloride films (A) before and (B) after reaction with allylamine vapor.

Attempts to couple allylamine to the acryloyl chloride plasma-polymerized surfaces using solution processes (either neat allylamine liquid or aqueous solutions of allylamine) proved unsuccessful. In every case, the plasma film was apparently dissolved in these solutions. However, brief exposure of these films to allylamine vapor was successful in conversion of the acid chloride group to an amide and introduction of a carbon−carbon double bond into the film. The vapor-phase coupling reactions were carried out for a very brief periods (only 30 s) at room temperature, after which the allylamine vapor was removed from contact with the coated substrates by opening a stopcock to the vacuum pump. If the allylamine vapor exposure was extended for longer periods (e.g., a few minutes), film degeneration could be visually observed with an apparent loss of film from various areas on the substrate. XPS and FT-IR analyses of the films immediately after exposure provide clear evidence for reaction of the acid chloride groups with the allylamine vapor. For example, FT-IR absorption spectra of plasma films deposited on KCl substrates are shown in Figure 10 as measured before and after exposure to allylamine. The complete removal of the 1760-cm^{-1} acid chloride group during reaction with allylamine vapor indicates that the allylamine was able to penetrate through the entire film thickness. The presence of the amide group resulting from the NH_2 + C(O)Cl reaction is shown by the absorption peak at 1531 cm^{-1}. Also, the presence of the C=C functionality in the film after reaction is shown by the new absorption peak at 1644 cm^{-1}. The broad absorption bands in the 3500−3000-cm^{-1} region are consistent with the formation of amide salts, presumably of the form $C(O)NH_3^+Cl^-$. XPS analysis of the films after exposure to the allylamine reveals the virtual elimination of the C(O)Cl peak at 289.4 eV accompanied by significant increases in the peak at 285 eV and, to a lesser extent, the peak at 288.2 eV (Figure 11). The increase at 285 eV is attributed to the presence of additional unsubstituted C atoms from the allylamine coupling, while the increase at 288.2 eV is consistent with the formation of amide groups. The N(1s) XPS spectrum of the derivatized sample (not shown) was consistent with the above result in that it consisted of a single broad peak in accord with the selective formation of amide groups. Control experiments with uncoated PET substrates exposed to allylamine vapor showed no change in C(1s) XPS spectra over that expected of a clean uncoated PET sample,[15] as shown in Figure 11.

Discussion

It is generally acknowledged that the reaction conditions prevailing during plasma polymerization processes are sufficiently energetic to promote simultaneously numerous and diverse chemical processes. In fact, one frequently proclaimed feature of plasma polymerization is that it can provide unique films whose chemical compositions are decidedly different from those of the starting monomers.

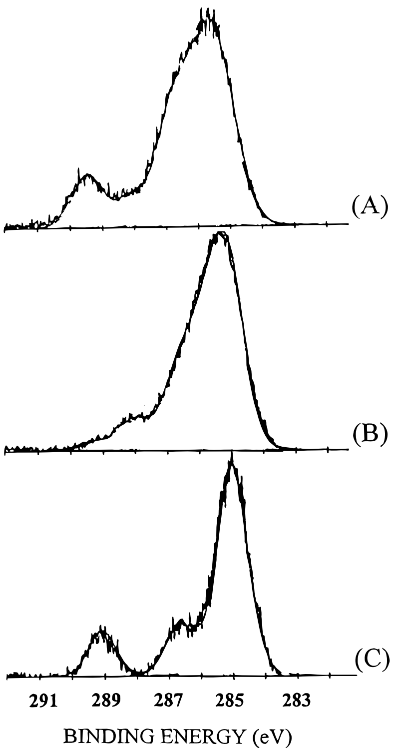


Figure 11. High-resolution C(1s) XPS spectra of pulsed plasma-polymerized acryloyl chloride films (A) before and (B) after exposure to allylamine vapor. The bottom spectrum (C) is that of a PET control subjected to the allylamine treatment only.

The present study examines plasma polymerization from an essentially opposite viewpoint. Namely, it evaluates the possibility of employing the plasma technique to generate polymers whose compositions retain, to as high a degree as possible, the monomer functionality in the plasma-generated films. Although there have been many other studies of this type, a distinguishing feature of the present work is to attempt to achieve this film chemistry controllability with the exceptionally reactive (by plasma standards) monomer acryloyl chloride. In fact, initial experiments confirmed the destructive nature of plasma polymerization in that film compositions obtained differed markedly from the C, Cl, and O atom percentages of the monomer (Table 1). This difference was very much apparent in all higher power runs, including CW plasmas operated at power inputs as low as 5 W. We believe this result reflects the efficient formation of CO groups under plasma operation. Overall, there is essentially no retention of the acid chloride groups initially present in the monomer in the plasma-deposited films at the higher input powers. As noted earlier, attempts to operate at powers of less than 5 W under CW conditions were unsuccessful in that the power density was insufficient to maintain the discharge and produce reasonable film formation rates.

In contrast with the above results, operation of the plasma under pulsed conditions permitted a much higher degree of film chemistry controllability to be achieved including retention of significant concentrations of acid chloride groups. Operation of the plasma in the pulsed mode permitted extension of these studies to much lower average power inputs than can be employed under CW conditions. Of particular significance, it is only at extremely low power input that the C(O)Cl retention in the films is observed, as shown in Figure 12, with the degree of C(O)Cl retention increasing exponentially with decreasing input power at average power input below roughly 5 W. This highly nonlinear power dependence of film composition suggests that there is a lower limit power input threshold below which dramatic changes in plasma dynamics begin to occur. In general, the film compositional variations observed with acryloyl chloride parallel to a high degree those recently observed during plasma polymerization of maleic anhydride.[9]

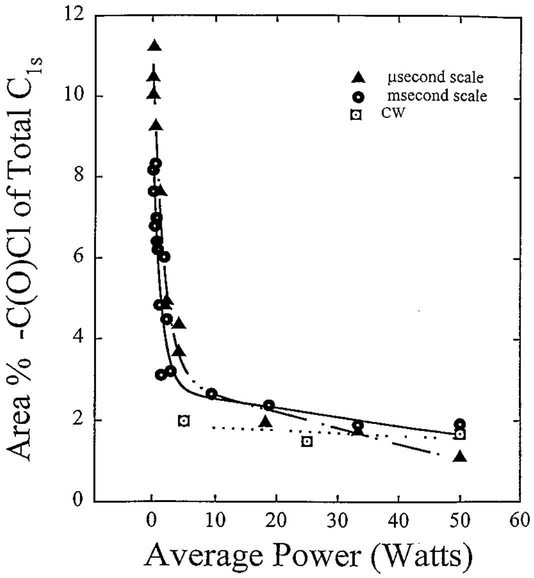


Figure 12. Variation of the relative surface concentration of C(O)Cl groups as a function of average power input during plasma polymerization of acryloyl chloride films. Millisecond (▲), microsecond (●), and CW (□) conditions employed during film formation are distinguished.

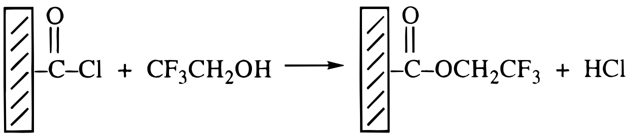
In addition to making polymerization available at lower average power inputs, a second important aspect of pulsed versus CW depositions is the generally much higher film formation thickness per joule under pulsed operation (Figure 7). We believe this result indicates that significant film formation is taking place during the plasma-off periods. Thus, reactive species produced during the plasma-on periods initiate polymerization of the monomer, and the polymers continue to form during the subsequent plasma-off relaxation periods. Furthermore, during these plasma-off periods the oligomers would not be subjected to ionization or fragmentation from collisions with high-energy electrons. Additionally, the more reactive species (e.g., radical ions) presumably disappear during the initial moments following cutoff of the rf power. The net effect of these changes would be to introduce a more selective chemistry during plasma-off, relative to that occurring during plasma-on, periods, reflecting the less energetic conditions prevailing during off times. If film growth during the plasma-off periods dominates over that observed during the plasma-on periods, then increased C(O)Cl retention would be expected at longer plasma-off times, as observed in this work.

However, as noted previously,[4] there are several other factors which may contribute to dynamic differences in contrasting pulsed and CW plasma polymerizations. These factors include the reduced importance of substrate bias, surface ion bombardment, vacuum UV photodecompositions, and substrate heating when contrasting pulsed versus CW processes. All of these factors will contribute to increased film chemistry selectivity under pulsed relative to CW plasma conditions. For example, it has long been recognized that large negative substrate bias potentials during plasma operation promote high-energy collisions of charged particles with surfaces. These collisions are believed to be responsible for ablation processes from these surfaces with accompanying bond breaking and overall surface randomization.[17] However, ablation processes are minimized under plasma-off periods in that substrate bias potentials decay rapidly (<1 ms) after power cutoff. In a similar vein, short-wavelength photons generated during plasma-on periods and known to produce significant photodecomposition of plasma films[18,19] will be absent during the plasma-off periods. Finally, lower substrate temperatures, as achieved during pulsed operation, would also promote increased chemical selectivity by minimizing competition from higher activation energy reactions during film formation.

It is of interest to note that the large decreases in film surface roughness observed as the rf duty cycles employed during pulsed operation are decreased (Figures 5 and 6) are also consistent with a diminution of ablation processes during plasma-off periods. This decrease in surface roughness with decreasing plasma duty cycle appears to be a general feature of pulsed plasma polymerizations, having now been observed with a variety of different monomers.[8,16] Thus, both film formation rates and surface roughness changes are consistent with the suggestion that significant film formation occurs during plasma-off periods.

In view of the complexity of processes occurring during plasma polymerizations, it is not possible at this stage to identify which of the above factors is most responsible for the observed differences in comparing film compositions, formation rates, and roughness under pulsed and CW conditions. It suffices to say that all of the potential dynamic factors identified above would be expected to influence the variation in film properties (i.e., increased retention of monomer functionality, decreased surface roughness, increased film formation rates per joule) with decreased rf duty cycles in the direction observed in this work and prior studies.

The retention of acid chloride groups in these films made available via use of ultralow-average-energy pulsed plasma polymerizations was utilized in subsequent derivatization reactions. The reaction of plasma-modified PET substrates with trifluoroethanol represents a nucleophilic reaction on the C(O)Cl group:



$$-C(=O)-Cl + CF_3CH_2OH \longrightarrow -C(=O)-OCH_2CF_3 + HCl$$

As shown in Figure 8, XPS analysis of the films after reaction reveals the presence of CF_3 groups on the surface. Thus, although CF_3CH_2OH is not a very strong nucleophile, its reaction with the C(O)Cl groups is sufficiently fast to result in attachment of significant amounts of fluorine to these surfaces (Figure 9). Although there is clear evidence for this attachment reaction, the total fluorine atom surface incorporation is less than that anticipated from reaction of all the C(O)Cl groups. For example, the original atomic compositions of the samples employed in these reactions were C = 63%, O = 16%, and $[Cl]_0 = 21\%$. This ignores the hydrogen atoms, which are not detected by XPS. The Cl atom content is divided into two fractions—those Cl atoms involved in the acid chloride groups and thus reactive toward CF_3CH_2OH and those Cl atoms involved in alkyl chloride bonds and thus not reactive toward the alcohol. XPS analysis revealed that 11.2% of the C atoms are involved in acid chloride groups. Thus $11.2/100 \times 63 = 7.1\%$ of the surface atoms are Cl's in acid chloride groups with 13.9% (i.e., $21-7.1$) of the Cl atoms present in nonreactive groups. Occurrence of reaction 1 introduces one O atom, two C atoms, and three F atoms for every Cl atom lost. Thus, by taking the conversion factor of acid chloride groups to be x (i.e., $x = 0$ for no reaction, $x = 1$ for complete reaction), the fluorine atom incorporation is related to x by the following equation:

$$\%\ F = \frac{3x\cdot[Cl]_0^*}{[C]_0 + [O]_0 + [Cl]_0 + (6-1)x\ Cl_0^*} \qquad (2)$$

where $[Cl]_0^*$ and $[Cl]_0$ represent the initial atom percentages of the reactive and nonreactive Cl's and $[C]_0$ and $[O]_0$ represent the initial C and O atom percentages. This equation assumes that all elements are homogeneously distributed within the XPS sampling depth before and after reaction. Using eq 2 and the maximum loading of 9% F (Figure 9), a value of $x = 0.46$ is obtained. On this basis, apparently only approximately half of the C(O)Cl groups available reacted with the CF_3CH_2OH. Conceivably, this may reflect that the assumption of homogeneous distribution within the XPS sampling depth is not valid and diffusional constraints have limited the conversion to the outermost monolayer. However, angle-dependent measurements revealed only a slight increase in F atom loading with decreased XPS takeout angle. Alternately, it is possible that some of the C(O)Cl groups are inaccessible for reaction in view of stereochemical constraints and/or that electron-withdrawing groups have reduced the reactivity of some of the acid chloride units. Similar observations of less than complete conversion have been reported by other workers in the XPS study of the derivatization of surface reactive groups using CF_3CH_2OH.[20,21]

The reaction of the plasma-generated acryloyl chloride films with allylamine provides evidence of facile reaction and coupling of the amine to the surface via amide bond formation. Since allylamine is a much stronger nucleophile than the trifluoroethanol, the enhanced reactivity with this reagent is expected. The resultant film after reaction includes the presence of unsaturated C=C bonds which could presumably be employed for subsequent addition reactions to molecularly tailor the surface of these substrates.

Conclusion

The pulsed plasma polymerization of acryloyl chloride can be adjusted to permit synthesis of polymer films having significant concentrations of acid chloride groups. However, this functional group retention is observed only under exceptionally low average power input, as made available by the pulsed plasma technique. Successful control of film chemistry in a monomer as reactive as acryloyl chloride suggests that the pulsed plasma polymerization approach should be usable to introduce a wide variety of reactive surface group functionalities at controllable concentrations via appropriate choice of reactant monomer.

As shown in this work, with two reactants differing markedly in nucleophilic character, the plasma films generated can be employed for subsequent attachment of target molecules to the plasma-modified substrates. Thus, the pulsed plasma surface modification process is proposed as the first step of a two-step treatment which can provide a very wide range of surface molecular tailoring for various applications.

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