Ring Retention via Pulsed Plasma Polymerization of Heterocyclic Aromatic Compounds

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Polymerization of two isomeric heterocyclic monomers, 3-methyl-1-vinylpyrazole and 1-allylimidazole, was investigated under pulsed plasma conditions. Large-scale, progressive variations in polymer compositions were observed with sequential changes in the plasma duty cycles employed, all other plasma variables being held constant. In particular, unusually linear polymers (by normal plasma polymerization standards) are achieved at exceptionally low average power inputs, employed when the pulsed plasma technique is operated at low duty cycles. With both monomers, a pronounced increased retention of their aromatic rings is observed in the plasma-synthesized polymers as the duty cycle employed during film formation is reduced. Overall, a higher ring retention is achieved with the imidazole, compared to the pyrazole, reflecting bond energy differences in these two isomers. This study also includes synthesis and spectral characterization of a conventionally prepared linear poly(3-methyl-1-vinylpyrazole) which was employed to assess the degree of ring retention in the plasma polymers. On the basis of the results of this study, it appears that relatively linear polymers of fairly complex molecules are readily synthesized using the low duty cycle pulsed plasma technique. Accordingly, this approach is useful in extending the utility of plasma polymerizations which have heretofore tended to focus on synthesis of unique, relatively highly cross-linked materials. The pulsed technique provides synthesis of these polymers while maintaining the many inherent advantages of the plasma polymerization technique, including particularly the pinhole-free, conformal, and adhesive qualities of these films.

Introduction

The use of plasma polymerization for synthesis of novel thin film materials, particularly for use in surface modifications, has become an increasingly active research area in recent years. Although originally employed primarily for passivation coatings, current interest centers on extension of this technology to numerous other applications in which surface compositions exert critical influences on device performances. Examples include sensors, dielectric films, antireflective (AR) coatings, biomaterials, and heterogeneous catalysts to identify but a few of the potential applications. The recent reviews by Shi[1] and Dénes[2] provide excellent overviews of the state-of-the-art in this field.

Each of the potential applications noted above place a heavy emphasis on exacting compositional controllability of the plasma coatings in order to maximize device performances. Accordingly, an increasing emphasis in current plasma polymerization research has focused on providing improved film chemistry controllability. It is now well established that several reaction parameters exert measurable influences on the structure and composition of plasma polymers. Examples include power input, monomer flow rates and pressures, substrate temperatures, and positioning of substrates relative to the plasma zone.[1,2] In particular, a composite variable W/FM (in which W is the power, F is the monomer flow rate, and M the molecular mass of the monomer), introduced by Yasuda, has been employed extensively in analyzing the effects of changes in plasma variables on film compositions.[3,4]

The present paper focuses on an alternate approach to achieving the desired film chemistry controllability during plasma polymerizations, namely, power input in a pulsed manner in lieu of the traditional continuous-wave (CW) operational mode. Specifically, the film

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[1] Shi, F. F. *Surf. Coat. Technol.* **1996**, *82*, 1.

[2] Dénes, F. *Trends Polym. Res.* **1997**, *5*, 23.

[3] Yasuda, H. *J. Polym. Sci. Macromol. Rev.* **1981**, *16*, 199.

[4] Yasuda, H. *Plasma Polymerization*; Academic Press: Orlando, FL, 1985.

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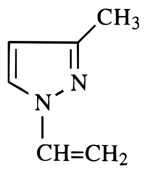
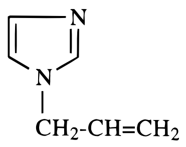
compositions are characterized as a function of the plasma duty cycles (defined simply as the plasma on to plasma off time) employed during polymerization, all other plasma variables remaining constant. As illustrated in previous work from this laboratory,[5−13] as well as by other workers,[14−16] relatively large-scale progressive changes in film compositions are observed with sequential variations in the plasma duty cycles employed during polymerization. This film chemistry controllability has been demonstrated with various functionalized monomers,[8,10,11,13,14] several perfluorocarbons,[5−7,9,15] organometallics,[11,12] and mixtures[16] illustrating the general utility of this approach. Of particular significance is the fact that the pulsed plasma technique permits synthesis of high-quality films at exceptionally low average power inputs. In effect, this permits examination of a composite variable such as *W*/*FM* over a significantly wider range of values than typically accessible under CW conditions. Most importantly, it is becoming increasingly apparent that it is precisely under ultralow power input conditions that dramatic increases in the retention of reactive functional groups of the starting monomer can be achieved in the plasma films.[13,14]

The present paper reports on the extension of the pulsed plasma technique to examination of the polymerization of two isomeric heteroaromatic dinitrogen compounds, namely 3-methyl-1-vinylpyrazole (MVP) (I) and 1-allylimidazole (AI) (II). The emphasis in this study was examination of the extent of aromatic ring retention in the resultant polymers, particularly those synthesized at ultralow power input. These monomers represent a very stringent test of the film chemistry controllability concept in view of the presence of relatively weak chemical bonds in these aromatic rings. This is particularly true for the pyrazole with its N−N bond (~170 kJ/mol).



(I)



(II)

As described below, progressive changes in film compositions with varying plasma duty cycles during polymerizations are observed with both monomers. However, a significant difference in the polymerization dynamics exists for these two compounds in that a higher ring retention is observed with the imidazole compared to the pyrazole. With both compounds unusually highly structured polymers (by normal plasma synthesis standards) are produced at exceptionally low power inputs, as shown by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FT-IR) characterizations of these films. In fact, imidazole films obtained under these conditions are spectroscopically comparable to those of other conventionally polymerized imidazoles, suggesting that relatively linear polymers are achievable under pulsed plasma conditions.

Experimental Section

The radio frequency (RF) (13.56 MHz) plasma reactor and associated electronics employed in this study have been described previously.[7,17] Substrates were located in the center of the cylindrical Pyrex glass reactor between the two external RF electrodes. Substrates employed were either polished silicon (for XPS and film thickness measurements) or KCl disks (for FT-IR transmission spectra). Substrates were subjected to a brief pulsed Ar plasma after insertion in the reactor to provide additional surface cleaning before exposure to the MVP or AI monomer.

The MVP and AI monomers (Aldrich Chemical) were thoroughly degassed by freeze−thaw procedures but were not subjected to any additional purification prior to use. The vapor from each monomer was allowed to diffuse directly into the plasma reactor from a sample reservoir located slightly upstream of the leading (hot) RF electrode. A baratron-controlled butterfly valve located downstream of the reactor was employed to maintain constant monomer pressure during plasma polymerizations. The reactant pressures, prior to plasma ignition, were typically of the order of 40 mTorr relative to the background pressure of 1 or 2 mTorr. Monomer flow rates were approximately 0.2 cm^3/min (STP), as estimated from pressure rise measurements in a known volume. Despite the relatively low pressures and monomer flow rates employed, film deposition rates were high with the exception of runs carried out at the very lowest power inputs. In general, film thicknesses deposited were of the order of 1000−2000 Å as achieved in runs of 15−30 min (total elapsed time).

Film characterizations were made using XPS and FT-IR analyses. The XPS spectrometer (Physical Electronics, Model Psi 5000) is equipped with a monochromator, thus providing high-resolution spectra. The XPS operating conditions and resolution specifications have been described elsewhere.[8] FT-IR transmission spectra were recorded at 8 cm^{-1} resolution (Brucker, Vector 22). Film thicknesses were determined using a profilometer (Tencor Alpha Step 200).

On the basis of previous studies in our laboratory, plasma on and off times employed were limited to millisecond and microsecond pulse widths. If too long plasma on times are employed (e.g., above 200 ms) film compositions become similar to those obtained under CW conditions. In general, plasma on periods were limited to times less than 10 ms in the present study. The duty cycles employed are presented as a simple ratio, in which the numerator is the plasma on time and the denominator the plasma off time, with these ratios expressed as either milliseconds or microseconds.

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(5) Savage, C. R.; Timmons, R. B.; Lin, J. W. *Chem. Mater.* **1991**, *3*, 575.

(6) Panchalingam, V.; Poon, B.; Huo, H.-H.; Savage, C. R.; Timmons, R. B.; Eberhart, R. C. *J. Biomater. Sci. Polym. Ed.* **1993**, *5*, 131.

(7) Panchalingam, V.; Chen, X.; Savage, C. R.; Timmons, R. B.; Eberhart, R. C. *J. Appl. Polym. Sci. Appl. Polym. Symp.* **1994**, *54*, 123.

(8) Rinsch, C. L.; Chen, X.; Panchalingam, V.; Eberhart, R. C.; Wang, J.-H.; Timmons, R. B. *Langmuir* **1996**, *12*, 2995.

(9) Wang, J.-H.; Chen, J.-J.; Timmons, R. B. *Chem. Mater.* **1996**, *8*, 2212.

(10) Beyer, D.; Knoll, W.; Ringsdorf, H.; Wang, J.-H.; Sluka, P.; Timmons, R. B. *J. Biomed. Mater. Res.* **1997**, *36*, 181.

(11) Chen, X.; Rajeshwar, K.; Timmons, R. B. *Chem. Mater.* **1996**, *8*, 1067.

(12) Han, L. M.; Rajeshwar, K.; Timmons, R. B. *Langmuir* **1997**, *13*, 5941.

(13) Calderon, J.; Timmons, R. B. *Polym. Prep.* **1997**, *38*, 1073.

(14) Ryan, M. E.; Hynes, A. M.; Badyal, J. P. S. *Chem. Mater.* **1996**, *8*, 37.

(15) Hynes, A. M.; Shenton, M. J.; Badyal, J. P. S. *Macromolecules* **1996**, *29*, 4220.

(16) Mackie, N. M.; Dalleska, N. F.; Castner, D. G.; Fisher, E. R. *Chem. Mater.* **1997**, *9*, 349.

(17) Savage, C. R.; Lin, J. W.; Timmons, R. B. Spectroscopic Characterization of Films Obtained in Pulsed RF Plasma Polymerization of Fluorocarbon Monomers. In *Structure-Property Relations in Polymers*; Urban, M. W., Craver, C. D., Eds.; Advances in Chemistry Series 236; American Chemical Society: Washington, DC, 1993, p 745.

Of particular significance were runs carried out at low plasma duty cycles corresponding to ultralow total power input. The average power, $\langle P \rangle$, during pulsed polymerizations is calculated from the definition

$$\langle P \rangle = \frac{\tau_{\text{on}}}{\tau_{\text{on}} + \tau_{\text{off}}} \cdot \text{peak power}$$

in which τ_{on} and τ_{off} are the plasma on and off times and the peak power refers to power input during the plasma on period of the duty cycle. We have consistently observed that it is possible to produce significant polymerization under pulsed conditions at $\langle P \rangle$ values that are much lower than the lowest CW wattage required to maintain a steady plasma. For example, films were synthesized in this study under pulsed conditions at $\langle P \rangle$ values as low as 0.05 W whereas approximately 5 W was the lowest power practicable to maintain a steady plasma under CW conditions with the relatively large (2 L) reaction vessel employed in this work. As shown in this study, as well as in previous studies employing the pulsed technique,[11,13,14] dramatic changes in the plasma film compositions are frequently observed at these ultralow power input values. Despite the low power input, both film deposition rates and adhesion to the substrates are generally satisfactory, along with good film quality. Presumably the relatively high peak powers employed during the brief plasma on periods aid in achieving surface grafting and thus the desired film adhesion. Film deposition data, as shown below, reveal significant film formation during plasma off periods, as illustrated both in the present study and in previous investigations.[8,11,17]

Samples of conventional free-radical-synthesized poly-MVP material were prepared for comparison with the plasma-generated films. A 10% MVP monomer solution dissolved in tetrahydrofuran was polymerized using 0.5% tertbutyllithium as initiator. The polymerization was carried out under N_2 at 50−60 °C with constant stirring for 24 h. Subsequently, films of this polymer were cast on Si or KCl substrates by evaporation of the tetrahydrofuran solvent under vacuum at 80 °C. A number of attempts to synthesize a conventional poly-AI sample were unsuccessful. Therefore, the comparison of plasma-generated AI films with conventional polymer was carried out using literature IR data on polyvinylimidazoles,[18] as well as utilizing XPS data from the conventionally synthesized poly-MVP.

The freshly prepared samples were stored in a desiccator prior to spectroscopic characterization with analyses carried out as soon as possible after synthesis. An interesting aspect of the polymers synthesized in this work was the relative lack of oxygen atom incorporation in these films. The only exceptions to this observation were several higher plasma duty cycle runs carried out with AI in which XPS analyses revealed approximately 3−7% O atom content. The low oxygen atom content of these films is unusual for plasma-synthesized polymers which are generally prone to post-plasma oxidations from free radicals trapped in these materials during film formation.[1−4]

Results

3-Methyl-1-vinylpyrazole (MVP). Large-scale changes in film compositions were observed as a function of the plasma duty cycle employed during polymerization of the pyrazole, as demonstrated by XPS and FT-IR analyses of these polymers. The high-resolution N(1s) and C(1s) spectra of these materials are shown in Figures 1 and 2, respectively. In both cases the spectra are arranged in order of decreasing plasma duty cycles employed during polymerization, reading bottom to top. The deconvoluted N(1s) spectra were accomplished employing three separate peaks corresponding to C≡*N*, C=*N*, and C−*N* functionalities at binding energies of 397.4, 398.4, and 399.9 eV, respectively. The C(1s) spectra were deconvoluted using four peaks corresponding to *C*−C, *C*−N, *C*=N, and *C*≡N functionalities at binding energies of 284.6, 285.2, 286.1, and 287.1 eV, respectively. These binding energies were computed relative to assignment of the lowest *C*−C peak to 284.6 eV.[19]

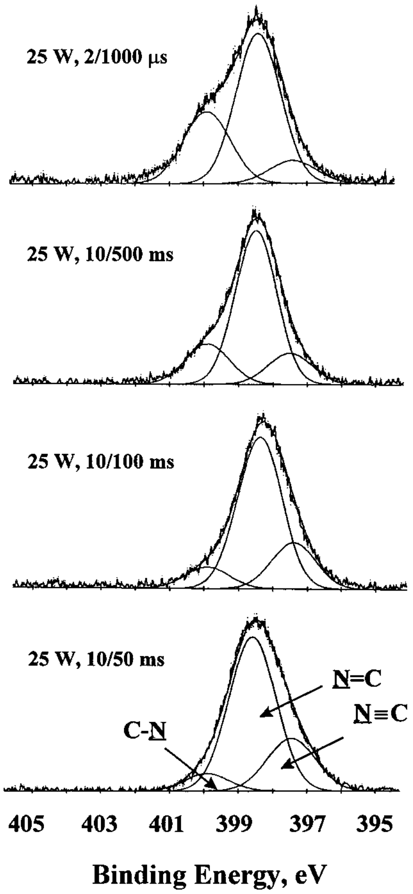
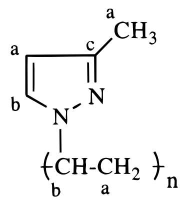


Figure 1. High-resolution N(1s) XPS spectra of films obtained from the pulsed plasma polymerization of the MVP monomer arranged in order of decreasing plasma duty cycles employed during film synthesis (bottom to top).

As shown in Figure 3, the above assignments are consistent with analysis of N(1s) and C(1s) spectra obtained from the non-plasma-synthesized linear MVP polymer. The two equal peak areas of the N(1s) spectrum are as expected for this polymer, reflecting the equal distribution of N atoms involved in C−*N* and C=*N* bonds in the starting monomer. The three peaks shown in the C(1s) spectrum have peak areas in the ratio of 3:2:1, consistent with the relative C atom abundancies labeled a, b, and c anticipated in the linear polymer:



The binding energies of the peaks shown in Figure 3 agree with the various peak assignments shown in

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(18) Eng, F. P.; Ishida, H. *J. Appl. Polym. Sci.* **1986**, *32*, 5021.

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

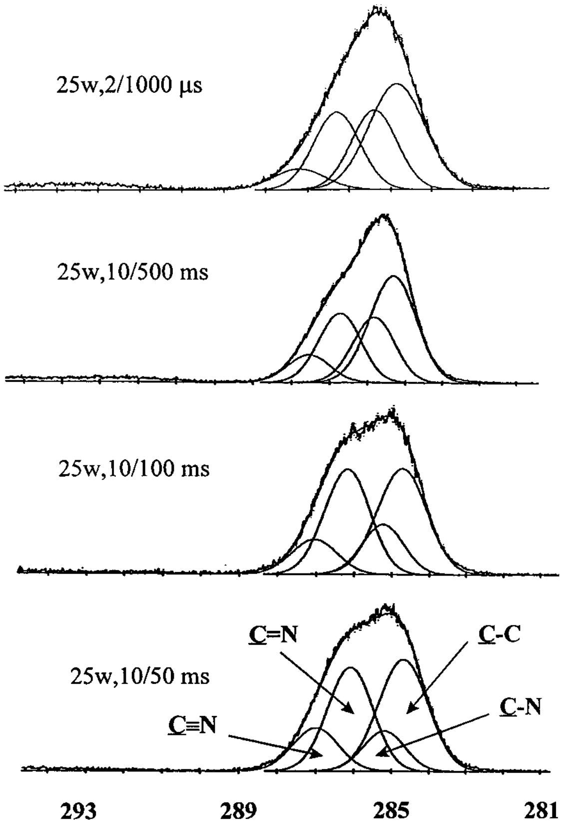

Figure 2. High-resolution C(1s) XPS spectra of the same films shown in Figure 1.

Figures 1 and 2 for both N and C photoelectrons. The analysis procedure and peak assignments employed here are similar to those employed by Beamson and Briggs in their analysis of XPS spectra of other linear, heteroatom-containing polymers.[20]

A comparison of the spectra shown in Figures 1−3 clearly reveal that the composition of the plasma-generated polymers bear an increasing similarity to the non-plasma-synthesized linear poly-MVP standard as the plasma duty cycle employed during film formation is reduced. These results are consistent with increased retention of the monomer ring system in these plasma polymers with reduced duty cycles employed during synthesis. Additional striking spectral evidence for increased aromatic ring content in these films is the appearance of high binding energy shake-up peaks in films obtained at the lowest plasma duty cycles, as shown in both Figures 1 and 2. These shake-up peaks are attributable to the increased presence of π bonding and thus higher ring content in these films.[20]

Although an obvious increased ring incorporation is achieved in the films deposited at the lowest plasma duty cycles, the ring content of these films remain less than that of the non-plasma-synthesized linear polymer standard. In particular, even films plasma synthesized at extraordinarily low average power input (i.e., 0.05 W) exhibit the presence of some C≡N groups which, of course, are not present in the completely linear polymer.

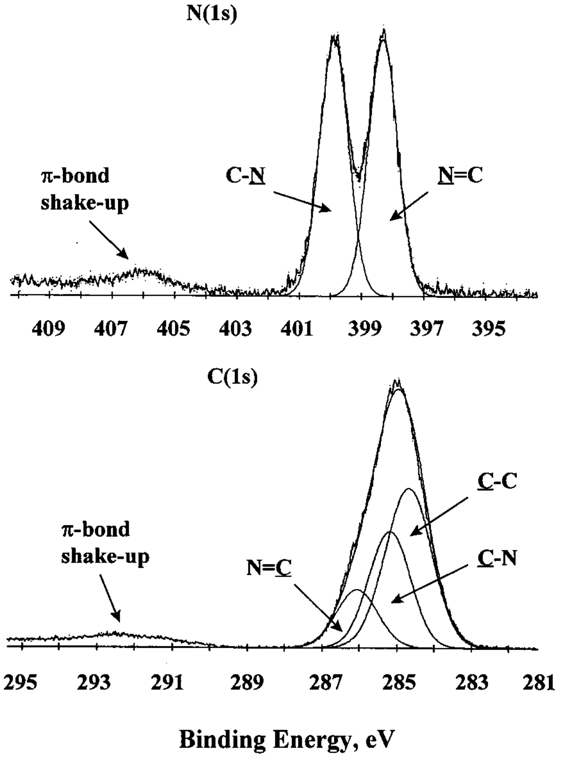

Figure 3. N(1s) (top) and C(1s) (bottom) high-resolution XPS spectra obtained from a non-plasma, conventionally synthesized linear MVP polymer.

FT-IR film characterization of these polymers provides additional support of the above analysis. IR transmission spectra of films polymerized at 25 W peak power and various plasma duty cycles are shown in Figure 4, in this case arranged in order of decreasing duty cycles top to bottom. Additionally, the transmission spectra of the starting monomer, non-plasma-synthesized linear polymer, and a pulsed plasma film generated at the lowest average power input of 0.05 W are shown in Figure 5. The spectra in Figure 4 reveal increasingly sharp bands from top to bottom, reflecting progressively more highly ordered polymeric structures as the plasma duty cycle employed during synthesis was reduced. In particular, increasingly prominent absorption bands appear at 3113, 1535, 1366, 1200, 1071, and 756 cm^{-1}. As shown in Figure 5 these frequencies are also prominent in the non-plasma linear polymer and in the starting monomer. All of these bands have been associated with ring vibrations of pyrazoles.[21,22] However, it is also important to recognize key differences between the plasma polymers and the linear poly-MVP standard, including films synthesized at ultralow power inputs. For example, the plasma polymers contain absorption bands at 2200 and 1628 cm^{-1} which are not present in the linear polymer or the starting monomer. These bands are assigned to −C≡N and nonring C=N stretching vibrations representing functionalities created during plasma operation.[22] Although the relative areas of these bands decrease as the duty cycles employed during plasma polymerization are reduced, these bands remain

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(20) Beamson, G.; Briggs, D. *High Resolution XPS of Organic Polymers. The Scienta ESCA Data Base*; J. Wiley and Sons: New York, 1993.

(21) cf. Elguero, J. Pyrazoles and Their Benzo Derivatives. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Potts, K. T., Eds.; Pergamon Press: New York, 1984.

(22) Socrates, G. *Infrared Characteristic Group Frequencies*, 2nd ed.; J. Wiley and Sons: New York, 1994.

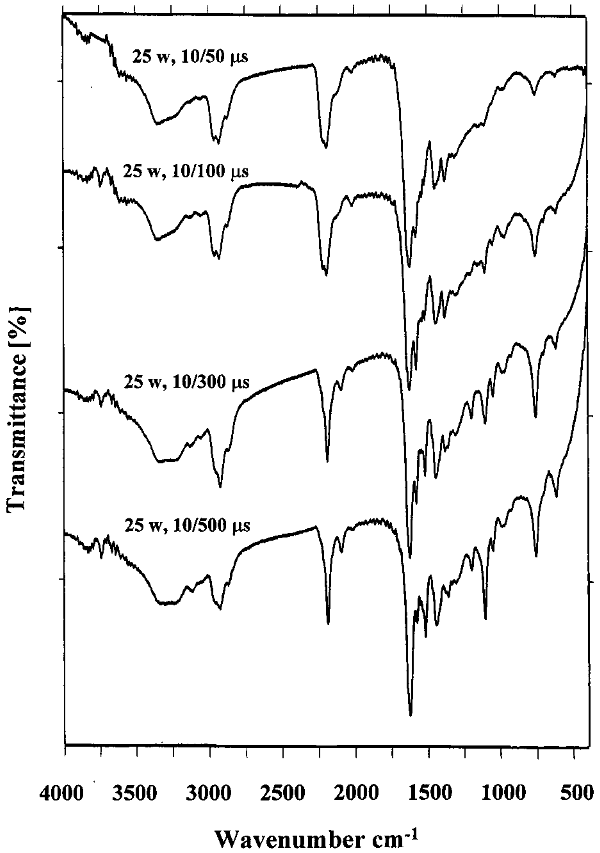


Figure 4. FT-IR transmission spectra of a series of MVP polymeric films obtained during pulsed plasma polymerization of MVP monomer. The spectra are arranged in order of decreasing plasma duty cycles employed during deposition reading top to bottom.

well pronounced even in the films produced under the least energetic plasma conditions. The IR spectra correlate with the XPS results in that the deconvoluted N(1s) and C(1s) spectra also reveal the presence of the $-C{\equiv}N$ groups. In terms of IR spectral analysis, it should also be noted that the prominent C=C stretching band of the starting MVP monomer (1644 cm^{-1}) is not present in either the plasma polymers or the non-plasma standard, indicating polymerization through this functionality under both sets of polymerization conditions.

1-Allylimidazole (AI). The compositional changes with variations in plasma duty cycle observed with the AI monomer parallel those of the MVP reactant with respect to increasing ring retention with decreasing average power input during synthesis. However, the overall extent of this ring retention is significantly higher with the AI polymers, as revealed by N(1s) (Figure 6) and C(1s) (Figure 7) XPS spectra of these films. These films were deposited at a peak power input of 50 W and variable duty cycles, as shown. The spectral analysis was carried out using the same functionalities as employed with the MVP films. Again a pronounced increase in the C−*N* group is observed as the duty cycle during synthesis is reduced, as shown in Figure 6. The two peaks shown approach, but do not equal, the 1:1 ratio anticipated for a completely linear AI polymer. Additionally, the C≡*N* contribution is significantly less with the low duty cycle AI films relative to that observed with MVP polymers. The same general pattern of functional group contributions is observed with the C(1s) spectra; however, this analysis is complicated somewhat by the presence of oxygen atoms in AI films deposited at higher plasma duty cycles (i.e., the bottom two spectra of Figure 7). The oxygen content of these films, 7.4% and 3.7% in the 10/50 and 10/100 ms runs, respectively, result in assignment of additional peaks at 288.5 and 286.2 eV corresponding to *C*=O and *C*−O groups. Plasma films deposited at the lower duty cycles of 10/200 and 10/500 ms were essentially devoid of oxygen content. As shown in Figure 7, a large progressive increase in the *C*−N peak area relative to the *C*=N peak area is observed as the duty cycle employed during synthesis was reduced. The relative areas of the *C*−C, *C*−N, and *C*=N peaks approach, but do not equal, the theoretical ratio of 2:3:1 for carbon atoms labeled a, b, and c anticipated for a completely linear polymer, as illustrated below:

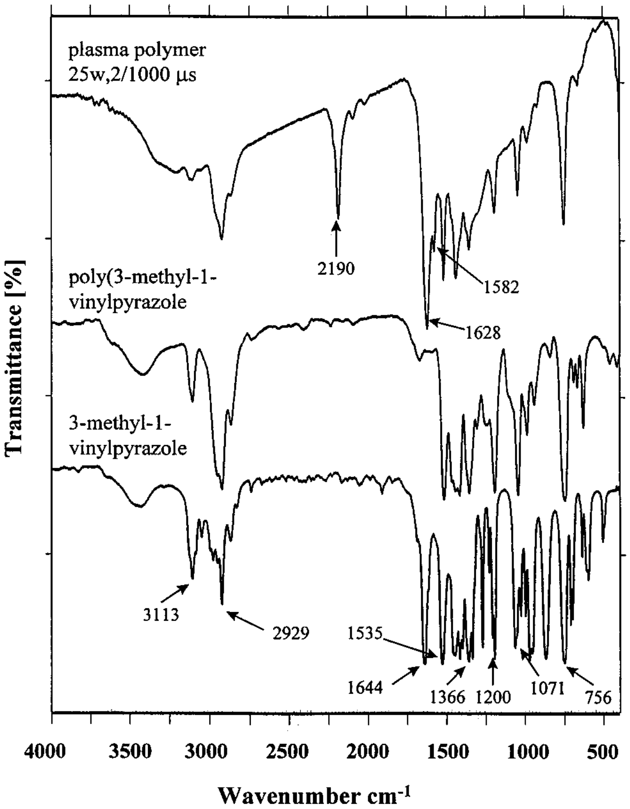
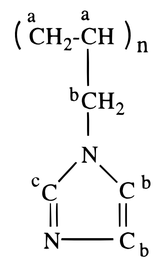


Figure 5. Comparison of the FT-IR transmission spectra of the lowest duty cycle pulsed plasma-synthesized MVP polymer (top), non-plasma-synthesized linear MVP polymer (middle), MVP monomer (bottom).



The increased ring retention in these polymers, at lower power inputs, is also evidenced by the shake-up peaks present in both the N(1s) and C(1s) spectra. As shown in Figures 6 and 7 the magnitude of these high binding

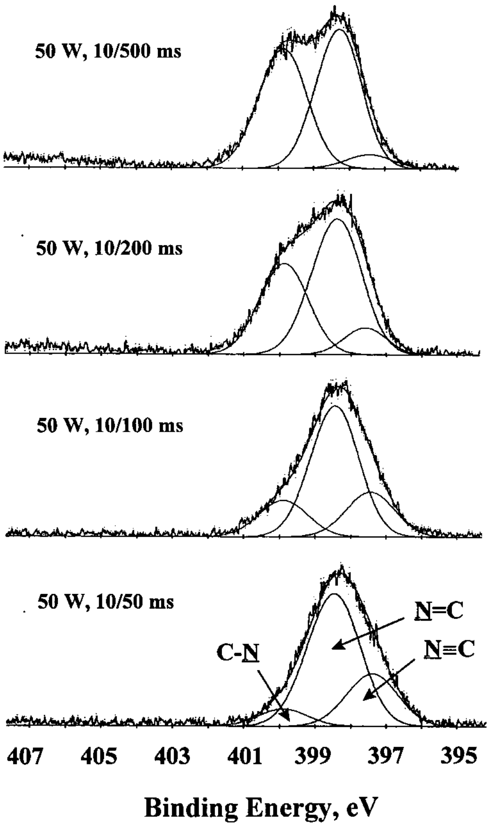


Figure 6. High-resolution N(1s) XPS spectra of plasma films obtained from the AI monomer arranged in order of decreasing plasma duty cycle during synthesis reading bottom to top.

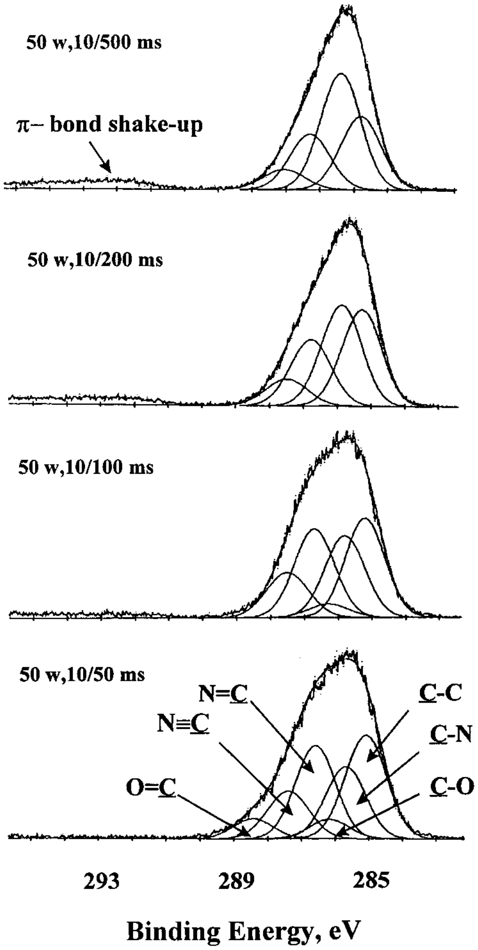


Figure 7. High-resolution C(1s) XPS spectra of the same films shown in Figure 6.

energy shake-up peaks increased as the duty cycles employed during film synthesis was reduced.

FT-IR spectra of the poly-AI films obtained at different plasma duty cycles are shown in Figure 8 along with the spectrum of the AI monomer. The plasma polymer spectra are arranged in order of decreasing duty cycles during synthesis, reading top to bottom. Clearly, increasingly sharp and more structured bands are observed as the duty cycle employed during synthesis was reduced. In the absence of a standard linear poly-AI film, the comparison of these spectra with a non-plasma-synthesized linear poly(vinylimidazole) spectrum is instructive.[23] For example, bands at 3110, 1502, 1230, and 1100 cm^{-1}, present in the plasma polymers, can be assigned to various ring vibrations. The 3110 and 1100 cm^{-1} bands have been assigned to stretching and in-plane bending of C=C−H and N=C−H ring vibrations. The 1502 cm^{-1} band is assigned to C=N ring stretching whereas that at 1230 cm^{-1} is attributed to an unspecified ring vibration.[23] All of these bands increase in intensity with decreasing duty cycle employed during film formation. The relatively strong band at 750 cm^{-1} is attributed to a CH_2 rocking vibration which would be consistent with an overall decreased cross-linking of the plasma polymers, reading top to bottom.

A very broad band extending from approximately 3500 to 2700 cm^{-1}, superimposed above the C−H stretching vibrations from 3100 to 2900 cm^{-1}, appears in the plasma films. The lower wavenumber portion of this broad adsorption can be attributed to NH···N hydrogen-bonding interactions known to occur in solid imidazoles.[22] The higher wavenumber portion of this band can be attributed to H_2O absorption by these films as reported in conventional linear poly(vinylimidazole) polymers.[23] On the basis of the results in Figure 8 it is apparent that more pronounced H_2O adsorption occurs in films polymerized under lower plasma duty cycles. This observation would be consistent with the less cross-linked nature of the lower duty cycle polymerized films. Vacuum heating of these films at 80 °C followed by subsequent FT-IR absorption measurements resulted in relatively little change in the IR absorption spectra.

As in the case of the plasma MVP films, absorption bands at 2230 and 1650 cm^{-1}, representing creation of −C≡N and nonring C=N groups during plasma synthesis, are observed in the poly-AI films. Although the relative intensities of these bands decrease with decreasing plasma duty cycles during synthesis, they remain clearly prominent even in films produced under exceptionally low power input conditions.

Film Deposition Rates. An interesting feature of the pulsed duty cycle technique is that relating to film formation rates under the intermittent plasma operation. In view of the intermittent operation, including relatively long plasma off periods, it is more informative to analyze film formation as a function of energy input in lieu of the traditional deposition rates (e.g., Å/min) employed in CW studies. As noted in previous studies, increases in film thickness per unit energy input are

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(23) Kumagi, M.; Tsuchida, K.; Ogino, Y.; Hansen, J.; Ishida, H. *Polymer* **1995**, *36*, 535.

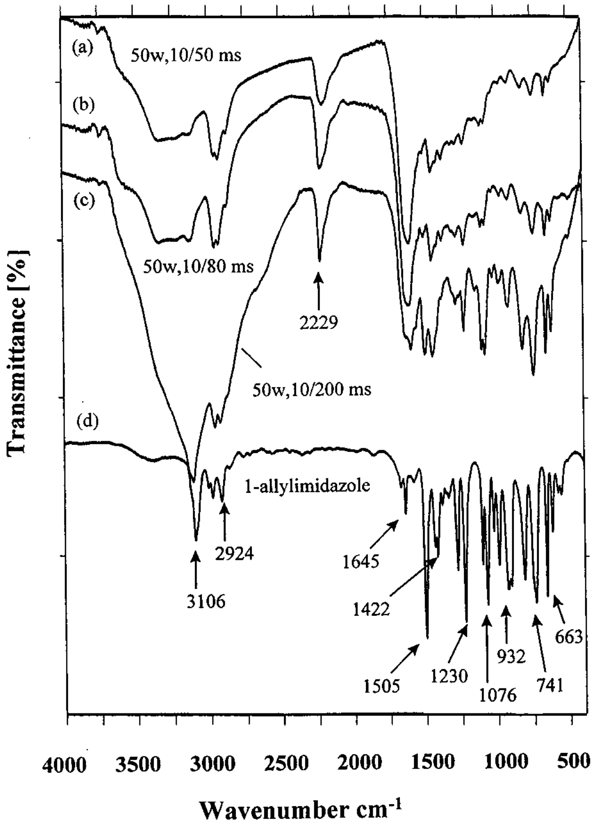

Figure 8. FT-IR transmission spectra of pulsed plasma-polymerized AI films deposited at 50 W peak power and duty cycles of 10/50 (a), 10/80 (b), and 10/200 ms (c). The spectrum of the AI monomer is shown for reference (d).

frequently observed as the plasma off times are increased during pulsed plasma polymerizations.[7,8,11,12,16] In fact, an increase in film thickness/J was observed in the present study as illustrated in Figure 9 with data obtained during the polymerization of the AI monomer. Comparable results (not shown) were obtained with the MVP polymer. This increase in film thickness/J with increasing plasma off times is indicative of significant film formation during plasma off periods. We believe this observation is important with respect to plasma dynamics, as discussed below.

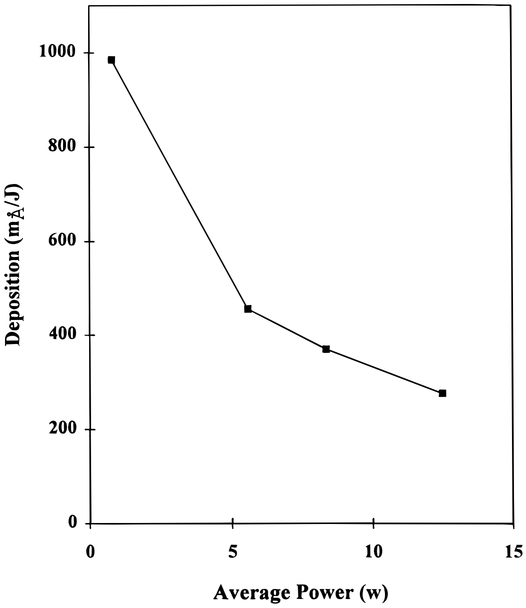

Figure 9. Variation in film thickness per joule of input energy as a function of the average power employed during the pulsed polymerizations

Discussion

The spectral data obtained in this study are internally consistent in showing progressive variations in film compositions with changes in the plasma duty cycles employed during polymerizations. With both monomers, the compositional changes involve an increased retention of the aromatic ring systems of these monomers in the resultant films, as the average power input during polymerization is decreased (i.e., duty cycles are lowered). At the same time, a significant difference is observed in contrasting the polymer compositions obtained from these two monomers. Specifically, a higher ring retention is observed in the case of the imidazole compared to the pyrazole. This difference is most clearly evident in comparing the N(1s) XPS spectra from these polymers obtained under the lowest duty cycles employed (Figures 2 and 6). Presumably, this result reflects differences in the bond energies of the starting monomers in that the pyrazole contains weak N−N bonds. Thus, even though the pyrazole studies were extended to exceptionally low average power inputs, it was simply not possible to identify reaction conditions which provided the same degree of ring retention as achieved with the imidazole. As shown in the imidazole studies, it is possible to achieve exceptionally high ring retention, thus forming unusually linear polymers in comparison with the typically more highly cross-linked polymers produced under CW conditions. The high degree of ring retention is evidenced by the close to 1 ratio of the C−*N* and C=*N* peaks in the top spectrum of Figure 6, which compares closely to that observed for the linear poly-MVP (Figure 3).

A second distinguishing feature, in contrasting polymer compositions from these two monomers, is the variation of N/C atom ratios with changes in the average power input. As shown in Figure 10, this ratio increases in the AI polymers, but decreases with the MVP polymers, as the average power input during polymerization is decreased. The MVP results are considered more typical of plasma results in that the N/C ratios of the polymers approach that of the starting monomer (i.e., $^1/_3$) as the plasma duty cycles are reduced. This type of atomic composition variation has been observed in several other pulsed plasma investigations. Although the exact origin of this effect is not known, it most likely involves the presence of the exceptionally weak N−N bond of this monomer. Preferential scission of this bond can lead to formation of relatively stable C≡N and C=N units which apparently are readily incorporated in the plasma polymers as shown by the spectroscopic results. If this is indeed the case, formation of such groups involves selective elimination of carbon atoms to account for the higher N/C atom ratios observed in polymers produced at the higher plasma duty cycles. As shown in Figure 10a, the N/C ratio of these polymers approximates more closely that of the starting monomer as the average power input employed during plasma operation is decreased. This trend is consistent with decreased N−N bond scission at lower power inputs. In

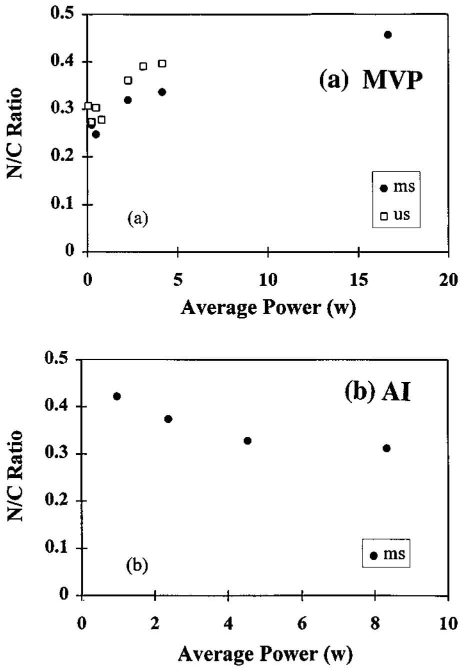

Figure 10. Variation of the N/C atom ratios in the pulsed plasma-polymerized films obtained from MVP (a) and AI (b) as a function of the average power employed during synthesis. The MVP study included both millisecond and microsecond pulse widths, as shown.

contrast, the AI results indicate increased selective N atom retention in the films as the plasma duty cycles employed during film formation are reduced, as shown in Figure 10b. It is only at the higher duty cycles (i.e., at higher average power inputs) that the N/C atom ratios of the polymers approach that of the starting monomer. The variation of the N/C ratios with power input in the case of the AI polymers is totally unexpected in comparison with plasma studies on numerous other monomers. Unfortunately, we are unable to offer an explanation of these latter results at this time.

A rough estimate of the overall ring retention in these plasma polymers can be obtained from the N(1s) XPS spectra. This estimate is based on the assumption that all of the C−*N* peak area is attributable to ring retention. On this basis we calculate maximum ring retention of approximately 50% in the MVP films and 86% in the AI polymers, both numbers coming from runs at the lowest average power input values. In view of the above assumption, these numbers must clearly be recognized as upper limits to the percentage ring retentions.

The results of the present study provide additional support for the unusual level of film chemistry controllability inherently available via the pulsed plasma technique. The highly structured, relatively linear polymers synthesized in this work at low duty cycles, particularly in the case of the imidazole, are quite unusual by plasma polymerization standards. The formation of a plasma polymer which so closely parallels the structure of that anticipated for a linear, conventional polymer, such as allylimidazole, is significant in terms of future applications of plasma polymerization technology. Most importantly, this film chemistry controllability has been achieved while retaining the many unique advantages of the plasma surface modification technique including conformal, pinhole-free coatings deposited in a single-step, all-dry process.

Summation

The film chemistry controllability made available by the pulsed plasma polymerization technique has been successfully employed to synthesize relatively linear polymeric materials. This controllability has been achieved despite the presence of weak bonds in these fairly complex molecules. The results obtained suggest that the pulsed plasma surface modification technique can be successfully employed to extend this polymerization method to synthesis of relatively ordered new materials, including work with larger monomers. Despite the use of low average power inputs, the pulsed technique permits synthesis of these films while maintaining all of the many advantages of plasma polymerization coating technology.

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