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CHARACTERIZATION AND PROPERTIES OF PLASMA
POLYMERIZED 2-VINYLPYRIDINE

K. W. BIEG, D. K. OTTESEN, AND K. L. BROWER

Sandia Laboratories

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K. W. Bieg, D. K. Ottesen, and K. L. Brower
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CHARACTERIZATION AND PROPERTIES OF PLASMA POLYMERIZED 2-VINYLPYRIDINE

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ABSTRACT

The chemical structure, aging, thermal, and adhesive behavior of plasma-deposited 2-vinylpyridine has been investigated. The molecular structure of the plasma polymer is significantly different from the conventional, linear polymer and is strongly dependent on plasma reactor variables. Additional cyano, methyl, and olefinic groups were identified in the plasma polymer, and aromaticity retention was reduced at the more severe (low pressure, high rf power) reactor conditions studied. Post-deposition oxidation occurred, which followed approximately first order kinetics initially ($\Delta E \sim 11.6$ Kcal/mole, with $\sim 25\%$ conversion of aromatic rings to an aromatic ketone in 4.5 months at 23°C). Oxidation was significantly reduced in vacuum, inert gas, and hydrogen atmospheres. Thermal weight loss began at relatively low temperatures and appeared to accompany an exothermic, irreversible cross-linking reaction which began at about 100°C . Principle low temperature decomposition products were low molecular weight gases (primarily, CO_2) and 2-methylpyridine. A quantitative tensile-pull adhesion test was developed. Using this technique, the plasma polymer-aluminum cohesive bond strength was found to be 480 psi and was degraded at high humidity levels.

INTRODUCTION

Plasma-deposited poly (2-vinylpyridine) is being considered as a thin film dielectric material in a high reliability, long life capacitor application. For this reason and the fact that plasma polymerization is an extremely complex and poorly understood process, a study was undertaken

in order to characterize the chemical nature of the as-deposited polymer material. Plasma polymerization involves the synthesis of thin (generally less than 50,000 Å) polymer films in a low-pressure radio frequency electrical discharge of the monomer and, typically, a suitable inert carrier gas. It is generally believed that polymerization occurs as the result of the generation of reactive free radicals and ionic intermediates from electro-monomer and accompanying fragmentation and secondary reactions in the plasma. However, the details of the polymer initiation, propagation, and termination reactions are not well understood due to the multitude of processes possible. For example, Vasile and Smolinsky¹ have identified at least 30 ionic and neutral species in a radiofrequency discharge of the simplest possible organic molecule, methane. Furthermore, Tibbitt, et al., have presented a "simplified" chemical reaction mechanism involving twenty steps² to explain the plasma polymerization of ethylene and have postulated an extremely complicated molecular structure for this material³. Therefore, it appears hopeless to identify a credible, all inclusive reaction sequence for more complicated organic molecules such as 2-vinylpyridine. In light of this, it was decided to undertake a more general investigation to identify the major chemical functional groups present in the as-deposited 2 vinyl-pyridine plasma polymer and to establish the significant chemical aging, thermal, and adhesive properties of the material.

Because of their irregular structure, insolubility in organic solvents, and availability in only milligram quantities, the characterization of plasma polymers is especially difficult. In particular, conventional dispersive infrared transmission techniques have traditionally used artificially thick films on other than metallic substrates and have generally yielded poorly resolved spectra. We have found Fourier transform infrared reflectance

spectroscopy (FTIR) to be a useful technique for the characterization of these thin (1,000-40,000 Å) polymer films deposited on aluminum substrates. In addition, we have explored the use of conventional chemical analysis, carbon-13 nuclear magnetic resonance (on the soluble polymer samples) and x-ray photoelectron spectroscopy to obtain complimentary structural information. We have extensively followed the chemical aging behavior of these thin films, particularly in oxidative environments, through the use of FTIR difference spectroscopy and electron spin resonance. Furthermore, we have performed a number of thermal analyses to identify possible phase transitions and thermal degradation/decomposition behavior using differential scanning calorimetry, thermogravimetry, and pyrolysis/gas chromatography mass spectrometry. Finally, a means of performing tensile pull adhesion testing on thin polymer films has been developed, and some initial results are presented.

EXPERIMENTAL

The equipment used in this study (Fig. 1) consisted of a capacitively coupled plasma reactor similar to the apparatus described by Poulsen⁴ for the plasma etching of integrated circuits. This arrangement resulted in uniform depositions over a range of flow rates and improved utilization of monomer compared to common plasma reactor designs. Monomer and carrier gas are introduced beneath the lower (ground) electrode and are forced to sweep radially inward across the 5 in diameter aluminum electrodes. The gases are pumped out through the tube in the center of the lower electrode. Substrates were mounted on the lower electrode. Electrode spacing was maintained at 2.3 cm. Power is supplied by an International Plasma Model PM 101 rf power generator operating at 13.56 MHz. Chamber pressure was monitored with a MKS Baratron Type 90B-1 capacitance manometer. The reactor

Figure 1. Capacitively-coupled plasma reactor.

was evacuated to less than 10^{-6} Torr with a diffusion pump prior to introduction of monomer. During the actual deposition, a mechanical pump with an in-line liquid nitrogen cold trap was used to maintain monomer and carrier gas flow.

2-Vinylpyridine (2-VP) monomer was used as received from ICN-K&K Laboratories. However, no impurities were detected by gel permeation chromatography or infrared spectroscopy. The monomer was thoroughly degassed by repeated freeze-pump-thawing under vacuum prior to use. Research grade argon (99.99% purity, Matheson Gas Products) was used as the carrier gas. Substrates were prepared by vapor deposition of an opaque layer of aluminum on glass micro-scope slides. Polymer film thicknesses were determined by measuring the step height between a masked and unmasked portion of the specimen with a Rank, Taylor, and Hobson Talystep 1 traversing stylus. Deposited films were generally stored in a vacuum desiccator prior to analysis to minimize absorption of moisture from the atmosphere, unless otherwise noted. During the aging studies, samples were contained in vacuum tight cannisters which could be backfilled with the respective aging gases and could then be stored in aging ovens at elevated temperatures.

Infrared spectra were obtained with a Digilab FTS-14 FTIR spectrometer in the reflection-absorption mode. A single external reflection from the sample surface was used, with an angle of incidence of 75° . The spectra were taken at a resolution of 6 cm^{-1} while the instrument was purged with dry nitrogen. Elemental analyses were performed on a Perkin-Elmer Model 240 elemental analyzer. Oxygen content was determined by difference. Molecular weights of samples soluble in THF were determined on a Waters' Associates ALC/GPC 502/401 dual detector liquid chromatograph using standard Waters' micro Styragel columns.

Carbon-13 nuclear magnetic resonance spectra were obtained on the polymer soluble in deuterated chloroform using Varian XL-100 and Bruker SXP spectrometers operating at 25.2 MHz. ESCA spectra were obtained on a PHI Model 548 ESCA/Auger Electron Spectrometer. For electron spin resonance measurements, polymer films ($\approx 28,000$ Å thickness) were plasma deposited directly onto sapphire or glass ESR substrates. Since the ESR spectrometer cavity⁵ operated at near-liquid helium temperatures, it was found desirable to roughen the substrate surface prior to polymer deposition to prevent flaking off of the polymer film as a result of thermal cycling.

Thermal analyses in dry argon were obtained with a DuPont Model 951 thermogravimetric analyzer. Sample weight was approximately 1 mg. with a heating rate of 10°C/min. Differential scanning calorimetry data was obtained with a Perkin-Elmer Model DSC-2 differential scanning calorimeter. Approximately ten milligram samples were run in dry nitrogen. Thermal decomposition products were determined using pyrolysis/gas chromatography-mass spectrometry at a heating rate of approximately 5°C/msec onto a 6' x 1/8" 4% SE-30 column programmed from 30°C to 220°C at 10°C/min. Tensile pull adhesion tests were performed on an Instron Model TTB. Samples were prepared by depositing films directly onto polished (600 grit) aluminum tensile plugs of one square inch surface area and assembled using appropriate adhesives. Pull rate was 0.05 inch/min.

RESULTS AND DISCUSSION

Effect of Reactor Conditions on Form of Polymer

The form of polymer produced during plasma deposition depends on reactor conditions during the polymerization⁶. The important reactor variables are monomer pressure, flow rate, and the reactor power level. Figure 2 shows a characteristic map of the dependence of type of polymer formed as a function

Figure 2. Dependence of 2-vinylpyridine polymer form on reactor variables at low power.

of 2-vinylpyridine monomer flow and pressure at a 10 watt power level. At monomer pressures above approximately 70 microns, a 'tacky' film only is produced in the stable discharge region. This polymer is soluble in polar solvents and may therefore be characterized using conventional chemical techniques. Gel permeation chromatograms (GPC) of plasma polymers synthesized at 0.13 Torr and 0.23 Torr monomer pressure were obtained and compared to a similar chromatogram of a special styrene oligomer mixture in order to obtain an approximate molecular weight for the soluble plasma material, as shown in Fig. 3. Resolution using this technique was not sufficient to detect individual oligomer units in the standard mixture. However, given the standard oligomer mixture molecular weight range of 208-1458, and a maximum concentration at 729 molecular weight one can obtain an estimate of the molecular weight of the plasma polymers soluble in tetrahydrofuran. The chromatogram of the plasma polymer synthesized at 0.13 Torr monomer pressure indicates a rather uniform distribution of oligomer units from approximately 300-800 molecular weight, with lesser amounts at lower and higher elution times. This corresponds to oligomers of 3-8 monomer units which appears to agree with approximate crosslink densities calculated for typical plasma polymers³ using other methods. The chromatogram of the plasma polymer synthesized at the higher monomer pressure, 0.23 torr, indicates an oligomer distribution which maximizes later, at approximately 300-400 molecular weight. Useful polymers for thin film capacitors were synthesized at 0.03 Torr monomer pressure and are not known to be soluble in any common organic solvent, though they swell in water owing to their high crosslink density.

Figure 3. Gel permeation chromatograms of linear and soluble plasma polymers.

Chemical Structure Characterization

Polymer films were synthesized under a variety of plasma reactor conditions in order to investigate these effects on polymer structure. Plasma conditions under which the various films were prepared are presented in Table 1. Figure 4 illustrates the Fourier transform infrared transmission spectrum of conventional, linear poly (2-vinylpyridine) (Polyaciencies #1050). The broad feature at 3450 cm^{-1} is due to water which was difficult to eliminate from the KBr pellet. The assignments for major bands in this spectrum (Table II) are relatively straight-forward based on the assignments for polystyrene⁷, poly(4-vinylpyridine)⁸, and substituted pyridines⁹. The reflectance FTIR spectrum for the plasma polymerized film prepared under the conditions specified for Sample 1 in Table I is also shown in Fig. 4. This spectrum is quite similar to that for the linear polymer. In particular, the plasma polymer spectrum contains the strong ring CH stretch at 3060 cm^{-1} along with the aromatic CH wagging vibration at 745 cm^{-1} characteristic of the expected 2-substituted pyridine ring. Also, the CH_2 backbone stretching and wagging bands are observed at 2930 cm^{-1} and 2870 cm^{-1} , and 1470 cm^{-1} , respectively. The presence of the intense CC and CN ring stretching bands at 1590 cm^{-1} indicates a substantial retention of aromaticity in the plasma polymer.

A number of important differences are also apparent. Additional relatively strong absorptions are present at 2200 cm^{-1} and 2165 cm^{-1} . Considering the starting material and lack of other absorptions in this region, these bands can clearly be assigned to a nitrile group indicating pyridine ring cleavage (an alkyne stretch is also a possibility, but this band is generally very weak, due to symmetry). The abnormally low energy at which

Figure 4. Fourier transform infrared spectra of poly (2-vinylpyridines).

this group absorbs suggests it is in a highly conjugated, electron-rich environment. The absorption at 1630 cm^{-1} may be identified as an olefinic ($\text{C}=\text{C}$) or imino ($\text{C}=\text{N}$) stretching band. Also noteworthy in the spectrum of the plasma polymer is the strong new band at 2965 cm^{-1} and the rather weak band at 1370 cm^{-1} . These absorptions may be assigned to methyl CH_3 stretching and deformation vibrations, suggesting a significant amount of branching or chain ends in this polymer.

The FTIR spectrum of a thinner film (Sample 2, Table I) of this same material is shown in Fig. 4. The same bands are observed as for the thicker film. However, the CH stretching bands in the $2900\text{--}3100\text{ cm}^{-1}$ region are noticeably more intense relative to the ring and deformation band in the $600\text{--}1600\text{ cm}^{-1}$ portion of the spectrum. Calculations¹¹ indicate that the major contribution to this observation is due to optical effects unique to reflection techniques, rather than actual structural differences in the films.

Figure 5 shows the FTIR spectrum of a film (Sample 3, Table I) prepared at the same total pressure but at a much lower monomer pressure than Samples 1 and 2. The balance was argon carrier gas. This spectrum displays structural features similar to the preceding samples. However, the nitrile bands are no longer clearly resolved and are shifted by approximately 20 cm^{-1} to higher energy, suggesting that this group does not exist in the same electron-rich environment of Samples 1 and 2. Further, the presence of a new CH_2 , CH_3 deformation band at 1450 cm^{-1} indicates that additional branching and crosslinking is present.

An FTIR spectrum of a polymer prepared under similar conditions but without the argon carrier gas (Sample 4, Table I), is also shown in Fig. 5.

Figure 5. Fourier transform infrared spectra of poly (2-vinylpyridines).

In general, the same bands are present as were observed with films prepared with the argon implying that the rare gas has no substantial influence on the resulting structure of these plasma polymers. This conclusion is not surprising in view of the fact that the addition of rare gases has little apparent effect on the ion chemistry of comparable benzene discharges¹². Also shown in Fig. 5 is the FTIR spectrum of a film prepared at a high rf power level. It is clear from the presence of only a few, broad absorption bands that substantial degradation of the monomer occurred under these conditions. In particular, the ring CH stretch is no longer apparent, indicating nearly complete breakup of the aromatic pyridine ring. Also, the previously well-resolved features at $1550\text{--}1600\text{ cm}^{-1}$ are manifested as a broad band at 1630 cm^{-1} , assignable primarily to $\text{C}=\text{C}$ and $\text{C}=\text{N}$ vibrations. The remaining features are the CH_2 and CH_3 deformation bands at 1450 cm^{-1} and 1370 cm^{-1} . This structure is one of a highly branched, unsaturated aliphatic polymer.

It is interesting to compare the relative degree of aromaticity retained by the polymers of Table I. This may be accomplished roughly by calculating the ratio of the ring CH stretch peak height at 3060 cm^{-1} to the aliphatic CH_2 stretch band at 2930 cm^{-1} . These comparisons are presented in Table III. It is apparent that aromatic degradation in the plasma polymers is most severe at conditions of lower monomer pressure or high power.

Table IV shows the results of the elemental analyses of the plasma polymers, kept in dry air for 20 days prior to analysis. All the plasma polymers have a relatively high concentration of oxygen. In addition, this percentage is highest for the polymers prepared under the more severe

conditions, suggesting that the concentration of trapped free radicals is higher for these films. Nitrogen retention is nearly stoichiometric with the linear polymer in all cases. Hydrogen yield is also quite low, as has been observed for plasma polymers formed from other types of aromatic monomers¹³. The hydrogen-carbon ratio was found to be a rather sensitive function of plasma reactor conditions as well. Figure 6 illustrates the variation of the H/C ratio with monomer pressure and reactor power level for polymer deposited on the ground electrode. The H/C ratio decreases rather slowly with increasing pressure, $\sim 0.025/100$ micron, but increases dramatically with reactor power level, $\sim 0.05/10$ watt. These variations are opposite those obtained for aliphatic starting monomers, and appear to correlate with the increasing proportion of aliphatic to aromatic groups at low pressures or high power, as noted previously by infrared spectroscopy. In fact, the infrared spectra of polymers synthesized under these severe conditions suggest an aliphatic structure similar to that obtained for plasma polymerized ethylene.³

These results suggest that under mild plasma reactor conditions, at low power levels and high pressures, polymerization occurs preferentially as a result of plasma-induced polymerization, in which polymerization is initiated by a reactive species created in the electrical discharge but polymer growth occurs essentially by a conventional chain propagation mechanism, in this case through the vinyl group of the monomer. Conversely, under more severe reactor conditions, plasma-state polymerization is favored in which the gaseous monomer is broken down into reactive fragment species, producing a plasma polymer that bears little resemblance to the starting material.

Figure 6. Hydrogen/carbon elemental ratios as a function of plasma reactor conditions.

An attempt was made to analyze the plasma polymer by means of ^{13}C nuclear magnetic resonance spectroscopy. This technique offers the potential advantages of increased sensitivity, particularly to aromatic carbons, and more easily quantifiable results in providing structural information complementary to the infrared method. Unfortunately, the technique requires a substantial quantity of sample (several tenths of a gram) and magic angle spinning in order to provide adequate resolution to analyze solid samples. However, it has been possible to obtain ^{13}C NMR spectra of plasma polymer samples soluble in polar solvents (in this case, those synthesized at pressures above 70 microns and soluble in deuterated chloroform).

Figure 7 shows the ^{13}C NMR spectrum of the conventional, linear polymer dissolved in deuterated chloroform. Aromatic and aliphatic peaks are well separated. Five distinct bands are evident in the aromatic region, corresponding to the five distinct carbons of the pyridine ring. The narrowness of these absorptions (particularly of the C_c and C_g carbons) indicates that this polymer is very stereoregular.¹⁵ A single, unresolved, aliphatic peak is present attributable to the secondary and tertiary chain carbons. The ^{13}C NMR spectrum of the soluble plasma polymer synthesized at a reactor pressure of 0.23 Torr is shown in Fig. 8. The peaks labeled e, d, f, and g are only slightly broadened and are clearly assignable to the unsubstituted aromatic carbons identified for the linear polymer. These observations indicate that very little rearrangement of the pyridine rings has occurred. However, the bands due to the tertiary ring carbon and the aliphatic CH and CH_2 carbons are significantly broadened relative to the linear polymer, indicating that substantial irregularities exist in the plasma polymer chain. Furthermore, a new peak due to methyl carbons is evident in the aliphatic region.

Figure 7. ^{13}C nuclear magnetic resonance spectrum of linear poly (2-vinylpyridine).

Figure 8. ^{13}C nuclear magnetic resonance spectrum of plasma poly (2-vinylpyridine).

This latter group, accounting for approximately 20% of the aliphatic carbons, was also observed in the infrared spectrum of the same material. The ^{13}C spectrum also contains a reasonably sharp peak in the region expected for a cyano group carbon, corresponding to that found by infrared.

An attempt was also made to analyze the surface structure of these polymer thin films by means of x-ray photoelectron spectroscopy (ESCA). The results of these analyses are tabulated in Table V. Unfortunately, it is difficult to obtain detailed structural information with this method due to the relative insensitivity to different types of carbon hybridization¹⁶ and the experimental uncertainties in the ESCA technique. However, a number of important trends may be noted. The carbon (1s) and nitrogen (1s) bands are significantly broadened for the plasma polymers relative to the linear polymer, indicating these atoms see a wider variety of chemical environments in the plasma materials. Only a rough estimate of the surface aromaticity was made by observing the very weak $n \rightarrow \pi^*$ 'shake-up' satellite¹⁶ at approximately 7 eV higher binding energy relative to the main C(1s) band. This satellite, attributable to aromatic carbons, was definitely observable in the linear polymer and the plasma polymer synthesized at high pressure but was not detectable above the noise for the other plasma polymers, implying substantial loss of aromaticity in these latter materials. The binding energies for N(1s) electrons for the plasma samples is generally higher than the linear polymer. This suggests the nitrogen atom exists in environments of higher electron density, probably as nitrile or imine-type functionalities. Finally, a high surface concentration of oxygen was noted for all samples. An attempt was made to sputter-etch away the surface layer in order to obtain compositional information about the bulk material using

ESCA. Unfortunately, this technique proved unsuccessful as sputtering induced artificial, rapid carbonization of the surface.¹⁷ However, the ESCA observations are in general agreement with the conclusions obtained from the infrared spectroscopy studies, suggesting the surface layer does not differ significantly from the bulk.

The distribution of polymer deposition was also noted to vary with reactor conditions. In particular, as the reactor power level is increased, the glow is extended to well outside of the interelectrode region, resulting in significant deposition on the walls of the vacuum chamber. As has been noted for the deposition for polytetrafluoroethylene in an inductive plasma reactor,¹⁸ the elemental composition of the polymer deposit was also dependent upon position in the reactor. Polymer deposited on the lower (ground) electrode at a 2 VP monomer pressure of 30 micron, argon pressure of 200 micron, and a power level of 20 watts has a molecular formula $C_7N_{0.96}H_{7.52}O_{0.35}$. However, polymer collected from the upper (rf) electrode had a much higher hydrogen concentration, $C_7N_{0.98}H_{8.56}O_{0.58}$, whereas that collected from the partial glow region, two inches beneath the lower electrode had an elemental composition $C_7N_{0.99}H_{6.92}O_{0.32}$. These results suggest that polymer deposited in the intense glow regions are much degraded relative to that obtained outside of the plasma zone.

Chemical Aging

Plasma deposited polymer films are known to contain high concentrations of residual trapped radicals subsequent to polymerization¹⁹. Post reaction of these radicals with oxygen upon exposure to air has been postulated to explain polymer oxidation. Correspondingly, the introduction of additional dielectric relaxation mechanisms attributable to the polar carbonyl

groups^{20,21}, a decrease in conduction current and an increase in capacitance have been found to result from post-deposition exposure of plasma polymerized films to air. The dielectric loss factor for plasma-polymerized polystyrene has been found to be an order of magnitude larger than the conventional material²² for this reason. In order to further quantify the chemical aging and longterm stability of plasma polymerized 2-vinylpyridine thin films, an investigation of the oxidation process was undertaken using FTIR difference spectroscopy, electron spin resonance (ESR) spectroscopy, and elemental analysis.

Radical decay in the plasma polymer films was followed in vacuum, hydrogen, and dry air atmospheres by electron spin resonance spectroscopy. Samples were aged at elevated temperatures (94°C or 130°C) in order to accelerate the aging process. A typical isotropic resonance, illustrated in Fig. 9, had a g-value of 2.0033 ± 0.0005 and a near-Lorentzian line shape. The measured spin density was 2.7×10^{19} spins/gm immediately after plasma deposition. Due to the lack of hyperfine structure, it was not possible to identify a unique free radical species. A number of radical species probably contribute to the observed signal. However, based on the types of radicals formed in irradiated linear polyvinylpyridines²³ and polystyrenes^{24,25} inferences can be made as to the types of radicals which might be present in the plasma polymer. Possible radicals which are reasonable are the alkyl,

Figure 9. Initial electron spin resonance signal for plasma polymer (Sample 3, Table I).

azabenzyl,

pyridyl,

pyridinyl,

and azacyclohexadieny radical,

Pyridinyl radicals appear to be responsible for the ESR signal in γ -irradiated linear poly (2-vinylpyridine), whereas benzyl-type radicals are formed in polystyrene. However, little pyridine ring modifications were apparent in the infrared and ^{13}C NMR analyses of the plasma polymers, suggesting that alkyl- and azabenzyl-type radicals are more common in these materials. In addition, pyridyl- and azacyclohexadienyl-radicals are stable only at very low temperatures. Azabenzyl-type radicals are especially stable at room temperatures, due to resonance stabilization. Of course, other types of aliphatic radicals are certainly present also, owing to the complicated structure of the plasma polymer and the variety of fragmentation²⁶ and excitation processes likely to occur in an organic plasma.

The spin density (Fig. 10) was observed to change upon aging, depending on the environment. A corresponding narrowing of the ESR line width from 18 gauss to 13 gauss was observed to accompany the reduction in spin concentration. The relatively slow spin decay rate in vacuum ($t_{1/2} \approx 23$ hrs at 94°C) probably results from the formation of crosslinks by radicals in close proximity, either by the migration of radical sites or the annihilation of radical pairs in a single absorption step. The decay process appears

Figure 10. Decay of electron spin density with time in various aging environments.

to be essentially halted at about 60% conversion, likely due to the limited mobility of the remaining radicals or conversion to relatively stable species. Subsequent exposure to air resulted in a rapid decay of the residual ESR signal. Aging in a 130°C vacuum yielded a slightly higher initial decay rate ($t_{1/2} \approx 12$ hrs) and a residual free radical concentration of only about 30% of the initial concentration.

Recombination is apparently catalyzed in the presence of hydrogen, as has been observed for the free radical decay in irradiated polyethylene²⁷. It is postulated that the presence of hydrogen provides a mechanism for the radicals to migrate to an appropriate reactive site, according to the following mechanism:

The $R_2^{\bullet}$ radical may therefore be more available to participate in a termination reaction (recombination, disproportionation, etc.). The initial spin decay is quite rapid ($t_{1/2} \approx 2$ hrs at 94° C), but the rate slows considerably by 80% conversion. Again, these residual radicals are probably quite stable (e.g., szabenzyl-type radicals) and less susceptible to migration.

Exposure of the freshly-deposited plasma polymer thin ($\approx 25,000$ Å) films to dry air at 94°C resulted in a rapid initial decay ($t_{1/2} < 1$ hr), followed by a much slower rate at $\approx 88\%$ conversion. Two explanations for this abrupt change of rate are possible. First, this behavior may indicate the presence of two distinct polymer phases (i.e., amorphous and crystalline), as has been proposed to explain the oxidation of radicals in irradiated semi-crystalline polyethylene.²⁸ In that polymer, an initial reaction period of 400 seconds was attributed to the rapid diffusion and subsequent reaction of oxygen in

the amorphous fraction. This was followed by a rate approximately 13 times slower, owing to the slow diffusion of free radicals (in the crystalline regions) to oxygen accessible areas. Recently, Oberbeck, et al.²⁹ have postulated the existence of structural order (crystallinity) in the sub-phases which are known to exist in plasma polymer deposits and are believed to originate from particulate formation in the gas phase during polymerization. However, little direct evidence for this hypothesis was given, and it has been generally accepted that plasma polymers are completely amorphous.^{3,30}

A more plausible explanation for the two-rate behavior is the formation of peroxy groups,³¹ for example by the reactions:

Presumably, the new radical $R'\cdot$ would then be in a more favorable position to recombine with another radical, resulting initially in the rapid decay of unpaired spins. The peroxy group may then further react to produce a carbonyl group and yield hydroxides or water:

Alternatively, the peroxide radical may split off CO_2 (along with a chain scission), as has been postulated to occur during the oxidation of irradiated polyethylene²⁸;

Yet another possibility would be the annihilation of radicals as a result of the formation of peroxide crosslinks:²⁸

These crosslinks might then slowly decompose to form carbonyl groups.

The elemental compositions of films aged in dry air, vacuum, inert gas, and hydrogen at 94°C for 20 days are given in Table VI. Hydrogen content is appreciably lower for the polymer aged in dry air, supporting an oxidation mechanism which results, for example, in the evolution of water. Furthermore, the hydrogen content of the films aged in hydrogen was essentially the same as those aged in inert gas and vacuum. This indicates that the radical decay is indeed hydrogen-catalyzed and that no net hydrogen uptake occurs when aging in this atmosphere. The residual oxygen content in the latter three polymers is apparently a result of reaction with the ambient atmosphere following removal from the respective aging environments. As can be seen, the amount of oxygen incorporated in the sample aged in hydrogen is significantly lower than that sample aged in dry air, in agreement with the ESR aging studies. Aging in vacuum and helium also yielded reduced oxygen concentrations, but to a lesser extent.

Figure 11 shows the mass spectrum of the off-gasing products of 31 milligrams of the plasma polymer (density = 1.43 gm/cm³) aged in 145 cm³ of 760 torr dry air at 94°C. Significant peaks occur at mass 44 (CO₂) and mass 29 (probably C₂H₅⁺). The concentration of carbon dioxide is approximately 1.05 wt.%, obtained by comparing the mass 44 peak height to mass 40 (argon, which has a natural abundance of 0.934% in air). Lesser peaks are apparent

1466 PVP IN DRY AIR

* 35

M/E 44 = 100%

Figure 11. Mass spectrum of plasma polymer outgassing products
in dry air (20 days at 94° C).

at mass 12 (C^+), mass 20, mass 27 (HCN^+ , or $C_2H_3^+$) and mass 34. The presence of water as an outgassing product is not precluded, however, since water was present in the mass spectrometer background and was therefore subtracted out. Also, the polymer itself may effectively scavenge moisture.

Chemical aging of the films was also followed by FTIR difference spectroscopy at 23°, 50°, 94°, and 130°C. With this technique, the spectrum of the unaged film is subtracted from the aged film spectrum, allowing quantitative detection of the growth of new absorption bands as well as more subtle shifts in existing absorptions. Figure 12 illustrates a typical difference spectrum, obtained after aging a 15,000 Å thick PVP film for 735 hours at 50°C in dry air. Subtraction was scaled to cancel the pyridine ring mode at 1596 cm^{-1} . Close examination of the difference spectra indicate the growth of the carbonyl band at 1700 cm^{-1} ,¹ correlates with a shift in the ring bands at 1591 cm^{-1} and 1433 cm^{-1} to 1597 cm^{-1} ,⁽²⁾ and 1436 cm^{-1} ,⁵ respectively. The low energy location of the carbonyl absorption suggests an aromatic ketone-type structure. The carbonyl stretching vibration in 2-acetyl pyridine has been found to absorb at 1702 cm^{-1} .³² Furthermore, the slight shifts to higher energy observed for the latter two ring deformation bands suggests the addition of an electron-withdrawing group in the vicinity of the aromatic ring. In analogy with that proposed to explain the thermooxidative degradation of polystyrene,^{33,34} it is likely that the dominant oxidation mechanism involves carbonyl formation α to the pyridine ring, accompanied by a chain scission:

Figure 12. Fourier transform infrared spectra of plasma poly (2-vinylpyridine) aged in dry air at 50° C.

Changes in the CR deformation region⁹ (as noted by the growth of a broad feature at 1200-1400 cm^{-1}) indicate that additional reactions (e.g., cross-linking, chain scissions, disproportionations) occur in the aliphatic chain. These latter processes appear to be accelerated at elevated temperature, as seen in a Fig. 13 by the much increased intensity of the CR deformation bands at 94°C. The growth of the bands at 1700 and 1597 cm^{-1} are in the same proportion, however, suggesting that the oxidation mechanism is not altered at the higher temperature. A comparison of difference spectra for PVP films aged at 94°C in dry air and inert gas (argon) is shown in Fig. 14. Oxidation has been drastically reduced in the argon atmosphere. Similar results were obtained for films aged in a hydrogen atmosphere and at 23, 50, and 130°C. The kinetics of the oxidation were studied by following the growth of the carbonyl peak with time (Fig. 15). The 130°C data did not fit conveniently on this plot. An excellent linear fit was obtained at all four aging temperatures for the initial oxidation process. However, the rate slows markedly beyond 25% conversion. The time for this break point was measured to be 4.5 months at 23°C. The rates for this initial oxidation are plotted versus inverse temperature Fig. 16. The Arrhenius activation energy was found to be approximately 11.6 kcal/mole. A similar number has been quoted for the growth of the dielectric loss peak in plasma polymerized tetrafluoroethylene, attributed to carbonyl formation.³¹

Thermal Analysis

The thermal behavior of the polymer was explored in order to assess the effects of subsequent manufacturing steps (some of which may subject the polymer to high temperatures) and the validity of extrapolating accelerated aging data to use temperatures.

Figure 13. Fourier transform infrared spectra of plasma polymers aged in dry air at 50° and 94° C.

Figure 14. Fourier transform infrared spectra of plasma polymers aged in dry air and argon at 94°C.

Figure 15. Oxidation of plasma polymer with time in dry air at various temperatures.

Figure 16. Calculation of Arrhenius activation energy for plasma polymer oxidation.

Differential scanning calorimetry was used to explore phase transitions in the polymer. Figure 17 illustrates the DSC scans for both the linear and plasma 2-vinylpyridine polymers. The scan of the linear polymer displays the expected endothermic behavior at the glass transition temperature, $T_g = 104^\circ\text{C}$. However, the plasma polymer scan reveals the onset of an irreversible, exothermic reaction near this temperature, continuing to approximately 600°C . This behavior is suggestive of an additional cross-linking reaction which is allowed to occur above $\approx 100^\circ\text{C}$, owing to increased segmental mobility of the polymer in the rubbery state. This post-reactivity may indicate residual reactive radical species or reactive groups (e.g., dangling vinyl groups) present in the polymer after deposition. Interestingly, the degradation reaction seems to be essentially unaffected when the heating atmosphere is changed from inert gas to air. Thermal stability of the various plasma polymers, synthesized according to the reactor conditions given in Table I, were determined by thermogravimetric analysis (Fig. 18). The conventional, linear poly (2-vinylpyridine) begins to unzip to monomer at about 370° . Invariably, the plasma polymers began to lose weight at a lower temperature than the conventional polymer. Due to its low molecular weight, the 'tacky' polymer synthesized at a high monomer pressure (Sample 1, Table I) began to lose substantial weight at a fairly low temperature, $< 150^\circ\text{C}$. The plasma polymers synthesized in the presence of argon were the most thermally stable. For example, the polymer synthesized under the 'nominal' reactor conditions of 0.03 torr 2 VP, 0.2 torr Ar, and 4 watt (Sample 3, Table I) showed only a 5% weight loss by 250°C at a $10^\circ\text{C}/\text{minute}$ heating rate. All plasma polymer scans displayed a relative plateau at $450\text{--}650^\circ\text{C}$, suggesting the occurrence of a thermally stable product in this region.

Figure 17. Differential scanning calorimetry of poly (2-vinylpyridines).

Figure 18. Thermograms of poly (2-vinylpyridines) in argon.

Pyrolysis gas-chromatography mass spectroscopy was used to obtain a more detailed analysis of the degradation process. Figure 19 compares the weight loss versus temperature for the slow heating rate, 10°C/min, used in the TGA analysis and the rapid heating rate, 5°C/msec, used in the flash pyrolysis GC-MS technique. It is evident that weight loss is more severe at the faster heating rate (10% at 250°C versus 5% at 250°C). Apparently, at the slower heating rate, a stabilizing reaction is allowed to occur (e.g., crosslinking) which slows further weight loss. Figure 20 shows a pyrogram of the conventional, linear polymer obtained at 700°C. By far the largest component is 2-vinyl pyridine monomer resulting from chain depolymerization ('unzipping'). Lesser components were identified as benzene, 2-methylpyridine, and various low molecular weight volatiles. Figure 20 also illustrates the 700°C pyrogram of the plasma polymer (Sample 3, Table I) which yielded primarily the low molecular weight volatiles. The presence of these pyrolysis products may indicate excessive branch points in the plasma polymer or secondary reactions occurring in the pyrolysis unit. Table VII identifies the various peaks in the pyrograms at 300, 400, 500, 600, and 700°C as well as these relative concentrations at the various temperatures. In all cases, the main components are 2-methylpyridine, 2-ethylpyridine, or low molecular weight gases. Monomer was apparent in the degradation products only in minute quantities. Methyl- and ethyl-pyridines may result from the interaction of methyl and ethylene radicals with pyridyl radicals, as has been suggested for the presence of analogous components in the pyrograms of polystyrene.³⁵ These observations suggest the presence of a high concentration of 'weak' bonds which are not present in the linear polymer and which lead to thermal decomposition at lower temperatures.

Figure 19. Thermograms of Sample 3 at two heating rates.

F1332.PYROLYSIS OF CONV.POLY(2-VINYLPYRIDINE)
CH 276 = 100%

1412C PLASMA POLYMERIZED 2-VINYLPYRIDINE 700C
TOTAL ION PROFILE

Figure 20. GC/MS pyrograms of linear and plasma polymers at 700°C.

Adhesion of Plasma Polymerized Films to Aluminum Substrates

As an initial step toward assessing the mechanical integrity of capacitors made with plasma deposited 2-vinylpyridine thin film dielectrics, it was necessary to establish an appropriate adhesion test method. After some consideration, it was decided to develop the tensile-pull method, as this technique could potentially yield quantitative information. An important initial consideration, in order to achieve meaningful results, was to determine an appropriate adhesive which could be used to assemble the tensile pull specimens, yet would not diffuse through the very thin poly (2-vinylpyridine) film and therefore influence the strength of the plasma polymer-metal bond. Three candidate adhesives were explored: EPON 828/ VERSAMID 140 epoxy, EPIBOND 104/VERSAMID 140 (a thixotropic epoxy), and Eastman 910 (a fast curing, non-viscous adhesive). The results of these experiments, for a range of poly (2-vinylpyridine) film thicknesses, are shown in Fig. 21. The pull strength for the specimens assembled with the two epoxies was found to be quite high and increased as the poly (2-vinylpyridine) film thickness was decreased, indicating that these adhesives did, in fact, influence the measured strength of the PVP-aluminum bond, apparently as a result of diffusion through the thin polymer film. The strength of specimens assembled with a sparing amount of Eastman 910 were found to be low and independent of PVP film thickness down to 2500 Å, indicating that the measured tensile pull strength of approximately 480 psi is a true measure of the plasma polymer aluminum bond strength. Failures appeared to be primarily adhesive in nature, as it was observed visually that a clean separation occurred at the polymer-metal interface in all cases. Further evidence for this observation was obtained with Auger spectroscopy.

Figure 21. Effect of various adhesives on the measured strengths of plasma poly (2-vinylpyridine) tensile specimens.

Figure 22 shows the Auger spectrum of an aluminum plug surface subsequent to rupture. Although the Auger spectrum indicates primarily carbon and nitrogen from the polymer material, some evidence for the aluminum (actually, oxidized aluminum) is apparent. This aluminum peak increased dramatically after only twelve minutes (approximately 100 Å) of sputtering, as shown in Fig. 23, again indicating a cohesive failure.

An important concern is the mechanical integrity of the thin film capacitors in high humidity environments, as electrical testing has indicated that irreversible damage results from exposure to high humidity.³⁶ Tensile pull specimens, assembled with Eastman 910 adhesive, were subjected to a 100% relative humidity environment at room temperature. The results of these tests are shown in Fig. 24. Storage in the high humidity environment resulted in a slight decrease in the measured pull strength with exposure time, apparently on account of the slow diffusion of humidity into the specimens. However, a rather catastrophic drop in strength was noted when the specimens were removed to a dry atmosphere. This may be a result of shrinkage as moisture is removed from the plasma polymer, resulting in weakening or actual delamination at the polymer-aluminum interface.

Tensile pull strengths were also determined for specimens which had various candidate protective coating materials sprayed directly onto the plasma polymer films prior to specimen assembly. In these cases, the objective was to examine suitability of plasma poly (2-vinylpyridine) thin (5500 Å) films as barrier coatings. The results of these tests for the various specimen configurations are shown in Table VIII. As can be seen, the PVP barrier layer does serve to reduce adhesion of the Laminar X500 protective coating to the aluminum substrate (1470 psi. vs 285 psi). However, failure

Figure 22. Auger spectrum of tensile pull specimen rupture surface.

Figure 23. Auger spectrum of tensile pull specimen rupture surface after twelve minute sputter.

Figure 24. Effect of 100% relative humidity on plasma polymer - aluminum adhesive strength.

in the case was found to be cohesive, in the PVP film itself, rather than adhesive (285 psi. vs 480 psi). This observation suggests that solvents present in the Laminar X500 material during processing decreased the cohesive strength of the plasma polymer. Conversely, the strength of the Epon 828/Zsubstrate bond was virtually unaffected by the presence of the intervening PVP barrier layer, even up to PVP film thicknesses of 17,000 Å. This indicates the likelihood of diffusion of the 828Z adhesive through the plasma polymer. Finally, the PVP layer appears to be an adequate barrier material when Kraton is used as the protective coating material (170 psi vs. 1000 psi.). However, in this case adhesive failure occurred at the PVP-kraton interface and was unusually low.

CONCLUSIONS

Plasma deposited poly (2-vinylpyridine) was found to have a chemical structure significantly differing from that of the conventional, linear polymer. In particular, infrared and carbon-13 nuclear magnetic resonance spectroscopies have shown the presence of cyano, methyl, and olefinic groups which are not present in the linear polymer, and a reduced concentration of aromatic pyridine ring functionalities. Furthermore, the molecular structure of the deposited polymer appears to depend rather strongly on the plasma reactor conditions, particularly the rf power level and monomer pressure. At high monomer pressures and a low power level (> 70 microns at 10 watts), one obtains a low molecular weight (< 1500) oligomeric material which is soluble in polar solvents and has a structure similar to that of the starting monomer. Conversely, at low pressures and high powers, one obtains a highly branched, crosslinked, unsaturated, aliphatic polymer which bears little structural resemblance to the linear polymer. This material is not known to be soluble in any organic solvents, but does appear to swell in water.

Specifically, aromaticity retention decreases markedly in plasma polymers synthesized at high powers or low pressures.

Plasma polymerized 2-vinylpyridine was observed to react with oxygen rather dramatically when exposed to air subsequent to deposition. This post-reaction is apparently due to the high concentration of trapped reactive radicals ($\sim 2.7 \times 10^{19}$ spins/gm) remaining in the films from the polymerization process. Fourier transform infrared difference spectroscopy suggested that oxidation at 23°, 50°, 94°, and 130°C occurs preferentially at a position α to the pyridine ring, resulting in an aromatic ketone-type structure. It is likely that this oxidation is accompanied by chain scissions. For the 'standard' (Sample 3, Table I) plasma polymer, the oxidation reaction appeared to be first order up to about 25% modification of the aromatic rings (with an activation energy of ≈ 11.6 kcal/mole and a reaction time of 4.5 months at room temperature) followed by a much slower rate thereafter. However, electron spin resonance spectroscopy and chemical analysis indicated that this oxidation could be reduced significantly by aging in vacuum or inert gas environments and, in particular, in a hydrogen atmosphere. Only slight modifications, primarily in the carbon-hydrogen deformation region, were observed in the infrared spectra of films aged in these latter environments, suggesting that additional crosslinking was the predominant mechanism.

Thermal analyses revealed a behavior consistent with the molecular structure observations mentioned previously. Thermogravimetry indicated a cross-linked polymer which began to lose weight at a rather low temperature ($\sim 5\%$ by 250°C in argon or air) but showed a slow rate-of-weight-loss thereafter. Furthermore, differential scanning calorimetry revealed the onset of an exothermic, irreversible crosslinking reaction near 100°C. This reaction

appears to correlate with the glass transition temperature in the linear polymer and suggests a reaction which is accelerated above 100°C due to increased segmental mobility of the polymer chains. Finally, thermal degradation/decomposition products have been observed by pyrolysis gas chromatography/mass spectrometry. Whereas the principle decomposition product of the linear polymer was simply monomer from the chain-unzipping reaction, the plasma polymer gave a variety of pyrolysis products. At low decomposition temperatures (< 300°C), one obtains primarily 2-methylpyridine and low molecular weight gases (mainly, CO₂), apparently due to the splitting off of chain branches and scission at 'weak bonds.' At higher temperatures, increasing evolution of ethylpyridine and low molecular weight gases was noticed.

A technique was developed to quantitatively measure adhesive bond strengths for thin (< 10,000 Å) plasma polymer films on metal substrates. This involved the assembly of a tensile pull specimen using Eastman 910 adhesive. With this method, the adhesive strength of the plasma poly (2-vinylpyridine) - aluminum bond was found to be 480 psi. Also, cycling at 100% relative humidity environment degraded the integrity of this bond. Finally, this technique was used to investigate the adequacy of the plasma polymer as a 'barrier coating' assuming three varieties of overlying 'protective coatings.' Plasma poly (2-vinylpyridine) was found to be a suitable barrier coating for Laminar X500 and Kraton overlayers, but not for Epon 828Z.

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TABLE I

Plasma Reactor Conditions

<u>Sample</u>	<u>Power (Watts)</u>	<u>Voltage P to P, Volts</u>	<u>2 VP Pressure (Torr)</u>	<u>Ar Pressure (Torr)</u>	<u>Thickness (Angstrom)</u>
1	10	250	0.23	---	28,000
2	10	250	0.23	---	5,500
3	4	150	0.03	0.20	38,000
4	4	180	0.03	---	5,000
5	40	250	0.03	0.20	9,000

TABLE II

Infrared Frequencies and Band Assignments for Linear
Poly(2-vinylpyridine) (From Figure 4)

<u>Frequency, cm^{-1}</u>	<u>Band Assignments*</u>
3060	ν_{20b}
3002	ν_{7b}
2930	$\nu(\text{CH}_2)$
2860	$\nu(\text{CH}_2)$
1590	ν_{8a}
1570	ν_{8b}
1470	$\nu_{19a}, \delta(\text{CH}_2)$
1430	ν_{19b}
1150	ν_{18b}
1050	ν_{18a}
995	ν_{12}
775	ν_{10a}
745	ν_{10b}

*Wilson (10) Nomenclature

TABLE III
Aromaticity Retention of Plasma Polymers
as Indicated by Infrared Peak Height Ratios

<u>Sample</u>	<u>(3060 cm⁻¹/2930 cm⁻¹)</u>	<u>Aromaticity Retention (%)</u>
Linear	0.58	100
1	0.41	70.7
2	0.45	77.6
3	0.26	44.8
4	0.15	25.9
5	-0-	-0-

TABLE IV
Elemental Analyses of Plasma-Deposited
Poly(2-vinylpyridine)

<u>Sample</u>	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% O</u>	<u>Formula</u>
Linear	80.0	6.7	13.3	---	C ₇ H ₇ N
1	77.0	6.15	13.0	3.9	C ₇ H _{6.71} N _{1.01} O _{0.26}
3	73.8	6.01	12.2	8.0	C ₇ H _{6.84} N _{0.99} O _{0.57}
4	74.2	6.20	12.0	7.6	C ₇ H _{7.02} N _{0.97} O _{0.54}
5	71.8	6.54	11.9	9.8	C ₇ H _{7.66} N _{0.99} O _{0.71}

TABLE V

ESCA Analysis of Plasma - Deposited Poly(2-vinylpyridine) Surfaces

SAMPLE	CARBON				NITROGEN			OXYGEN		
	BE(eV)	HW(eV)	%	%C(1s) Shake-up	BE(eV)	HW(eV)	%	BE(eV)	HW(eV)	%
Linear	285.3	2.8	86	5	399.1	2.5	9	532.9	3.2	5
1,2	285.3	3.1	83	1	399.9	3.0	8	532.4	3.6	8
3	285.3	3.7	78	NT*	399.4	3.8	7	532.0	3.9 ¹	15
4	285.3	3.1	80	NT	399.1	2.8	9	532.3	3.0	11
5	285.3	2.9	84	NT	399.7	2.8	4	532.5	3.1	12

* Not detected

TABLE VI

Elemental Compositions of Plasma Poly(2-Vinylpyridines)
(Sample 3, Table I) Aged for 20 Days at 94°C

<u>Environment</u>	<u>Composition</u>
dry air	C ₇ N _{1.02} H _{6.20} O _{0.80}
vacuum	C ₇ N _{0.99} H _{6.74} O _{0.26}
helium	C ₇ N _{1.00} H _{6.80} O _{0.27}
hydrogen	C ₇ N _{1.00} H _{6.67} O _{0.08}

TABLE VII

Pyrolysis Products of Plasma Polymer
(Sample 3, Table I) at Various Temperatures

	<u>300°C</u>	<u>400°C</u>	<u>500°C</u>	<u>600°C</u>	<u>700°C</u>
% Weight Loss	15.26	34.21	58.65	61.52	62.20
CH ₄ +CO ₂ +C ₂ H ₄ , #1	32.2	21.5	39.1	42.0	90.1
Unidentified #2	N. D.				
Unidentified #3	N. D.	4.2	4.6	7.5	.2 .3
Tolvene	N. D.	1.1	1.5	2.5	.7
2-Methylpyridine, #5	67.8	10.1	8.8	9.5	1.5
Unidentified #6	N. D.	N. D.	N. D.	.5	.1
2-Ethylpyridine, #7	N. D.	50.2	39.2	29.3	5.6
Unidentified #8	N. D.	2.6	1.6	2.6	.8
Unidentified #9	N. D.	3.9	1.9	2.2	.4
Unidentified #10	N. D.	2.6	.8	.9	.3
Unidentified #11	N. D.	3.7	2.4	3.0	N. D.

TABLE VIII

Tensile Pull Strengths for Candidate Barrier PVP-Protective Coating Combination

<u>Specimen Configuration</u>	<u>Measured Tensile Pull Strength (psi)</u>	<u>Mode of Rupture</u>
Al-PVP-Eastman 910-Al	480	Adhesive, at PVP-Al interface
Al-X500-X1	1470	Cohesive, in X500
Al-PVP-X500-Al	285	Cohesive, in PVP film
Al-828Z-Al	1675	Adhesive, at 828Z-Al interface
Al-(5500-17000A) PVP-828Z-Al	1600	Adhesive, at PVP-Al interface
Al-Kraton-Al	> 1000	Adhesive
Al-PVP-Kraton-Al	170	Adhesive, at PVP-Kraton interface

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