

Correlated Electron Spin-Resonance and Infrared Spectroscopic Study of the Postformation Auto-Oxidation Phenomenon in Plasma-Polymerized 4-Vinyl Pyridine Films

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SYNOPSIS

Plasma polymerization of 4-vinyl pyridine (4-VP) proceeds through a gas-phase free radical mechanism to yield a film that retains much of the organic functionality of the monomer. During the deposition process, free radicals, which have been shown to quickly react with oxygen, are trapped to yield a film with a nascent peroxy radical density of 2.9×10^{18} spins/g as quantified by electron spin resonance (ESR) spectroscopy. In air at room temperature, peroxy radicals in the film react to produce carbonyl, hydroxyl, and ether structures in the polymer that was monitored using infrared (IR) spectroscopy. The free radical population was found to decay rapidly at first and then reach an apparent steady state after 30 hr. As the spin density decreases, a concomitant growth of vibrational modes associated with oxygen-containing functional groups was observed in the IR spectrum of the film. The relative population of oxygen-containing groups continued to increase even after the free radical population reached steady state. This slow, auto-oxidative effect may be attributed, in part, to free radical centers that are anchored to the polymer chain in regions of high crosslinking. In such regions, limited segmental mobility may limit the rate of radical-radical recombination (termination) processes relative to oxidative radical-center. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Plasma (or glow discharge) polymerization¹ is quite different from conventional chemically initiated or radiation-initiated addition polymerization. In conventional polymerization of vinyl monomers, numerous means of initiation may be used to produce various kinds of reactive (polymerizable) species, but the propagation step of the polymerization always involves the addition reaction to the double bond of the monomer. Therefore, the reactivity of the vinyl double bond towards the reactive species created in the initiation step is an important factor that influences the overall polymerization rate. Accordingly, the presence of a double bond is usually necessary for all conventional addition polymerization, and its absence rules out polymerization (i.e.,

styrene vs. ethyl benzene). However, in the case of plasma polymerization, an organic compound such as ethyl benzene not only polymerizes, but exhibits a deposition rate similar to that of styrene.² The properties of the plasma-produced polymers are, however, quite different from those produced by conventional polymerization, and it is best to consider them not the same polymer (i.e., plasma-polymerized styrene is not a kind of polystyrene).

The formation of high molecular weight materials can be induced through the process of plasma polymerization in a gas-phase system. A plasma is a partially ionized gas comprised of free electrons, photons, polyatomic and atomic ions, energetic neutrals, and various free radical species. The characteristic glow of a plasma results from the decay of species from highly excited electronic, vibrational, and rotational states through photon emission mechanisms. The photons present in a low-pressure plasma may have energies spanning from the soft x-ray and deep ultraviolet region to the far infrared

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region. Typically, a plasma is ignited in a low pressure (<1 Torr) precursor vapor with an electric discharge. In these "cold" or low-temperature plasmas the extent of ionization is usually much less than 1%. However, the free radical population in the plasma may be more than an order of magnitude higher than the ion population.³ Polymer formation occurs primarily through the reaction of radical species formed in the discharge. The mechanism of polymer formation is termed rapid step growth polymerization (RSGP).⁴ In this mechanism, radical species formed in the gas-phase first condense on a substrate surface. The radical species present on the surface can then react with more radical or nonradical neutral species from the gas phase. In this manner a polymer film is deposited on (or actually grown from) a surface. The plasma polymerization process may be controlled to produce a contiguous polymer film with unique properties such as a high degree of crosslinking and branching.

Under certain plasma conditions, the rate of radical deposition and formation in the growing film is greater than the rate of the elementary steps that lead to radical termination. Thus, free radical species may be trapped within the plasma-produced polymer.⁵ The growing polymer film is also subjected to continuous bombardment by high energy photons, electrons, and ions present in the plasma environment. These bombardment processes may also lead to free radical formation on the surface of the growing film. The films produced from plasma polymerization are usually quite dense and exhibit a high degree of crosslinking, which results in low segmental mobility. In such films, free radical centers may be isolated from structural moieties that would react to terminate or dissipate the free radical site.

High rates of gas-phase and surface activation as well as ion bombardment may lead to long-lived free radicals in plasma-produced polymers. The extent of free radical formation in plasma polymer film, however, is strongly dependent on the specific monomers or precursors used in polymerization and on the various plasma reaction parameters such as power density, monomer flow rate, reactor pressure, etc. In addition, conventional polymers exposed to plasma-irradiation often exhibit a large population of free radicals on the polymeric surface. This can lead to the formation of a surface layer with highly crosslinked network structure.⁶ In fact, even a few seconds of plasma irradiation are long enough to cause substantial changes in the surface properties.

Generally, free radicals are highly reactive and their presence in a polymer film results in time-dependent phenomena or aging effects in the film mo-

lecular structure as the free radicals react and eventually terminate. Film properties and end-use performance may be expected to change with time or age as time-dependent chemical and structural changes occur. Therefore, it is of critical importance to characterize and understand the extent of free radical formation, the reaction paths associated with free radicals, and the free radical lifetime in plasma-produced polymer films.

Electron spin resonance (ESR) spectroscopy has been used to study free radicals that are formed in plasma polymerization and plasma treatment processes.⁷⁻¹² The significance of these fundamental studies on plasma-induced radical formation was to understand the degradation phenomena in the polymer and the molecular mechanism of "plasma treatment" for polymer surface modification. These studies provide a basis for future experimental design of plasma treatment on various kinds of polymers, because the resulting surface properties apparently depend on the nature of the radical formed.

Early work by Yasuda and co-workers showed that free radical densities in plasma produced polymer films ranged from 10^{16} to 10^{20} spins/cm³, as measured by ESR.¹ Plasma-polymerized films from a large number of monomers were investigated. It was also observed that the free radical density and lifetime was strongly dependent on the structure of the organic precursor and on the mechanism of monomer activation. Siloxane monomers produced films with the lowest free radical populations. Aliphatic and aromatic monomers yielded films with intermediate spin densities, whereas the highest spin densities were observed in films produced from fluorinated precursors such as hexafluoroethene. In Yasuda's study the effect of pulsing the plasma source was also investigated.

The structure and free radical characterization of plasma-polymerized hexafluoropropene was recently investigated by Wang and Chen.⁸ By measuring time-dependent free radical populations in both inert and ambient atmospheres at various temperatures, the activation energy and mechanisms of free radical termination were determined for this polymer film.

The formation of free radicals in polymers induced by plasma irradiation has also been reported. Kuzuya and co-workers have studied free radicals in polyethylene¹⁰ and methacrylic polymers⁷ after exposure to an inert-gas plasma. High-resolution ESR measurements yielded information on the specific structure of the free radical site in the polymer. The effect of plasma treatment on free radical formation in both synthetic and natural fibers was also

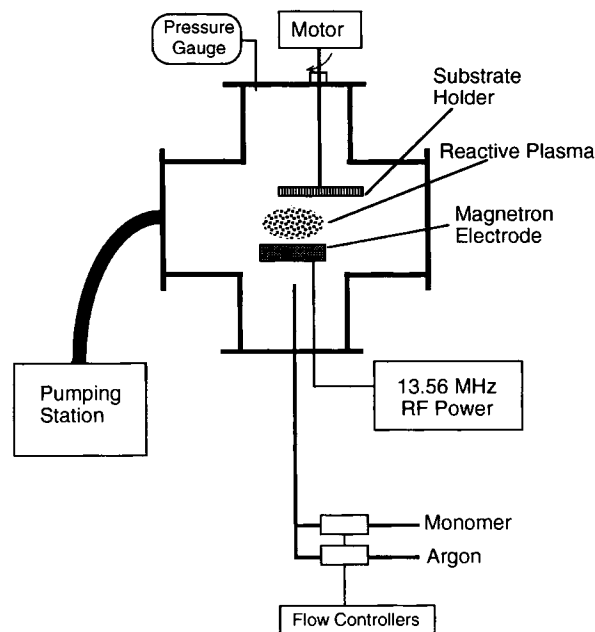


Figure 1 Schematic diagram of plasma polymerization reactor.

studied by Chen.⁹ In that study, fibers of cotton, rayon, linen, nylon, and polyethylene terephthalate were exposed to plasmas produced from nitrogen, argon, oxygen, carbon monoxide, or tetrafluoromethane. The surface free radical concentration was monitored by ESR to determine the radical half-life.

In this article, the free radical population in a plasma-polymerized 4-vinyl pyridine (PP 4-VP) film is quantified, for the first time, using electron spin resonance spectroscopy. The free radical population is monitored as a function of time to determine the free radical lifetime. In addition, Fourier transform infrared (FT-IR) spectroscopy is used to characterize the molecular structure of the nascent PP 4-VP film. Time-dependent changes in the molecular structure are also observed by FT-IR spectroscopy that can be compared with the decay of free radicals as measured by ESR. This combination of ESR and FT-IR spectroscopies provides a unique platform

on which to observe the postformation free radical reaction processes in plasma-polymerized films.

EXPERIMENTAL

Plasma Polymerization

The plasma-polymerized film for both IR and ESR analysis was prepared by simultaneous deposition to assure accurate time correlation in this multi-technique study. A schematic diagram of the plasma polymerization reactor is shown in Figure 1. The basic vacuum chamber was comprised of a six-inch i.d. glass cross from Konex. The pumping station consisted of an Edwards EH-500 booster pump backed by an Edwards E2M80 mechanical pump charged with perfluorinated polyether fluid. This pumping system provides a pumping speed of 400 m³/h at 0.3 Torr. Chamber pressure was monitored with an MKS Baratron 122AA capacitance manometer.

The single electrode was an unbalanced magnetron type. This cathode design utilizes a magnetic field to spatially confine the plasma discharge to the region just above the cathode surface. The plasma discharged was powered by a 13.56 MHz Advanced Energy RFX 6000 supply and impedance matching network. The substrate holder was a 5.5 inch diameter polycarbonate disk spaced 25 mm above the cathode surface. The holder was rotated at 30 rpm. Permanent gases were metered into the vacuum chamber using MKS 1159 flow controllers and low-pressure monomer vapor is introduced using an MKS 1150C flow controller. In these experiments, 99.995% argon was obtained from Scott specialty gases. The 4-vinyl pyridine monomer was > 95% purity from Aldrich and was used without any additional purification or degassing.

For the simultaneous/correlated ESR and IR experiments, a 4 mm thick KBr plate was mounted on the substrate holder along with several precleaned glass microscope slides. This run is designated F1 and the reactor operational parameters are listed in

Table I Plasma Polymerization Operational Parameters

Film Designation	Monomer Flow (sccm)	Argon Flow (sccm)	Power (watts)	Composite Power	Cathode-Substrate	Deposition Rate (Å/s)
				Density (J/kg)	Distance (cm)	
F1	7.0	20	10	1.4×10^7	2.5	11
F2	12.5	20	30	3.1×10^7	2.5	52

Table I. The holder was placed into the vacuum chamber and evacuated to base pressure of approximately 0.001 Torr for about 20 min. Argon was introduced into the vacuum chamber at a flow rate of 20 sccm. The 4-vinyl pyridine vapor was directed into the chamber at a flow rate of 7.5 sccm. The chamber pressure was 0.011 Torr, with both the argon and 4-vinyl pyridine flowing through the chamber. The discharge was ignited by applying 11 watts rf power forward to the cathode. The reflected rf power was 1 watt to yield a net discharge power of 10 watts. The duration of the deposition was 900 s. This yielded a polymer film with a thickness of 10,000 Å as subsequently measured by a stylus profilometer.

After the rf power was turned off, the monomer and argon flows were terminated and the gate valve to the pumping station was closed. The chamber was backfilled with house nitrogen to a pressure of 10 Torr and then immediately pumped down to base pressure. This back flushing process was repeated four times to remove any residual monomer vapor from the chamber. The chamber was then held at base pressure for about 10 min and then backfilled with nitrogen to 400 Torr and followed by evacuation. This second backflushing and evacuation was repeated, after which the chamber was backfilled with nitrogen to atmospheric pressure and the chamber opened. Less than 25 min elapsed between the end of the deposition and opening the chamber to atmosphere.

The substrate holder was then immediately removed from the chamber and 4.5 mg of the polymer deposit was removed from the glass slides with a razor blade, placed into an ESR tube, and transferred to the ESR spectrometer. During the ESR analysis the end of the ESR tube was not capped so that the sample would be exposed to room atmosphere.

Another experiment was performed to measure time-dependent changes in the IR spectrum for a film (designated F2) prepared under the conditions listed in Table I.

ESR Analysis

ESR measurements were performed on a Bruker X-band ESP 300e spectrometer, which operates at a frequency of 9.4 GHz. The ESR spectra were recorded in the first derivative mode using a modulation frequency of 100 KHz. The modulation amplitude was kept small compared to the ESR line width to avoid any line shape distortion. The spectrometer frequency was measured to an accuracy of

± 1 KHz with the aid of a microwave frequency counter, EIP model 625A. The spectrometer is also equipped with an NMR Gaussmeter, model ER035M-IEC located very close to the center of the ESR cavity and capable of measuring the magnetic field to the nearest 0.01 Gauss. A variable temperature unit was used to control and measure the temperature of the sample to an accuracy of $\pm 1^\circ\text{C}$.

Infrared Analysis

Infrared analysis was performed on the polymer deposited on the KBr in the transmission mode using a Perkin-Elmer 1760 FT-IR with a DOS-based Spectracalc control and data reduction software package. Thirty scans at a resolution of 4 cm^{-1} were summed for each IR spectrum. Between IR spectral acquisitions, the KBr plate coated with PP 4-VP was stored in a desiccator to minimize water uptake and clouding of the KBr plate.

RESULTS AND DISCUSSION

Time-dependent changes in the PP 4-VP film were quantified using ESR and FT-IR spectroscopies. The point of removal of the PP 4-VP sample from the chamber is established as zero time for these experiments. This is approximately 25 min after the end of the deposition cycle, as described in the Experimental section.

The time-dependent ESR spectra of a 10,000 Å thick PP 4-VP film are shown in Figure 2. The first spectrum was acquired 50 min after removal from the vacuum chamber. Subsequent spectra were acquired at 30-min intervals. All of the spectra exhibit a single asymmetric line centered at a g -value of 2.00352 ± 0.00002 and peak-to-peak line width, ΔH_{p-p} , of 10.5 Gauss characteristic of peroxidic radicals.¹³ The plasma activation of 4-vinyl pyridine would be expected to produce nonperoxy radical species from the activation of the 4-vinyl pyridine vinyl site or aromatic ring. Thus, the peroxy radical species would not be anticipated as the primary free radical species in the nascent film. However, some of the peroxy radicals may be directly formed during the polymerization process from reactions involving background oxygen and oxygen-containing species (e.g. water) in the vacuum chamber. The abundance of the peroxy radical in the postformation ESR spectrum suggests that a rapid and relatively complete reaction of the primary radicals occurs upon exposure to residual oxygen in the chamber or atmospheric oxygen after removal from vacuum. The

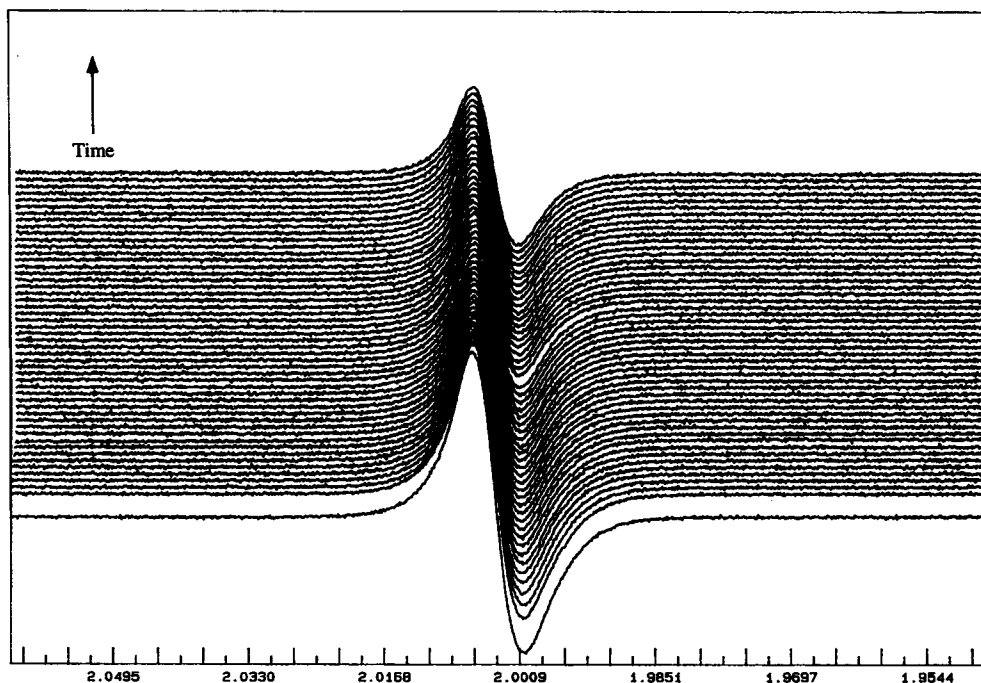
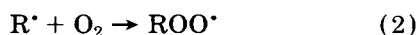
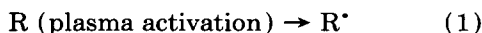
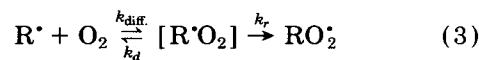


Figure 2 Time-dependent electron spin resonance signal for plasma-polymerized 4-vinyl pyridine (F1). Spectra were acquired at 30-min intervals.

peroxy radical formation mechanism may be expressed in a two-step process as follows:



where R represents a nonradical atom or group on the polymer network, R^{\bullet} represents the primary radical(s) created by plasma activation and ROO^{\bullet} represents the peroxy radical. The free radical centers are essentially immobile and react when oxygen diffuses to the site. The oxygen diffusion and reaction sequence can be written explicitly as shown below.



In this expression, $[R^{\bullet}O_2]$ represents an intermediate structure, k_{diff} , the coefficient of diffusion process and, k_d , the dissociation of the intermediate back into reacting species, whereas k_r is the reaction rate constant of the final step for peroxy radical formation. The reaction rate between a radical and scavenger oxygen molecule is very fast compared to the rate of oxygen diffusion to the site. Measurements of oxygen permeation rates in similar PP 4-VP films yielded permeability constants on order of $10^{-11} \text{ (cm}^3 \text{ (stp) cm) (cm}^2 \text{ s cm Hg)}^{-1}$. In the thin

structures studied here ($10,000 \text{ \AA}$), the films are expected to equilibrate with atmospheric oxygen within a few minutes after removal from the vacuum chamber. Therefore, the kinetics of formation of the peroxy radical is not observed on the time scale of these ESR measurements.

The free radical concentration or spin density at the time of the first measurement ($t = 50 \text{ min}$) was quantified by calibrating the ESR spectrometer using 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). The spin density in the PP 4-VP film was 2.5×10^{18} spins/g. Assuming that the major structural unit in the film is the 4-vinyl pyridine structure, this spin density corresponds approximately to one free radical site for every 2,300 repeat units (or molecular-structural equivalents).

From the time-dependent ESR signal shown in Figure 2 the radical intensity is observed to decay with time. Figure 2 shows that the spectral lineshape and linewidth as well as the g -value remain constant over the duration of the experiment. Under the limitations of the room temperature ESR measurement, only the oxygen-center spin system is observed. Thus, the depletion of the total free radical signal with time is attributed to quenching reactions of the peroxy radical in the PP 4-VP film. This also suggests that the dissociation constant, k_r , is negligible.

Information concerning the structure of the plasma-polymerized 4-vinyl pyridine film may be

obtained from the IR spectrum acquired 24 min after removal from the reactor, as shown in upper trace of Figure 3. It is also useful to compare the IR spectrum of PP 4-VP to that of solution polymerized poly(4-vinyl pyridine), as shown in the lower trace of Figure 3. Vibrational modes associated with the major absorption bands in the IR spectrum of the plasma-polymerized 4-VP are listed in Table II. Both spectra are dominated by the strong pyridine ring bend-stretch vibrations centered at 1414 cm^{-1} and 1597 cm^{-1} . This indicates that substantial retention of the monomer structure is achieved under these plasma polymerization conditions. Another band of interest in Figure 3 is the C—H stretch absorption found in the 2966 cm^{-1} region. This vibration suggests that free methyl groups are formed in the plasma polymerization process and are incorporated into the film structure. Absorptions at 2216 cm^{-1} and 2171 cm^{-1} may be attributed to the conjugated $\text{—C}\equiv\text{N}$ structure and $\text{—N—C}\equiv\text{N}$ aminonitrile structure, respectively.¹⁴ These vibrations are indicative of pyridine ring-opening processes occurring in the plasma environment. However, because the absolute extinction coefficients for all of the IR bands are not known, it is difficult to quantify the extent of 4-vinyl pyridine structural transformations that occur as a consequence of plasma activation.

As the peroxy radical termination reactions occur, concomitant changes in the PP 4-VP infrared spectra are observed. Representative IR spectra exhib-

iting time-dependent changes are plotted in Figure 4. The spectra were acquired at 0.4, 30, 165, and 1080 h after the film was removed from the vacuum chamber. The spectral changes may be characterized by the growth of bands in three frequency regions. In the $2800\text{--}3400\text{ cm}^{-1}$ regime a very broad band develops with time. This absorption may be attributed to the carboxylic O—H stretching mode. A strong absorption in the $1690\text{--}1712\text{ cm}^{-1}$ region is also observed to increase with time. This spectral region corresponds to the C=O stretching vibration related to carboxylic acid, ketone, and/or aldehyde structures. Broad and/or overlapping absorptions preclude specific carbonyl assignment. Another broad absorbance band grows in the $1000\text{--}1500\text{ cm}^{-1}$ region with time. This broad absorbance may be attributed to a variety of structures of known peroxy radical reaction products. Several vibrational modes may contribute to the $1000\text{--}1500\text{ cm}^{-1}$ region including the C—OH stretch and —O—H bending modes of carboxylic acids, the ester C—O stretch, and the asymmetric ether C—O—C stretch.

Time-dependent changes in the IR spectra were quantified by obtaining the absorbance ratio for the C=O stretching band at 1700 cm^{-1} relative to the pyridine bend-stretch peak found at 1597 cm^{-1} . The baseline for measuring the peak height was imposed between the absorption minima at 600 cm^{-1} and 1730 cm^{-1} . This analysis assumes that the population of the pyridine rings does not change with time

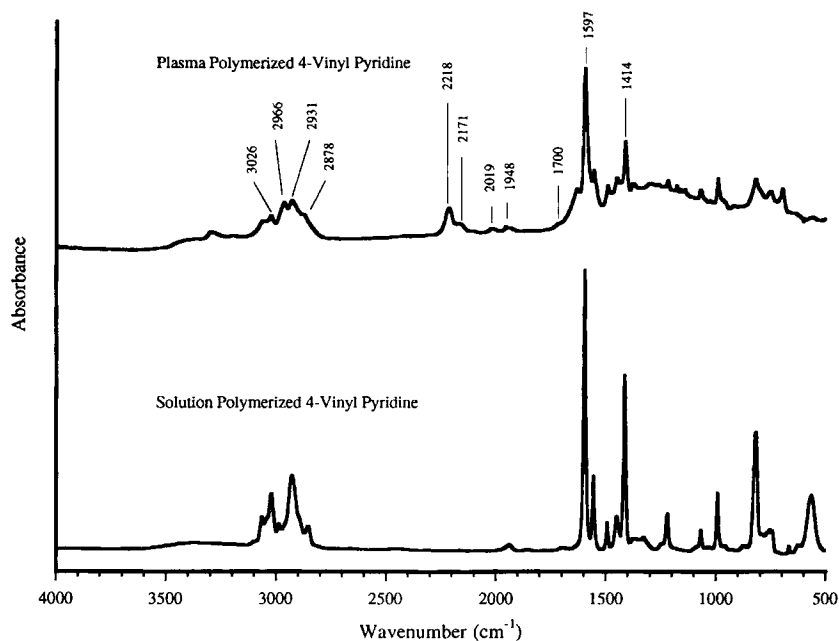


Figure 3 Comparison of plasma-polymerized, sample F1 (upper trace), and solution polymerized 4-vinyl pyridine infrared spectra (lower trace).

Table II Tentative Assignment of Selected Infrared Absorption Bands of Plasma-Polymerized 4-Vinyl Pyridine

Frequency (cm ⁻¹)	Assignment
1000–1500	C—OH stretch, Carboxylic—O—H bend, ester C—O
1414, 1597	Asymmetric ether C—O—C
1690–1712	Pyridine ring bend-stretch
1948	—C=O stretch
2019	Ring combination band
2171	Ring combination band
2218	—N—C≡N stretch
2800–3400	Conjugated—C=N stretch
Broad underlying absorption	carboxylic O—H stretch
2800–3200	Aliphatic and conjugated C—H stretches

(i.e., this structure does not participate in the peroxy radical reaction sequence).

The relative intensity of the ESR peroxy radical signal and the relative absorbance of the $\nu(\text{C}=\text{O})$ band are plotted together in Figure 5. The integrated ESR signal is arbitrarily normalized to the first value recorded ($t = 0.8$ h). Both data sets were fit using double exponential functions. As shown in Figure 5, the ESR signal decays rapidly at first and asymptotically approaches a stable value after approximately 30 h. The relative free radical concentration in the film at the time of removal from the chamber ($t = 0$) may be calculated from the line equation to yield a spin density of 2.9×10^{18} spins/g in the nascent film. The relative free radical concentration at $t = \infty$ represents a spin density loss of 65% of the initial ($t = 0$) concentration. This long-lived

peroxy radical concentration corresponds to a spin density of 1.3×10^{18} spins/g.

In the relative $\nu(\text{C}=\text{O})$ curve shown in Figure 5, the absorption signal is found to increase with time. The rate of carbonyl production does not correspond exactly to the rate of peroxy radical decay. In fact, the relative $\nu(\text{C}=\text{O})$ signal continues to increase even after 160 h, whereas the extrapolated ESR signal remains relatively constant after ~ 35 h. For comparison, both the decay of the normalized ESR signal and the growth of the relative $\nu(\text{C}=\text{O})$ band in the IR spectrum with time were fit with arbitrary double-exponential functions. Neither the decay or growth curves could be directly ascribed to first- or second-order kinetic processes. These correlated ESR and IR time-dependent spectra suggest

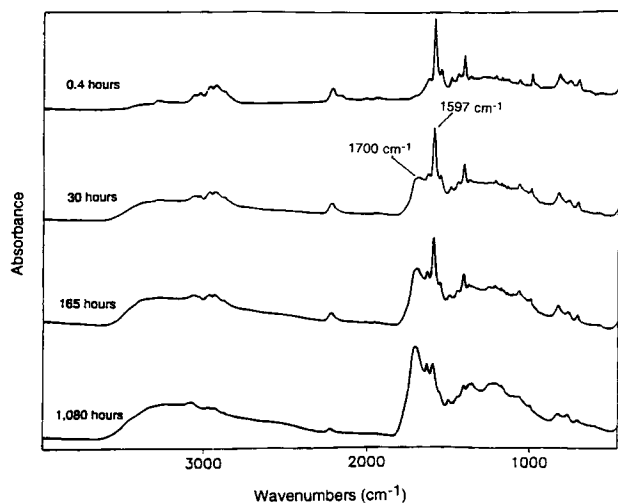


Figure 4 Time-dependent IR spectra for plasma-polymerized 4-vinyl pyridine sample F1.

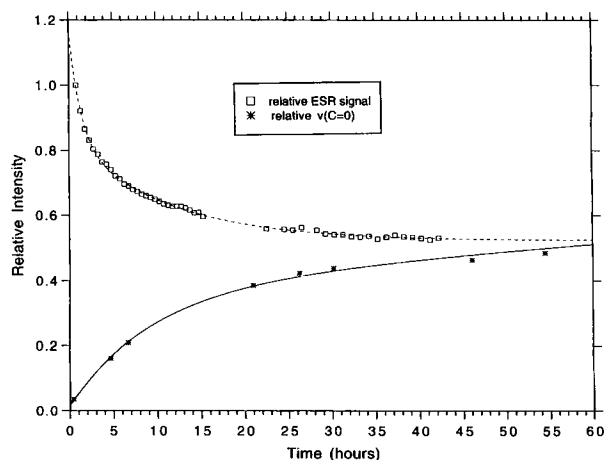


Figure 5 Time-dependent relative ESR intensity and relative $\nu(\text{C}=\text{O})$ absorbance for plasma-polymerized 4-vinyl pyridine sample F1.

that there are concurrent postformation free radical reactions occurring in the plasma-polymerized 4-vinyl pyridine.

Postformation free radical reactions in the PP 4-VP film may be similar to thermally induced oxidative processes, which have been studied extensively in for a variety of polymer systems.¹⁵ There are several reaction mechanisms for peroxy radicals that result in migration, as opposed to termination, of the spin center. For example, a peroxy may insert into an carbon-carbon double bond (or other unsaturated site) to form a peroxy group with the spin center transferred to a carbon center adjacent to the point of unsaturation. Other free radical propagation mechanisms involve hydrogen abstraction from the same or neighboring chain. These processes can yield a hydroperoxy species and an alkyl free radical. The alkyl free radical center can quickly react with molecular oxygen to create another peroxy radical site. The hydroperoxy species may be considered a metastable intermediate that can further react to yield species containing carbonyl as well as hydroxy structure. These propagation reactions produce carbonyl and other oxygen functionality in the plasma polymer but do not deplete the free radical population. This may explain the continued growth of $\nu(\text{C}=\text{O})$ in the PP 4-VP film while the radical concentration remains constant as measured by ESR.

The depletion of the free radical population in the PP 4-VP film occurs through radical-radical recombination reactions. These termination reactions requires that the free radical centers be in close proximity. For a condensed phase system, such as a polymer, free radical sites migrate spatially via propagation reactions that are facilitated by molecular oxygen as described previously. In other work, the postformation film atmosphere has been shown to influence the rate of free radical decay in plasma-produced polymers.⁸ For the plasma-polymerized 4-vinyl pyridine films studied here, the films may be considered to be saturated with atmospheric oxygen. Thus, long-lived free radical sites will mainly be of the peroxy structure. Thus, termination reactions will most likely occur by the reaction of two peroxy species.

The time-dependent free radical behavior observed here gives information about postformation film oxidation processes as well as insight into the film growth mechanism and structure. Plasma excitation of cyclic structures such as 4-vinyl pyridine can result in the cleavage of a covalent bond to yield both mono- and diradical species.⁴ Diradical species can be incorporated into a polymer film while retaining an active free radical center. This anchored

free radical site can continue to react with nonactivated 4-VP molecules from the gas phase to propagate a branched chain. Propagation in the growing film will continue until the free radical site is terminated by reaction with a monoradical species or by hydride extraction from a gas-phase molecule or fragment. The film structural growth may proceed over and around an anchored free radical site and, thus, block access to the site for a terminating species. Hence, the free radical center lies trapped in the polymer film. In the plasma-polymerized 4-vinyl pyridine F1, the spin density in the nascent film corresponds to approximately only one free radical site for every 2,000 vinyl pyridine repeat units. Thus, the free radical centers are present at low concentrations and may be highly dispersed. In a plasma-produced polymer there is usually a high level of crosslinking that contributes to low molecular mobility. Plasma-polymerized 4-vinyl pyridine films similar to those used in this study have been characterized in our laboratories by solubility studies and NMR molecular dynamics measurements. These measurements have suggested that the PP 4-VP films are highly crosslinked and exhibit limited molecular motions at room temperature.

Both free radical propagation reactions and termination reactions can contribute to the observed formation of carbonyl and other oxygen-containing functionality in the plasma-produced 4-vinyl pyridine polymer film. The rate of formation of carbonyl and other oxygenated species can be correlated with the decay of the free radical population in the film. However, after the initial rapid decay process, a long-lived peroxy free radical population persists in the film. This population can continue to produce oxygenated polymer species through the propagation reactions and maintain a constant free radical spin density.

The rapid initial decay process and the long-lived free radical population may be rationalized, in part, by considering the distribution of crosslinking, branching, and heterogeneous structure present in the polymer film. In regions of the network structure that have fewer chemical crosslinks (higher segmental mobility) and higher levels of branching, the propagation and termination reactions can proceed relatively rapidly. However, in regions of the structure that are highly crosslinked (lower segmental mobility) and pendant side chains are more dispersed (isolated), the propagation and termination reaction rates are attenuated.

The trapped free radical population and chemical structure of the polymer film is dependent on the plasma polymerization conditions. One of the pri-

mary factors that influences the plasma process is the power supplied to the discharge relative to the monomer feed to the reactor. This can be quantified for a given reactor by calculating the composite power density¹⁶ as expressed below.

Composite Power Density (J/kg)

$$= (W/FM) \times 1.34 \times 10^9$$

In this equation, W is the power applied to the plasma in watts, F is the monomer flow rate in standard cm^3/min , and M is the molecular weight of the monomer in g/mol . In the present study, the mass flow-rate of argon was not included in the composite power density calculations.

To test the effect of power density on postformation carbonyl production, another PP 4-VP film, F2, was prepared using a higher monomer flow rate and composite power density as listed in Table I. The initial ($t = 10$ min) IR spectrum for this sample was similar to that for F1 found in Figure 3. It is interesting to compare the relative growth of $\nu(\text{C}=\text{O})$ for F1 and F2 films as plotted in Figure 6. As can be seen in Figure 6, the PP 4-VP film prepared using the higher composite power density exhibits a higher rate and higher extent of carbonyl formation. The extent of activation and free radical formation and fragmentation of the precursor structure increases as plasma power density increases. Thus, the film produced under the higher composite power density results in a higher concen-

tration of free radical species trapped in the film, which ultimately results in higher carbonyl production. Also, Figure 6 shows the continued growth of $\nu(\text{C}=\text{O})$ in the F2 PP 4-VP film even after 720 h (30 days) since formation.

In addition to free radical mechanisms for plasma-polymerized 4-vinyl pyridine, there may be a other chemical structures in the polymer system that play a direct or intermediate role in the auto-oxidation processes. For example, the relative intensity of the vibrational modes assigned to $-\text{C}\equiv\text{N}$ (2218 cm^{-1}) and $-\text{N}-\text{C}\equiv\text{N}$ (2171 cm^{-1}) decrease with time for both Film 1 and Film 2, as shown in Figure 7. It may also be noted that the initial relative intensity of vibrational bands associated with both nitrile structures was higher in the sample prepared under a higher composite power density. These labile structures may generate oxidated functionality in the film through hydrolysis or direct oxidation.

CONCLUSIONS

Plasma polymerization of 4-vinyl pyridine proceeds through a gas-phase free radical mechanism that produces a highly crosslinked film. As initially measured by infrared spectroscopy, the film retains much of the organic functionality of the monomer. However, during the deposition process, free radicals are trapped in the film, which are localized and isolated from structural moieties that would react to ter-

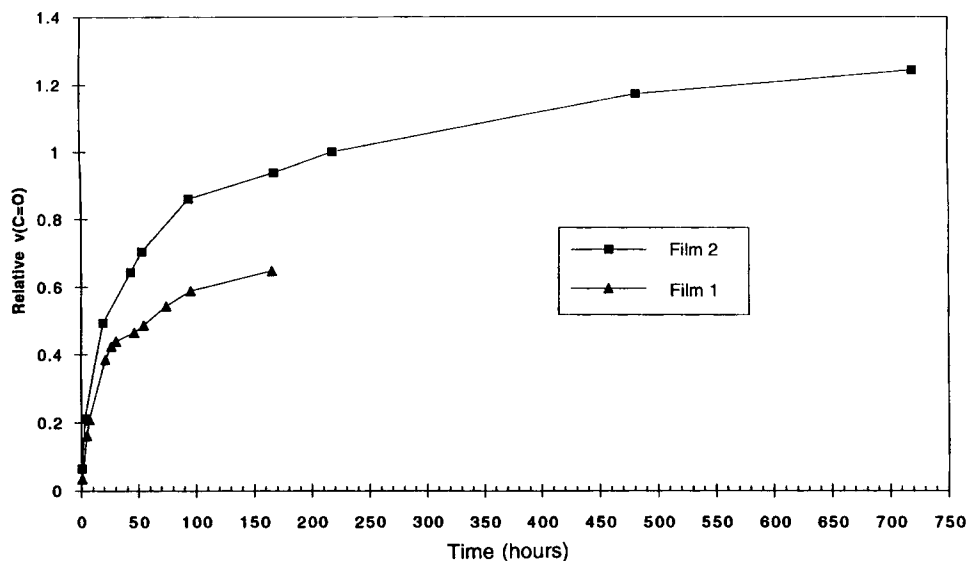


Figure 6 Time-dependent relative $-\text{C}\equiv\text{N}$ (2218 cm^{-1}) and $-\text{N}-\text{C}\equiv\text{N}$ (2171 cm^{-1}) absorbance for plasma-polymerized 4-vinyl pyridine films (F1 = 1.4×10^7 and F2 = 3.1×10^7 J/kg).

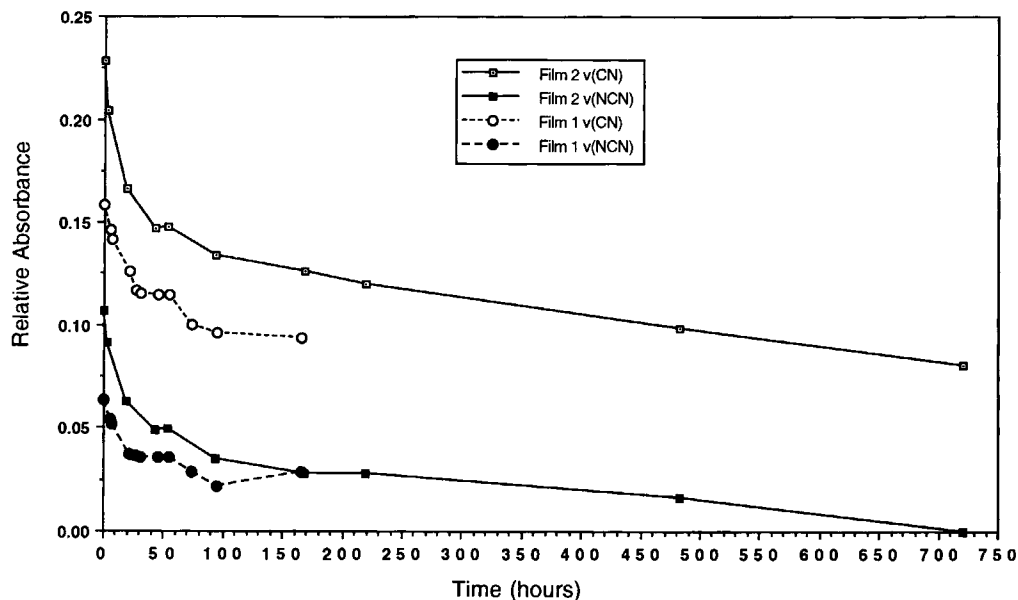


Figure 7 Time-dependent relative $\nu(\text{C}=\text{O})$ absorbance for plasma-polymerized 4-vinyl pyridine prepared at different composite power densities ($F1 = 1.4 \times 10^7$ and $F2 = 3.1 \times 10^7$ J/kg).

minate or dissipate the free radical site. Using ESR, these primary free radicals have been shown to quickly react with atmospheric oxygen to yield a film with a nascent peroxy radical density of 2.9×10^{18} spins/g. This corresponds to 1 free radical site for every 2,000 4-VP monomer or equivalent structural units in the structure. The peroxy radicals react through mechanisms, which involve hydride extraction followed by oxidation to produce carbonyl, hydroxyl, ether, and other oxygenated structures in the polymer chain that can be monitored using infrared spectroscopy.

Depletion of the free radical population with time was tracked using ESR. The signal decays rapidly at first and then reaches a long-lived value corresponding to 1.3×10^{18} spins/g after approximately 30 h. As the free radical population decreases, a concomitant growth of vibrational modes associated with oxygen-containing functional groups is observed in the IR spectrum of the film. A continued increase of carbonyl functionality is observed even as the peroxy radical population remains level. This slow, auto-oxidative effect may be attributed, in part, to free radical centers that are anchored to the polymer chain in regions of high crosslinking. In such regions, limited segmental mobility would limit the rate of radical-center migration and radical-radical recombination (termination) processes.

The free radical decay and the growth of carbonyl in the polymer cannot be ascribed to first- or second-

order kinetic processes. The mechanisms involved in the propagation and eventual termination of free radicals in PP 4-VP are complex and not completely understood. The time-dependent changes observed in the structure of PP 4-VP films are anticipated to affect the physical and chemical properties of the polymer. Thus, it is important to understand the time-dependent behavior of plasma-polymerized films and plasma-treated polymers if they are to be implemented in commercial processes and products.

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