Fourier Transform Infrared Studies on the Thermal Degradation of Polyvinylimidazoles. Part II

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Synopsis

Oxidative thermal degradation of polyvinylimidazoles on copper have been studied. Degraded products include olefinic, saturated, and α,β-unsaturated ketones, α,β-unsaturated and β-iminonitriles, C≡N conjugated and —NH—C≡C— components. At 150°C, the rate of degradation of the polymers is relatively slow. For PVI(1), approximately 50% of the polymer remained nonoxidized after 64 h of heating, whereas 80% of PVI(4) remained nonoxidized after 47 h of heat treatment. At 210°C, the degradation mechanisms involved three stages, with the duration of each stage quite different between the two polymers. No degradation of polyvinylimidazoles is observed in vacuum initially at 400°C. Prolonged heat treatment leads to evaporation of residual water, further complex formation, and, finally, evaporation of the polymer films.

INTRODUCTION

As reported previously[1,2] poly-*N*-vinylimidazole [PVI(1)] and poly-4(5)-vinylimidazole [PVI(4)] have been demonstrated to be effective new polymeric anticorrosion agents for copper at high temperatures. Oxidation of copper is suppressed even at 400°C. A series of experiments was undertaken to elucidate the degradation mechanisms of these polymers by Fourier transform infrared (FT-IR) spectroscopy. The main goal of this paper is the understanding of the inhibition mechanism by the polyvinylimidazole polymers on copper.

It has been known that thermal oxidation of polymer coating is accelerated appreciably in the presence of copper, copper salts, and copper oxides.[3-7] The catalytic mechanisms, however, are not well understood. Many investigators have stressed that copper and its compounds promote the decomposition of hydroperoxides, which are formed in the beginning of the thermal oxidation of polymer films coated on copper.[3-9] For example, thermal degradation of vinyl polymer, such as polypropylene, leads initially to the formation of hydroperoxide groups. These groups then decompose and lead to main chain scission and/or possibly cross-linking. Also, complex multifunctional compounds with various oxygen-containing groups are produced as low-molecular-weight species and formed along the polymer chain as keto, aldehyde, or carboxyl groups.[10,11] Termination then takes place with the formation of inert products or with the use of an inhibitor, such as oxamide.[3] Figure 1 shows a plausible mechanism for the interaction of copper with a
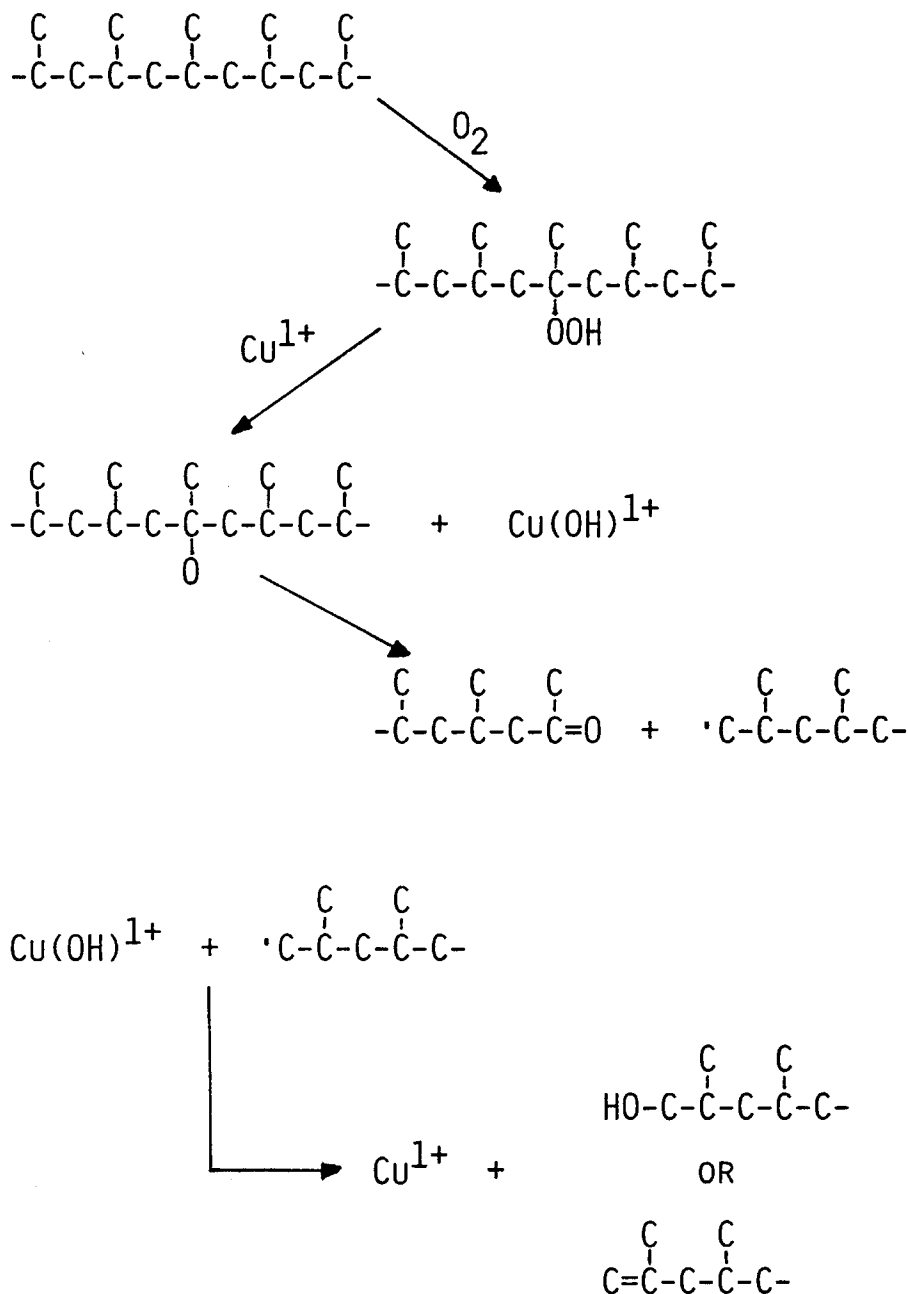
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Fig. 1. A plausible mechanism for the interaction of copper with a hydroperoxide.

hydroperoxide.[3] Cuprous copper can be readily produced in the polymer from copper or from cupric compounds. It then reacts with hydroperoxides formed during incipient oxidation of the polymer to form alkoxy radicals that propagate the oxidative chain reaction. And the cupric copper can be reduced to cuprous by the hydrocarbon itself or by an antioxidant. This mechanism

assumes that cuprous ions diffuse into the polymer to promote hydroperoxide decomposition. However, how cuprous, cupric, or both ions diffuse into the polymer is not understood. Jellinek et al.,[12] based on their physicochemical and ion-scattering spectrometry (ISS) results, explained that the catalytic action of copper oxides was due to an initiation reaction consisting of abstraction of tertiary H atoms producing R· radicals, reducing copper oxide in the process. The ROOH groups are decomposed by Cu^+ ions, which are oxidized to Cu^{2+} ions in the polymer film. The Cu^{2+} ions, in turn, decomposed further ROOH groups and were reduced to Cu^+, with RO· and ROO· radicals produced during these reactions, leading to accelerated oxidation.

In Part I of this two-part series,[13] we have investigated the thermal degradation of PVI(1) and PVI(4) films on potassium bromide (KBr) plates at elevated temperatures in air. It was found that the thermal degradation reactions of both polymers were very similar except that degradation of PVI(4) takes place before PVI(1) at 250°C. When the temperature is elevated to 330°C, the occurrence of oxidation and dehydrogenation leads to the formation of saturated ketones and unconjugated C=C bonds in the polymer backbone, respectively. The combination of the two types of reactions also yields α,β-unsaturated keto compounds. Then at prolonged heat treatment at 330°C, cleavage of imidazole rings also occurs and α,β-unsaturated cyano structures are formed. At 400°C, a new class of compound, carbodiimides, is being produced and the amount of the α,β-unsaturated cyano compounds is greatly reduced. Upon further heat treatment at 400°C, carbodiimides are mostly evaporated and degraded.

In this paper, we shall continue to study the degradation mechanisms of PVI(1) and PVI(4) films on copper mirrors at elevated temperatures in air and in reduced pressures by FT-IR spectroscopy using reflection-absorption (R-A) technique. By examining the degradation under reduced pressures, it is possible to retard the reaction kinetics so that oxidative degradation, which complicates the spectral interpretation, is of secondary importance.

Adsorption characteristics and rate of complex formation of small imidazoles, such as imidazole and undecylimidazole, are different from polyvinylimidazoles because of their smaller molecular size. However, they all bear the imidazole moiety, which is capable of forming a complex with copper. In fact, recently, small imidazoles have been used as effective corrosion inhibitors for copper.[14–18] At the end of the discussion, we also compare the thermal degradation mechanisms between the smaller imidazoles and polyvinylimidazoles.

EXPERIMENTAL

Oxidative thermal degradations were performed on 2.5 × 5.0 × 0.2 cm copper mirrors (ASTM B125, type ETP). Copper mirrors were mechanically polished with no. 5 chromeoxide, ultrasonically washed with acetone, rinsed with 2% dilute hydrochloric acid and distilled water, and dried with a stream of nitrogen gas. PVI(1) and PVI(4) were first dissolved in anhydrous ethanol and methanol, respectively, to yield a concentration near 0.68 g/L. Then using a 50-μL microsyringe, the polymers were solution cast onto copper

substrates and air dried. Film thickness was calculated based on the concentration of the solution, the quantity used, the area of the substrate, and the density of the sample. Unless specified, the typical thickness of the films used on copper mirrors was 150 nm. Films of undecylimidazole on copper mirrors were similarly prepared. Thermal degradations in vacuum were studied on $1.25 \times 5.0 \times 0.2$ cm copper mirrors. After the deposition of a PVI film, it was placed into a Kimax test-tube (15 mm diameter by 150 mm length), which was then stoppered with a one-hole rubber cork. Afterward, glass tubing that connected to a mechanical vacuum pump was inserted into the hole of the rubber cork. The sample was degassed for 5 min before inserting into a Thermolyne furnace (model 10500).

For reflection experiments, the reflection-absorption attachment (Harrick Scientific) along with a gold wire grid polarizer (Perkin-Elmer) were mounted in a Digilab FTS-14 Fourier transform infrared spectrometer equipped with a triglycine sulfate detector and purged with dry air. Spectra collected were the average of 200 scans at 4 cm^{-1} resolution using an optical velocity of 0.3 cm/s. The angle of incidence used was 75°. Syntheses of PVI(1), PVI(4), PVI(1)-Cu(II) complex, and PVI(4)-Cu(II) complex were carried out as reported previously.[1]

RESULTS AND DISCUSSION

Band Assignments

Experimentally, the R-A technique is not as straightforward as transmission, and difficulties often occur in quantitative interpretation because R-A spectra may be distorted relative to transmission with significant shifting in peak maxima. The reason for such distortion is the contribution of the refractive index to the reflectivity of a sample with the abrupt changes in the refractive index in the region of an absorption band (the anomalous dispersion). Frequency shift is often interpreted as a chemical structural change. Optical effects must be considered prior to the attribution of the frequency shift to the chemical structure change. However, for the polyvinylimidazole films, no significant shifting to higher frequencies relative to transmission (due to the optical effects) is observed as polyvinylimidazoles do not absorb strongly.[19,20] Thus, tentative band assignments for the reflection spectra of the polyvinylimidazoles are the same as the transmission spectra, as reported previously in Part I.[13]

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PVI-Copper (II) Complexes. Figure 2 shows the transmission spectra of PVI(1) powder and PVI(1)-Cu(II) complex. Basically the two spectra are quite similar. The band at 920 cm^{-1} in PVI(1) was assigned previously[13] as the C—H out-of-plane bending mode. The intensity of this band in PVI(1)-Cu(II) complex was greatly reduced. The relative intensity between the bands at 1110 and 1090 cm^{-1} was also changed. These bands are assigned
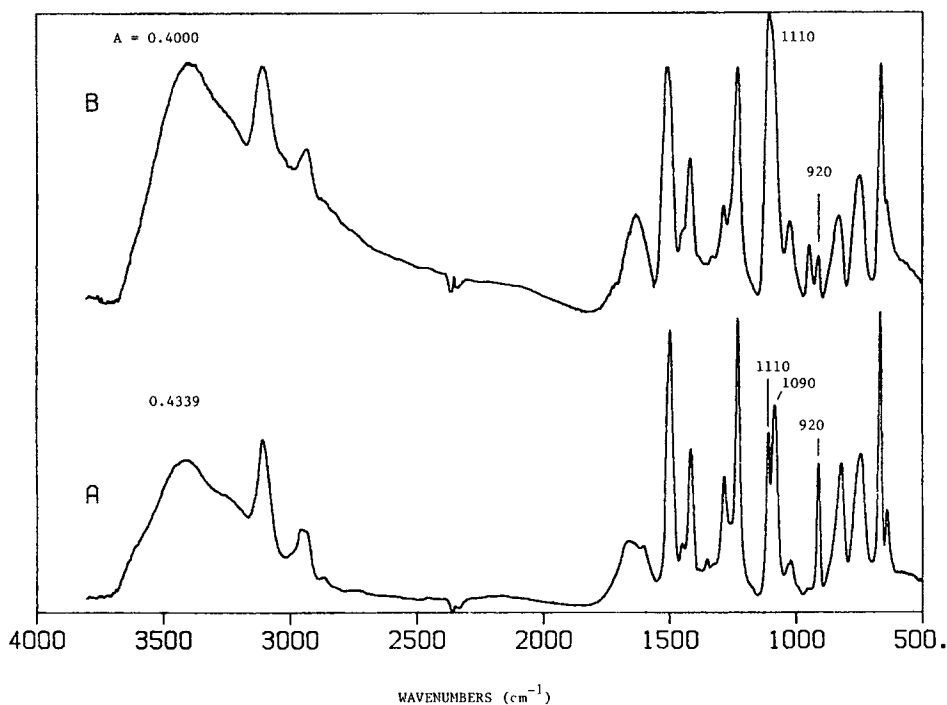
Fig. 2.   Infrared transmission spectra of (A) PVI(1) powder; (B) PVI(1)-Cu(II) complex.

to the C—H in-plane bending modes of the imidazole ring. In the PVI(1) spectrum, the band at 1110 cm^{-1} was less intense than the band at 1090 cm^{-1}. However, the reverse was true for the PVI(1)-Cu(II) spectrum. The bonding of the nitrogen atom with a heavy copper atom and the subsequent shifts in electron densities in the imidazole rings resulted in various shifts in position of some of the bands and in relative changes in intensity of various bands.

The transmission spectra of PVI(4) powder and PVI(4)-Cu(II) complex are shown in Fig. 3. The band at 940 cm^{-1} in PVI(4) was assigned previously to the N—H bending. This band was not present in the PVI(4)-Cu(II) complex, indicating the expected absence of the N—H band where the hydrogen atom was replaced by a much heavier copper atom. Again, the substitution of the copper atom caused the electron densities in the imidazole ring to shift because of the negative charge of the azole nitrogen. The result led to various changes in band positions and relative intensity. The band at 980 cm^{-1} was assigned to the C—H out-of-plane bending in the PVI(4) spectrum. Subsequently, the band was shifted to 970 cm^{-1} and the band shape became relatively sharper.

Degradation at 150°C

Figure 4 shows the changes occurring in the reflection spectra from 3600 to 600 cm^{-1} of PVI(1) film thermally degraded on copper at 150°C as a function of time. No degradation was observed after the film was heat treated for 5 min (spectrum B). Reduction of bands at 3400 and 1640 cm^{-1} was due
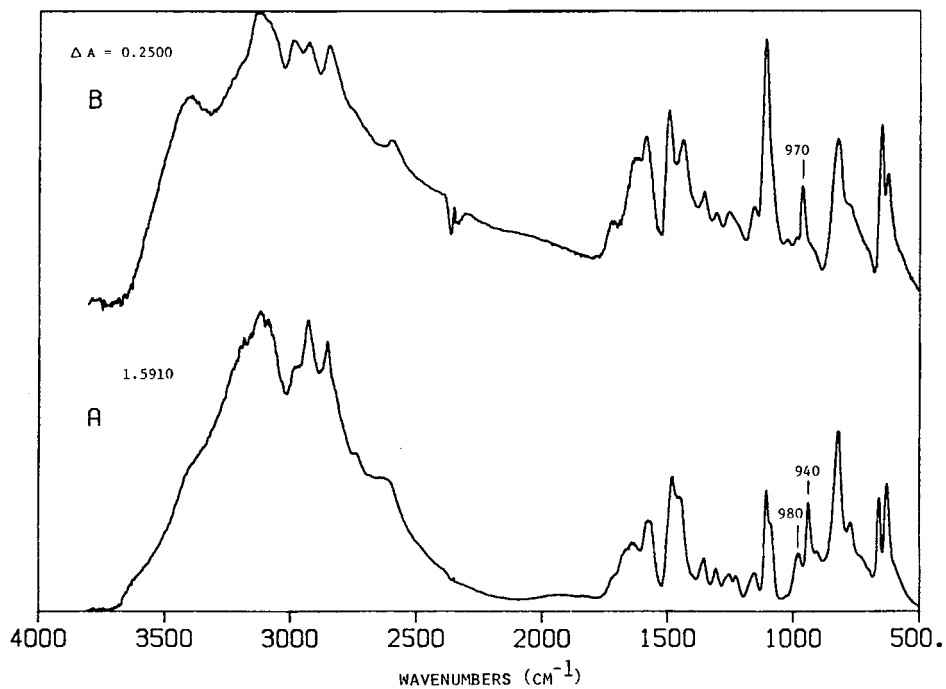
Fig. 3.   Infrared transmission spectra of (A) PVI(4) powder; (B) PVI(4)-Cu(II) complex.
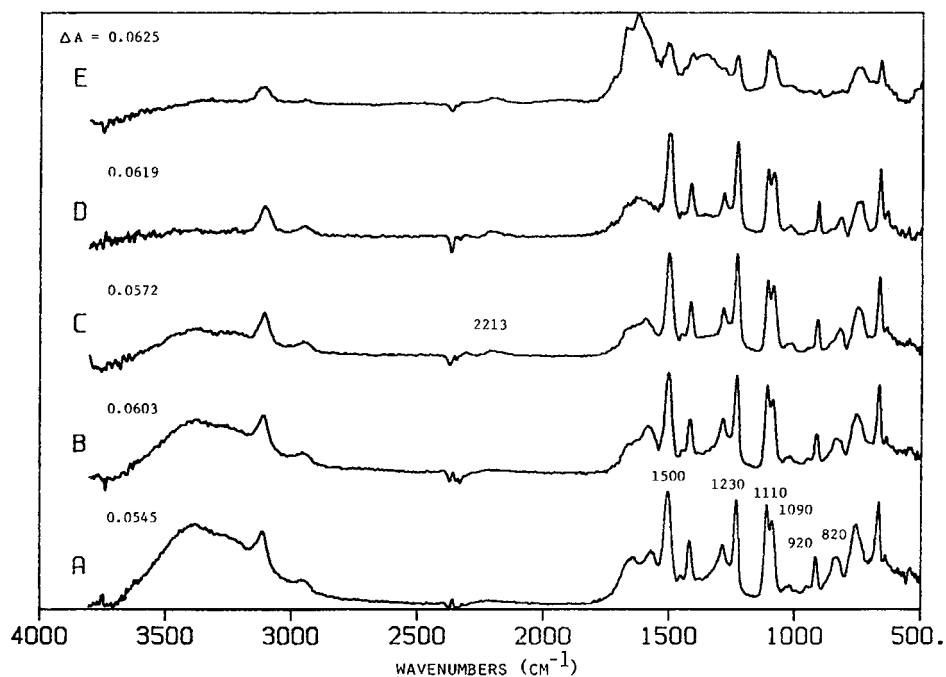

Fig. 4.   Infrared R-A spectra of PVI(1) with heat treatment at 150°C for (A) 0 min; (B) 5 min; (C) 2 h; (D) 6 h; (E) 64 h.

to the evaporation of residual water in the polymer, as reported previously.[13] The water was tightly bound through hydrogen bonding with the pyridine nitrogens of the imidazole rings and could not be readily removed. As PVI(1) was heated for 2 h (spectrum C), residual water continued to evaporate. At the same time, degradation occurred as observed by the reduction of the bands at 1110 and 1090 cm^{-1} the (C—H in-plane bending). These bands are useful for measuring the extent of imidazole ring cleavage by observing its area reduction versus time. The ring cleavage had led to the formation of nitrile as observed by the emergence of the band at 2213 cm^{-1} (spectrum C). This new band was assigned to α,β-unsaturated nitrile.[11,13,21] After 6 h of heating (spectrum D), all residual water was completely removed, as indicated by the disappearance of the broad band at 3400 cm^{-1}. Oxidation occurred and led to the formation of various oxidized products as shown by the multiple bands in the 1550–1750 cm^{-1} region. These bands were more pronounced as the polymer was heated for 64 h (spectrum E). The 1800–1500 cm^{-1} region of this spectrum was expanded and plotted in Fig. 5A.

New bands at 2213, 1724, 1677, 1665, 1631, and 1512 cm^{-1} were observed as the results of the degradation. The intensity of the original bands, such as 1414, 1286, 1230, 920, 820, and 641 cm^{-1}, was greatly reduced. All these bands were associated with the imidazole ring absorption modes, therefore indicating severe ring cleavages. The growing in intensity of the band at 2213 cm^{-1} also supported this finding.

Figure 6 shows the changes occurring in the reflection spectra from 3600 to 600 cm^{-1} of PVI(4) film thermally degraded on copper at 150°C as a
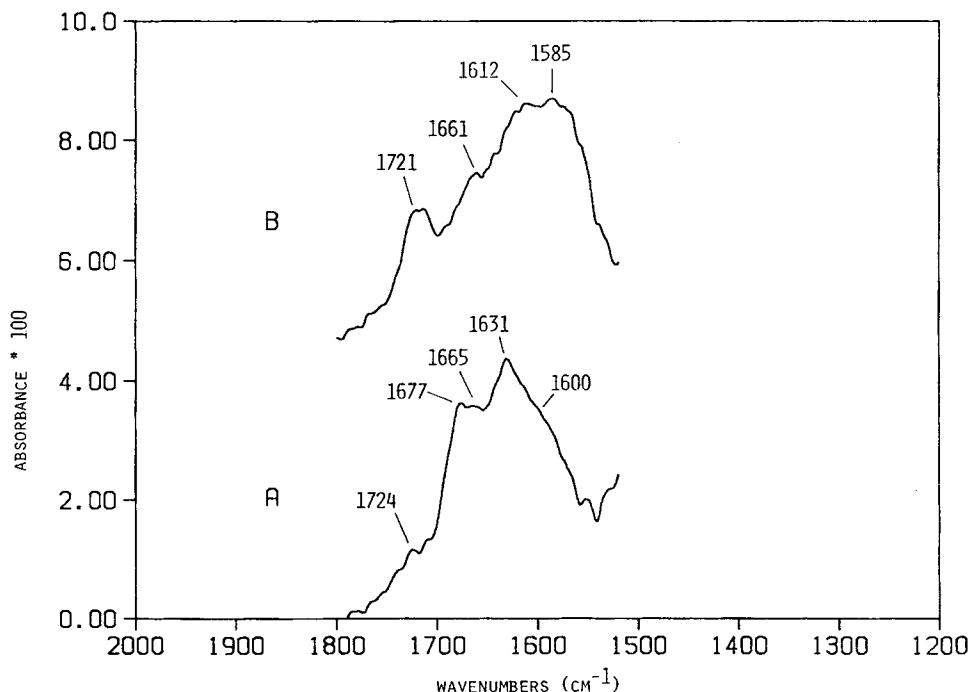

Fig. 5.   Infrared R-A spectra of (A) PVI(1) with heat treatment at 150°C for 64 h; (B) PVI(4) with heat treatment at 150°C for 47 h.
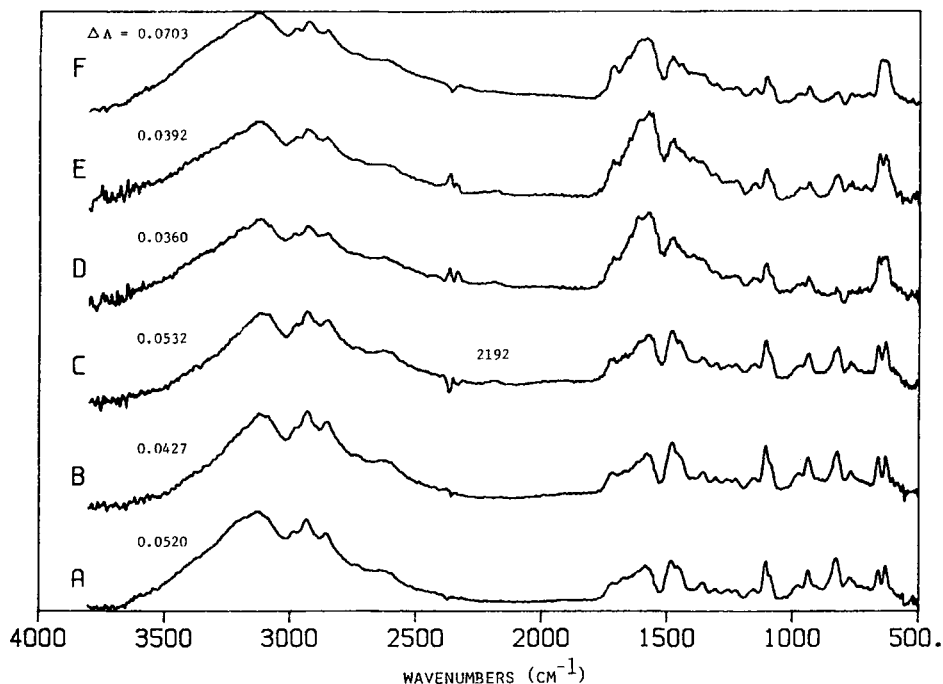
Fig. 6.   Infrared R-A spectra of PVI(4) with heat treatment at 150°C for (A) 0 min; (B) 10 min; (C) 4 h; (D) 23 h; (E) 28 h; (F) 47 h.

function of time. In the early stage of heat treatment (10 min, spectrum B), no change was observed except for a small reduction of the broad band at 3400 cm^{-1}, which was due to the evaporation of the residual water and the further transformation of N—H into N—Cu (complex formation) in the polymer.[13] When the polymer was heated for 4 h (spectrum C), imidazole ring cleavages led to the formation of nitriles, as indicated by the band at 2192 cm^{-1}. Grassie and McGuchan,[22] in their pyrolysis of polyacrylonitrile (PAN) study, postulated that when the cyclization of PAN was blocked at the initiation step, the structure obtained is a β-imino nitrile (Fig. 7). This β-imino nitrile absorbs near 2190 cm^{-1}. Unsaturated nitriles do not absorb as low as this,[23] but amino-substituted unsaturated nitriles do have abnormally low nitrile frequencies[24] and imino nitriles also have this characteristics. Therefore, the band at 2192 cm^{-1} in spectrum C was assigned to a β-imino nitrile. As PVI(4) was heat treated for 47 h (spectrum F), the new bands became more prominent as the result of the thermal degradation, and the 1800–1500 cm^{-1} region was expanded, as shown in Fig. 5B. These bands included 2192, 1721, 1661, 1612, and 1585 cm^{-1}.

Degradation of PVI(1) and PVI(4) appeared to be rather slow at 150°C. Both polymers were not completely degraded even after prolonged heating. For PVI(1), calculations of the area reduction of the band at 1110 cm^{-1} showed that approximately 50% of the polymer remained nonoxidized after 64 h of heating. On the other hand, using the area of the band at 1106 cm^{-1}, it was found that 80% of PVI(4) remained nonoxidized after 47 h of heat treatment.
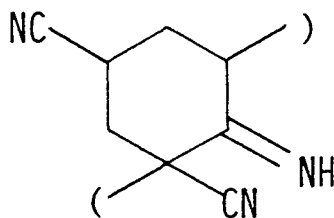
Fig. 7.   β-imino nitrile.

The tentative assignments for the new bands emerged from the thermally degraded polyvinylimidazoles are shown in Table I. The band assignments were similar to those assigned in Part I,[13] and the arguments for such assignments, therefore, would not be repeated here.

Degradation at 210°C

Figures 8 and 9 show the reflection spectra of PVI(1) with heat treatment at 210°C for various times. As mentioned earlier, the C—H in-plane bending mode, which occurs near 1110 cm^{-1}, is useful for measuring the extent of imidazole ring cleavage. On the other hand, the bands at 2960 and 1415 cm^{-1}, which have been assigned to the CH$_2$ asymmetric stretching and the CH$_2$ bending,[13] are useful for measuring the extent of the polymer chain oxidation and/or scission. Figure 10 shows the curves of the area reduction of the bands at 1110, 1415 and 2960 cm^{-1} versus log time in seconds. For the band at 1110 cm^{-1}, the initial linear decrease was observed up to 7 min, followed by another linear decrease with a steeper slope. There was no change in the area of both bands at 1415 and 2960 cm^{-1} initially. Then, after 7 min of heat treatment, a linear decrease of the area was observed in both cases. Oxidation is commonly described in terms of the mathematical relationship found between the oxide thickness x, which is assumed to be uniform, and time t. For thin films, the relationships are of the form

$$x = k \log t$$

where k is the rate constant.[25,26] Therefore, the linear relationships of the curves in Fig. 10 were likely caused by oxidation. The change of the slope

TABLE I
Tentative Band Assignments of Thermally Degraded PVI

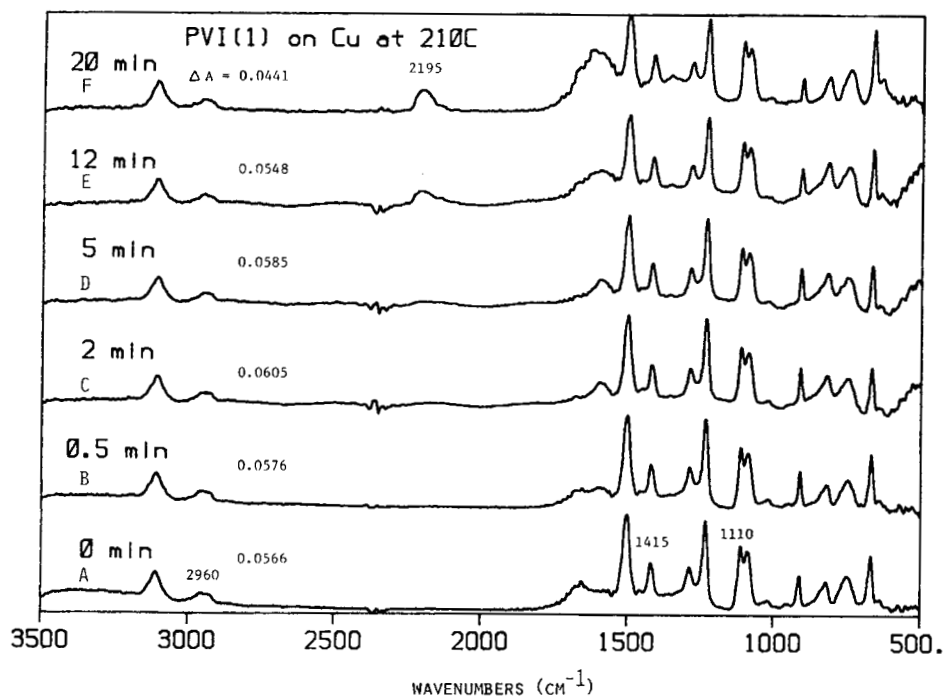| PVI(1) bands (cm^{-1})	PVI(4) bands (cm^{-1})	Tentative assignments
2213		α,β-Unsaturated nitrile
	2192	β-Imino nitrile
1724	1721	C=O ketonic stretching
1677		C=O α,β-Unsaturated ketone
1665	1661	C=C unconjugated
1600	1612	C=N conjugated; C=O + C=C (mixed mode); C=C + N—H (mixed mode)

Fig. 8.   Infrared R-A spectra of PVI(1) with heat treatment at 210°C for (A) 0 min; (B) 0.5 min; (C) 2 min; (D) 5 min; (E) 12 min; (F) 20 min.
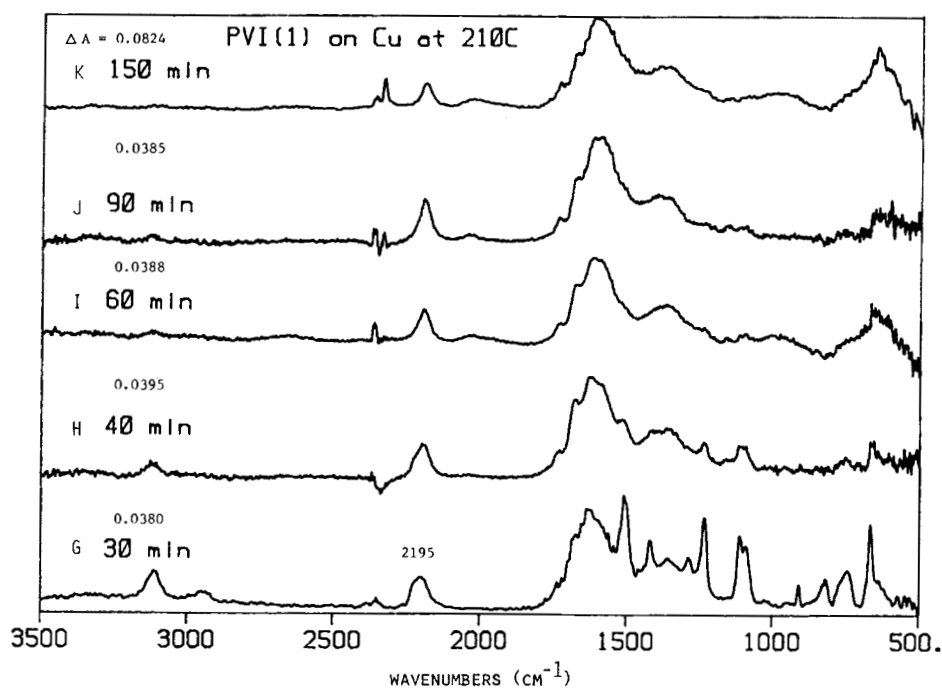

Fig. 9.   Infrared R-A spectra of PVI(1) with heat treatment at 210°C for (G) 30 min; (H) 40 min; (I) 60 min; (J) 90 min; (K) 150 min.
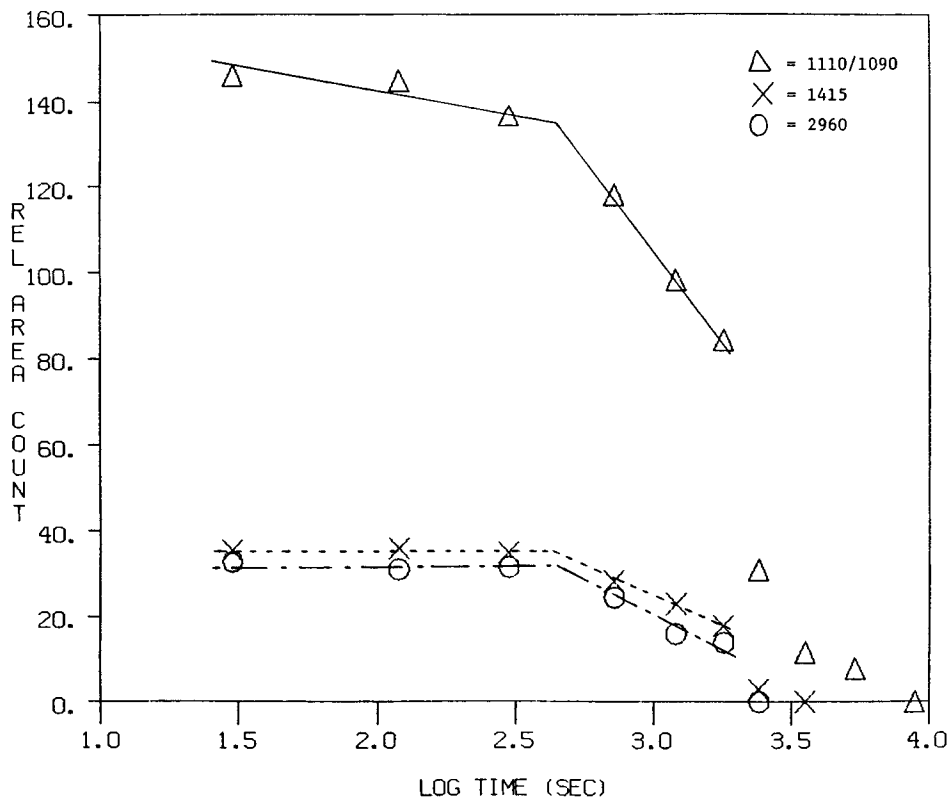
Fig. 10. Relative intensity of the bands at 2960, 1415, and 1110 cm^{-1} of thermally treated PVI(1) (210°C) versus log time in seconds.

implies the change of the degradation mechanism. Thus, the degradation or oxidation mechanism of imidazole rings in the first 7 min was different from that afterward. The second slope of the 1110 cm^{-1} curve was steeper than those of the bands at 1415 and 2960 cm^{-1} at the same time period, indicating that the ring opening took place faster than the oxidation or scission of the polymer chain. After 30 min of heat treatment, by measuring the relative area of the band at 1110 cm^{-1}, it appeared that 50% of the polymer film remained nonoxidized. Then a very drastic reduction of the three bands was observed, indicating a much faster rate of degradation. Finally, total degradation of the polymer film was completed after 3 h of heat treatment.

As shown in Figs. 8 and 9, heat treatments caused the cleavage of imidazole rings and led to the formation of nitrile, as indicated by the appearance of the band at 2195 cm^{-1}. The increase of the band area versus time in minutes was plotted and shown in Fig. 11. Nitrile formation took place only in the first 7 min. The cyano products appeared to be thermally very stable and were not further degraded even after 3 h of heat treatment.

In summary, the oxidative degradation of PVI(1) at 210°C involved three stages. The first stage of degradation took place in the first 7 min. The degradation mechanisms in this time period involved the cleavage of im-
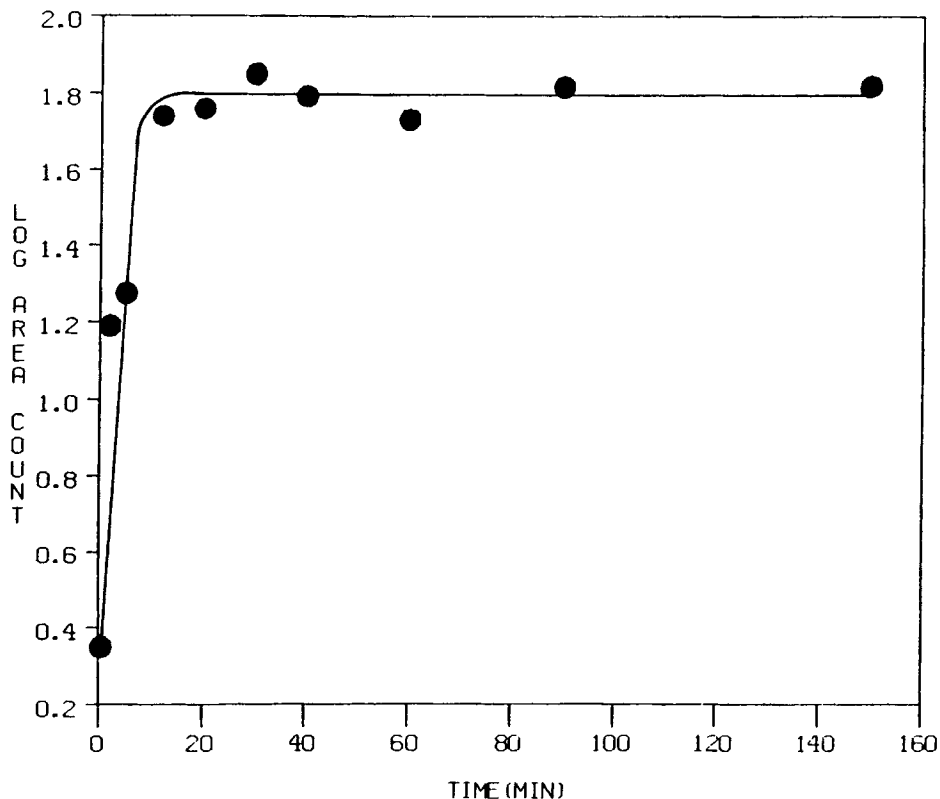
Fig. 11.   Relative intensity of the band at 2195 cm^{-1} of thermally treated PVI(1) (210°C) versus time in minutes.

idazole rings and nitrile formation, as indicated by the area reduction of the band at 1110 cm^{-1} and the increase of the band area at 2195 cm^{-1}, respectively. However, no degradation or chain scission of the polymer chain occurred in this first stage. The second stage lasted 23 min. During this time period, oxidation of imidazole continued and the rate of oxidation was faster than that of the first stage, with the degradation mechanism also different from the first. Besides ring opening, oxidation and/or scission of the polymer chain also occurred, but the rate was slower than that of the cleavage of the rings. The third stage took place after 30 min of heat treatment, when ring cleavage and degradation of the polymer were completed. The reduction in the band area of the transition from stage two to stage three was drastic, indicating a relatively faster rate of degradation than those observed earlier. It appeared that the initial oxidation mechanisms for PVI(1) at 150 and 210°C were different. The nitrile bands, which were the results of imidazole ring cleavages, appeared at 2213 and 2195 cm^{-1} for temperatures of 150 and 210°C, respectively. The former is assigned to α,β-unsaturated nitrile and the latter to β-imino nitrile. It must be emphasized that these band assignments can only be tentative. There is yet another possible assignment for these bands, as explained in the following. Cyano compounds coordinate to transition metals in two ways. Generally, nitriles

use the lone pair electrons of the nitrogen atom (σ electrons) to form linear R—C≡N—M bonds.[27-29] These σ-coordinated complexes increase the nitrile stretching frequency. However, it has been shown that isocyanate,[30] amine nitrile,[31-35] dinitrile,[36,37] phosphine nitrile,[38] and trifluoroacetonitrile[39] ligands are capable of coordination through the triple bond of their nitrile groups. Unlike the σ complexes, the π-coordinated complexes show a decrease in the nitrile stretching frequency. Thus, it is possible that the 2195 cm^{-1}, instead of arising from the β-imino nitrile, is actually the result of π-coordination complex formed between α,β-unsaturated nitrile ligand with copper. In consequence, the nitrile stretching frequency is shifted from 2213 to 2195 cm^{-1}.

Degradation of PVI(4) was also studied at 210°C for various periods of time, and the reflection spectra are shown in Figs. 12 and 13. Few spectral changes were observed during the first few minutes of heating (spectra A through D). Nitrile formation became noticeable after 12 min (spectrum E), as shown by the band at 2190 cm^{-1}. With prolonged heat treatments, the growth of the nitrile band was also accompanied by oxidatively degraded products, as shown by the emergence of multiple bands in the carbonyl region (spectra F through K).

Curves of the relative area reduction of bands at 2930, 1481, and 1106 cm^{-1} versus log time in seconds are shown in Fig. 14. The bands at 2930 and 1481 cm^{-1} were assigned to the CH$_2$ asymmetric stretching and the CH$_2$ bending modes, respectively, whereas the band at 1106 cm^{-1} was due
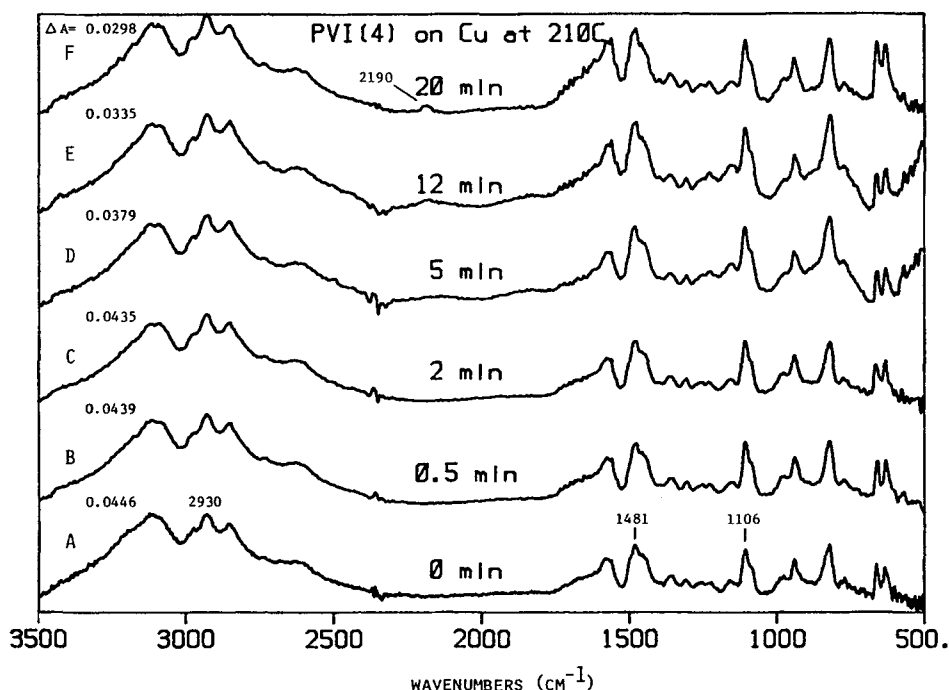

Fig. 12. Infrared R-A spectra of PVI(4) with heat treatment at 210°C for (A) 0 min; (B) 0.5 min; (C) 2 min; (D) 5 min; (E) 12 min; (F) 20 min.
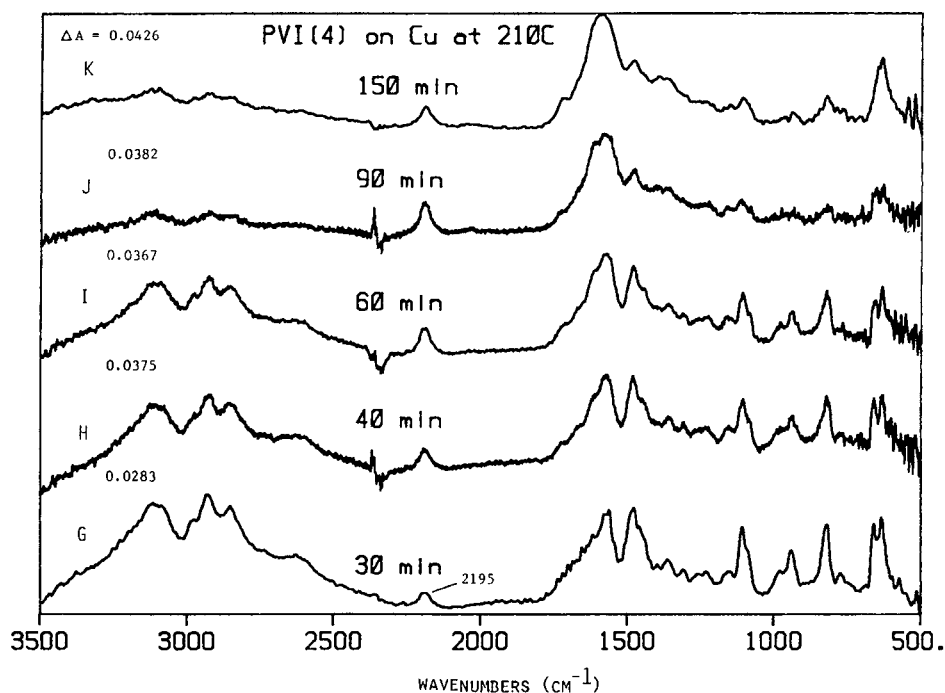
Fig. 13. Infrared R-A spectra of PVI(4) with heat treatment at 210°C for (G) 30 min; (H) 40 min; (I) 60 min; (J) 90 min; (K) 150 min.

to the C—H in-plane bending mode. No degradation of the polymer was observed in the first 4 min, as there was no change in the area for all three bands. Cleavage of imidazole rings occurred after 4 min, as seen by the reduction of the band at 1106 cm^{-1}. Then, after 7 min, there was also area reduction for the bands at 2930 and 1481 cm^{-1}. The linear relationship of the curves indicated, once again, that degradation was caused by oxidation. A drastic reduction in the band area was observed immediately after 60 min of heat treatment, indicating a rapid degradation. Calculations from the relative area reduction of the bands at 2930, 1481, and 1106 cm^{-1} showed that approximately 20% of PVI(4) was left nonoxidized.

Figure 15 shows the band area at 2190 cm^{-1} versus time in minutes. Nitrile formation started after 4 min into heat treatment and lasted for approximately 50 min. The cyano compounds formed appeared to be thermally stable and did not degrade even after prolonged heating at 210°C.

Similar to PVI(1), the oxidative degradation of PVI(4) can also be divided into three stages; however, the degradation mechanism and duration of each stage differ. The first stage covered the first 4 min when no degradation occurred. Thus, in comparison with PVI(1), for which the oxidation occurred immediately, PVI(4) appeared to be thermally more stable. In the second stage, the oxidation of imidazole rings occurred first and led to the nitrile formation, which lasted for 55 min, during which no change of the mechanism was observed. Oxidation and/or scission of the polymer chain was also observed later in the stage. The third stage began after the film was
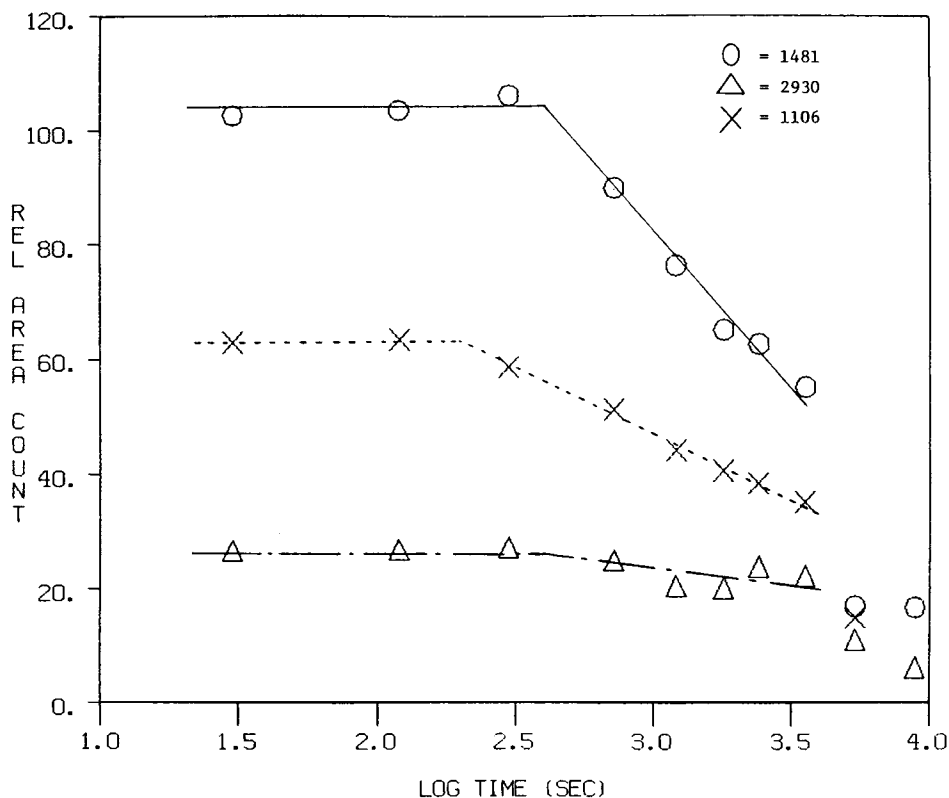
Fig. 14. Relative intensity of the bands at 2930, 1481, and 1106 cm⁻¹ of thermally treated PVI(4) (210°C) versus log time in seconds.

heated for 60 min. Band area reduction of the transition from stage two to stage three was sharp, implying that there was a change in the degradation mechanisms, with the rates relatively faster than the previous oxidation rates. Unlike PVI(1), only 80% of the PVI(4) film was degraded. Stage three, which lasted 1.5 h, was the longest stage of the three. When compared to the heat treatment at 150°C, it appeared that the initial oxidation mechanisms of PVI(4) in both cases were the same. As indicated by the band near 2190 cm⁻¹, β-imino nitrile was produced in both thermal conditions as the result of the imidazole ring cleavages.

DEGRADATION ON COPPER MIRROR IN VACUUM

Figure 16 shows the spectral changes of PVI(1) under vacuum at 400°C for various lengths of time. It is assumed that, at high vacuum, oxidative degradation is of secondary importance in interpreting the observed results. Therefore, in this part of the study, we are dealing essentially with a thermal decomposition. The above statement is supported by the fact that no oxidative species were produced, as no new bands were observed in either the nitrile or the carbonyl regions (spectra B, C, and D). After 3 min of heat treatment, tightly hydrogen bonded residual water was mostly evaporated,
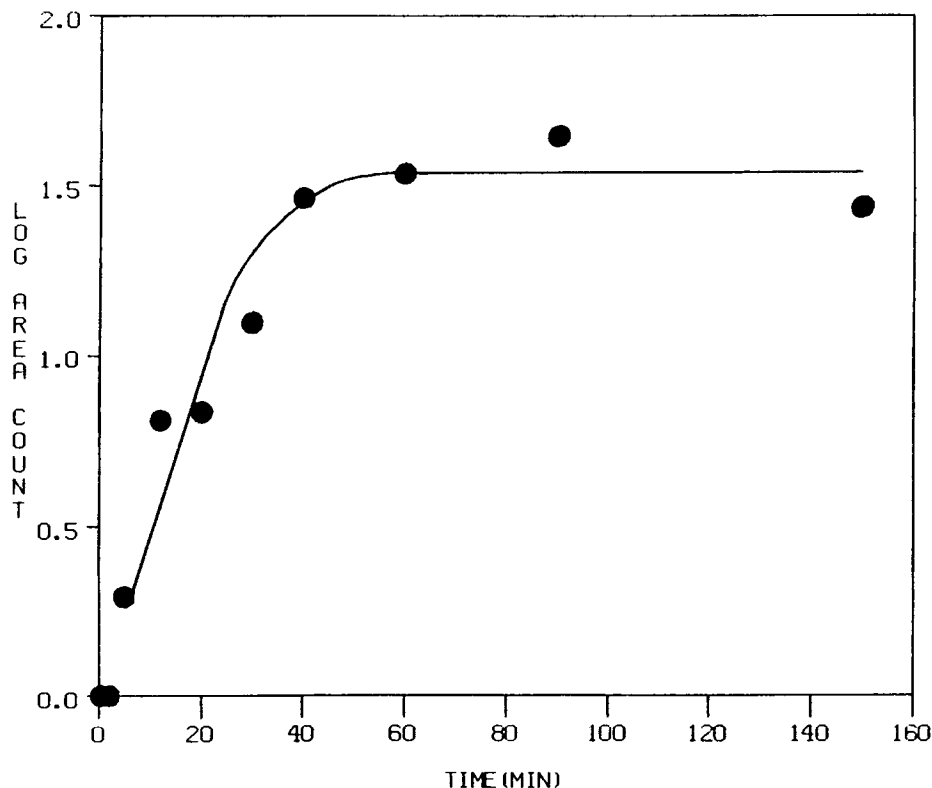
Fig. 15. Relative intensity of the band at 2190 cm^{-1} of thermally treated PVI(4) (210°C) versus time in minutes.

as noted by the reduction of the band near 1640 cm^{-1}. In general, there was no change in the spectrum, except for the relative reduction of the intensity of the band at 1110 cm^{-1} when compared with the band at 1090 cm^{-1}. It appears that the above phenomena may be due to more copper complex formation. The argument follows that since the evaporation of the residual water has led to the breakdown of the hydrogen bonding between the water molecules and the nitrogen atoms of the imidazole rings, more free imidazole rings are available for interacting with the copper ions. However, this argument does not hold since there is no reduction in the intensity of the band at 920 cm^{-1} as it is essential for the PVI(1) complex formation (see PVI-Copper (II) Complexes). The reduction of the band is probably due to the orientation effect of the imidazole rings. As the residual water was evaporating, the imidazole rings were "relaxed" and preferentially lay more parallel to the surface. The band at 1110 cm^{-1} has previously been assigned to the C—H in-plane bending mode. This mode of vibration involved a changing dipole moment parallel to the plane of the ring. One of the characteristics of infrared R-A spectroscopy of metals is that it is sensitive to the change of dipole moments normal to the metal surface. Therefore, because of this selection rule, a weaker C—H in-plane bending mode has been
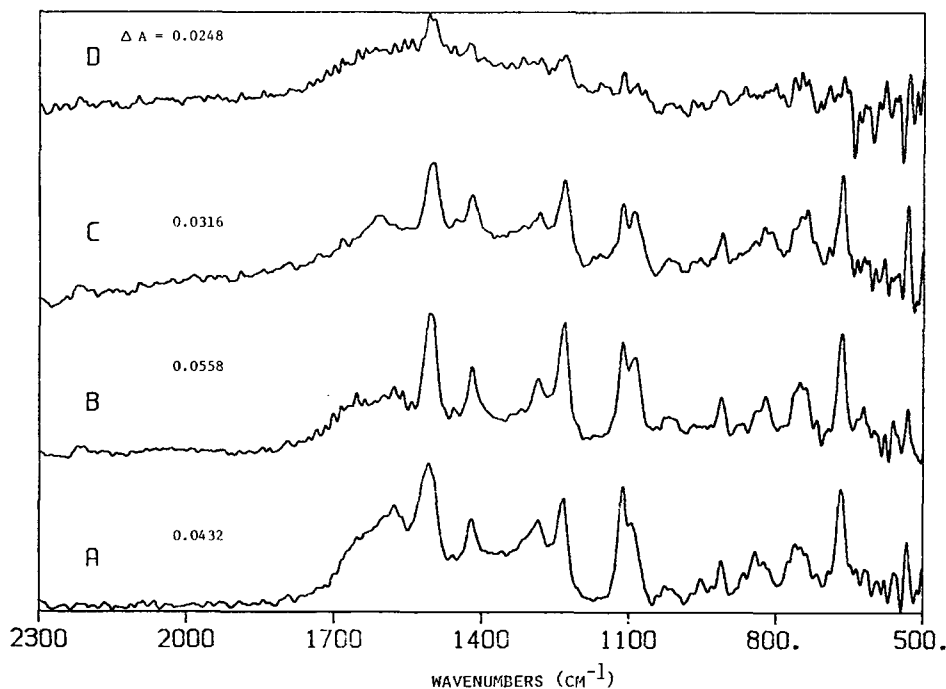
Fig. 16. Infrared R-A spectra of PVI(1) treated in vacuum at 400°C for (A) 0 min; (B) 3 min; (C) 7 min; (D) 10 min.

detected. It must be emphasized that the orientation represents an average value for all parts of the film. Thus, it was also likely that the interfacial layer next to the copper might be more highly oriented than the outer layer exposed to the air. Prolonged heat treatment of the sample led to further evaporation of the polymer, as shown in spectra C and D.

Figure 17 shows the spectral changes of PVI(4) under vacuum at 400°C at different degrees of heat treatment. After 15 min, it was observed that the bands at 940 and 627 cm^{-1} were mostly reduced. These two bands have been assigned previously to the N—H bending modes. The reduction of these bands indicated that there was complex formation between the protonated nitrogen atoms of the rings and the copper ions. As the result, formation of Cu—N bond displaced the hydrogen atom from the nitrogen atom and, thus, greatly suppressed the intensity of the N—H bending bands. The reduction of the previously assigned N—H stretching band at 3120 cm^{-1} (Fig. 18) further supported this finding. It is interesting to note that the intensity of the band at 1480 cm^{-1} increased after 15 min of heating. This band was assigned to the ring stretching and CH$_2$ bending modes previously. The enhancement of the intensity was probably due to the stretching of the unassociated rings because of the elimination of hydrogen bonding through water evaporation.

Similar to PVI(1), no degraded product was observed except for the continual evaporation of PVI(4) at prolonged heat treatment, as shown in spectra C and D.
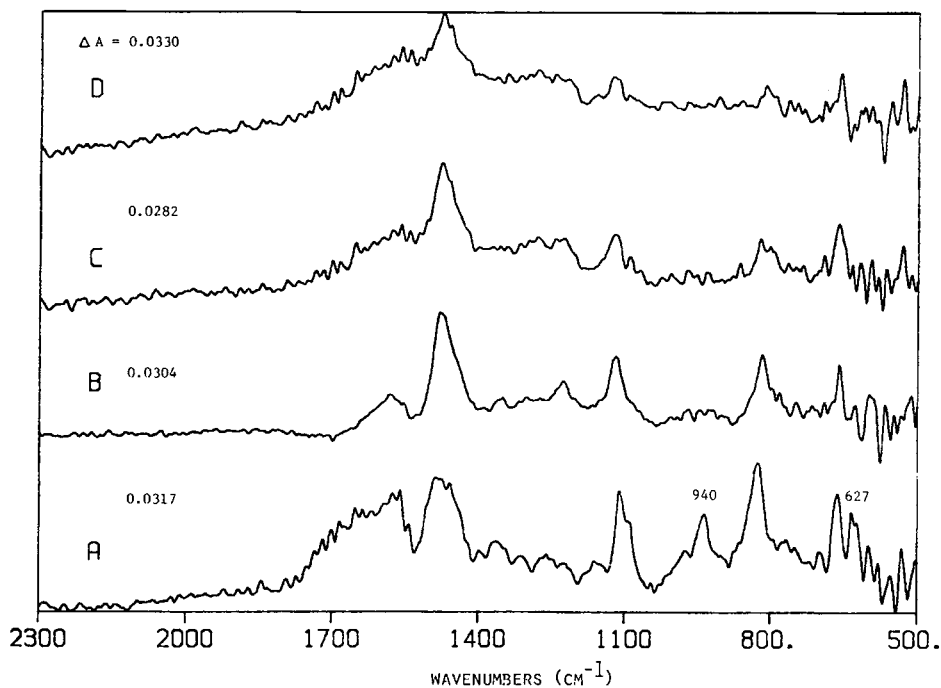
Fig. 17.   Infrared R-A spectra of PVI(4) treated in vacuum at 400°C for (A) 0 min; (B) 15 min; (C) 30 min; (D) 45 min.
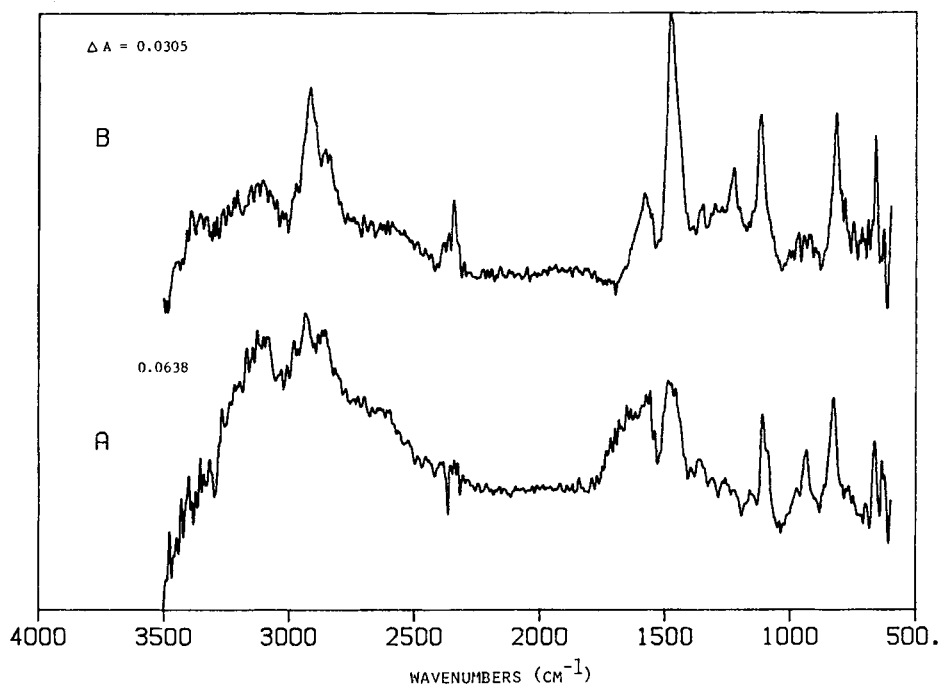
Fig. 18.   Infrared R-A spectra of PVI(4) treated in vacuum at 400°C for (A) 0 min; (B) 15 min.

COMPARISON WITH SMALL IMIDAZOLE DEGRADATION

From previous high-temperature studies,[1] we have demonstrated that PVI(1) and PVI(4) are more effective antioxidants than undecylimidazole, one of the commonly used corrosion inhibitors for copper. Yoshida and Ishida[40] have done extensive investigation of the thermal stability of undecylimidazole on copper using Fourier transform infrared R-A spectroscopy. At 150°C, they found that ring cleavage took place first and was followed by the elimination of the alkyl group and the oxidation of the imidazole. Cleavage of the ring occurred between C_4 and C_5 and led to the formation of the first degradation product, as shown in Fig. 19A. Upon further heat treatment, the final decomposition product with the perpendicular nitrile-metal interaction was suggested, as shown in Fig. 19B.

Similar to undecylimidazole at 150°C, ring cleavage of polyvinylimidazoles occurs prior to the oxidation and/or scission of the main polymer chain, and the rate of the former is faster than that of the latter. Unlike undecylimidazole, where total degradation of the film takes place after 22 h, polyvinylimidazoles suffer relatively little degradation under the same conditions. After 64 h at 150°C, 50% of PVI(1) film degraded. For PVI(4), 20% of the film degraded after 47 h at the same temperature.

In summary, because of cleavage from the ring and evaporation, the alkyl chain of undecylimidazole does not play a role in the final degradation products. Conversely, the polymer alkyl chain (backbone) was readily oxidized and complex multifunctional compounds with carbonyl and olefinic groups were produced along the polymer chain. The type of carbonyl of degraded undecylimidazole is exclusively aldehyde, whereas in polyvinylimidazoles it consists of saturated and α,β-unsaturated ketones. Cleavage of imidazole ring in both cases has led to nitrile formation also. Polyvinyl-
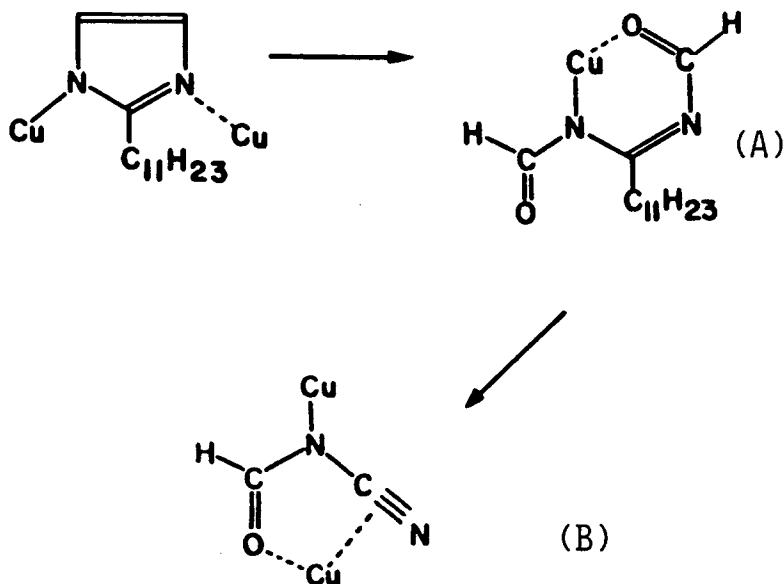

Fig. 19.   Oxidative degradation products of undecylimidazole at 150°C.

imidazoles yielded α,β-unsaturated and possibly β-imino nitriles, whereas the cyanamide type of nitrile was formed from undecylimidazole. As expected, the thermal degradation mechanism of polyvinylimidazoles is much more complicated than that of undecylimidazole. Other than what has been mentioned, conjugated C=N, C=C, and NH are also produced in the polymer systems.

CONCLUSION

Degraded products of the polyvinylimidazoles include olefinic, saturated, and α,β-unsaturated ketones, α,β-unsaturated and β-imino nitriles, and C=N conjugated and —NH—C=C— components. At 150°C, the rate of degradation of the polymers is relatively slow. Both polymers were not completely degraded even after prolonged heating. For PVI(1), approximately 50% of the polymer remained nonoxidized after 64 h of heating, whereas 80% of PVI(4) remained nonoxidized after 47 h of heat treatment. The oxidative degradation of the polyvinylimidazoles at 210°C involved three stages, and the degradation mechanisms and duration of each stage are quite different for the two polymers. For PVI(1), the degradation mechanisms in the first stage involved the cleavage of imidazole rings and β-imino nitrile formation. For PVI(4), no degradation of any kind occurred. In the second stage, oxidation of imidazole rings in PVI(1) continued. However, the rate was faster than that in the first stage, with the degradation mechanisms also different from the first. For PVI(4), ring cleavage occurred for the first time and led to the formation of β-imino nitrile. Besides ring opening, oxidation and/or scission of the polymer chain also occurred in the two polymers, but the rate was slower than that of the cleavage of the rings. Both PVI(1) and PVI(4) shared similar degradation mechanisms in the last stage. The transition from stage two to stage three was drastic, indicating a relatively faster rate of degradation than those observed earlier. Ring cleavage and degradation of the PVI(1) film were completed, whereas only 80% of the PVI(4) film was degraded.

No degradation of polyvinylimidazoles is observed in vacuum initially at 400°C. Prolonged heat treatment leads to evaporation of residual water, further complex formation, and, finally, evaporation of the polymer films.

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