

# Fourier Transform Infrared Studies on the Thermal Degradation of Polyvinylimidazoles: Part I

FREDERICK P. ENG and HATSUO ISHIDA, *Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106*

## Synopsis

Thermal degradation of polyvinylimidazoles on potassium bromide plate has been studied. At 300°C heat treatment, 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  $\alpha,\beta$ -unsaturated keto compounds. Then at prolonged heat treatment at 300°C, cleavage of imidazole rings also occurs and  $\alpha,\beta$ -unsaturated cyano structures are formed. At 400°C, a new class of compound, carbodiimides, is being produced while the amount of the  $\alpha,\beta$ -unsaturated cyano compounds is greatly reduced. Similar to polyacrylonitrile, ladder-type structures for degraded PVI(1) and PVI(4) are proposed probable.

## INTRODUCTION

The catalytic properties of synthetic polymers containing pendant imidazole groups have been explored by a number of workers.<sup>1-9</sup> The catalytic effects of some of these polymers in esterolytic reactions have exhibited several similarities with those of enzymic reactions.<sup>1-3</sup> Several of these polymers also show unusual specificity to the substrate in their catalytic action and so have been considered as possible models for enzymes<sup>4-6</sup> since the imidazole groups also bind metals very strongly<sup>7-9</sup> and, in that sense, are analogous to the metal-containing enzymes in which the imidazole groups are found in the histidyl residue.

Recently, two of these imidazole-containing polymers, poly-*N*-vinylimidazole [PVI(1)] and poly-4(5)-vinylimidazole [PVI(4)], have been demonstrated in our laboratory<sup>10</sup> for the first time to be effective new polymeric anticorrosion agents for copper at elevated temperatures. Oxidation of copper is suppressed even at 400°C. PVI(1) and PVI(4) are proven to be more effective antioxidants than the most commonly used corrosion inhibitors, benzotriazole and undecylimidazole, at high temperatures. These polymeric agents are water soluble and can be used to treat the metal surface easily.

In the past, many experimental techniques<sup>11-15</sup> have been used to study the corrosion-inhibition mechanisms of different anticorrosion agents for copper; however, the mechanisms are still not well understood. In this two-part series, we shall investigate the thermal degradation of PVI(1) and PVI(4) films on potassium bromide (KBr) plate and copper mirrors. Through these studies, we are seeking to better understand the inhibition mechanisms of these polymers on copper.

In this paper, we shall study the thermal degradation mechanisms of both PVI(1) and PVI(4) films on KBr plates at elevated temperatures in air by Fourier transform infrared (FTIR) spectroscopy.

## EXPERIMENTAL

Thermal degradations were performed on KBr plates (20 × 2.5 mm) purchased from Optovac, Inc. PVI(1) and PVI(4) were first dissolved in anhydrous ethanol to yield a concentration of 0.68 g/L. Then using a 50  $\mu$ L microsyringe, the polymers were solution cast on the KBr plates and air dried to form the polymeric films. Afterward, the films were further dried in a vacuum oven (30 mm Hg) at 30°C overnight. Film thickness was calculated based on the concentration of the solution, the quantity used, the area of the KBr plate, and the density of the sample. The thickness of the PVI(1) and PVI(4) films were 6 and 2  $\mu$ m, respectively. A Digilab FTS-14 Fourier transform infrared spectrometer equipped with a triglycine sulfate detector was used. The instrument was purged with dry air to prevent the interference of atmospheric moisture on the spectra. Spectra collected were the average of 100 scans at 4  $\text{cm}^{-1}$  resolution using an optical velocity of 0.3 cm/s. Spectra were plotted in the absorbance mode, with the most intense peak representing the highest absorption. The absorption difference between the maximum and minimum absorbance is designated as  $\Delta A$ . Overlapped bands were deconvoluted using a Lorentzian curve-resolving computer program (see Ref. 34).

As reported previously,<sup>10,16</sup> PVI(1) and PVI(4) were synthesized by free-radical polymerizations of *N*-vinylimidazole and 4(5)-vinylimidazole, respectively, in benzene using azobis(isobutyronitrile) as initiator.

## RESULTS AND DISCUSSION

### Band Assignments of PVI(1) and PVI(4)

The transmission spectra of PVI(1) and PVI(4) are shown in Fig. 1. Tentative band assignments of the polymers are listed in Table I. Work done on normal coordinate analyses of *n*-paraffins and imidazole by Schachtschneider and Snyder<sup>17</sup> and Cordes and Walter,<sup>18</sup> respectively, along with band assignments from Bellamy,<sup>19</sup> Colthup et al.,<sup>20</sup> Bassignana et al.,<sup>21</sup> and Carlson and Brown,<sup>22</sup> were used as references.

The polymerizations of *N*-vinylimidazole and 4(5)-vinylimidazole by free-radical initiation proceed normally in benzene solution, affording PVI(1) and PVI(4) with one-third and one-half mole of bound water per mole of monomer, respectively.<sup>1,23</sup> The water is tightly bound and cannot be removed by heating at 40°C in a vacuum oven (30 mm Hg) for 3 days. The O—H stretching from the residual water is observed at 3400 and 3380  $\text{cm}^{-1}$ . The pendant imidazole groups were complicated by resonance and, in the case of PVI(4), hydrogen bonding, which make spectral interpretation more complicated. Nevertheless, band assignments for both polymers are very similar. The C—H stretching mode of the imidazole ring is observed in the 3300–2980  $\text{cm}^{-1}$  region, with N—H stretching of PVI(4) at 3120  $\text{cm}^{-1}$ . The  $\text{CH}_2$

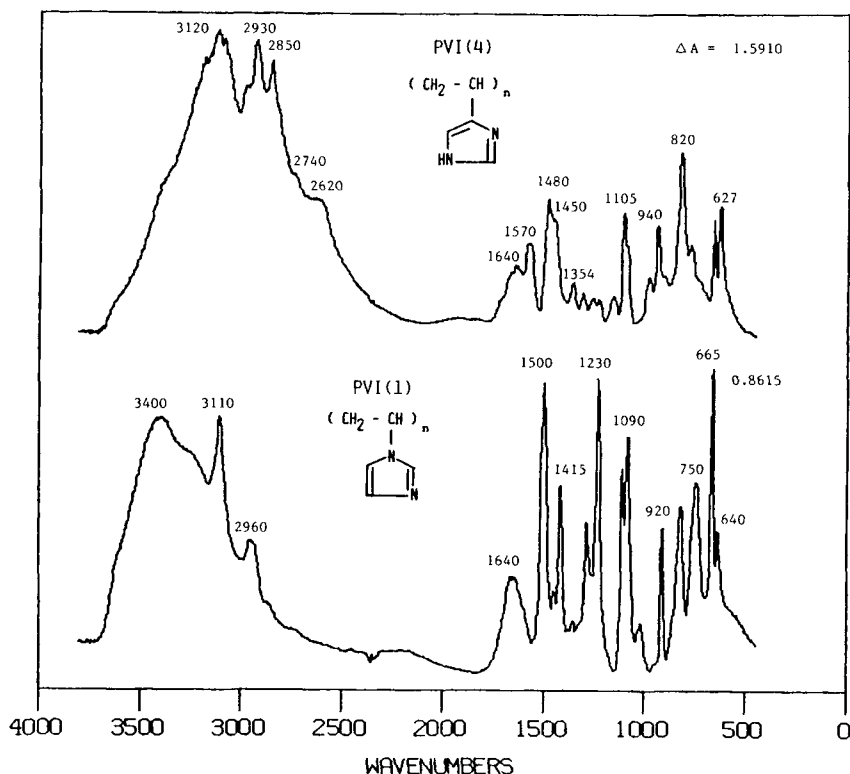


Fig. 1. Transmission spectra of PVI(1) and PVI(4).

stretching of the polymer backbone occurs in the 2960–2850  $\text{cm}^{-1}$  region. For PVI(1), the broad feature in the 3700–2800  $\text{cm}^{-1}$  region is due to associated hydrogen bonding with the residual bound water. A similar phenomenon is observed for PVI(4), except the region is extended from 3700 to 2400  $\text{cm}^{-1}$  and the hydrogen bondings are contributed by both the bound water and the N—H of the imidazole groups. The ring stretching-breathing and  $\text{CH}_2$  deformation modes are overlapped in the 1640–1150  $\text{cm}^{-1}$  region. The CH in-plane bending mode, which occurs near 1110  $\text{cm}^{-1}$ , is useful for measuring the extent of imidazole ring cleavage.

### DEGRADATION OF PVI(1)

Figures 2 and 3 show the changes occurring in the transmission spectra from 3600 to 500  $\text{cm}^{-1}$  of PVI(1) film as a function of temperature and time. Spectrum A represents the original spectrum of PVI(1) before heat treatment; spectra B through G give the changes occurring when heated at 250, 330, or 400°C for various lengths of time. It was found that the degradation below 300°C was too slow for practical observation. Conversely, degradation near 400°C was too rapid. The spectral changes that occurred at 330°C are best visualized by comparison with the nonoxidized film spectrum, as illustrated in the following sections.

TABLE I.  
 Tentative Infrared Band Assignments of PVI(1) and PVI(2)

PVI(1) bands ( $\text{cm}^{-1}$ )	PVI(4) bands ( $\text{cm}^{-1}$ )	Tentative assignments
3400 S	3380 M	O—H from residual water
	3120 M	N—H stretching
3110 M	2980 W	C=C—H/N=C—H stretching
2960 M	2930 M	CH <sub>2</sub> asymmetric stretching
	2850 M	CH <sub>2</sub> symmetric stretching
	2740 W	Combination (1261 + 1480)
	2620 W	Combination (1359 + 1261)
1640 S	1640 M	O—H deformation (water)/C=N stretching
1500 S	1570 M	C=N/C=C stretching
1450 W	1480 M	CH <sub>2</sub> bending (mostly) + ring stretching
1415 W	1450 M	CH <sub>2</sub> bending (mostly) + ring stretching
1350 VW	1354 W	CH and CH <sub>2</sub> wagging
1330 VW	1306 W	CH and CH <sub>2</sub> wagging
1275 M	1261 W	Ring vibrations
1230 S	1230 W	Ring vibrations
1110 S	1105 M	CH in-plane bending
1090 S	1090 M	CH in-plane bending
920 M	980 W	CH out-of-plane bending
	940 M	N—H bending
825 S	820 M	CH out-of-plane bending
750 S	770 W	CH <sub>2</sub> rocking
665 S	660 M	Ring torsion
	627 M	N—H out-of-plane bending
640 W		C=C—H/N=C—H wagging

S;strong, M;medium, W;weak and VW;very weak.

As shown in spectrum B, no degradation was observed after the sample was heated at 250°C for 15 min. However, after 15 min at 330°C, PVI(1) began to degrade as a result of competitive oxidative reactions (spectrum C). Cleavage of imidazole rings led to the formation of nitrile groups as indicated by a band near 2222  $\text{cm}^{-1}$ . This band has been assigned to  $\alpha,\beta$ -unsaturated nitrile.<sup>19</sup> The other interesting region lies in the 1800–1500  $\text{cm}^{-1}$  region. The bands in this region were more pronounced as the polymer was heated at a longer time to 45 min at 330°C (spectrum D). The result of deconvolution of this region is shown in Fig. 4. Curves A, B, and C represent the original spectrum, the spectrum constructed with the deconvoluted bands, and the difference between the two, respectively. Six bands are resolved in this region. The bands at 1497, 1451, and 1409  $\text{cm}^{-1}$  are the original bands of PVI(1). However, the formation of the bands at 1722, 1678, and 1596  $\text{cm}^{-1}$  is due to the oxidative degradation of PVI(1).

The band at 1722  $\text{cm}^{-1}$  has been reported and assigned by Conley and Bieron<sup>24</sup> to a ketonic carbonyl stretching frequency typical of a saturated aliphatic ketone.<sup>25</sup> The postulated ketonic structure of PVI(1) is shown in Fig. 5A. It can be formed from oxidative attack on the backbone of the polymer.<sup>26</sup>

Dehydrogenation reactions are also not uncommon in polymers. As a result, unconjugated C=C bonds, which absorb in the 1680–1620  $\text{cm}^{-1}$  range,<sup>19,25</sup> can be formed readily. Such reactions are shown in Fig. 5B. The

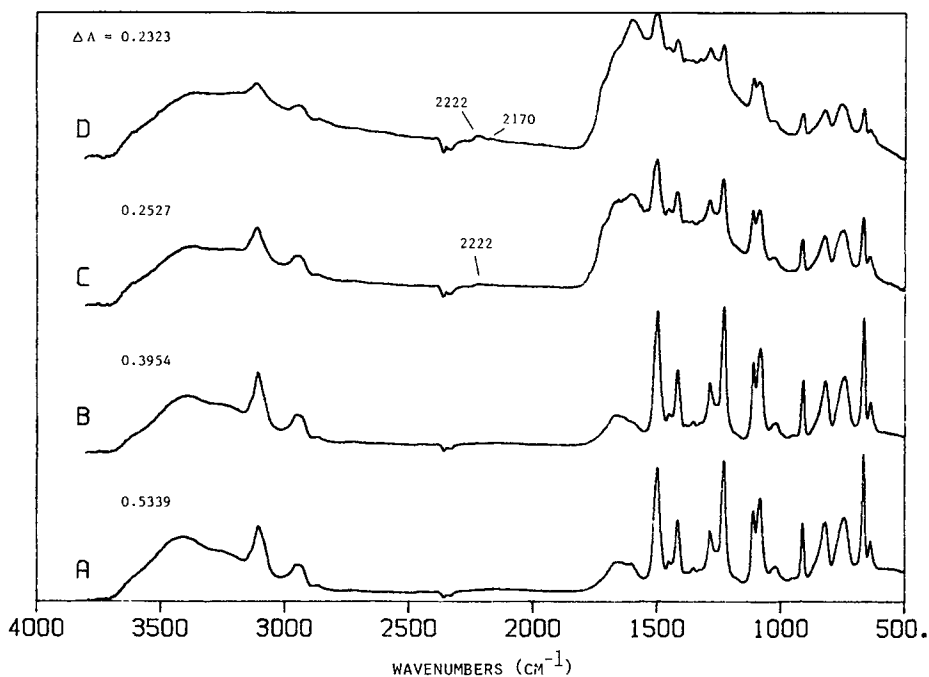


Fig. 2. Spectra of PVI(1) film with high-temperature treatments: (A) no heat treatment; (B) 250°C for 15 min; (C) 330°C for 15 min; (D) 330°C for 45 min.

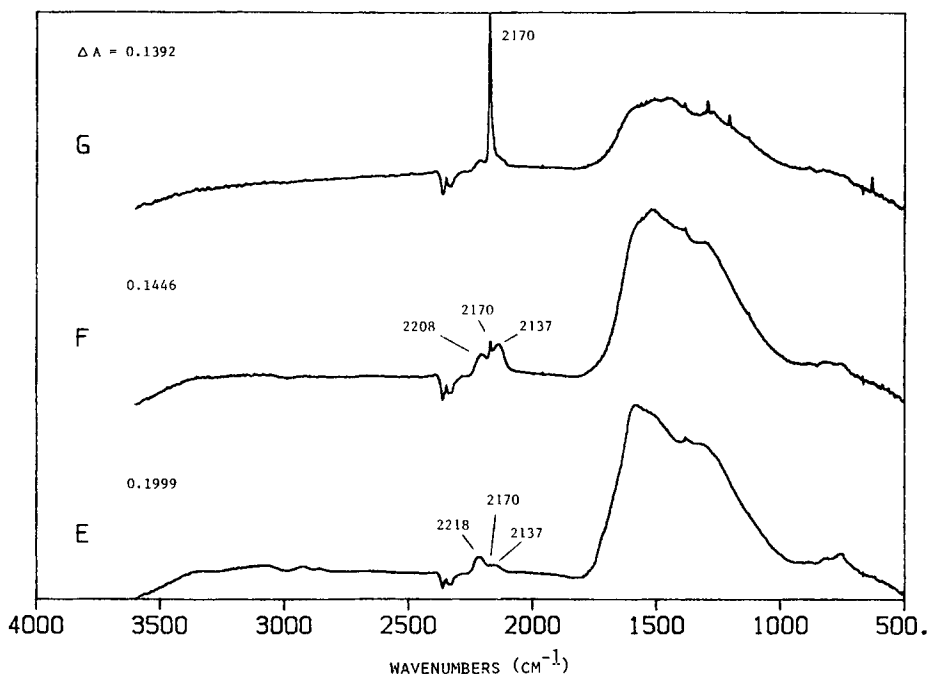


Fig. 3. Spectra of PVI(1) film with high-temperature treatments: (E) 400°C for 15 min; (F) 400°C for 45 min; (G) 400°C for 90 min.

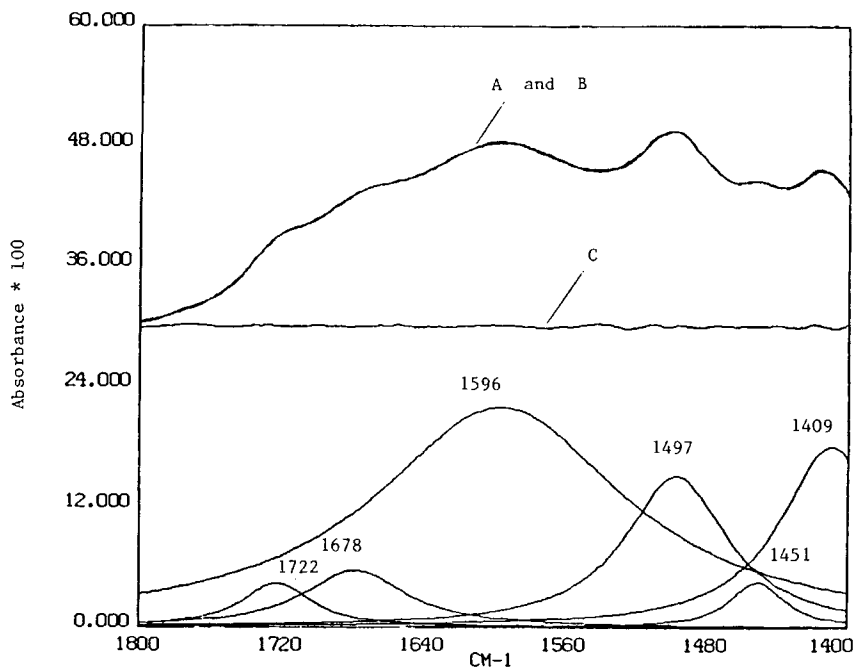
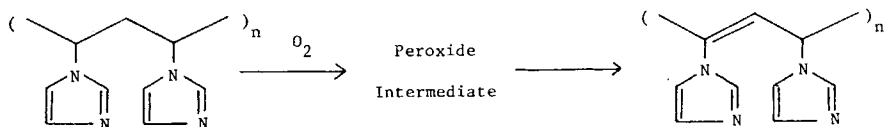


Fig. 4. Deconvolution result of the 1800–1400  $\text{cm}^{-1}$  region of PVI(1): (A) original spectrum; (B) constructed spectrum after deconvolution; (C) difference spectrum (A - B).

1678  $\text{cm}^{-1}$  band in Fig. 4 has been assigned to such an olefinic stretching frequency.<sup>26</sup>

Assignment for 1596  $\text{cm}^{-1}$  is not as trivial. It has been shown that it is due to conjugated C=N sequences in nitrogen-containing ring structures.<sup>27</sup> Yet, as assigned by Conley and Bieron<sup>24</sup> and Bellamy,<sup>19</sup> the absorption band at 1596  $\text{cm}^{-1}$  is due to conjugated C=C stretching vibration. The intensity of the band is enhanced when the double bond introduced into the polymer skeleton is conjugated with another unsaturated group. The shift of this frequency to 1600  $\text{cm}^{-1}$  from higher unconjugated C=C band frequencies is consistent with a neighboring electron-withdrawing group, such as the

B.



A.

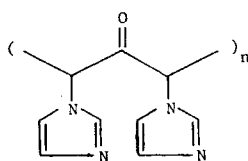


Fig. 5. Postulated structures of degraded PVI(1): (A) aliphatic ketone; (B) olefin.

nitrile group, in conjugation with the C=C bond. Then, Coleman and Petravich,<sup>28</sup> in studying the thermal degradation of polyacrylonitrile, have suggested that the actual band position is probably a combination of the 1610 and 1575  $\text{cm}^{-1}$  bands of the structure shown in Fig. 6. They have assigned the 1610  $\text{cm}^{-1}$  band to a mixed mode; mostly a C=O stretching vibration in conjugation with a C=C stretching vibration and the 1575  $\text{cm}^{-1}$  band, also a mixed mode, to mostly a C=C stretching and NH bending vibration. Their assignments were based on the study of the model compound  $\delta(8,9)$ -octahydro-7-quinoline.<sup>29</sup>

As PVI(1) was heated to 400°C (Fig. 3, spectra E, F, and G), the original polymer structure disappeared completely because of evaporation and degradation. No C—H stretching mode was observed after the film was heated for 15 min (spectrum E). It is interesting to note the emergence of the bands at 2170 and 2137  $\text{cm}^{-1}$ , which became more pronounced as PVI(1) was heated for 45 and 90 min at 400°C. The band at 2170  $\text{cm}^{-1}$  is assigned to potassium cyanide (KCN). In general, inorganic cyanides absorb in the 2180–2080  $\text{cm}^{-1}$  region.<sup>19</sup> KCN was formed as a result of the interaction between the KBr substrate and the degraded cyano compounds of PVI(1). The band at 2137  $\text{cm}^{-1}$  is assigned to carbodiimide stretching vibration. Compounds of this class have the structure R—N=C=N—R. Khorana<sup>35,36</sup> has studied a small number of examples and noted absorption at 2150  $\text{cm}^{-1}$ . Then Meakins and Moss<sup>37</sup> have made more detailed study of the frequency and intensity of nine carbodiimides. The result showed that absorption took place in the range 2152–2128  $\text{cm}^{-1}$ . Mogul<sup>38</sup> has reviewed the infrared and Raman spectra of carbodiimides and confirmed the results of Meakins and Moss. The formation of carbodiimides from PVI(1) is likely due to the cleavage of the bond between the number one nitrogen and the number five carbon atoms of the imidazole ring.

Figure 7 summarizes the band formations in the 2300–2100  $\text{cm}^{-1}$  region. Initially, imidazole ring cleavage has led to the formation of  $\alpha,\beta$ -unsaturated nitrile (2220  $\text{cm}^{-1}$ ) when PVI(1) film is heated at 330°C for 15 min (spectrum A). Then, at 330°C for 45 min (spectrum B), the byproduct KCN (2170  $\text{cm}^{-1}$ ) begins to form as a result of the interaction between the KBr substrate and the degraded cyano compounds. When the temperature is raised to 400°C (spectra C, D, and E), carbodiimides (2137  $\text{cm}^{-1}$ ) are also formed as a result of the ring cleavage. Then, after the prolonged heating at 400°C for 90 min (spectrum E), the amount of both the  $\alpha,\beta$ -unsaturated nitrile and carbodiimide products are greatly reduced, probably because of evaporation.

In summary, no degradation of PVI(1) film was observed below 250°C. Oxidation and dehydrogenation of PVI(1) occurred at 330°C and led to the formations of saturated aliphatic ketones and unconjugated C=C bonds at the polymer backbone, respectively. The combination of the two types of

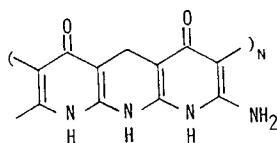


Fig. 6. Degraded PAN structure as postulated by Coleman et al.<sup>28</sup>

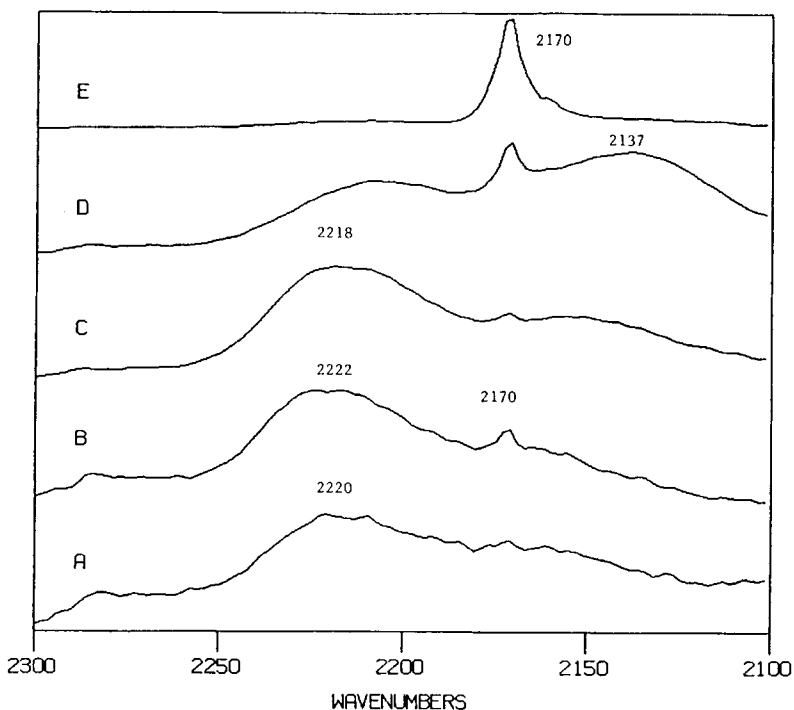


Fig. 7. Spectra of PVI(1) film with high-temperature treatments in the  $2300\text{--}2100\text{ cm}^{-1}$  region: (A)  $330^\circ\text{C}$  for 15 min; (B)  $330^\circ\text{C}$  for 45 min; (C)  $400^\circ\text{C}$  for 15 min; (D)  $400^\circ\text{C}$  for 45 min; (E)  $400^\circ\text{C}$  for 90 min.

reactions yielded  $\alpha,\beta$ -unsaturated keto compounds. Cleavage of imidazole rings occurred at both  $330$  and  $400^\circ\text{C}$  and formed  $\alpha,\beta$ -unsaturated cyano structures and carbodiimides, respectively. Then, complete evaporation and degradation occurred after 15 min of heating at  $400^\circ\text{C}$ , where no original PVI(1) structure was observed.

#### DEGRADATION OF PVI(4)

Figures 8 and 9 show the changes occurring in the transmission spectra from  $3800$  to  $500\text{ cm}^{-1}$  of PVI(4) film as a function of temperature and time. Unlike PVI(1), PVI(4) degraded after heating at  $250^\circ\text{C}$  for 15 min (spectrum B). Multiple bands were formed in the  $1800\text{--}1600\text{ cm}^{-1}$  region. However, no nitrile formation was observed. The newly formed bands became more pronounced as the film was heated at  $330^\circ\text{C}$  for 15 min (spectrum C). Figure 10 shows the relative enhancement of the intensity of these bands when compared with the existing PVI(4) bands at  $1570$ ,  $1480$ , and  $1450\text{ cm}^{-1}$ . Using spectrum C ( $330^\circ\text{C}$  for 15 min), the result of deconvolution of the  $1800\text{--}1465\text{ cm}^{-1}$  region is shown in Fig. 11. The bands at  $1564$  and  $1478\text{ cm}^{-1}$  are the original bands of PVI(4), whereas the bands at  $1721$ ,  $1677$ , and  $1613\text{ cm}^{-1}$  are due to the oxidative degradation of PVI(4). At  $300^\circ\text{C}$  for 15 min, ring cleavage is also observed, as noted by the emergence of the nitrile band at  $2224\text{ cm}^{-1}$ . The assignments of these bands are the same as those in PVI(1). Table II summarizes the major infrared bands occurring in the



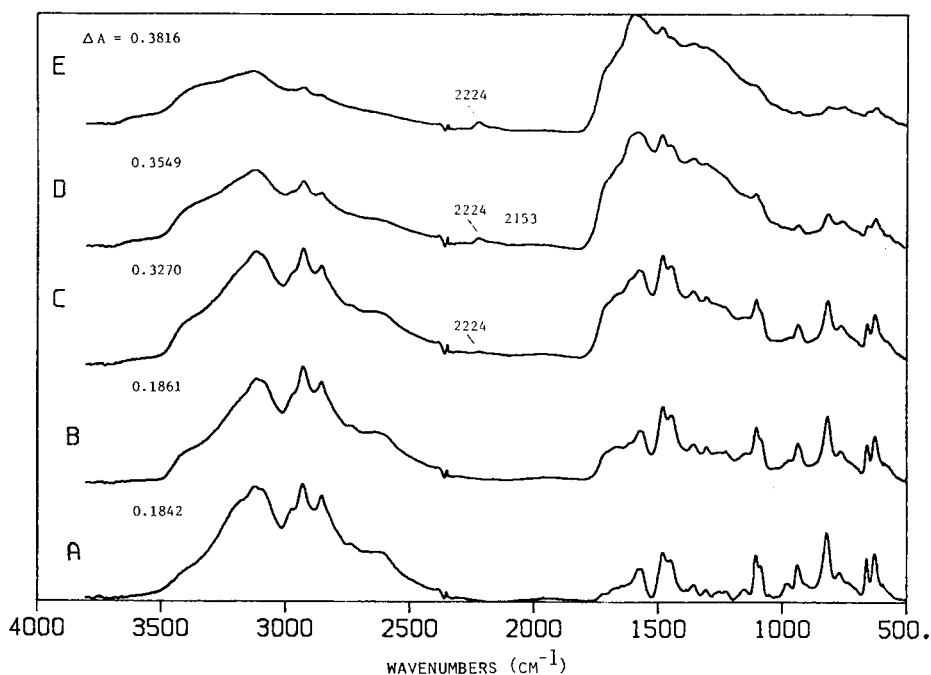


Fig. 8. Spectra of PVI(4) film with high-temperature treatments: (A) no heat treatment; (B) 250°C for 15 min; (C) 330°C for 15 min; (D) 330°C for 35 min; (E) 330°C for 60 min.

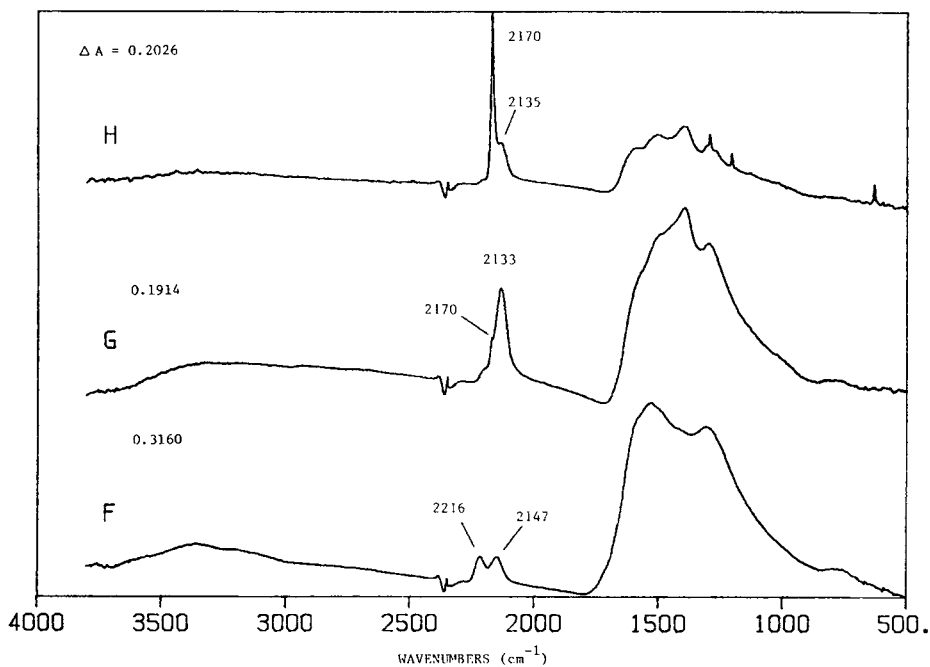


Fig. 9. Spectra of PVI(4) film with high-temperature treatments: (F) 400°C for 45 min; (G) 400°C for 90 min; (H) 400°C for 2 h and 15 min.

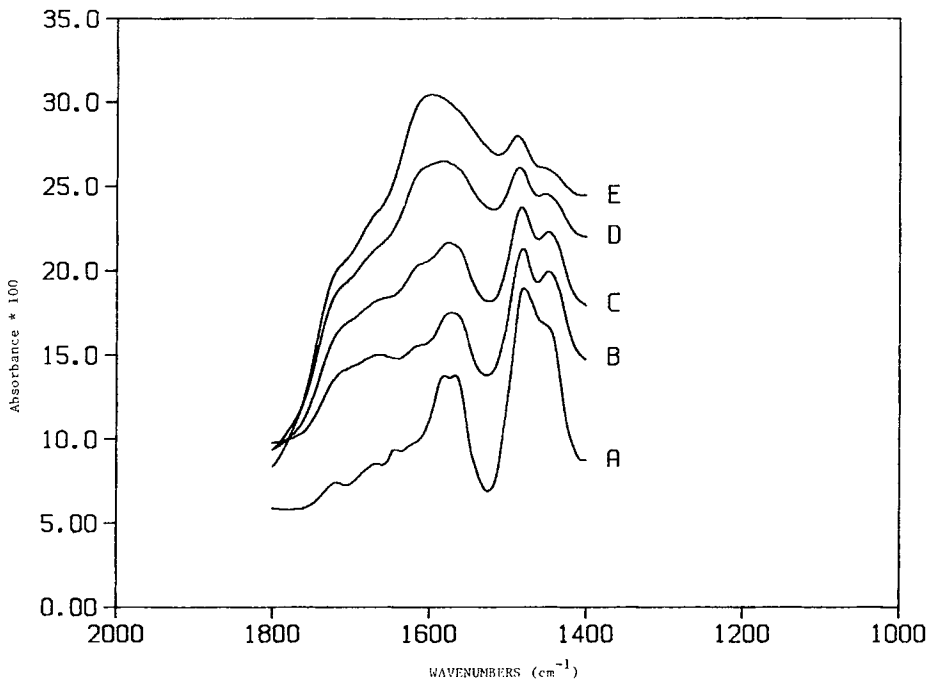


Fig. 10. Spectra of PVI(4) film with high-temperature treatments in the  $1800\text{--}1400\text{ cm}^{-1}$  region: (A) no heat treatment; (B)  $250^\circ\text{C}$  for 15 min; (C)  $330^\circ\text{C}$  for 15 min; (D)  $330^\circ\text{C}$  for 35 min; (E)  $330^\circ\text{C}$  for 60 min.

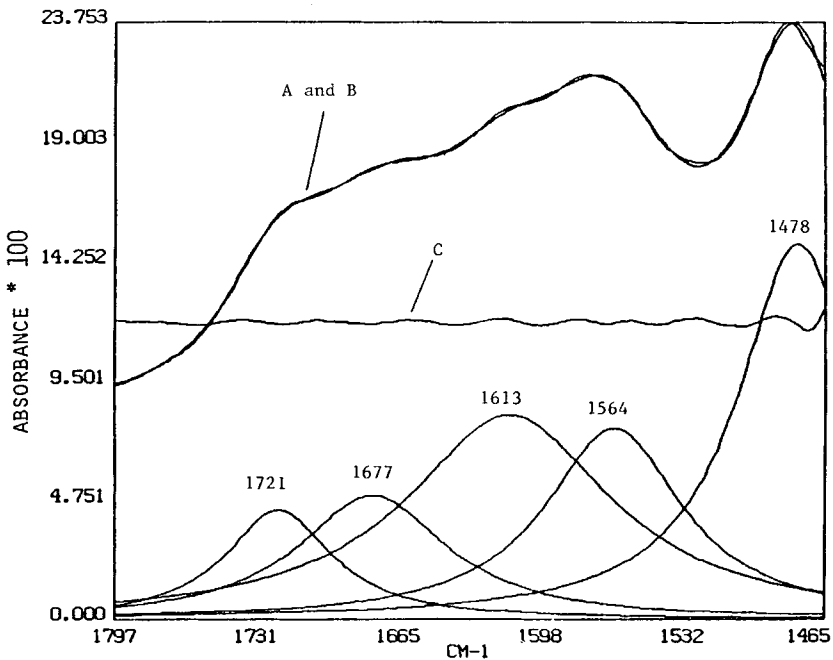


Fig. 11. Deconvolution result of the  $1800\text{--}1465\text{ cm}^{-1}$  region of PVI(4): (A) original spectrum; (B) constructed spectrum after deconvolution; (C) difference spectrum (A-B).

TABLE II.  
Major Infrared Bands of Air-Degraded PVI(1) and PVI(4)

PVI(1) bands ( $\text{cm}^{-1}$ )	PVI(4) bands ( $\text{cm}^{-1}$ )	Tentative assignment
2216	2224	CN ( $\alpha,\beta$ -unsaturated)
2137	2133	—N=C=N—
1722	1721	C=O (ketonic stretching)
1678	1677	C=C (unconjugated)
1596	1613	C=N (conjugated); C=O + C=C (mixed mode); C=C + N—H (mixed mode); C=C (conjugated)

air-degraded PVI(1) and PVI(4) spectra and shows tentative assignments of these bands.

As PVI(4) film was heated to 400°C (Fig. 9, spectra F, G, and H), total evaporation and degradation of PVI(4) occurred. After 15 min of heating, similar to PVI(1), carbodiimides were formed as noted by the appearance of the band at 2147  $\text{cm}^{-1}$  (spectrum F). The intensity of this band was greatly enhanced as the film was heat treated at a longer time to 90 min (spectrum G). At the same time, KCN began to form, as indicated by the band at 2170  $\text{cm}^{-1}$ . Then, after 2 h and 15 min of heat treatment, KCN continued to form and appeared to be the major product.

Figure 12 summarizes the band formation of PVI(4) film in the 2300–2100  $\text{cm}^{-1}$  region. Initially, ring cleavage occurs and leads to the formation of  $\alpha,\beta$ -unsaturated nitrile (2224  $\text{cm}^{-1}$ ) when the film is heated at 330°C for 35 or 60 min (spectra A and B). Then, at 400°C for 45 min (spectrum C), carbodiimide (2133  $\text{cm}^{-1}$ ) is also observed. At the same time, the by-product KCN begins to form. At 400°C for 90 min (spectrum D), the  $\alpha,\beta$ -unsaturated nitrile compounds were completely evaporated or degraded. Carbodiimide is left as the major compound with KCN continues to form. Lastly, after the prolonged heating for 2 h and 15 min, KCN remains as the major band with the carbodiimide band greatly reduced.

In summary, degradation of PVI(4) film took place after 15 min at 250°C. Similar to PVI(1), oxidation and dehydrogenation occurred and led to the formation of saturated aliphatic ketones, unconjugated C=C bonds at the polymer backbone, and  $\alpha,\beta$ -unsaturated keto compounds. Ring cleavage occurred at both 330 and 400°C and yielded  $\alpha,\beta$ -unsaturated cyano structures and carbodiimides, respectively. Prolonged heat treatment at 400°C led to the formation of KCN as the major component.

## CONCLUSION

The thermal degradation of polyvinylimidazoles on KBr plate has been studied using FTIR spectroscopy. The complete picture of the thermal degradation process in PVI(1) and PVI(4) is very complicated. With the inclusion of oxygen into the polymer systems along with olefinic species, the routes by which the systems degrade become extremely complex. Upon further

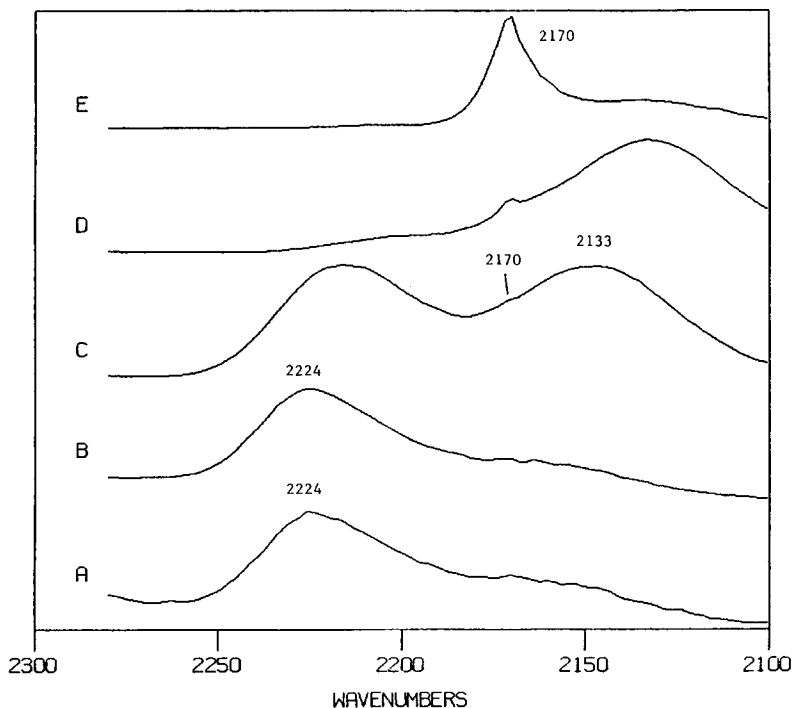


Fig. 12. Spectra of PVI(4) film with high-temperature treatments in the 2300–2100  $\text{cm}^{-1}$  region: (A) 330°C for 35 min; (B) 330°C for 60 min; (C) 400°C for 45 min; (D) 400°C for 90 min; (E) 400°C for 2 h and 15 min.

degradation, the broadly defined spectra obtained shed no light on these processes. In general, the thermal degradation reactions of PVI(1) and PVI(4) are very similar except that degradation of PVI(4) takes place before PVI(1) at 250°C. When the temperature is raised 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  $\alpha,\beta$ -unsaturated keto compounds. Then at prolonged heat treatment at 330°C, cleavage of imidazole rings also occurs and  $\alpha,\beta$ -unsaturated cyano structure are formed. At 400°C, a new class of compound, carbodiimides, is being produced while the amount of the  $\alpha,\beta$ -unsaturated cyano compounds is greatly reduced. Upon further heat treatment at 400°C, carbodiimides are mostly evaporated and degraded, leaving KCN as the major component.

In the past, thermal degradation of polyacrylonitrile (PAN) has been studied extensively by a number of research groups<sup>24,26–28,31–33</sup> in attempting to adequately explain the formation of color and the degradation reactions occurring in PAN. Most of the proposed reactions that occur during the thermal treatment of PAN lead to ladder-type structures (Fig. 13). Based on the major band positions, intensities, shapes, and assignments, comparisons between both air-degraded PAN<sup>24,28</sup> and PVI(1) or PVI(4) infrared spectra show remarkable similarities (Table III). Thus, similar to PAN, lad-

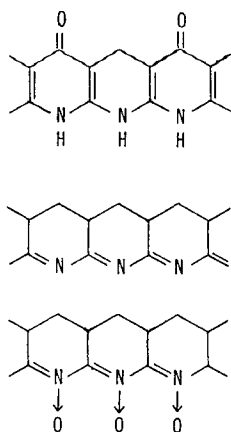


Fig. 13. Postulated ladder-type structures of degraded PAN.

TABLE III.  
Comparisons of Degraded PAN, PVI(1), and PVI(2) Infrared Bands

PVI(1) bands ( $\text{cm}^{-1}$ )	PVI(4) bands ( $\text{cm}^{-1}$ )	PAN bands ( $\text{cm}^{-1}$ )	Tentative assignment
2216M	2224M	2210M	CN ( $\alpha,\beta$ -unsaturated)
1722M	1721M	1715M	C=O (ketonic stretching)
1678M	1677M	1655M	C=C (unconjugated)
1596S	1613S	1592S	C=N (conjugated); C=O + C=C (mixed mode); C=C + N—H (mixed mode)

S;strong and M;medium

der-type structures for degraded PVI(1) and PVI(4) are also very probable. These ladder-type structures might have explained the high thermal stability of degraded PVI(1) and PVI(4) films on copper mirrors<sup>10</sup>; however, the mechanisms leading to these structures are not at present understood. The thermal degradation mechanisms of PVI(1) and PVI(4) on copper mirrors are discussed in Part II.

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