FT-RAMAN SPECTROSCOPIC STUDY OF THE FORMATION OF POLYENES DURING THERMAL DEGRADATION OF POLY(VINYL CHLORIDE) AND POLY (N-VINYL-2-PYRROLIDONE) BLENDS

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ABSTRACT

In situ degradation of poly(vinyl chloride)/poly (N-vinyl-2- pyrrolidone)
(PVC/PVP) blends has been studied by Fourier-transform Raman spec-
troscopy. PVP acts as a destabilizer in the thermal degradation of PVC as
manifested by the reduction of temperature for the onset of degradation and
the time the polymer is held at a particular temperature for this onset.
Increasing the amount of PVP in the blends decreases the dehydrochlorination
temperature and time. In blends containing high PVP concentrations, polyene
bands dominate over nondegraded PVC bands. Maximum polyene lengths of
around 35 were achieved. High PVP ratios and prolonged degradation at
higher temperatures resulted in a decrease in mean polyene length due to
crosslinking and oxidative scission.

Key Words: Polymer degradation; PVC blends; Raman spectroscopy

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INTRODUCTION

Homogeneous blends of poly (vinyl chloride) (PVC) and certain heteroatomic polymers, display degradation behavior, which is different from that of the individual homo-polymers, resulting in either an acceleration of the degradation rate or a stabilizing effect [1]. For example, the PVC/poly (N-vinyl-2-pyrrolidone) (PVP) blend degrades at temperatures below that at which PVC alone begins to degrade. It was proposed that the C=O groups accelerated the dehydrochlorination.

In PVC and its blends, degradation commences by the elimination of a HCl molecule, followed by the rapid loss of adjacent HCl molecules according to an unzipping reaction, catalyzed by the HCl formed, leading to formation of all-*trans* conjugated polyene sequences along the polymer chains [2, 3]. This results in the discoloration of the PVC and PVC/PVP blends even at very low concentrations of polyenes. It has been reported that [4] in contrast to the instability of their *cis*-isomers, the *trans*-polyene sequences are energetically favored at moderately higher temperatures. In previous studies, polyene lengths of around 20 have been obtained in neat PVC [5, 6].

Raman spectroscopy is particularly suited to the study of degradation of PVC blends as it is an extremely sensitive technique for detecting polyenes during the dehydrochlorination of PVC due to their hyperpolarizabilities [7]. FT-Raman spectroscopy is particularly favored over conventional Raman spectroscopy due to the elimination of laser induced sample fluorescence. This is due to the wavelength of the laser used (λ = 1064 nm) being far away from the frequency region where excitation of fluorescence emission occurs. The detection level of dehydrochlorination by this method is significantly lower than that obtained by FT-IR absorption or emission spectroscopy. Therefore, the temperature and time for the onset of dehydrochlorination can be more accurately determined. Raman spectroscopy has been successfully used in studies of oxidation of polyolefins and used to monitor changes in functional groups with time [8].

It has been suggested that the C-Cl$\cdots$O=C interaction is responsible for the miscibility of PVC/PVP blends [1]. The effect of this interaction was associated with the logarithmic increase of the C=O shift at about 1690 cm^{-1} with increasing PVC content. There was a blue shift of the C=O stretching mode as the PVP content decreased. The shift was most pronounced between 10 to 40% PVP blends. A total shift of 13 cm^{-1} was obtained corresponding to a change in composition from 40 to 100% PVP [1].

In this paper, *in situ* degradation of PVC/PVP blends by FT Raman spectroscopy as a function of blend composition and time while the polymer was held, exposed to air at elevated temperatures is presented.

EXPERIMENTAL

PVC (Sigma-Aldrich) with a molecular weight of 30 000 g/mol and PVP (Sigma-Aldrich) with a molecular weight of 24 000 g/mol were used. PVC/PVP

blends were obtained by dissolving measured amounts of PVC and PVP powders in cyclohexanone and casting on glass slides.

In situ thermal degradation of PVC/PVP blends was studied by a Perkin-Elmer Series 2000 FT-Raman spectrometer. The excitation source was a Nd^{3+}: YAG laser (λ = 1064 nm). 50 scans were employed at a resolution of 8 cm^{-1}. Laser power was fixed at 150 mW. The beam was aligned with BaSO$_4$ to optimize the Raman signal. The PVC/PVP film was compressed into a non-fluorescent quartz NMR tube and placed inside the aluminum heating block in which it was exposed to the laser beam through a quartz window. The temperature of the aluminum block was precisely controlled and stabilized at the test temperature before the sample was inserted in it. Experiments were carried out in an open tube exposed to air. Spectra were collected at 5-minute intervals while the polymer was kept in the heating block at the test temperature. Interval time was fixed at 5 minutes as 50 scans lasted approximately 5 minutes. Experimental band intensities were determined by peak height measurements from a fitted base line. The near infrared laser (NIR) did not contribute to any temperature rise above the controlled temperature of the sample.

In order to look at dehydrochlorination kinetics at times up to 6 minutes, 3 samples with compositions of 10% PVC 90% PVP, 50%PVC 50 % PVP, and 80% PVC 20% PVP were heated in a preheated furnace for times from 10 to about 400 seconds. Raman spectra of these samples were obtained at room temperature by quenching the samples in water at certain time intervals.

RESULTS AND DISCUSSION

The spectra of pure PVC and PVP have been reported [1]. Identical spectra were obtained in this study. The FT-Raman spectrum of degraded PVC/PVP blend showed intense bands around 1500, 1100, 610-690, and 1430 cm^{-1} corresponding to ((−C=C−) n), ((=C−C=) n), C−Cl stretching vibrations and CH$_2$ deformation bands respectively (Figures 1 and 2). The extent of dehydrochlorination and polyene formation of 10% PVC/90% PVP and 90% PVC/10% PVP blends with respect to time at 120°C can be seen in Figures 1 and 2, which show 11 and 13 consecutive spectra presented in stacked form, respectively. Each spectrum was recorded at 5-minute intervals at 50 scans, while keeping the temperature constant at 120°C.

The C−Cl stretching bands near 610-690 cm^{-1} decrease, whereas polyene bands (−C=C−) and (=C−C=) around 1490 and 1095 cm^{-1} increase with temperature and time. The effect of PVP on the degradation of PVC can clearly be seen when the spectra of 90% PVC/10% PVP and 10% PVC/90% PVP blends in Figures 1 and 2 are compared. Increasing the amount of PVP in the blends decreases the dehydrochlorination temperature and time. The polyene bands in the 10% PVC/90% PVP blend dominate the nondegraded PVC bands (Figure 1). On the other hand, even at the later stages of degradation of 90% PVC/10% PVP sample the C−Cl stretching and CH2 deformation bands are much stronger compared
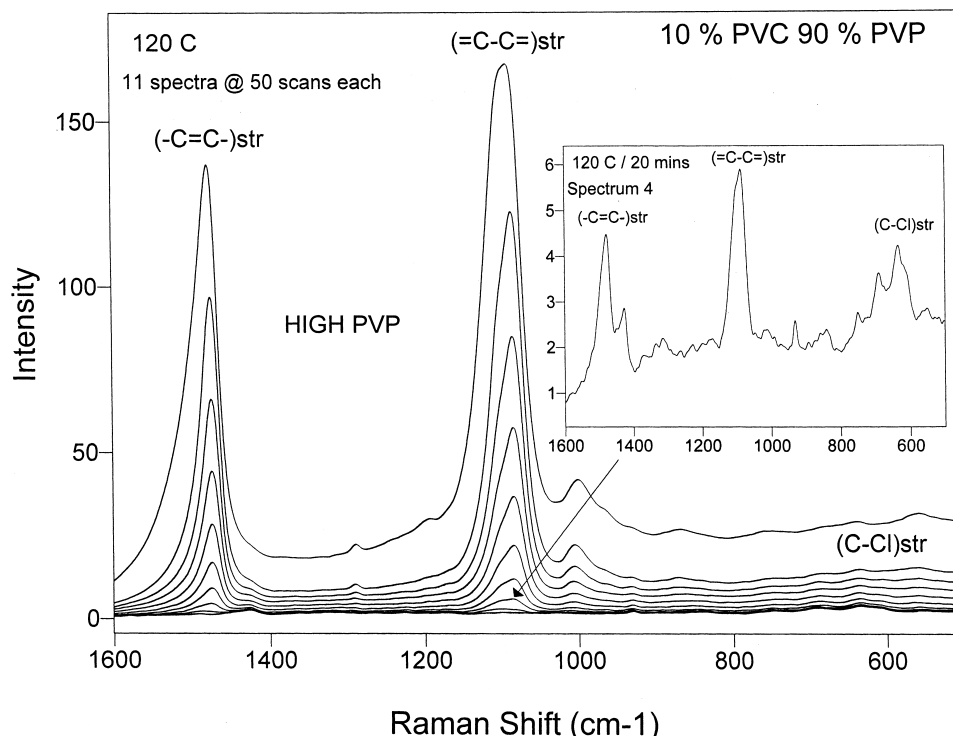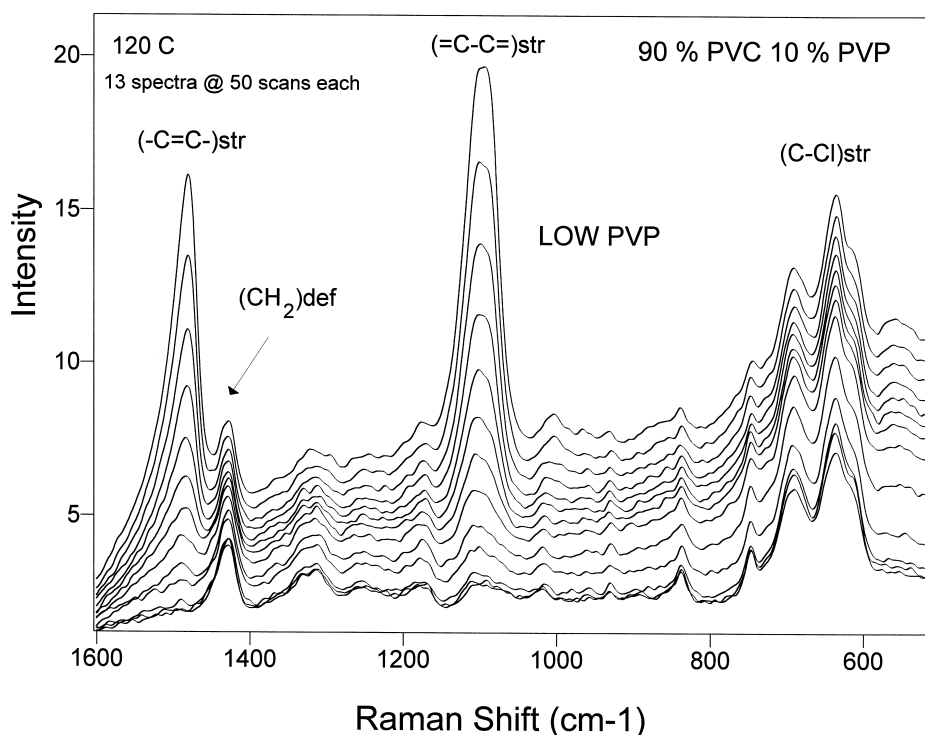
Figure 1. Raman spectra of 10% PVC/90% PVP blend as a function of time at 120°C.

to that of the 10% PVC/90% PVP blend (Figure 2). In Figure 1, the increased intensity of polyene bands suppresses the rest of the spectra, rendering the PVP spectrum invisible at such a compressed scale. The inset in Figure 1 shows the 4th spectrum from the stack, recorded after 20 minutes of degradation at 120°C, revealing the spectral details of both components that are otherwise masked due to the domination of the polyene peaks. Observation of the Spectra of 0, 10, 40, 50, 60, 90, and 100% PVC in PVC/PVP blends taken at room temperature, indicated that the Raman spectra are additive with band intensities proportional to the composition [9]. The increase in Raman intensity of the 930 and 850 cm^{-1} peaks correlates with increasing the PVP content as both peaks correspond to the lactam ring breathing.

The mean length of the polyenes *n* is estimated from the positions of the Raman bands by using the following equation [10, 11].

$$n = \frac{\ln\left(\dfrac{\bar{v} - 1461}{151.2}\right)}{-0.0708} \tag{1}$$

where $\bar{v}$ is the Raman shift of the C=C stretch. It was noted that the frequencies of the polyene bands were identical when excited by using wavelengths in range of

Figure 2.   Raman spectra of 90% PVC/10% PVP blend as a function of time at 120°C.

252.7 nm and 1064 nm [9, 10]. Hence, the empirical correlation between polyene length and Raman shift given in Equation 1 is valid irrespective of the excitation wavelength and applicable for both resonance and non-resonance Raman spectra. This was unexpected due to the resonance Raman effects at short wavelength. At certain excitation wavelength not only polyenes of length n determined by Equation 1, are at resonance, but polyenes with length n^{-1}, n^{-2}, ... and n^{+1}, n^{+2}, ... are at pre-resonance, and, although with smaller Raman intensity, also contribute to the ν band.

The polyene length was plotted as a function of time for a series of temperatures (120°C, 125°C, 130°C, 135°C, and 140°C) at compositions of 10% PVC, 50% PVC, 80 % PVC in Figures 3, 4, and 5, respectively. The general trend is that polyene growth takes place rapidly, reaching a maximum of about 32 to 35, followed by a decline in polyene length. The onset of both the increase and decrease in the polyene length depend on factors such as temperature, time the sample kept at that temperature and the composition of the blend.

In Figure 3a, the data of 130°C, 135°C, and 140°C are close to each other. However, 120°C curve separated from the rest with a slower rate of polyene length change with time. Further experiments were carried out to observe the rate of polyene formation at very early stages of exposure to heat. A further analysis was performed on the 10% PVC/90% PVP blend at 120°C by using the FT Raman
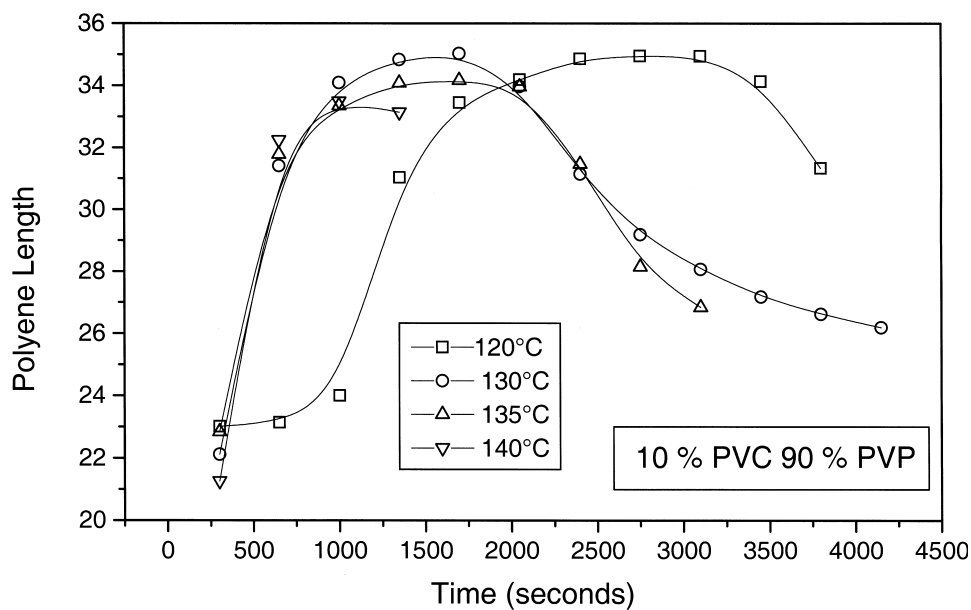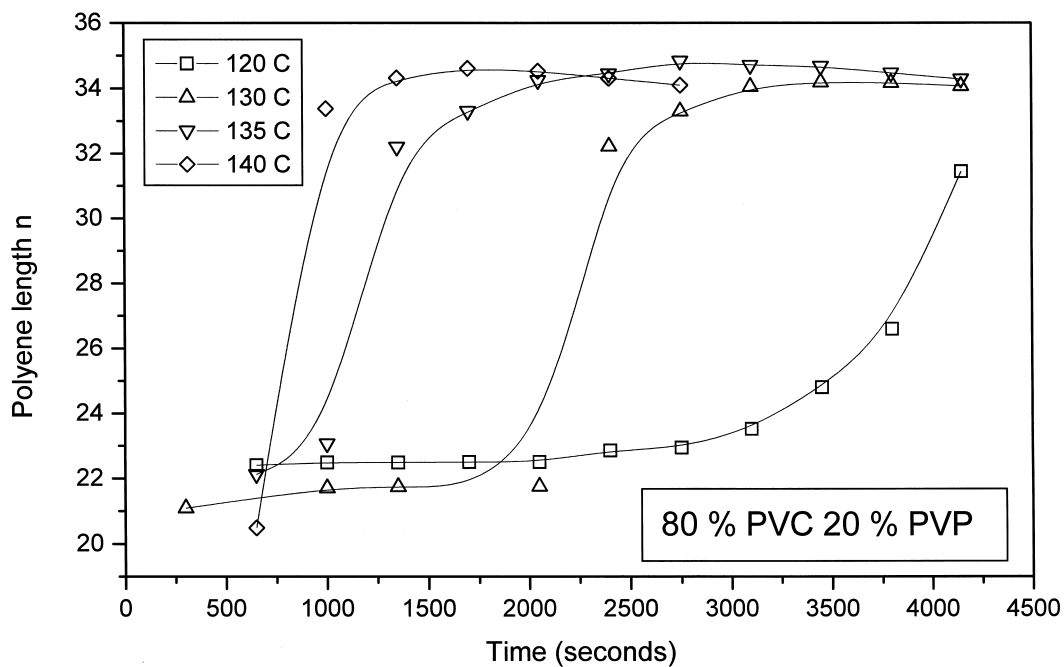
Figure 3a.   Change of polyene length with time for 10% PVC/90% PVP blends at 120°C, 130°C, 135°C, and 140°C.
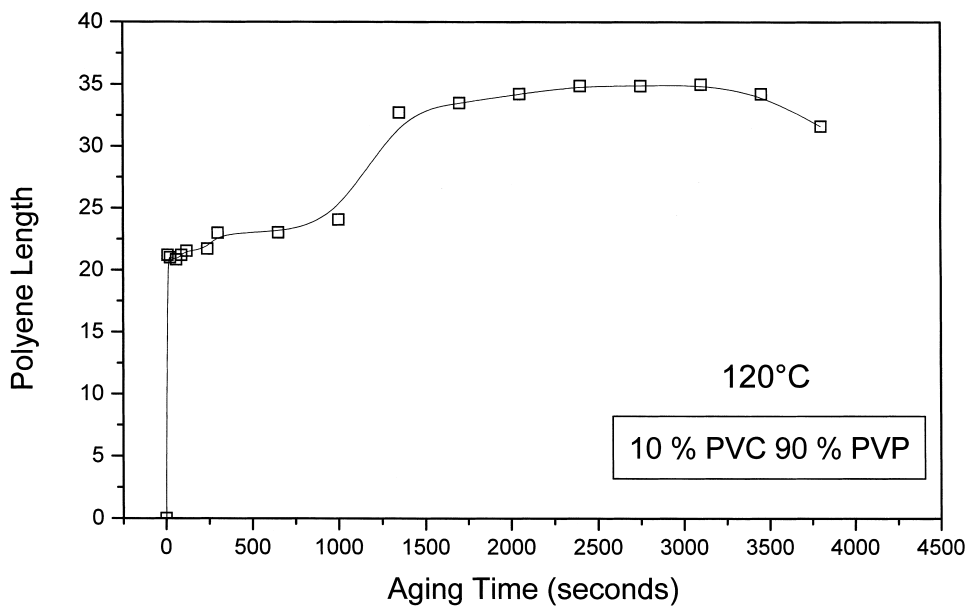
Figure 3b.   Change of polyene length with time for the 10% PVC/90% PVP blend at 120°C from 0 to 3500 seconds, showing the polyene growth in the initial period.
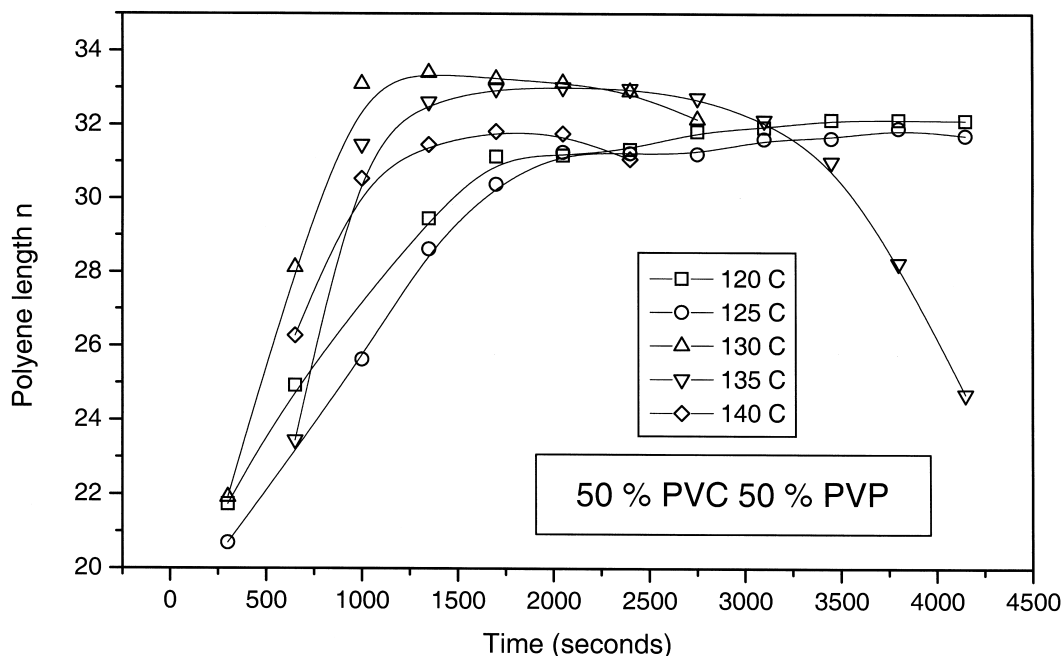
Figure 4. Change of polyene length with time for 50% PVC/50% PVP blends at 120°C, 125°C, 130°C, 135°C, and 140°C.
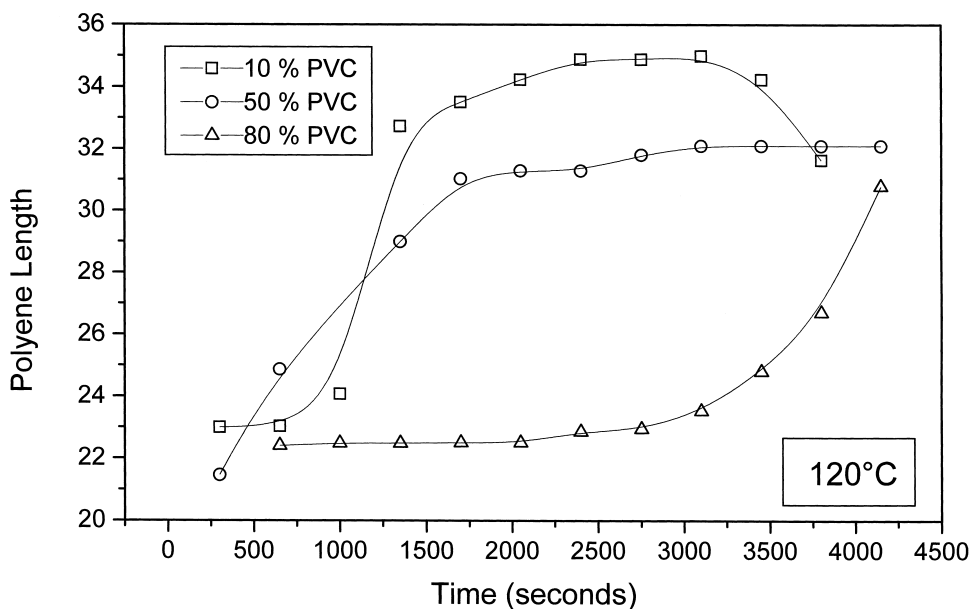
Figure 5. Change of polyene length with time for 80% PVC/20% PVP blends at 120°C, 130°C, 135°C, and 140°C.

spectrometer to see the polyene growth in the initial part of the experiment, from 10 to 400 seconds. The sudden increase in polyene length to about 22 confirms that the unzipping reaction is instantaneous (Figure 3b). Discoloration was observed even after 10 seconds exposure to 120°C supporting the latter observation. Initial instantaneous increase to a polyene length of around 20 is followed by another rapid increase to around 34 at 1250 seconds and the onset of the decrease in polyene length was observed at around 3500 seconds (Figure 3b). The transition temperature and times varied depending on the temperature of the experiment and composition of the blend.

At higher temperatures, the rate of increase of polyene growth is higher and a maximum polyene length between 32 and 35 is reached very rapidly. Generally, once achieved, the maximum polyene length remained approximately constant for a considerable length of time during the degradation of the blends. However, prolonged degradation beyond 2000 seconds of blends containing high PVP percentages, at higher temperatures of 135°C and 140°C resulted in a decrease of mean polyene length (Figures 3 and 4). The reduction in polyene length was observed earlier at higher temperatures in samples with high PVP concentrations. Comparison of Figures 3, 4, and 5 reveals that both the onset of increase and decrease in polyene length start earlier with the increase in PVP ratio in the blend at a given temperature. For example, at 135°C, the decrease of polyene length starts at around 1700 seconds for the 10% PVC/90% PVP blend, 3000 seconds for the 50% PVC/50% PVP blend respectively. For the 80% PVC 20% PVP blend there is not a decrease in the polyene length within the time frame of the experiment. The effect of temperature on the onset of the increase in the polyene length can clearly be seen in the polyene length vs. time curve of the 80% PVC/20% PVP blend (Figure 5) where each curve is well separated in time axis by the temperature of the experiment. There was a long induction period before the onset of final increase in the polyene length at 120°C and 130°C for this composition. At higher temperatures mobility of the chains increase, thus increasing frequencies of crosslinking and chain scission. Moreover, the presence of PVP accelerates degradation, which is manifested by the early onset of the acceleration in polyene growth and subsequent decrease in conjugation. The effect of blend composition can be seen more clearly in Figure 6, which shows polyene growth of 3 different blends at 120°C. The data of 10% and 50% PVC blends formed a group, as they exhibited similar behavior. They both rapidly reached maximum polyene lengths of 33 and 31, respectively. On the other hand, the 80% PVC blend had a much slower rate of increase of polyene length and a long induction period prior to the final acceleration in the polyene growth.

It has been reported that in later stages of degradation, long polyene linkages decompose into smaller ones as shown by mass spectroscopic data and these small polyene linkages may cyclize to form cyclic compounds via intra or intermolecular interactions [2, 12]. During degradation, a combination of processes take place at a molecular level such as crosslinking of polyene sequences [7], readdition of HCl, and oxidative scission in the presence of oxygen resulting in shortening of

Figure 6. Change of polyene length with time at 120°C for 10% PVC/90% PVP, 50% PVC/ 50% PVP, and 80% PVC/20% PVP blends.

the conjugation length. In another study, an increase in molecular weight during degradation in nitrogen was attributed to crosslinking, whereas a decrease in molecular weight during degradation in air was attributed to oxidative scission [13]. Further evidence of crosslinking and polyene chain scission is the red shift of the C=C peak and decrease in its intensity, which indicate shorter lengths and lower population densities of polyenes (Figures 7 and 8). The increase in intensity with time at a given temperature means increase of the number of polyene chains. The increase and the subsequent decrease in polyene intensities and the initial Raman shift to lower wavenumbers can be seen in a three dimensional representation of the change in intensity of the 10% PVC/90% PVP blend as a function of time at 130°C in Figure 7. Figures 8, 9, and 10 show the change in intensity of the polyene peak at 1490 cm^{-1} with time of 10% PVC/90% PVP 50% PVC/50% PVP and 80% PVC/20% PVP blends at 120°C, 130°C, 135°C, and 140°C. At 130°C, (Figure 8) the polyene length increased, reaching a peak, which is followed by a decline. At 120°C, the induction period is long and the rate of increase of polyene length is too slow to reveal the peak within the experimental time frame. At 140°C, at this composition, the polymer degraded early in the experiment resulting in termination of the experiment. Clearly, as the temperature increases the rate of change of intensity increases and the onset time for the changes in intensity decreases.

    Superimposition of the polyene length vs. time and intensity vs. time graphs at the same composition and temperature reveal that the rate of change of intensity
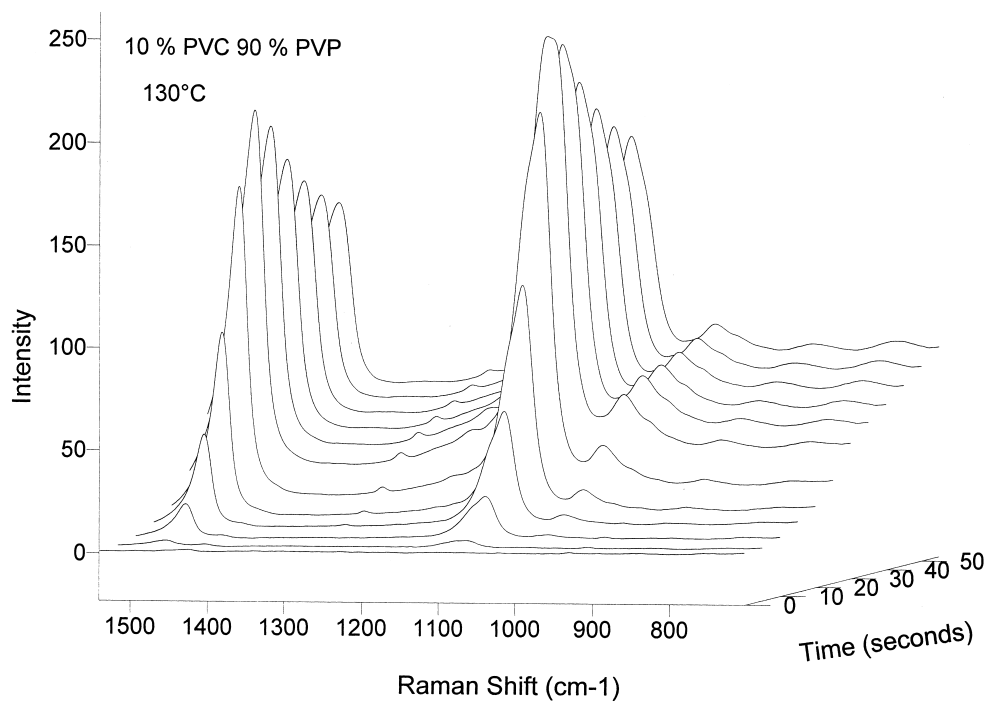
Figure 7. Three-dimensional representation of the Raman shift of polyene peaks in 90% PVP/ 10% PVC blends at 130°C as a function of time.
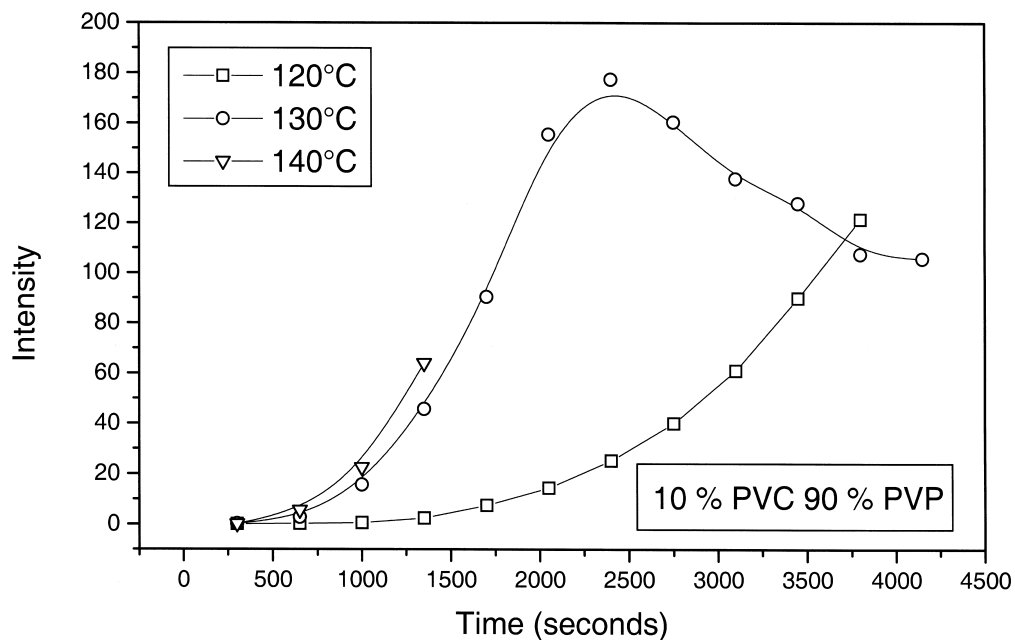
Figure 8. Intensity vs. time of the –C=C- peak (around 1490 cm^{-1}) for the 10% PVC/90% PVP blend at temperatures of 120°C, 130°C, and 140°C.
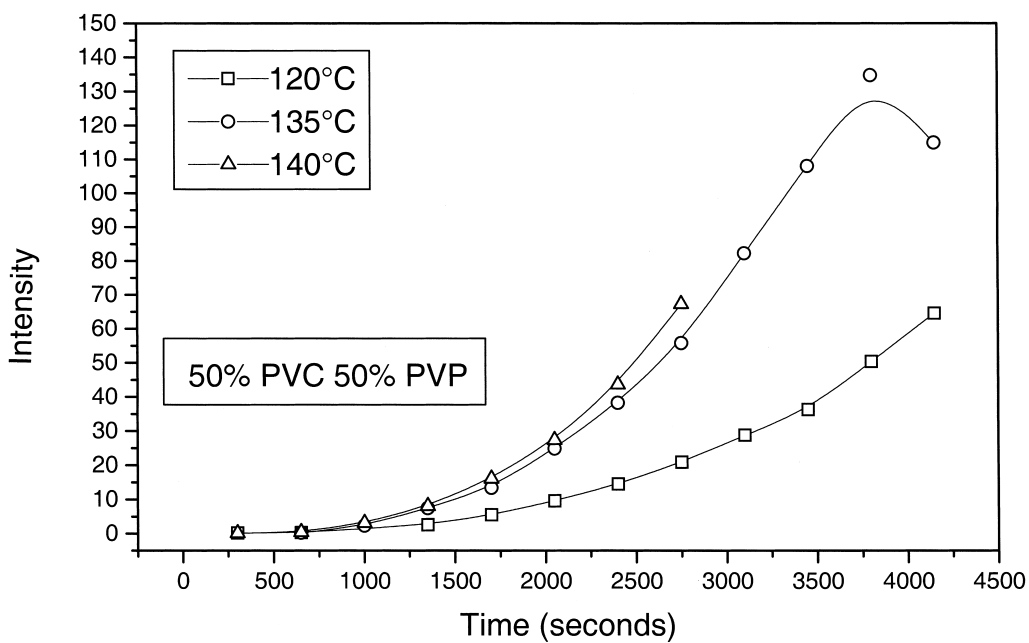
Figure 9. Intensity versus time of the –C=C- peak (around 1490 cm^{-1}) for the 50% PVC/50% PVP blend at temperatures of 120°C, 135°, and 140°C.
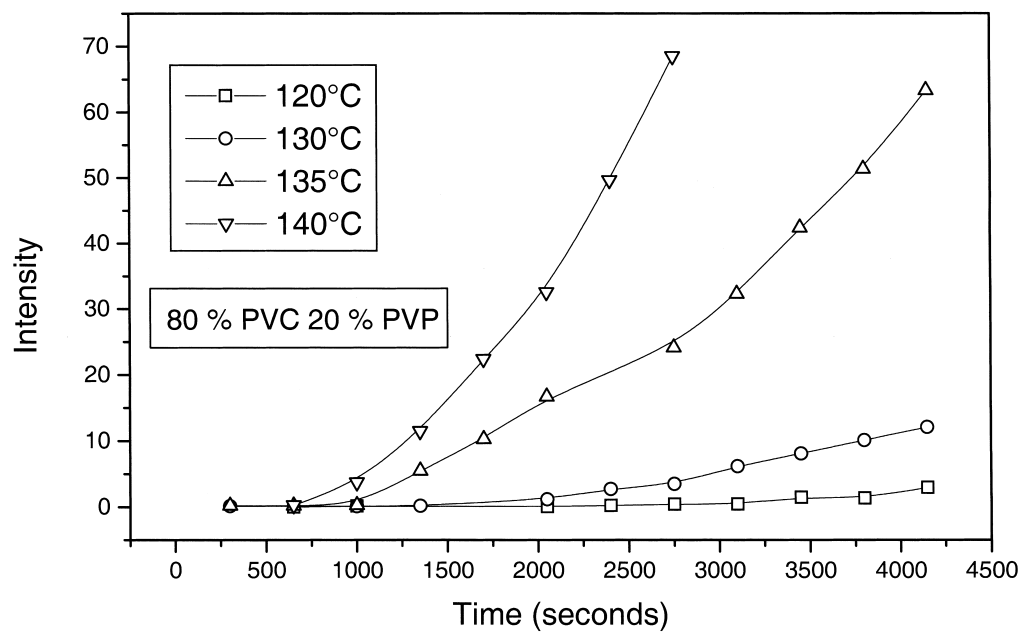
Figure 10. Intensity vs. time of the –C=C- peak (around 1490 cm^{-1}) for the 80% PVC/20% PVP blend at temperatures of 120°C, 130°C, 135°, and 140°C.

is much slower than change in polyene length with time. Polyene intensity change lags behind the polyene growth significantly. Polyene length increases early in the experiment and reaches a plateau followed by a sharp drop at prolonged aging times, particularly at high PVP compositions. Comparison of Figures 3a and 8 clearly shows that while the sharp drop in polyene length occurs, the polyene intensity is still increasing. This suggests that while longer polyene segments decompose into smaller ones, the population density of the polyenes is increasing. In other words, polyene formation is continuing but the sequence length is dropping. At higher PVC compositions the rates of change in intensity are much slower.

It was suggested that C-Cl···O=C interactions resulted in a good dispersion of PVP in PVC assisting in the formation of longer sequences of polyene formation. The presence of PVP between PVC chains was thought to form an impediment to further interaction between polyene sequences, hindering cross link formation and aromatization at the early stages of dehydrochlorination, hence resulting in longer polyene sequences [1]. It was also suggested that in neat PVC, interaction of polyenes with each other during formation might result in shorter polyene lengths as a result of crosslinking [1]. In contrast to the latter observation, results of this study indicated that increasing the PVP content gave rise to an earlier decrease in polyene length, particularly at higher temperatures. This would be consistent with mobility increases at high temperatures, facilitating crosslinking of polyene chains. The experiments in this study were carried out in open air, whereas the abovementioned study was done in nitrogen. Crosslinking of polyenes takes place in both inert and oxygen atmospheres but oxidative scission of polyenes occurs in oxygen atmospheres. Abbas and Sorvik [13] reported an increase in the molecular weight during degradation in nitrogen, which was attributed to cross-linking, and a decrease in molecular weight during degradation in air, which was attributed to oxidative scission. The release of HCl is faster at high temperatures and considerably higher in air than in an inert atmosphere or in vacuum [7]. Release of HCl also gives rise to chain scission, enhancing this effect. It was found that at low dehydrochlorination levels the number of polyenes increased rapidly parallel with the increase in the release rate of HCl.

FTIR emission spectroscopy was performed to investigate the influence of oxidation in polyene degradation of 90% PVP/10% PVC blend at 130°C, exposed to air for a period of 5000 seconds by observing the possible formation of carbonyl groups as Raman spectroscopy is less sensitive to the detection of this group. No spectral changes were observed at this temperature within the test period. Based on the literature, carbonyl formation would be expected to occur, but it must be below the detection limits of the technique. Alternatively, volatile oxidation products may be lost from the thin polymer film soon after formation.

Several mechanisms have been proposed for the interaction and degradation of these blends but it is difficult to obtain definitive proof of the processes involved. Dipole - dipole interaction proposed as a key step in the degradation process [1] is represented in Figure 11.
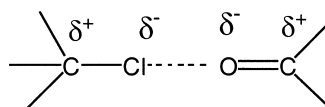
Figure 11. Dipole-dipole interactions suggested by Dong *et al.* [1].

The main support for this seems to come from the shift in the carbonyl stretching frequency with increasing concentrations of PVC. However, this interaction does not seem chemically reasonable and, in view of the relative electronegativities of the atoms involved, a much more likely interaction is shown in Figure 12.

However, the proposed mechanism [1], which involves this interaction, does not address the formation of the first double bond. In the case of the PVP/PVC degradation such an interaction is not necessarily involved and we believe that it is more likely that the process is a simple E_2 elimination as seen in Figure 13.
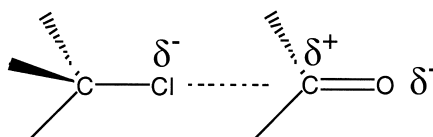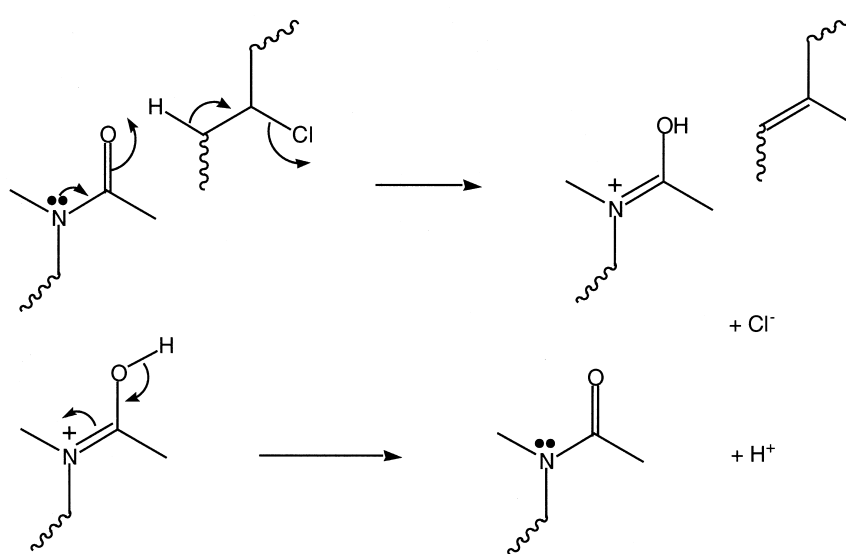
Figure 12. Proposed dipole-dipole interactions.

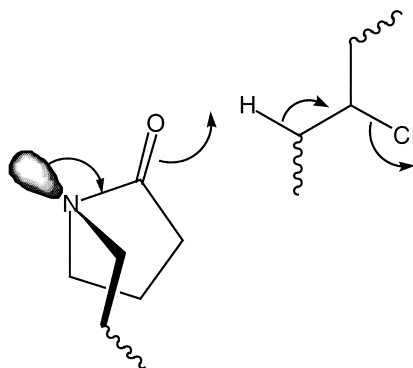**Figure 13.** A proposed mechanism for elimination of HCl.

Figure 14. Lone-pair electrons on nitrogen assist the elimination reaction.

This process is driven by the increase in base strength of the carbonyl oxygen resulting from the lone pair electrons on the neighboring nitrogen [14] and involves a "concerted" electron transfer process. While such process is not common for simple amides in solution, there are at least two important factors, which are specific to the present case:

1. The effective concentration is very high because there is no solvent and so although the base strength of the carbonyl is not dramatically high, it could be forced into close proximity to the α-hydrogen atom.

2. The lactam ring acts as a "strap" to force the lone pair electrons on the nitrogen to adopt a very favorable orientation and so assist the efficient transfer of electrons (Figure 14).

As mentioned by Dong *et al.* an E_1 (or ionic) mechanism is also possible (Figure 15):
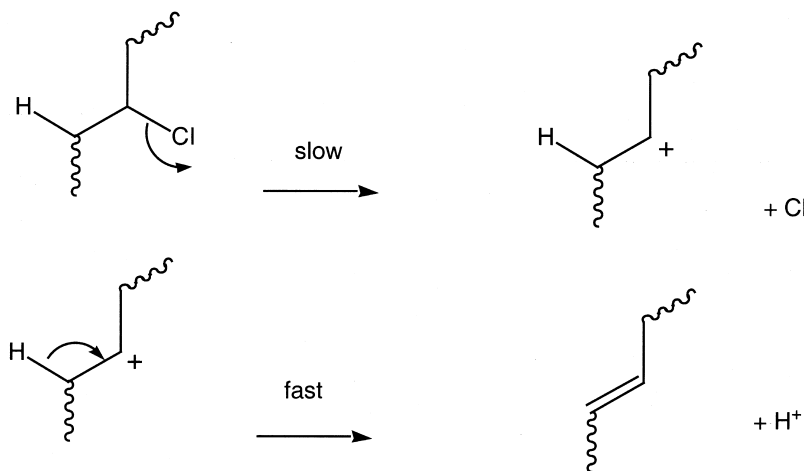

Figure 15. An E_1 (or ionic) mechanism for the elimination of HCl.

Such processes can be significant in secondary cases (as here), particularly in solvents, which favor ionization [15] or which help to "solvate" ions [16]. Since polyvinyl pyrrolidone is an extremely polar medium it may well encourage this process. Dong et alia invoke the C-Cl.....O=C dipole to explain the next elimination step. However, we believe this is unnecessary since a mole of HCl has now been produced, and subsequent steps are no more than acid catalyzed eliminations. This may proceed through an ion-pair mechanism such as that proposed by Starnes *et al*. [17].

CONCLUSION

Increasing the amount of PVP in the PVC/PVP blends decreased the dehydrochlorination temperature and time. Increasing PVP ratios, particularly at higher temperatures, resulted in an earlier decrease in the mean polyene length due to crosslinking and oxidative scission. We have proposed a mechanistic explanation of the elimination of HCl and polyene formation based on classical organic elimination reactions.

ACKNOWLEDGMENTS

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