Raman Spectroscopic Study of the Interaction of Iodine with Polyene Sequences Derived from the Phase-Transfer-Catalyzed Dehydrochlorination of Poly(vinyl chloride)

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Introduction. The degradation of poly(vinyl chloride) (PVC) under nonoxidative conditions, whether induced thermally (~200 °C) or photochemically or by ionizing radiation or base catalysis in the solution phase results in the evolution of HCl and formation of a distribution of polyene sequences[1] with values of n in the range 1 to about 15

$$\sim(\mathrm{CH_2CHCl})_n\sim \rightarrow \sim(\mathrm{CH{=}CH})_n\sim + n\mathrm{HCl} \quad (1)$$

As the value of n reaches about 4–5, even though the total extent of dehydrochlorination may be less than $10^{-2}\%$, the absorptions of the polyenes extend into the visible region and the polymer becomes colored but without any appreciable change in electrical or mechanical properties. In the presence of oxygen, the dehydrochlorination is accompanied by chain scission, cross-linking, and oxygenation of the polymer, processes which if allowed to continue unchecked would lead to disastrous changes in its physical properties. For more than 50 years, the history of the thermal and photochemical stabilization of PVC has centered around the prevention of polyene formation and minimization of their effects, since these structures play a central role in the degradation process.

In 1974, the preparation of polyacetylene (PA), in a form which could be oxidatively "doped" to produce a material whose electrical conductivity approached that of the metallic regime, led to the growth of intense interest in the synthesis and properties of linear polymers which contained extended π-conjugation.[2] The more recent realization that their nonlinear optical properties may be at least as important as their electrical characteristics has further stimulated research in this area.[3] The essential difference between polyenes in PA and those in degraded PVC is that the former extend throughout the polymer, whereas the latter are relatively short and are isolated from each other by long sequences of undegraded segments. PVC is, therefore, a potential "precursor polymer" for PA if the degree of dehydrochlorination can be made sufficiently high while cross-links and other undersirable side reactions are kept to an acceptable minimum.

Characterization of polyene systems has been studied mainly using ultraviolet–visible absorption, fluorescence emission, and Raman spectroscopies. Resonance Raman spectroscopy is a sensitive technique for studying the polyene sequences formed by elimination of HCl since, by varying the excitation wavelength, an estimate of sequence length and polydispersity can be obtained from the frequency of the ν_2 (C=C) mode near 1520 cm^{-1}. This application has been reported elsewhere[4,5] and is not discussed in detail here save to note the variations in numbering terminology for the modes which exists between authors. Raman analysis has also been used to investigate the effects of doping of conjugated polymers, in particular polyacetylene, in attempts to elucidate the structural details of the doped domains.

Our previous work[6–8] in this area has been concerned with metal chloride ($FeCl_3$, $SbCl_3$, $ZnCl_2$), catalyzed and photocatalyzed dehydrochlorination of PVC films in attempts to produce high concentrations of polyene sequences containing *in situ* dopants. We have also studied the dehydrochlorination of PVC using a phase-transfer catalysis (PTC) technique based on that described by Kise[9] and present here a preliminary study of both visible and near-infrared (near-IR) excited Raman spectroscopy of the polyenes formed and their interaction with molecular iodine.

Experimental Section. Sample Preparation. Suspension PVC (supplied by European Vinyl Corporation International) was catalytically dehydrochlorinated by a phase-transfer technique using essentially the conditions described by Kise.[9] The PTC catalyst used in this work was tetrabutylammonium hydrogen sulfate (TBAHS; typically 0.5 mM) in a 40–50% aqueous sodium hydroxide solution at 70 °C. Reaction times were varied from a few minutes up to 16 h. The color of the PVC began to darken almost immediately after it was added to the catalyst system and rapidly turned black. At the end of the required reaction time, the black product was filtered off, washed thoroughly with successive portions of water and ethanol, and dried by pumping under vacuum. If the dried product was not used immediately, it was stored under vacuum in the dark. Doping was carried out by adding the dried degraded polymer to a solution of iodine in dichloromethane (DCM) and stirring for up to 24 h. The doped product was dried and stored in a desiccator in the dark.

Raman spectra were obtained using two systems: the first was a dispersive Dilor XY spectrometer using an argon-ion laser oscillating at 488 nm for excitation and an intensified diode-array detector. Fourier transform (FT) Raman spectra were recorded using Perkin-Elmer 1760 spectrometer with a polarized Spectron Nd:YAG laser (1064 nm) for excitation and a liquid-nitrogen-cooled InGaAs detector. Degraded samples were analyzed *in situ* in evacuated tubes, while iodinated samples were analyzed as compacted disks in air. Acquisition conditions are specified in the figure captions.

Results. The Raman spectra recorded in this work are displayed in Figures 1 and 2. Figure 1 shows the spectra obtained under 488-nm excitation (<0.5 mW) of the samples degraded for (a) 15 min, (b) 8 h, and (c) 8 h followed by I_2 doping. Spectral manipulations made prior to display are noted in the figure caption. Although the samples were black, spectra in parts a and b of Figure 1 were of excellent quality and clearly confirmed the formation of polyenes. No PVC bands were visible owing to the dominance of the resonance-enhanced polyene bands. The ν_2 band positions (*ca.* 1527 cm^{-1}) indicate an average sequence length of *ca.* 10.5 units.[4] Although the I_2-doped material (Figure 1c) yielded a significantly poorer spectrum owing to its weaker intensity and higher background, it is apparent that the ν_2 position is upshifted slightly to *ca.* 1536 cm^{-1}, corresponding to a sequence length of 9 units.

Figure 2 shows the spectra obtained using 1064-nm excitation for the same samples. Some interesting differences compared with the 488-nm spectra are im-

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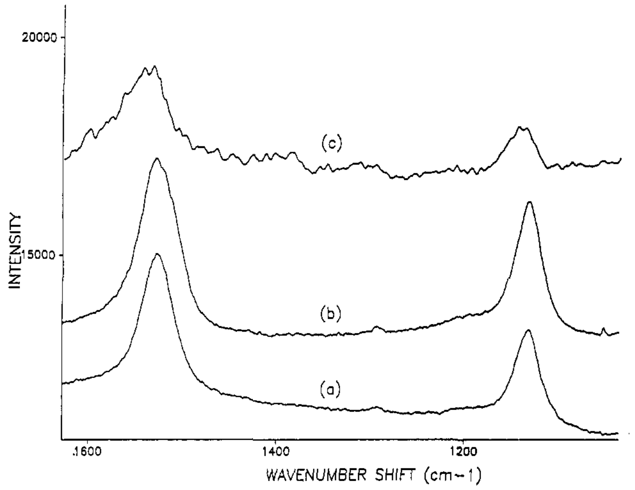

Figure 1. Spectra of dehydrochlorinated PVC under 488-nm excitation with <0.5 mW at the sample. Spectral resolution was *ca.* 4 cm^{-1}. Base lines were offset to allow easy comparison of spectra. (a) Degraded for 15 min. (b) Degraded for 8 h. (c) As for b but doped with iodine. The weaker spectrum (c) has been multiplied by a factor of 4 to allow easier comparison.

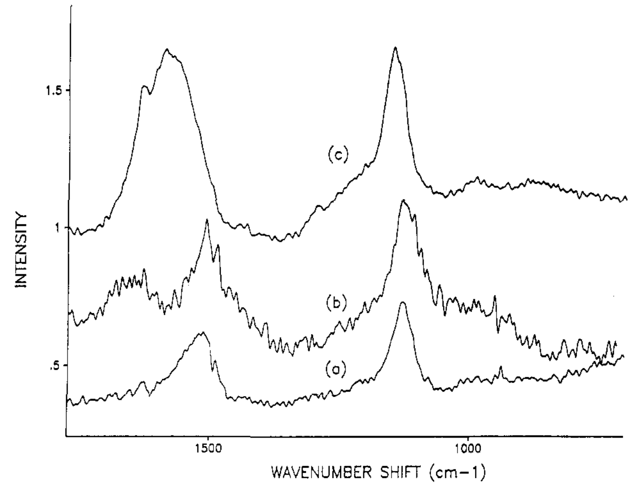

Figure 2. Spectra of dehydrochlorinated PVC under 1064-nm excitation and 4-cm^{-1} resolution. Spectrum labels are as in Figure 1. The 8-h nondoped sample (b) was on a high fluorescent background, hence the poor S/N. Base lines are offset to allow easier comparison of spectra.

mediately apparent. First, the spectra of the undoped samples (parts a and b of Figure 2) were of poorer S/N than the visibly excited spectra, and the ν_2 band positions were significantly lower (*ca.* 1517 and 1507 cm^{-1}), indicating conjugation lengths of 13 and 15 units for the 15-min and 8-h samples, respectively. Second, the spectrum of the iodine-doped sample was of better S/N than the corresponding 488-nm spectrum or the spectra in parts a and b of Figure 2, with a ν_2 position of 1590 cm^{-1} and a new band appearing at 1630 cm^{-1}. The spectra in Figure 2 were superimposed upon an oscillating background arising from sample thermal emission and broad-band fluorescence which was modulated by the instrument transmission function. The effect was most severe for the 8-h nondoped sample, which had a very large fluorescence background and hence a very poor S/N. Doping the sample gave a much better signal/background ratio and hence an improved S/N.

Discussion. The results summarized above can be partially rationalized by recourse to the literature. Data in Figure 1 clearly show that polyenes of moderate conjugation length were present in each sample, and the conjugation length was not greatly altered by the degradation time. Doping with iodine caused some reduction in spectral quality as samples were more prone to burn up in the laser beam, but the main effect was to slightly upshift the ν_2 band position. This can be readily understood from previous work and implies that doping has disrupted the conjugated sequences by effectively introducing a defect, thereby reducing the sequence length and increasing the C=C stretching frequency.[4,5] Modes due to the doped domains themselves would be expected to have a significantly different structure and should become obvious at high doping level.[5,10–13]

The IR excited spectra are actually more interesting in that their interpretation is not so straightforward. Spectra of undoped samples (Figure 2a,b) have ν_2 modes at significantly lower frequency than those measured with visible excitation (Figure 1a,b). This is entirely expected as the longer wavelength excitation should be resonant with the electronic absorption of longer polyene sequence lengths, which have correspondingly lower vibrational frequencies. This is the normally observed dispersion in Raman frequency.[4,5] However, the spectrum of the doped sample in Figure 2 is different in that it is more intense, the ν_2 mode is upshifted by nearly 80 cm^{-1}, and a new mode appears at *ca.* 1630 cm^{-1}. These effects cannot be explained simply by the reduction in the effective conjugation length on doping, as the upshift in frequency is far greater than was observed with visible excitation. Furthermore, the shorter sequence should be in closer resonance with the 488-nm excitation, so that a higher ν_2 frequency would be expected using visible rather than near-IR excitation of a polydisperse polyene sample. In contrast, we actually observed a much higher ν_2 frequency in the near-IR excited spectrum of the iodine-doped samples.

These observations lead to the conclusion that the near-IR and visible excitation spectra reveal completely different domains within the same sample in these experiments. The spectrum in Figure 1c is of "normal" polyene sequences, where the sequence length is simply shortened by doping-induced defects, and is consistent with spectra normally observed at low dopant concentrations.[5,11] The spectrum in Figure 2c is believed to be due to the actual doping-induced domains themselves. Clearly, the strength of the bands in Figure 2c indicates that these domains have an electronic absorption resonant with the 1064-nm laser, whereas the nondoped sample is more strongly resonant with visible excitation (contrast Figures 1b and 2b). This supposition is supported by the results of Harada *et al.*,[11] who showed that iodine doping of a model polyene, β-carotene, yielded an electronic absorption band at *ca.* 940 nm, which would be in approximate resonance with 1064-nm excitation. Unfortunately, these workers only presented Raman data for excitation up to 647-nm wavelength.

Observation of resonance-enhanced near-IR Raman spectra of polyenes is not new; for example, Furukawa *et al.*[10] made measurements on *trans*-polyacetylene (PA) using near-IR and visible excitation on both pristine and doped polymer. Similarly, Harada and co-workers[11] have made measurements on PA and β-carotene (pristine and doped) using excitation wavelengths from 325 to 647 nm. Williams and Gerrard[14] used FT-Raman spectroscopy to analyze thermally degraded PVC coupons, and there have been a number of studies using near-IR excitation on conducting polymers.[10,13] The common factor in all of these studies is that, while it is obvious that resonance-enhanced spectra of doped domains are readily obtainable and can often by rationalized as spectra of localized polarons or bipolarons,[10,13] in all cases the near-IR spectra yielded *lower* vibrational frequencies for the ν_2 bands than did visible excitation of the same samples. In other words, the visible and near-IR excitations were in resonance with the same doped domains, but near-IR excitation preferentially enhanced the feature due to the domains with the *longer* conjugation length. This is what would be expected from the normal dispersion behavior of polyene spectra.

Our results from I_2-doped samples are in marked contrast, since the near-IR data show higher ν_2 positions than the 488-nm spectra, implying that shorter effective sequence lengths exist in the doped domains. We conclude that in our doped samples, although the doped domains are of short sequence length, their structure is such that their electronic absorption maximum is in the near-IR and so they are only observed in the 1064-nm spectra, while the nondoped regions of the same samples are strongly resonant under visible excitation and are therefore seen only in the visible spectra. The extra band at ~1630 cm^{-1} is assigned to a possible bimodal distribution of sequence lengths in the doped domains. The nondoped sequences are apparently longer than the doped domains, given the relative ν_2 positions in both spectra, although gross differences in the domain structure compared with normal polyene could invalidate this assumption. We are not aware of this behavior being reported previously.

The structure of the actual doped domains is unclear at present but probably corresponds to a complex of a polyiodide ion with a polyene cation, where the charge is localized over a relatively short sequence of carbon atoms in the chain.[15] The extent of delocalization could be determined, in principle, by comparison with the spectra of cations of $-(C{=}C)_n-$ oligomers as a function of n.[10,13] This is currently being investigated and will be the subject of a future publication.

Conclusions. Phase-transfer catalysis has been shown to be an effective method for the dehydrochlorination of PVC to yield conjugated polyene sequences. The sequence lengths are not monodisperse since a different effective length is determined by visible and near-IR excited Raman spectra. However, no very long sequences were detected using the latter technique. Doping the system with iodine gave an unusual material. Visible Raman spectra showed a slight decrease of conjugation length due to chain disruption, but the doped domains were generated with a short sequence length and were strongly resonance-enhanced only under near-IR excitation—they were invisible under visible excitation! Normally the short sequences would be preferentially observed using a visible laser, so these results are very unusual and point to an interesting structure for the doped domain. Our results contrast with literature reports on doped polyacetylene, where even at high levels of doping the visible excited spectra are dominated by shorter sequence lengths than the near-IR spectra. We, therefore, conclude that with our samples only the near-IR excited spectra detect the doped domains, while the visibly excited spectra detect normal polyene, and so the doped domains in our samples are significantly different from those generated on doping polyacetylene.

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