# The Resonance Raman Spectrum of Degraded Poly(vinyl chloride). 2. $\gamma$-Irradiated Samples

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ABSTRACT: The resonance bands which appear in the Raman spectrum of poly(vinyl chloride) samples after degradation by $\gamma$ irradiation are examined in two samples of the polymer with different syndiotactic contents. The various lengths of conjugated sequences present in the degraded samples are studied by using four different laser frequencies as exciting lines and the effect of increasing radiation doses on the concentrations of these sequences is examined. The results indicate that the concentration of the longer conjugated sequences rises steadily with radiation dose in the case of the less syndiotactic polymer. With the more highly syndiotactic sample, however, the rate of increase falls off rapidly, and for the highest doses an actual decrease is observed; this effect appears to be associated with the occurrence of cross-linking in the polymer.

Although the structures present in thermally degraded poly(vinyl chloride) have been studied by many workers, and spectroscopic methods have played an important part in characterizing the conjugated polyene units formed by the sequential loss of hydrogen chloride, PVC degraded by $\gamma$-ray or high-energy electron irradiation has received much less attention. Ultraviolet/visible absorption spectroscopy and ESR spectroscopy have been used independently in one or two instances but most of the information currently available on $\gamma$-irradiated PVC has emerged from the application of the two techniques in combination.

Miller[1] noted that the presence of free radicals is associated with the development of color and, hence, absorption in the visible region of the spectrum of irradiated PVC. Atchison[2] deduced that there are three types of radicals, decaying exponentially with half-lives of 4.5, 63, and 1630 h at ambient temperature. He showed that the absorbance at 550 nm is inversely proportional to the concentration of the long-lived radicals; at shorter wavelengths discrete bands, indicative of conjugated polyenes of different sequence lengths, were observed. These results were confirmed by Loy,[3] who found that each of the three types of radicals yields a constant distribution of conjugated chain lengths. Ohnishi, Nakajima, and Nitta[4] concluded that the absorption in the visible region of the spectrum is caused by the formation of polyenyl radicals or polyene radicals, containing as many as nine conjugated double bonds.

Resonance Raman spectroscopy has been used recently[5–7] to characterize the conjugated polyene sequences present in thermally degraded PVC. It proved to be very sensitive, the limit of detection being less than 0.0001%, and it was possible to compare the levels of conjugated polyenes containing 9, 13, and 16/17 conjugated double bonds in a series of samples. The technique should therefore prove useful for the examination of $\gamma$-irradiated specimens and the purpose of the present study has been to confirm this surmise.

## Experimental Section

Two types of PVC were used for the degradation studies; the first a commercial polymer prepared by the mass polymerization method and the second the Montedison fibre-forming polymer. The syndiotactic contents of both have been determined by NMR spectroscopy[8] and are 55% in the case of the former and 67% for the latter.

The samples were sealed under vacuum in glass tubes and irradiated at a rate of 3 Mrad/h to give total dosages of 0.5, 1, and 2 Mrad for each of the polymers. The samples were examined where possible as solutions in tetrahydrofuran, the glass tubes being unsealed just before the solutions were made up in order to minimize any effects due to atmospheric oxidation. The concentrations were chosen to give solutions of approximately similar absorbance in the visible region of the spectrum to minimize any errors arising from partial absorption of the laser beam, although the concentrations used were sufficiently low to make such effects very small. All intensities were corrected to a constant PVC concentration of 30 mg cm$^{-3}$. The two most highly irradiated Montedison samples proved to be only partially soluble in tetrahydrofuran and so they were shaken continuously with the appropriate volume of tetrahydrofuran until a homogeneous gel had formed and spectra could then be obtained in the same way as for the solutions. In addition to the samples irradiated in vacuo, further samples of each polymer were irradiated to 0.5 and 1 Mrad in the presence of air and examined in the same way as described above.

The Raman spectra were obtained with a JEOL JRS-S1 spectrometer using the 457.9- and 488-nm lines of an argon ion source and with a Spex Ramalog 4 spectrometer using the 530.8 and 568.2-nm lines of a krypton ion laser.

## Results and Discussion

The degraded samples of both polymers were examined with the four exciting wavelengths 457.9, 488, 530.8, and 568.2 nm and the intensities of the resonance line at about 1120 cm$^{-1}$ ratioed against the tetrahydrofuran solvent line at 915 cm$^{-1}$ were measured, following the method previously used for the examination of thermally degraded samples.[5,6] Plots of this intensity ratio as a function of radiation dose for the mass polymer are given in Figure 1 and for the Montedison polymer in Figure 2. Several interesting features are apparent.

In the case of the mass polymer the intensity ratio increases with radiation dose at each of the four exciting wavelengths, showing that the concentration of conjugated double bonds with between 9 and 16/17 units increases as the degradation proceeds. As has already been pointed out in the case of the thermally degraded polymers, it is not easy to compare intensity ratios measured with two or more exciting wavelengths, because they are dependent upon several factors. However, the fact that the intensity ratio at the highest dose, 2 Mrad, decreases steadily as the exciting wavelength increases, from 0.46 with 457.9 nm to 0.165 with 568.2 nm, suggests that the concentration of the longer conjugated sequences is somewhat lower than the shorter ones. The various values indicate that the level of the degradation is a few hundredths of one percent, once again demonstrating the ability of the resonance Raman technique to give information at very low concentration levels of conjugated polyenes. There are clear indications that the concentration of a particular type of conjugated polyene is not a linear function of the radiation dose; however, no interpretation of this observation will be attempted on the basis of the limited results available.

The results of the measurements on the Montedison polymer differ considerably from those on the mass polymer, both with regard to the concentration of conjugated polyenes for a particular dose and the variation with irradiation. Only in the case of the 457.9-nm exciting line are the two sets of intensity ratios comparable and even here there is an indication

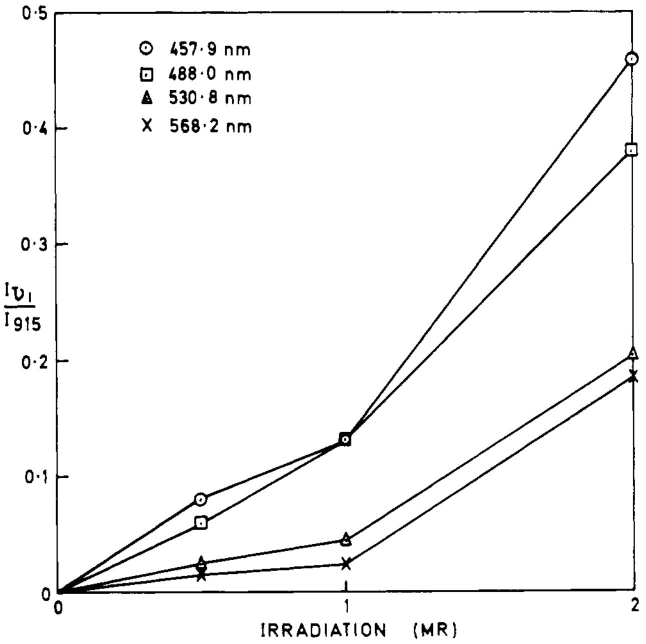


**Figure 1.** Intensity of the resonance Raman band $\nu_1$ of $\gamma$-irradiated mass polymerized PVC as a function of irradiation dose for the exciting wavelengths 457.9, 488, 530.8, and 568.2 nm.

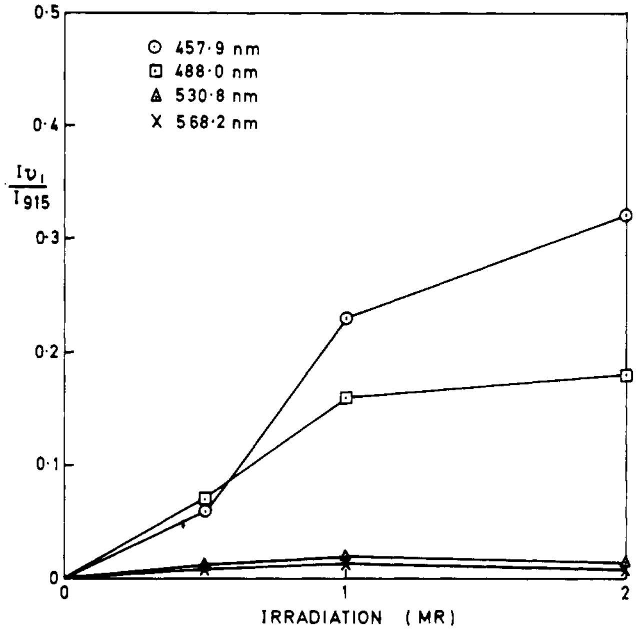


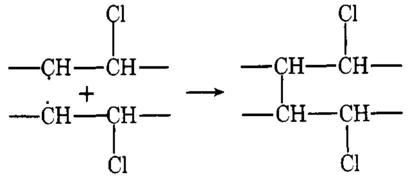
**Figure 2.** Intensity of the resonance Raman band $\nu_1$ of $\gamma$-irradiated Montedison PVC as a function of irradiation dose for the exciting wavelengths 457.9, 488, 530.8, and 568.2 nm.

that the rate of formation of conjugated polyenes with $n = 9$ as assessed by the changing slope of the line is falling off for higher radiation doses. This trend is confirmed by the results for the remaining exciting wavelengths. At 488 nm the ratios for 1 and 2 Mrad are very similar and with 530.8 and 568.2-nm excitation the ratio passes through a maximum at about 1 M rad. Furthermore, the overall level of conjugated unsaturation is an order of magnitude lower than for the mass polymer.

The overall concentration of conjugated polyenes and of conjugated sequences of different length is determined by their rate of formation and by subsequent losses from reactions such as cross-linking or others in which long conjugated sequences are converted to shorter ones. The fact that the longer sequences are formed readily in the case of the mass polymer suggests that they would also occur with the Montedison polymer if competing reactions were absent. Cross-linking reactions which lead to the formation of materials which are insoluble in or gel with normal solvents for PVC are well known in the degradation of PVC by $\gamma$ irradiation. This suggests that this type of reaction is occurring with the Montedison polymer, both on general grounds, and because of its low solubility in tetrahydrofuran after degradation. It is thus of interest to try to establish why cross-linking reactions occur much more readily in the case of the more syndiotactic Montedison polymer and at a very low level of conjugated unsaturation.

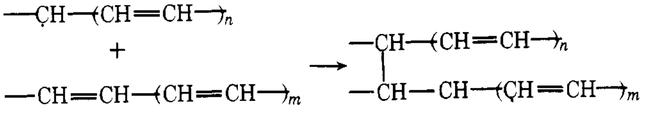
A number of mechanisms for the cross-linking of PVC have been proposed. Druesdow and Gibbs[9] have suggested four, namely copolymerization between polyene groups, chain transfer between a polyene group and a segment of the normal polymer, a Diels–Alder reaction, and cross dehydrochlorination between a point of high chlorine activity on one chain and a hydrogen atom on another. They favored the cross dehydrochlorination mechanism but Winkler,[10] noting that the first two reactions require radicals for initiation and believing that the normal reactions of free radicals can explain cross-linking in PVC, was in favor of them. As degradation by $\gamma$ irradiation is likely to lead to a relatively high concentration of radicals the first two mechanisms of Druesdow and Gibbs will be considered.

The most direct mechanism for cross-linking in vacuo or in an inert atmosphere involves the termination of two macroradicals:



$$\begin{array}{c}\text{—}\underset{\cdot}{\text{C}}\text{H—}\overset{\text{Cl}}{\overset{|}{\text{CH}}}\text{—}\\ + \\ \text{—}\dot{\text{C}}\text{H—}\underset{\text{Cl}}{\underset{|}{\text{CH}}}\text{—}\end{array}\longrightarrow\begin{array}{c}\text{—CH—}\overset{\text{Cl}}{\overset{|}{\text{CH}}}\text{—}\\ | \\ \text{—CH—}\underset{\text{Cl}}{\underset{|}{\text{CH}}}\text{—}\end{array}$$

The rate of this coupling reaction should be temperature dependent. At very low temperatures, when the molecular motion of the macroradicals is very small, the termination rate should be extremely low. On the other hand it should increase rapidly above the glass transition temperature. Rånby and co-workers[11] have recently proposed an alternative/additional process which involves an unpaired electron transfer from one polyenyl radical to a double bond in another conjugated system by the following reaction:



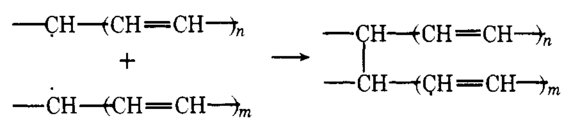
$$\begin{array}{c}\text{—}\underset{\cdot}{\text{C}}\text{H—(CH=CH—)}_n\\ + \\ \text{—CH=CH—(CH=CH—)}_m\end{array}\longrightarrow\begin{array}{l}\text{—CH—(CH=CH—)}_n\\ \quad| \\ \text{—CH—CH—(}\underset{\cdot}{\text{C}}\text{H=CH—)}_m\end{array}$$

The probability of occurrence of this reaction is high because of electron resonance transfer along the conjugated polyene structure:

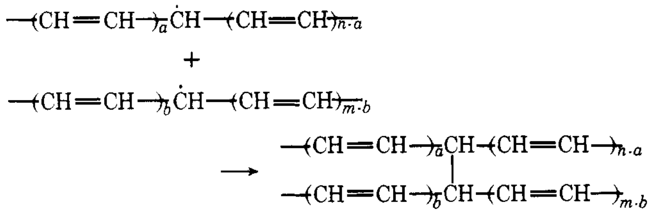
$$\begin{array}{c}\text{—}\dot{\text{C}}\text{H—CH=CH—CH=CH—CH=CH—}\\ \updownarrow \\ \text{—CH=CH—}\dot{\text{C}}\text{H—CH=CH—CH=CH—}\\ \updownarrow \\ \text{—CH=CH—CH=CH—}\dot{\text{C}}\text{H—CH=CH—}\end{array}$$

Such resonance structures allow for a transfer of the unpaired electron along the conjugated double bond sequence from one end to the other. The probabilities of reaction at different points in the polyenyl radical structure may vary widely because of differences in the free electron spin density on the various carbon atoms of this structure.

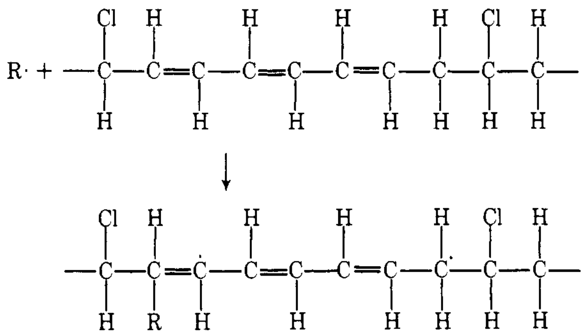
It also seems likely that two delocalized polyene radicals may combine as follows:



or



In the latter case the total amount of unsaturation is the same as in the former but the lengths of the conjugated sequences present after crosslinking are smaller, the shortest sequence being obtained when $a = n/2$ and $b = m/2$. With all of these cross-linking reactions there will, on average, be a substantial reduction in the conjugated sequence length. This will not necessarily be the case with the chain transfer between a polyene group and a segment of a normal polymer chain:



The resulting radical can then undergo normal radical reactions. This might occur preferentially via the terminal double bond at each end of a conjugated sequence, leading to a shortening by two double bonds. It is therefore a relatively inefficient mechanism for giving a substantial reduction in the average length of conjugated sequences.

It is possible to interpret the present results in a general way in terms of any of these mechanisms; however, none of them provide a ready explanation for the large difference in behavior between the mass and Montedison polymers. The ease with which the latter cross-links would seem to be explicable in terms of steric factors preventing the necessary spatial proximity of the radicals in the case of the mass polymer. This material contains a high proportion of bent syndictactic and isotactic structures and this is reflected in the low x-ray diffraction crystallinity value of about 10%. On the other hand, the more syndiotactic Montedison polymer contains a greater proportion of planar syndiotactic units, the chains pack more closely, and the crystallinity rises to about 25%. In these circumstances cross-linking reactions involving conjugated polyenes of a particular sequence length should occur more readily in the case of the Montedison polymer under the present conditions where the irradiation was undertaken below the glass transition temperature. This difference might not be so marked above $T_g$ or in solution.

It is interesting to compare these results with those of Mitani and Ogata[12] who studied the effect of polyene formation by ultraviolet photodegradation. They examined five materials of different syndiotacticities, in the temperature range 10 to 115 °C, and assessed polyene formation by ultraviolet/visible absorption spectroscopy. They found that the average polyene sequence length increased with increasing sample syndioacticity. They failed to find any change in molecular weight after irradiation and, in noting that their degradation conditions were very mild, suggested that the primary effect of the ultraviolet irradiation was dehydrochlorination and that other reactions such as cross-linking and chain scission could not conceivably play a significant role. The conditions during degradation by $\gamma$-irradiation are considerably more severe and radicals are produced much more abundantly. Hence, the difference in behavior with respect to sample tacticity is not surprising.

Although an explanation of the present results in terms of the steric probability of cross-linking reactions seems very plausible, other types of reactions, involving structural defects or impurities, cannot be excluded a priori. For example, the presence of chain branching would also presumably act in the same way as steric factors in limiting cross-linking reactions. However, it is now reasonably established that the level of chain branching decreases with decreasing polymerization temperature and therefore increasing syndiotacticity. Hence, if there is an effect it will complement the steric factor. A number of workers have examined the effect of extraneous impurities in initiating dehydrochlorination reactions; although the evidence is not completely unambiguous it does favor[13,14] these playing no more than a minor role. Hence, although there may be differences between the two samples used for the present work with respect to extraneous impuriites arising from the different types of polymerization processes used, these are unlikely to exert a significant effect on the degradation and subsequent cross-linking.

The cross-linking reaction will lead to a decrease in the average length of the conjugated polyene sequences. Consequently, as the concentration of longer sequences decreases the concentration of shorter sequences will increase. Hence, the parallel behavior of the intensity ratios for $n = 9$ as a function of radiation dose for the two polymers may be partly fortuitous and with higher doses than those studied the slope of the plot in the case of the Montedison material may decrease, and may even become negative as conversion to still shorter polyene units becomes considerable. In the absence of exciting wavelengths shorter than 458 nm it is not possible to explore this possibility. The marked dependence of the extent of cross-linking on the degree of syndiotacticity of the polymer suggests that with still more highly ordered specimens, such as may be prepared by low-temperature polymerizations, it will not be possible to build up a significant concentration of longer polyene sequences because of facile cross-linking.

In principle, the above results and conclusions, based on measurements on the $\nu_1$ band at about 1120 cm$^{-1}$, should be capable of confirmation by parallel measurements on $\nu_2$, at about 1500 cm$^{-1}$. In practice this was not possible because of the appearance of a broad band centered at about 1500 cm$^{-1}$, particularly in the case of the Montedison polymer. This band, which we are unable to account for, largely obscured $\nu_2$ at the lower dose levels and prevented quantitative measurements. However, as the results for the $\nu_1$ band are quite unambiguous this is not a practical drawback.

The limited number of samples irradiated in air gave no detectable resonance Raman bands. They showed a broad carbonyl band, centered at about 1700 cm$^{-1}$, in their infrared spectra. In view of the ease with which oxy and peroxy radicals participate in cross-linking reactions by termination[11] under these conditions it is not surprising that the concentrations of conjugated polyene units with $n = 9$ or greater is insignificant.

One additional point merits mention in the case of degradation by $\gamma$ ray irradiation, consequent upon the formation of radicals. Although there have been combined ESR/ultraviolet-visible absorption studies, such as those of Miller,[1] Atchison,[2] and Loy,[3] which show clearly that the appearance of UV-visible absorption parallels the formation of radicals, it has been the general practice to interpret the spectra on the same basis as with thermally degraded polymers.[15,16] In this latter case although the evidence is somewhat conflicting[11,17] it is clear that the radical concentrations must be very much lower than with the $\gamma$ irradiated specimens. However, Ohnishi, Nakajima, and Nitta,[4] citing unpublished calculations of Morokumo, have pointed out that the absorption bands of polyenyl radicals occur at significantly longer wavelengths than conventional conjugated polyenes of equal $n$ value. For example, with $n = 6$ the values are 430–435 nm and about 365 nm, respectively. If this can be substantiated it will be necessary to accept lower $n$ values than those previously suggested. The assignment of the $n$ values from the resonance Raman measurements does not depend upon the relationship between the wavelengths of the absorption maxima and the conjugated sequence length. It is dependent upon the empirical relation established[5] between the precise frequency of $\nu_1$ and $\nu_2$ and the $n$ value. However, in view of the effective increase in conjugation of the polyenyl radical of a given value it seems probable that the values of $\nu_1$ and $\nu_2$, for a given $n$, will be lower in the case of the polyene radical. Hence, equal doubt about the precise lengths of the conjugated polyene radicals may well exist in the case of the resonance Raman results. This uncertainty is of no consequence for the interpretation of the measurements reported above because we have been concerned with comparative rather than absolute $n$ values.

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# Inter- and Intramolecular Interactions of Polymers as Studied by Fluorescence Spectroscopy. 6. Exciplex of Poly[oxy-2-(9-anthryl)methylpropyleneoxy-(4-*N*,*N*-dimethylaminobenzyl)malonyl]

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ABSTRACT: Poly[oxy-2-(9-anthryl)methylpropyleneoxy(4-*N*,*N*-dimethylaminobenzyl)malonyl] (PE(A-1D)) was prepared by polycondensation of the corresponding 1,3-propanediol with the corresponding diethyl malonate. Anthryl groups as electron acceptors and *N*,*N*-dimethylanilino groups as electron donors were alternatively arranged along a polyester main chain so that strong exciplex emission was observed. From the results of absorption, emission, and excitation spectra, inter- and intramolecular interactions of the polymer were discussed. Comparison of absorption spectra of PE(A-1D) with the monomer model compounds 1,3-diacetoxy-2-(9-anthryl)methylpropylene (II) and diethyl (4-*N*,*N*-dimethylaminobenzyl)malonate (I) indicated the presence of weak ground state interactions between chromophores. Solvent effects on intensity, lifetime, and/or peaking wavelength of the exciplex emission from PE(A-1D) were compared with those on the exciplex emission from 1-anthryl-3-(4-*N*,*N*-dimethylanilino)propane(III) and the anthracene–*N*,*N*-dialkylaniline system. It was concluded that the exciplex by PE(A-1D) was less susceptible to solvent polarity in comparison with the exciplex by III and the anthracene–dialkylaniline system due to hindered solvation and restricted mobility of chromophores in PE(A-1D). The transient absorption spectrum of the exciplex by PE(A-1D) in DMF agreed with that of anthracene anion radical indicating the ion-paired state is still emissive in the polymeric system. The ratio of exciplex emission ($I_E$) to that of monomer emission from anthryl groups ($I_M$) increased with concentration suggesting the interpolymer association in the concentration region of $10^{-4}$ M. The driving force of interpolymer association was attributed to the weak ground state interactions. It was also confirmed that excitation of either anthryl groups or *N*,*N*-dimethylanilino groups equally brought about the exciplex formation.

Studies on the excited state interactions of chromophores which are chemically bound to polymers provide various information relevant to the segment mobility, the local concentration of polymer bound functional groups, the inter- and intramolecular interactions, and the environment surrounding the chromophores in polymeric systems.