Resonance Raman Spectrum of Degraded Poly(vinyl chloride). 4. Determination of Conjugated Polyene Sequence Lengths

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ABSTRACT: In order to establish the accurate relationship between ν_2, the C=C stretching frequency, and the conjugated polyene sequence length, n, required for the interpretation of the resonance Raman spectra of degraded poly(vinyl chloride) samples, it is necessary to obtain a reliable value for ν_2 for very long conjugated sequences. The previously adopted value, 1474 cm^{-1}, taken from a published Raman spectrum of polyacetylene, is shown to be in error. A critical survey of the literature, together with the results from new measurements, indicates that the correct value is 1461 cm^{-1}. The previously used exponential relationship between ν_2 and n has therefore been modified, giving $\nu_2 = 1461 + 151.24e^{-0.07808n}$. For $n \sim 20$, the longest sequences commonly encountered in degraded PVC, this revised equation gives an n value smaller by about 2 than that from the earlier exponential equation. Reciprocal equations of the type $\nu_2 = a + b/n$, used by some workers to interpret the resonance Raman spectra of polyacetylene samples, are not satisfactory.

Resonance Raman spectroscopy is now well established[1–5] as a valuable method for the characterization of the longer of the conjugated polyene sequences present in degraded poly(vinyl chloride). The technique has three major advantages: the high sensitivity, giving a limit of detection of about 0.00001%, its complementary role to ultraviolet/visible spectroscopy, as the latter is not useful for sequences longer than about ten conjugated units, and its selectivity, a consequence of the fact that ν_2, the C=C stretching mode, decreases in frequency as the conjugated sequence length, n, increases.

In order to utilize this selectivity effectively it is necessary to establish an explicit relation between ν_2 and n. The first approach[1] was to plot published ν_2 values for low molecular weight conjugated polyenes[6–8] against log n. A straight line is obtained and this may be used, by extrapolating beyond $n = 11$, the last of the calibration points, to find n values from the ν_2 values obtained from the spectra of degraded PVC samples.[1,3,4]

However, it has been pointed out recently[5] that the linear relation between ν_2 and log n can only be valid over a limited range because it implies that $\nu_2 \to -\infty$ as $n \to \infty$, and this is clearly erroneous. Hence, the validity of an accurate extrapolation to n values of about 20, to interpret the lowest ν_2 values found for degraded PVC, is suspect. Gerrard and Maddams[5] overcame this problem by using an additional calibration point. They assumed that the ν_2 value of 1474 cm^{-1}, reported by Shirakawa et al.[9] for polyacetylene, corresponds to very long sequences. They combined this data point with those for the low molecular weight conjugated polyenes and, by an asymptotic regression, obtained the equation $\nu_2 = 1474 + 141.67e^{-0.0925n}$. The use of this equation in place of $\nu_2 = k \log n$ gives significantly larger values for n; e.g., for $\nu_2 = 1491$ cm^{-1}, $n = 23.0$, not 19.0.

The recent marked interest in polyacetylene as the starting material for the preparation of electrically conducting polymers has led to the realization[10–13] that a range of conjugated sequence lengths occurs in these materials, and this is reflected in the reported values for ν_2 using exciting wavelengths in the range 600–700 nm. Some of these are lower than the figure of 1474 cm^{-1} used to establish the exponential relation between ν_2 and n. There is, therefore, the need to establish a reliable value for ν_2 for $n \to \infty$ and, if necessary, to revise the equation now in use. The purpose of the present work is to consider these points and also the merits of the simple inverse relation between ν_2 and n proposed by Lichtmann and Fitchen.[11]

Experimental Section

The *trans*-polyacetylene specimen, made by the Shirakawa method[9] and supplied by Dr. Weber of The Naval Research Laboratories, Washington, D.C., was examined in the solid state. The measurements were made on an Anaspec 33 Raman spectrometer whose frequency scale was calibrated with carbon tetrachloride and indene. The exciting lines, 676.4 and 752.5 nm, were obtained from a Spectra Physics Model 164-11 krypton ion laser.

Results and Discussion

Value of ν_2 for $n \to \infty$. Two factors are central to the estimation of a realistic value for ν_2 for $n \to \infty$. They are availability of a *trans*-polyacetylene sample containing very long conjugated sequences and the use of a wavelength that will excite resonance in them. It is clear, retrospectively, that these factors have not been satisfied in the measurements of Shirakawa et al.,[9] which gave the ν_2 value of 1474 cm^{-1}. Lichtmann and Fitchen[11] appear to have been the first to realize, on the basis of the shape of the ν_2 profile as a function of excitation wavelength, that *trans*-polyacetylene samples contain a range of conjugated sequence lengths. They have presented more detailed evidence in a recent publication.[12] Schügerl and Kuzmany[13] have given ν_2 profiles for a range of exciting wavelengths for a *trans*-polyacetylene sample prepared by the method of Ito et al.;[10] their results show very clearly that the sample contains a wide range of conjugated sequence lengths and this spread is confirmed by the results of measurements in our laboratory.[14] Schügerl and Kuzmany[13] estimate that the average value of n for their sample is 30.

In the present context it is the maximum value for n that is of primary importance. The failure of some earlier workers to appreciate that comparatively short conjugated sequences are present in polyacetylene samples largely accounts for the spread of ν_2 values reported in the literature. It is on these grounds that the value of 1474 cm^{-1} is not acceptable, and the figure of 1470 cm^{-1} reported by Lefrant et al.[15] is rejected for the same reason, together with the fact that an exciting wavelength of 605 nm was used. The effect of exciting wavelength is clearly illustrated by the results of Harada et al.;[16] using 568.2, 647.1, and 676.4 nm, they found corresponding ν_2 values of 1474, 1469, and 1466 cm^{-1}. They suggested that the value of 1466 cm^{-1} corresponds to a conjugated sequence length of at least 100 units and that approximate n values can be deduced from measured ν_2 values for n as large as 50.

Nevertheless, it is clear that the sample used for this work contained shorter sequences than had been envisaged

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Table I
Conjugated Polyene Sequence Lengths, n, for Various Values of ν_2 Using Three Methods of Calculation

	calculated n		
ν_2, cm^{-1}	exponential equation	revised exponential equation	equation based on Litchmann and Fitchen
1510	14.8	14.4	7.9
1506	16.1	15.5	8.6
1502	17.6	16.7	9.5
1498	19.3	18.0	10.5
1495	20.8	19.1	11.4
1493	21.8	19.8	12.1
1491	23.0	20.7	12.9
1489	24.3	21.6	13.8
1487	25.7	22.5	14.9
1485	27.6	23.5	16.1

because, 2 years later, Harada et al.[17] reported a ν_2 value of 1462 cm^{-1} for an excitation wavelength of 647.1 nm, with no significant change when the wavelength was increased to 676.4 nm. They suggested a value of 1460 cm^{-1} for $n \rightarrow \infty$ Values in close proximity have emerged from other recent work. Kuzmany[18] has proposed 1459 cm^{-1} and Kletter et al.[19] find 1457 cm^{-1} for $\lambda = 676.4$ nm. The value obtained in the present work is 1461 cm^{-1}, from measurements with the excitation wavelengths 676.4 and 752.5 nm. As this last result is the only one for which there is stated evidence for spectrometer calibration, it will be adopted for the purpose of calculating a revised experimental relation between ν_2 and n.

Revised Relation between ν_2 and n and Its Implications. When the literature ν_2 values for low molecular weight conjugated polyenes[6-8] are combined with 1461 cm^{-1} for $n \rightarrow \infty$, asymptotic regression gives the equation $\nu_2 = 1461 + 151.24e^{-0.07808n}$. The practical implications of this revised equation have been assessed by calculating n values for a series of ν_2 values and comparing the results with those from the original exponential equation. The results are given in Table I. For ν_2 values below about 1500 cm^{-1} the difference in n values becomes appreciable and increases rapidly with decreasing ν_2, as anticipated. The difference is approximately two conjugated double bonds in the case of the longest sequences found in most types of thermally degraded PVC, although unpublished results from this laboratory show that the highly syndiotactic urea clathrate polymer degraded at 190 °C to 0.1% HCl loss gives $\nu_2 = 1468$ cm^{-1} for an exciting wavelength of 647.1 nm. It would not have been possible to interpret this measurement using the equation based on $\nu_2 = 1474$ cm^{-1} for $n \rightarrow \infty$, but the revised equation gives an n value of 43. The revised (and lower) n values in column 3 of Table I would also be particularly important in the use of the resonance Raman technique for the study of polyacetylenes and degraded poly(vinyl bromide). In the case of the latter, on the basis of one study involving ultraviolet/visible spectroscopy,[20] there is evidence for the presence of sequences with n appreciably in excess of 20.

This emphasizes the need for a reliable value of ν_2 for $n \rightarrow \infty$ as the measured n values are rather critically dependent on it in the case of longer sequences. The present evidence suggests that the adopted value of 1461 cm^{-1} is unlikely to be in error by more than 2 cm^{-1}. Consequently, the n values in column 3 of Table I should be correct to about 0.3 for sequence lengths in the vicinity of 20. This uncertainty is appreciably smaller than that likely to occur because of the lack of specificity of the resonance Raman technique for longer sequences. This factor leads to a ν_2 profile that is the concentration-weighted sum of the individual peaks for the various n values excited by a particular wavelength and, in general, this results in a displacement of the ν_2 profiles to lower frequencies, giving erroneously high values for n.[5]

Evaluation of Other Proposed Relations between ν_2 and n. Lichtmann and Fitchen[11] in their work on polyacetylenes have proposed the simple equation $\nu_2 = b/x + a$, where x is the number of carbon atoms in the conjugated sequence and a is the value of ν_2 for $n \rightarrow \infty$. They used the value 1450 cm^{-1} but did not justify the choice. This equation has been evaluated in the slightly modified form $\nu_2 = a + b/n$. Using $a = 1461$ cm^{-1}, together with the usual data for the low molecular weight conjugated polyenes, one finds that the best-fit routine then gives $\nu_2 = 1461 + 387.69/n$. n values calculated from this equation are given in column 4 of Table I and it is clear that they are wholly unsatisfactory. This is a consequence of the poor goodness of fit that is achieved over the whole of the calibration range. If the equation is fitted to the low molecular weight polyene data only, the goodness of fit is comparable to that obtained with the experimental equation. However, when it is constrained to fit the additional data point $\nu_2 = 1461$ cm^{-1} for $n \rightarrow \infty$, the goodness of fit is poor and there is a large bias. This behavior is markedly different from that of the exponential equation, for which the goodness of fit over the whole range is only marginally worse than that over the limited range covered by the low molecular weight polyenes. Hence, the equation of Lichtmann and Fitchen is not of value for the determination of the sequence lengths of the conjugated polyenes present in degraded PVC and polyacetylene samples. It may also be concluded from this result that the essentially similar equation $\nu_2 = 1459 + 720/(n + 1)$, proposed by Kuzmany,[18] will also not be of value.

Conclusions

1. The best value for ν_2, the C═C stretching mode, for a very long conjugated polyene sequence, is 1461 cm^{-1}, not the figure 1474 cm^{-1} used previously.

2. The variation of ν_2 with conjugated sequence length n is best represented by the exponential equation $\nu_2 = 1461 + 151.24e^{-0.07808n}$. This may be used with confidence to interpret the resonance Raman spectra of degraded PVC and polyacetylene samples. The lack of specificity of the spectra for larger n values is the principal source of error in the determination of conjugated sequence lengths.

3. The errors resulting from the use of the now superseded exponential equation, $\nu_2 = 1474 + 141.67e^{-0.0925n}$, increase rapidly with increasing n. For $n = 20$, the longest sequences commonly encountered in degraded PVC samples, the revised equation gives an n value smaller by about 2.

4. Reciprocal equations of the type $\nu_2 = a + b/n$, proposed by Lichtmann and Fitchen and by Kuzmany, are not satisfactory.

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Investigation by Small-Angle Neutron Scattering of the Chain Conformation in Equilibrium-Swollen Poly(dimethylsiloxane) Networks

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ABSTRACT: The influence of swelling on the dimensions of the elastic chains in poly(dimethylsiloxane) (PDMS) networks prepared by "end-linking" has been investigated by small-angle neutron scattering. Within the limit of experimental accuracy the radius of gyration of the elastic chains in a network swollen in a good solvent of PDMS is the same as that of the linear homologue of the same molecular weight in dilute solution. The functionality of the cross-links and the conditions of network preparation such as the polymer concentration at network formation have no influence on the chain dimensions. No simple general relation exists between the macroscopic and the molecular behavior. However, the results obtained strongly support de Gennes' approach based on the analogy between a semidilute solution of high molecular weight polymer and a cross-linked gel swollen to equilibrium in a good solvent.

Introduction

Swollen networks have been the subject of many investigations during the past 30 years. The experimental results reported in the literature concern mainly their macroscopic behavior, for example, equilibrium swelling and modulus. The interpretation of the network behavior upon swelling in relation to the deformation thus involved at the molecular level has given rise to many controversial discussions.

The recent development of the SANS technique allows one to obtain quantitative information concerning the dimensions of the network strands: the radius of gyration of an elastic chain can be measured accurately and it can be compared with theoretically predicted values.

A recent investigation by SANS of poly(dimethylsiloxane) (PDMS) model networks in the dry state has led to the conclusion that cross-linking (by an "end-linking" reaction) does not affect the dimensions of the polymer chains.[1] This is established regardless of the concentration at which the networks have been generated. Thus, at the molecular level, no memory effect or supercoiling of the elastic chains can be detected.

In the present paper the experimental results of a SANS investigation on the same type of PDMS networks, swollen to equilibrium in cyclohexane, a good solvent of PDMS, are reported and discussed.

Theory of the Swelling Process

In the early theories of rubber elasticity,[2-4] the cross-links of a rubbery network were considered to be firmly embedded in the medium. As a consequence, in a deformed network, the displacement of the cross-links is affine in the macroscopic strain, i.e., the macroscopic swelling.

An alternative approach to rubber elasticity was first developed by James and Guth.[5,6] In their model called "phantom network", the physical role of the chains is to transmit the forces exerted on the junctions. The volume and material existence of the chains are ignored: the latter may go through one another freely and they are consequently not restricted by neighboring chains. The junction points of a phantom network can be characterized by the following behavior: (i) their mean positions are defined by the macroscopic dimensions, (ii) the displacements of these mean positions are affine in the macroscopic strain, and (iii), the fluctuations of the junctions from these mean positions are Gaussian and their magnitude is independent of the strain.

Recently, Flory[7,8] reviewed these rubber elasticity theories. He suggests that these two deformation processes correspond to the upper and lower limits of a chain deformation in a real network. The experimentally observed discrepancies from the phantom network theory could be due to restrictions of the fluctuations around the mean positions of the cross-links. These restrictions are imposed by the neighboring chains and are the chief consequence of entanglements in polymer networks.

de Gennes[9] has proposed a more intuitive model based on the analogy between a swollen gel and a semidilute solution of high molecular weight polymer chains. The mesh size of the network corresponds to the "screening length" of the polymer solution.

As a consequence, the equilibrium segment concentration c_e of the swollen gel is related to the c^* concentration

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