the resonance frequency, as well as collecting data as a function of temperature and coupling this with a more complete theoretical analysis, it will be possible to obtain a more complete characterization of the complex motion found in such systems as these.

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The Resonance Raman Spectrum of Thermally Degraded Poly(vinyl chloride)

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ABSTRACT: The bands which appear in the Raman spectra of poly(vinyl chloride) samples after thermal degradation are shown to be the result of a resonance Raman effect from conjugated polyene sequences formed during the degradation. This is demonstrated by the band intensities, their dependence on the wavelength of the exciting line in relation to the visible absorption spectra of the degraded polymers, the appearance of strong harmonic and combination bands, and the systematic variation of their half-widths. Intensity measurements on the two strongest resonance lines for a series of samples degraded to known extents at 160 and 190° indicate that the average sequence length of the conjugated polyenes increases with increasing time and temperature of degradation.

Liebman, Foltz, Reuwer, and Obremski[1] have recently found bands at 1124 and 1511 cm^{-1} in the Raman spectra of poly(vinyl chloride) samples subjected to various heat treatments. The intensities of these two bands were greater the higher the temperature to which the samples were taken and, for a given temperature, were more intense for slow cooling than for quenching. They concluded that the appearance of the two bands was indicative of a degradation process rather than a predegradative structural reorientation, and they suggested that conjugated polyene sequences were responsible. They did not give quantitative information on the extent to which conjugated polyene sequences were formed but it is evident that, with the conditions employed and in the light of the results reported below, the level must have been below 0.01%. They refer to work by Rimai, Kilponen, and Gill[2] on intense bands at 1158 and 1527 cm^{-1} for β-carotene and at 1158 and 1515 cm^{-1} for lycopene, which were shown to be of enhanced intensity because of the resonance Raman effect, and conclude[1b] that resonance enhancement is the reason why the 1124- and 1511-cm^{-1} bands appear so strongly in degraded PVC samples containing rather low levels of conjugated polyene sequences.

The purpose of the present study has been twofold. The first objective has been to demonstrate unequivocally that the 1124- and 1511-cm^{-1} bands arise from a resonance Raman effect involving the conjugated polyene sequences formed during the thermal degradation of PVC. Second, in view of the high intensity of the two resonance bands it is clearly of interest to study the feasibility of estimating low levels of degradation and, possibly, of obtaining information on the nature of the conjugated polyene sequences.

Experimental Section

The degraded poly(vinyl chloride) samples were prepared from a commercial polymer made by a mass polymerization process. Two series of materials, degraded at 160 and 190° for varying times, were examined. The methods used to degrade the polymer and to estimate the amount of hydrogen chloride evolved, to obtain a quantitative value for the degree of degradation, were improvements on the procedure of Marks, Benton, and Thomas[3] and were introduced to increase the precision of the measurements on lightly degraded materials. The degradation apparatus was flushed with dry nitrogen until the pH titrating–recording system showed no further change, indicating that any atmospheric carbon dioxide admitted with the sample had been expelled. The nitrogen flow was continued for a further 10 min during which time the pH remained constant, indicating the absence of zero drift. The sample well of the heating furnance contained a small quantity of thermally stable oil, to ensure rapid equilibration when the tube containing the polymer was introduced. The hydrogen chloride evolved was carried by the nitrogen stream into a slightly alkaline trap liq-

Table I
Details of Degraded PVC Samples Studied

Degradation temp, °C	Degradation time, min	Degradation, %
150	320	0.11
160	80	0.016
160	104	0.036
160	168	0.0625
160	200	0.1
190	2	0.01
190	8	0.05
190	15	0.1

uid whose pH of about 8 was held constant by the controlled addition of 0.01 *N* caustic soda solution. The volume of added NaOH, equivalent to the level of hydrogen chloride evolved, was recorded continuously as a function of time. Details of the degraded samples used for the Raman measurements are given in Table I.

The Raman spectra were measured with a JEOL JRS-S1 spectrometer, using the 488- and 515-nm lines of an argon ion laser source, and with a Spex Ramalog 4 spectrometer, using the 568- and 647-nm lines of a krypton ion laser. The samples were examined in the solid state, in powdered form in capillary tubes, and in solution in tetrahydrofuran stablized with 0.1% hydroquinone. The ultraviolet–visible absorption spectrum of a typical degraded specimen was measured in solution in tetrahydrofuran on a Beckman DK-2 spectrometer. A commercial sample of β-carotene, giving a 98% assay in terms of the all-trans isomer by ultraviolet spectrophotometry, was used without further purification. It was examined in solution in tetrahydrofuran.

Results and Discussion

Qualitative Studies. Raman spectra of solutions of the degraded polymers were measured using the four exciting lines at 488, 515, 568, and 647 nm. The spectra recorded with the 647-nm line gave no indication of bands in the vicinity of 1124 and 1511 cm^{-1} whereas the 568-nm line gave strong bands at 1113 and 1498 cm^{-1} and the two lines at 488 and 515 nm gave strong bands at 1123 and 1511 cm^{-1}, in good agreement with the frequencies reported by Liebman, *et al.*[1] These results can be interpreted more fully by reference to the ultraviolet–visible absorption spectrum of degraded PVC shown in Figure 1.

The 647-nm exciting line lies to the long wavelength side of the absorption arising from the conjugated polyene sequences resulting from the thermal degradation. Hence, there cannot be a resonance effect, in agreement with the absence of bands near 1120 and 1510 cm^{-1}. The three remaining exciting lines fall within the wavelength region where there is significant polyene absorption and the appearance of two strong bands in each case is a clear indication that they are the result of the resonance Raman effect. The difference in the frequencies of the two when the exciting line is changed from 568 to 515 and 488 nm can be understood from a more detailed consideration of the visible absorption spectrum shown in Figure 1, and from the behavior of the two resonance frequencies as a function of the conjugated sequence length for a number of simple polyenes.

The spectrum of degraded PVC shows discrete band structure in the ultraviolet region and in the visible spectrum to about 450 nm. This is the combined result of two factors.[3] There are present sequences of conjugated double bonds of varying length, each sequence giving three or four well-defined peaks, and as the sequence length increases these peaks move to longer wavelengths, but at a decreasing rate.[4] For a given sequence length three types of conjugated unsaturation occur in degraded PVC and these result from the initial dehydrochlorination step commencing at a

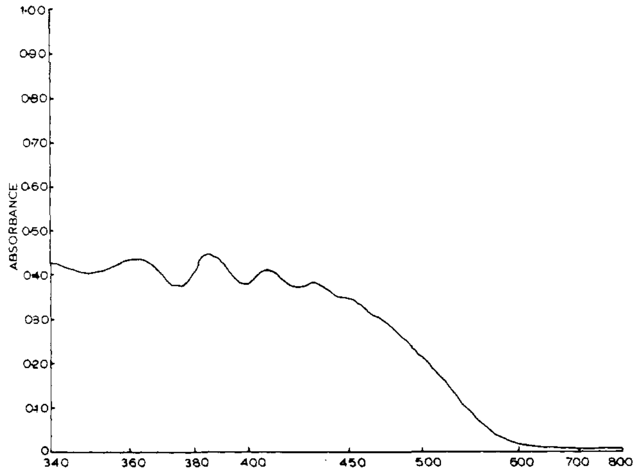

Figure 1. The ultraviolet–visible absorption spectrum of a typical thermally degraded poly(vinyl chloride) sample.

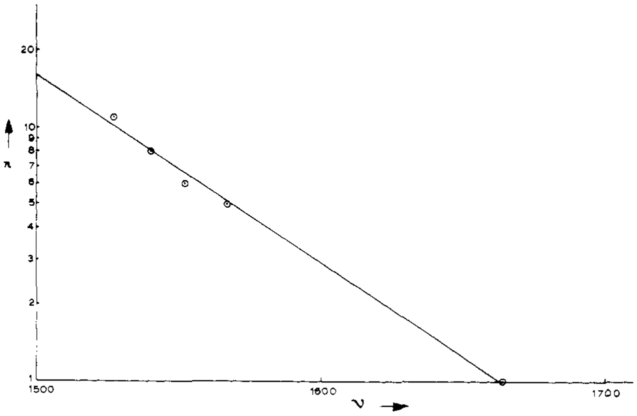

Figure 2. Relation between the C═C stretching frequency and the number of conjugated double bonds in the Raman spectra of polyenes.

chain end, somewhere along a chain and at a branch point, respectively. These three processes result in structures of the type $R_1HC{=}CH\cdot(CH{=}CH)_n\cdot CH{=}CH_2$, $R_1HC{=}CH\cdot(CH{=}CH)_n\cdot CH{=}CHR_2$, and $R_1R_2C{=}CH\cdot(CH{=}CH)_n\cdot CH{=}CHR_3$. With these three structures the three peaks are displaced, respectively, by about 5, 10, and 15 nm from their positions with the unsubstituted polyene structure $H_2C{=}CH\cdot(CH{=}CH)_n\cdot CH{=}CH_2$. The result is that as the conjugated sequence length increases the overlap between the various bands increases and leads to the increased loss of fine structure shown in Figure 1, until it vanishes beyond about 450 nm. However, as the wavelength of the exciting radiation is changed beyond 450 nm it will excite resonance in conjugated polyenes of varying sequence lengths despite the fact that their presence is not wholly apparent from the absorption spectrum.

Several workers[2,5,6] have reported Raman measurements on the C═C stretching mode, which is responsible for the band in the vicinity of 1510 cm^{-1}, for conjugated polyenes of varying sequence lengths and it is clear that the frequency decreases with increasing conjugation. Hence, the frequency of the resonance line should decrease with increasing wavelength of the excitation line, in agreement with the experimental results. Information of a more quantitative nature may be obtained by plotting the published frequencies as a function of the logarithm of the number of conjugated double bonds. The result, shown in Figure 2, is a straight line. When the frequencies obtained from the 488- and 568-nm exciting lines are interpreted on the basis of

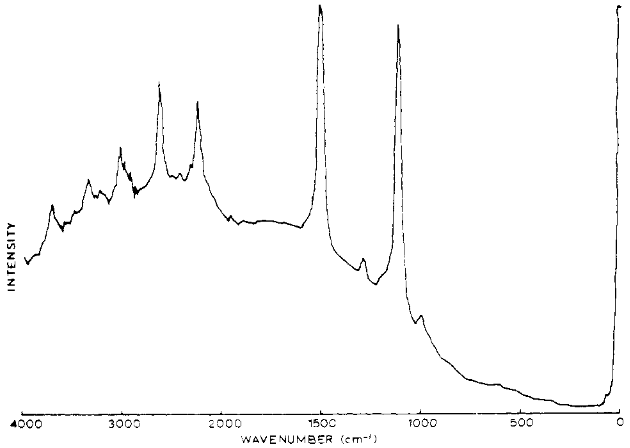

Figure 3. The resonance Raman spectrum of a thermally degraded sample of poly(vinyl chloride).

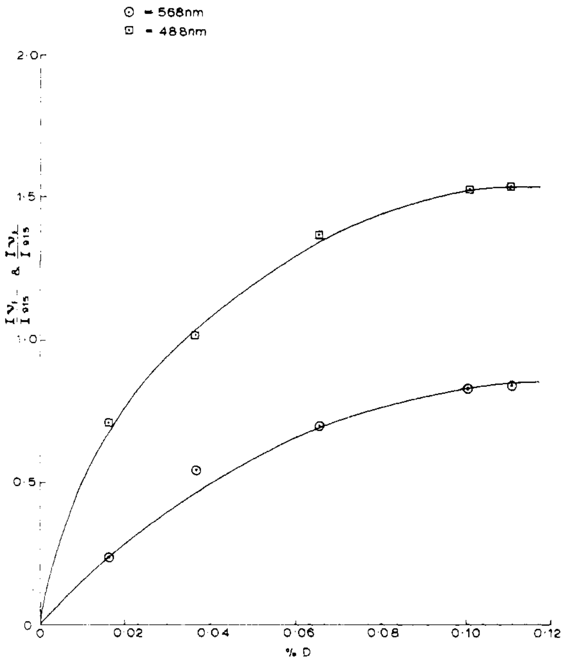

Figure 4. Intensity of the resonance Raman band ν_1 of thermally degraded PVC as a function of percentage degradation, for the exciting wavelengths 488 and 568 nm.

Figure 2 it is evident that resonance is being excited in sequences of approximately 13 and 16 or 17 conjugated double bonds, respectively. The fact that the 488- and 515-nm lines give the same frequency, 1511 cm^{-1}, shows that they are both inducing resonance in polyenes with 13 conjugated double bonds. The frequency of the second resonance band, at about 1120 cm^{-1}, is less sensitive to the conjugation length and is clearly of less value for diagnostic purposes.

Although it is possible[3] to separate the overall ultraviolet–visible absorption spectrum of degraded PVC into the component overlapping bands and, by means of some reasonable assumptions as to their molecular extinction coefficients, obtain quantitative values for conjugated polyene concentration this type of calculation becomes very difficult for the structureless absorption beyond 450 nm. Hence, the availability of a more selective approach, the characteristic C=C stretching frequency (ν_2) in the resonance Raman spectrum, is useful. The present limitation to this new method is the limited number of exciting lines available but the increasing use of tunable dye lasers may soon provide the answer. It would be of considerable value to measure ν_2 as a function of the exciting wavelength at intervals of approximately 10 nm over the range 400 to 600 nm.

Table II
The Resonance Raman Bands of Thermally Degraded PVC Excited by the 515-nm Argon Ion Line

Band position, cm^{-1}	Band half-width, cm^{-1}	Band assignment
1123	32	ν_1
1511	37	ν_2
2242	62	$2\nu_1$
2623	64	$\nu_1 + \nu_2$
3018	~80	$2\nu_2$
3335	~80	$3\nu_1$
3700	~80	$2\nu_1 + \nu_2$
4380	15	?
4473	11	?
4738	13	?

When the degraded samples are examined in the solid state additional weaker bands appear at higher frequencies (Figure 3). These may be assigned to harmonics and combinations of the two strong bands at about 1120 and 1510 cm^{-1}, as given in Table II. The nature of the weak peaks at 4380, 4473, and 4738 cm^{-1} will be discussed below, in connection with their half-widths. Liebman, *et al.*,[1] noted the appearance of some of these bands but did not comment on their significance. One consequence of the resonance Raman effect is the apparent breakdown in the harmonic oscillator selection rules, permitting vibrational overtones and harmonics to appear with intensities comparable to those of the fundamentals.[7] The work of Clark and Mitchell[8] on titanium tetraiodide provides an elegant example of this effect as harmonics of the low-lying fundamental at 161 cm^{-1} as high as the twelfth were observed. The appearance of harmonics and combinations of ν_1 and ν_2 in a variety of substituted conjugated polyenes is also well documented.[2,6,9,10] Another feature of the harmonic and combination bands arising from the resonance Raman effect is that their half-widths increase as the vibrational quantum number increases.[7] This behavior is readily discernible in the results given in Table II and this evidence, together with the high intensity of ν_1 and ν_2, their dependence on the wavelength of the exciting line, and the appearance of harmonic and combination bands, demonstrates unequivocally that the bands at about 1120 and 1510 cm^{-1} in the Raman spectra of thermally degraded PVC samples result from a resonance process. The weak bands at 4380, 4473, and 4738 cm^{-1} are very much sharper than the harmonic and combination bands and obviously are not a result of the resonance effect. They were observed under conditions of relatively high spectrometer gain and are probably instrumental artifacts.

Quantitative Studies. In order to avoid the various problems that arise when making direct intensity measurements the intensities of the 1123- and 1511-cm^{-1} bands were determined as ratios against the solvent tetrahydrofuran band at 915 cm^{-1}. The concentrations of the various degraded samples were adjusted to give solutions of approximately similar absorbance in the visible region of the spectrum, to minimize any errors arising from partial absorption of the exciting radiation, 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 variation of I_{ν_1}/I_{915}, where

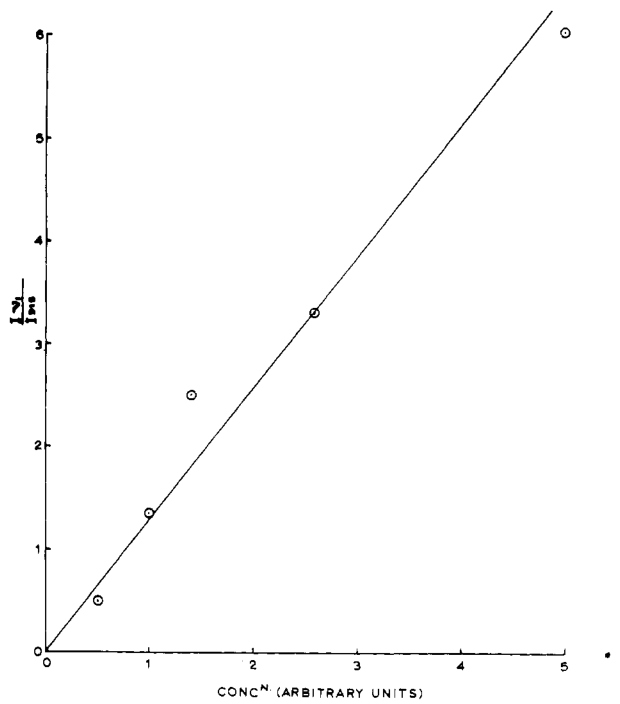

Figure 5. Intensity of the resonance Raman line ν_1 of β-carotene as a function of concentration.

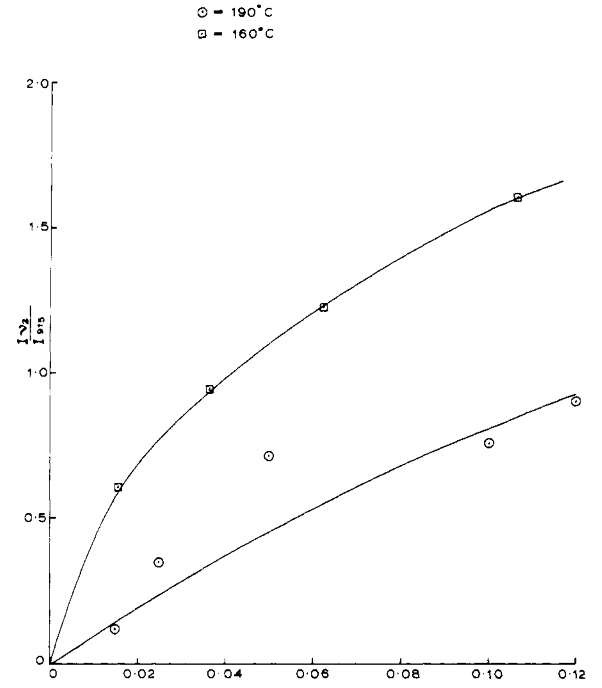

Figure 6. Intensity of the resonance Raman line ν_1 of thermally degraded PVC as a function of percentage degradation for samples degraded at 160 and 190°.

I is the intensity, as a function of percentage degradation at a given temperature for the 488- and 568-nm exciting lines is shown in Figure 4. The corresponding plots of $I\nu_2/I_{915}$ as a function of degradation are similar.

Two features of these curves are of particular interest, namely the markedly nonlinear relation between the intensity ratio and the degree of degradation and the relative intensity ratios for the two exciting wavelengths as a function of the degree of degradation. Although a wholly satisfying explanation of both observations is not possible without a wider range of measurements it is possible to do so tentatively, and in a way which relates the two features. In order to place an interpretation on the nonlinear intensity–degradation curves it is first necessary to establish that instrumental factors are not the cause. This is conveniently done with the model compound β-carotene for which measurements on solutions in tetrahydrofuran gave the linear relationship shown in Figure 5. Hence, it is reasonable to seek an explanation in terms of the molecular structures of the degradation products.

It is not particularly meaningful to compare intensity ratios at the two exciting wavelengths 488 and 568 nm for one sample only because several factors determine the intensity and they are wavelength dependent. The absorbance values of such a sample will not be equal at the two wavelengths; neither are the molar absorptivities nor the concentrations of the polyenes excited to resonance by these two wavelengths equal. However, if the relative intensity ratios at the two wavelengths changes in a systematic way with the percentage degradation this may be interpreted rationally in terms of a change in the average length of the conjugated polyene sequences. Visual inspection of Figure 4 indicates that the ratio of the slopes of the two curves becomes more nearly unity as the percentage degradation increases and this is confirmed by a detailed numerical comparison. This strongly suggests that as the degradation proceeds the proportion of longer conjugated sequences, characterized by use of the 568-nm line, increases relative to the somewhat shorter sequences excited by the 488-nm line.

When the intensity ratios for the two series of samples degraded at 160 and 190° are compared (Figure 6) a clear difference in behavior is evident. An interpretation of the results on a comparative basis presents fewer problems than those shown as Figure 4, because only one exciting wavelength is involved. It is concluded that at the lower degradation temperature the proportion of conjugated sequences excited by the 515-nm line is greater than at the higher degradation temperature. Thus, the concentration of a conjugated polyene of a particular length is a function both of the degradation temperature and the degree of degradation. The greater scatter of the points from the 190° degraded samples in Figure 6 is a consequence of the fact that very short heating times only were required to obtain the smaller extents of degradation and it is difficult to obtain wholly reproducible conditions. The line drawn for these samples, although not the best line through the points indicated, was obtained from a larger number of samples with degradations up to 1.1%, enabling it to be defined more exactly (Figure 7). However, as the maximum degradation at 160° only reached 0.12% a limited part of the 190° curve is shown for comparison purposes in Figure 6.

It is also possible to determine the degree of degradation at very low levels, from measurements on solid samples, by using the intensity ratio of ν_1 or ν_2 against that of a convenient PVC band such as the one at 2915 cm^{-1} arising from the C–H stretching vibration. $I\nu_1/I_{2915}$ or $I\nu_2/I_{2915}$ is then plotted against the degree of degradation measured by HCl evolution, as with the solution measurements, to obtain a calibration curve. In practice only the two samples with the smallest amounts of degradation are really suitable for this purpose because the intensity ratio is too large to measure accurately in the case of the more degraded polymers. In this way it is possible to detect conjugated polyenes down to a level of at least 0.0001%, although a quantitative calibration is not possible because the titrimetric method for measuring hydrogen chloride evolution lacks the sensitivity to be useful at such low levels of degradation. The value of the resonance Raman technique, so far

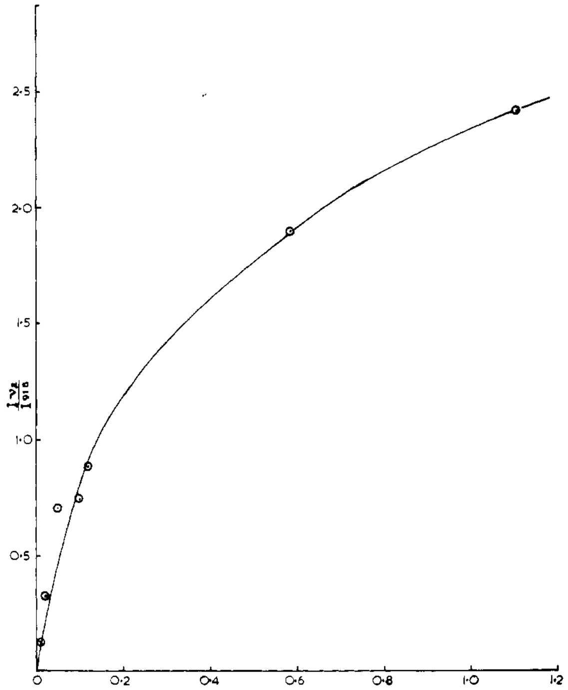

Figure 7. Intensity of the resonance Raman line ν_1 as a function of percentage degradation for PVC samples degraded at 190°.

as its very high sensitivity is concerned, is that it permits solution studies on comparatively insoluble samples with normal levels of degradation. It is interesting to note that the results obtained from measurements on solid samples enable values to be obtained for the approximate degree of degradation of the samples examined by Liebman, *et al.* The most heavily degraded of these contains about 0.003% of conjugated polyenes only, making the assumption that the distribution of sequence lengths is not markedly different from that of the samples examined in the present work. This provides another cogent example of the very high sensitivity of the technique.

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Partially Melted Rodlike Molecules. Light-Scattering and Translational Diffusion

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ABSTRACT: A simple method is presented for determining physical properties of partially melted polymers. The model employed treats "unmelted" regions as rigid rods and "melted" regions as Gaussian random coils. The regions are separated by universal joints. The physical properties explicitly considered are the structure factor for scattered light intensity and the Kirkwood translational diffusion coefficient. Four cases of melting are considered: melting at one end into a single strand; melting at one end into two strands; melting at both ends; and interior melting.

We present a method for determining physical properties of partially melted polymers. The simple model we employ replaces the "unmelted" regions by rigid rods and the "melted" regions by Gaussian random coils. The two properties that are explicitly considered are the Debye intramolecular structure factor $P_n(\theta)$ for the angular distribution of scattered light intensity from a single chain[1]

$$P_n(\theta) = \frac{1}{n^2}\sum_{i=1}^{n}\sum_{j=1}^{n}\langle\exp[i\mathbf{q}\cdot\mathbf{R}_{ij}]\rangle \tag{1}$$

and the Kirkwood expression[2] for the translational diffusion coefficient D

$$D = \frac{kT}{n\zeta}\left[1 + (\zeta/6\pi\eta_0 n)\sum_{i=1}^{n}\sum_{j=1(\neq i)}^{n}\langle\mathbf{R}_{ij}^{-1}\rangle\right] \tag{2}$$

In eq 1 n is the number of segments in the chain; the sums are over all the segments; $|\mathbf{q}| = (4\pi/\lambda_0)\sin\theta$ is the scattering wave vector for light of wavelength λ_0, scattered at angle θ; and $\mathbf{R}_{ij}$ is the vector position between segments i and j. In eq 2 T is the temperature, k is Boltzmann's constant, ζ is the friction coefficient for an individual segment, and η_0 is the solvent viscosity. While the expression for D