LINEAR OPTICAL PROPERTIES OF A SERIES OF POLYACETYLENE Oligomers

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ABSTRACT. A homologous series of polyacetylene oligomers having up to 13 double bonds has been prepared, thus allowing, for the first time, an examination of optical properties of polyenes having enough conjugation length to suggest extrapolation to the polymer. We have measured two linear optical properties, the uv-visible absorption spectra in solid and solution form and the Raman scattering spectra in solid form. Both the lowest energy electronic absorption peak and the frequency of the Raman band associated with the carbon-carbon double bond stretch become linear in 1/n for n ≥ 7. Assuming the validity of the 1/n extrapolation, the results suggest that the familiar forms of polyacetylene have effective conjugation lengths of no more than approximately 30 double bonds.

1. Introduction

Polyacetylene has attracted considerable attention over the past decade as the prototypical conjugated polymer.1 It is now well established that an understanding of the electronic properties of oligomers can contribute significantly to the understanding of conjugated polymers such as polyacetylene. This is particularly true given the highly disordered nature of polyacetylene and other conjugated polymers, since disorder leads to a dispersion in conjugation length, defined as the length over which the π electron structure remains ordered (i.e. planar). Both a chemical defect (chain end, crosslink, or impurity) or a structural defect (rotation out of planarity) can serve to interrupt conjugation. A segment of conjugation length n, where n is the number of double bonds, in a long polymer chain is proposed to have electronic behavior similar to that of an oligomer of length n. There is now much support for and general acceptance of this idea in the literature.2-4

The electronic properties of oligomers generally extrapolate close to those of the corresponding polymer with a 1/n dependence. This has been shown, at least semi-quantitatively, for numerous conjugated polymers (polyacetylene, polydiacetylenes, polythiophene, polyphenylene, etc.) for a variety of
electronic properties, such as optical properties (linear and nonlinear), oxidation/reduction potentials, and ionization potentials. Detailed examination of the n dependence of the electronic properties requires preparation of oligomers over a large range in n approaching as close as possible (in a 1/n sense) to the infinite chain limit. They must also be chemically and isomerically pure.

In this paper we present such a detailed examination of the linear optical properties of a homologous polyene series prepared as described elsewhere by Knoll and Schrock:5

![Polyene structure](image)

These molecules have well-defined n values that range from 1 to 13 and are pure all trans. Specifically, we present and discuss (Section III) the UV-visible adsorption spectra in various solvents and in the solid state. We also present and discuss (Section IV) the n dependence of Raman frequencies and relate these results to the dispersion in these vibrational frequencies that are observed in polyacetylene. Experimental details are given in Section II.

II. Experimental Section

The t-butyl-capped polyenes were prepared via ring-opening of 7,8-Bis(trifluoromethyl)tricyclo[4.2.2.02,5]deca-3,7,9-triene by W(CH-t-Bu)(N-2,6-C6H3-1-Pr2)(O-t-Bu)2 followed by reaction with pivaldehyde or 4,4-dimethyl-trans-2-pentanal. After heating the resulting mixture, the t-butyl capped polyenes, with n from 1 to 13, were isolated by column chromatography and characterized by 1H and 13C NMR studies.5

The samples, in the form of powder or small crystallites, used for Raman scattering and optical absorption were stored under argon in glass vials having Teflon-lined screw-on tops. When not in use in the experiments, the vials were stored at dry ice temperature (-78°C) in the dark. The quality of the sample was checked by noting the absence of any ice on the inside of the cooled vials, as well as the reproducibility of spectra taken before and after several weeks of storage. For the Raman scattering measurements, the vials were allowed to warm to room temperature and then placed directly into the spectrometer such that the sample within the vial was at the focal point of the collecting optics, which were set in near-backscattering geometry. The n-1 polyene was, unlike all the other molecules, a liquid at ambient temperature, and condensing the sample on a wall of the vial with dry ice enabled collection of scattered radiation with the same backscattering geometry. For the optical absorption studies, the vials were opened in an argon dry box to allow removal of small amounts (<1 mg) of sample to several vials, one for each solvent. These vials were capped in the above described manner and transported into the spectroscopy laboratory. There, they were opened to
allow introduction of a several mls of spectroscopy grade solvent (one of sodium dodecyl sulfate in water, and the resulting solution (or, in the case of SDS/H₂O, the suspension obtained after brief sonication of the mixture) was immediately transferred to a quartz cell for absorption measurement with a Perkin-Elmer Lambda 9 spectrophotometer. In some cases, measurements were made on thin films deposited on glass slides by evaporation of dilute solution in a volatile solvent.

Raman spectra were recorded with either of two instruments. The first was a Spex Triplmate spectrometer terminated with a EG&G Princeton Applied Research model 1420 silicon photodiode array detector. The diode array provided a range of approximately 350 cm⁻¹ centered at the set wavelength of the Triplmate; the range was calibrated for wavenumber Raman shift from a particular exciting laser wavelength using known emission lines from low pressure inert gas bulbs. The data collection was managed by a PAR model 1460 optical multi-channel analyzer. The resolution of the diode array was approximately 0.7 cm⁻¹. However, the relatively large slit settings needed to illuminate enough of the diode array to provide the above spectral range contributed a significant instrumental line width to the spectra.

The second instrument was a Spex scanning triple monochromator terminated with a C31034 photomultiplier tube operating in photon-counting mode. In this case the collection of data, at 2 cm⁻¹ resolution, was managed by a Spex Datamate computer. The entrance slit was set at 1 mm, providing a band pass of approximately 10 cm⁻¹.

In both cases, the resulting spectra were transferred to a PC for analysis. No correction for absorption of scattered light by the sample was attempted. For some of the samples that showed significant fluorescence below the Raman bands, a polynomial-fit baseline was subtracted before peak center determination. Peak positions were determined using a center of mass algorithm with the half-maximum intensity used as the cut-off, coded for SpectraCalc software.

III. UV-Visible Spectra

UV-visible spectra of the our model polyenes have been measured in a variety of solvents and in the solid state. As noted in the experimental section, solid-state spectra were recorded for thin films on glass slides or for water dispersions. In both cases, scattering distorts the spectra considerably, though we have been able to ascertain the peak positions for the lowest energy absorption peaks.

Some examples of solution spectra are shown in Figure 1. All solution spectra show a well-defined 0-0 transition followed by a vibrational progression with a spacing on the order of 0.2 eV. As expected, the position of the 0-0 band (E₀) decreases smoothly with increasing chain length. The vibrational spacing also decreases somewhat as chain length increases.
Figure 1. Solution phase uv-vis absorption spectra of four of the t-butyl capped polyenes, n=7-10, as labelled.

Figure 2 summarizes some of the $E_0$ data for our model polyenes. The data for pentane solution are consistent with literature results for other polyene series, though the Figure 2 data are more complete and extend to larger n. For example, the data for dimethylpolyenes for n=1 to 10 would essentially superimpose on our pentane data. We have also studied the solvent dependence of electronic absorption. The solvent series chosen was pentane, cyclohexane, benzene, and carbon disulfide; this series covers a large range in refractive index (1.36 to 1.62) so that solvent polarizability effects on electronic absorption can be determined. We find results which are quite consistent with those of Sklar et al., who studied diphenyl polyenes over the chain length range 1 to 8, and of D'Amico et al. for regular polyenes with n=4-6.

As can be seen in Figure 2, $E_0$ is linear in 1/n at large n, becoming sublinear for n less than roughly 7. This is true for all solvents studied. Solvent polarizability has a substantial effect on $E_0$ but little or no effect on the
Figure 2. Energy of O-O transition ($E_0$) vs. the inverse of the number of double bonds in the molecule. Squares are in pentane solution, diamonds are in CS$_2$ solution, and inverted triangles are in solid form.

The slope of $E_0$ versus $1/n$ in the linear regime. Extrapolation of the curves to the infinite chain limit ($1/n=0$) yields $E_0$ values which are greater than that of polyacetylene ($E_0=1.55$ eV).\textsuperscript{11} This is to be expected since the polymer data are only available for the solid state where the surrounding molecules are polymers with polarizability substantially greater than that of the solvents we have used.

The $E_0$ data for thin films of the model polyenes are significantly lower than those for solutions again because of the higher polarizability of the medium. Analysis of the solid-solvent $E_0$ shifts is complicated by the fact that polyene polarizabilities are expected to vary as a function of $n$. According to recent theoretical studies,\textsuperscript{12} the molecular polarizability of polyenes increases roughly as $n^2$ for small $n$ and begins to approach a linear dependence at roughly $n=10$. The latter is the trivial increase due to the increase in molecular size; therefore in the range the polarizability of the medium would be approaching a constant which would also be expected to be characteristic of the polymer. The consequences for solid-state $E_0$ data such as those shown in
Figure 2 would be a solid-solvent shift which increases as $n$ increases, consistent with our results. We would also expect a saturation in this shift as $n$ increases; our data do not extend to large enough $n$ to state whether this is the case or not. In a more detailed analysis of these results to be published elsewhere, we have shown that molecular polarizabilities derived from the solid-solvent shifts in Figure 2 are consistent with recent theoretical results.\textsuperscript{12}

Extrapolation of the $E_0$ data for the solids to infinite chain length yields 1.33 eV, a value which is significantly less than that observed for polyacetylene. One interpretation of this result is that polyacetylene contains conjugated segments that are no more than 20-30 units in conjugation length. As will be seen in the next section, Raman results are consistent with this interpretation. However, there are several arguments against this interpretation. First, absorption spectra for polyacetylene are generally independent of preparation method; we would expect preparation method to have a significant effect on chemical and physical defects present at a concentration sufficient to produce a limiting chain length of 20-30 double bonds. However, to our knowledge a clear 0-0 transition energy for polymer ($E_p$) has been obtained only for Shirakawa polyacetylene.\textsuperscript{11} Secondly, the solid-solvent shift is expected to saturate for large $n$,\textsuperscript{12} invalidating the extrapolation of the solid-state data. In fact one would expect the solid-state data to eventually parallel solution data (where the polarizability of the medium is constant) as $n$ increases. Finally, it is possible that further theoretical developments will reveal higher order terms in the $n$ dependence of electronic absorption which will cause a sublinear dependence at small values of $n$. Therefore the theoretical justification for the $1/n$ extrapolation is not rigorous.

**IV. Raman Spectra**

Raman scattering has been a prime probe of the structure of conducting polymers, in particular of both cis and trans isomers of polyacetylene.\textsuperscript{14-18} The most salient feature of the Raman spectra obtained from undoped trans-polyacetylene, as by now observed by numerous workers, is the dependence of Raman shift upon excitation wavelength, or dispersion. The two strongest Raman bands in the range corresponding to mid-infrared strength vibration are nominally the carbon-carbon single bond stretch and double bond stretch, although both modes involve a mixture of single and double bond stretches and CCH angle bend. For red excitation, the first appears as an asymmetric band at about 1060 cm\textsuperscript{-1} and the second similarly at about 1460 cm\textsuperscript{-1}; these frequencies are referred to as the primary peaks. As the excitation wavelength is decreased toward the blue, high frequency shoulders develop and increase both in intensity and frequency with decreasing excitation wavelength. For violet excitation they are resolved as satellites on the high energy side of the primary peaks. It has been found that the shapes of the Raman bands, and in particular the relative strengths of the primary and satellite peaks, are dependent upon sample preparation and history, sometimes varying for different sections of a single sample. However, the frequencies of both primary and satellite peaks depend only upon excitation wavelength.

A number of models\textsuperscript{18-23} have been proposed to account for this dispersion, and two are currently in the greatest favor.\textsuperscript{23,24} In the first,\textsuperscript{20,21} the Raman
frequency of either of the two strongest modes is assumed to decrease with increasing conjugation length as is found for the double bond vibration in finite molecular polyenes, according to the form

\[ \nu_{1,2} = (A_{1,2} + B_{1,2}/n) \]  

where 1,2 denote the "single bond" and "double bond" stretch, respectively. The most recently quoted values of the parameters are \( A_1 = 1060 \), \( B_1 = 600 \), \( A_2 = 1450 \), \( B_2 = 500 \), all in \( \text{cm}^{-1} \). As noted above, the lowest electronic excitation energy is also assumed to decrease with increasing conjugation length, consistent with experimental and various theoretical models. According to this model, red excitation probes only those segments with relatively long conjugation lengths, providing their characteristic Raman frequency. As the excitation wavelength is decreased, excitation of the shorter, segments is also allowed, thus showing the characteristic Raman shifts of both. When applied to the Raman spectra of polyacetylene, this model suggests a bimodal distribution of conjugation lengths. The details of the determined distribution of conjugation lengths depends upon the details of the model connecting the shape of the measured Raman spectrum to the excitation wavelength via the conjugation length, and in particular upon the assumed dependencies of excitation energy and Raman shift with respect to that length. It may also be noted that another recent model has proposed a direct relationship between the double bond stretch frequency and the excitation energy, as was previously suggested.

In the second model the cross-section for Raman scattering is expressed as the product of two functions. The independent variable is not the conjugation length, but rather a parameter, \( \lambda \), which is indirectly related to the electron-phonon coupling constant \( \lambda \); the form of the relationship of these two parameters is determined by the specific model for electron-phonon interaction. The Raman frequencies (or, more precisely, the product of the frequencies of three coupled modes) are found to increase with increasing \( \lambda \), while the lowest electronic excitation energy is found to depend upon the related parameter \( \lambda \), e.g., as in a Peierls model. Thus, a correspondence between Raman shift and electronic excitation is determined, as in the previous model. A (unimodal) distribution of values of \( \lambda \) within a particular sample is then allowed. The first component function is peaked at the Raman frequency characteristic of chain segments described by the mode of the population distribution in \( \lambda \). The second component function is peaked at the Raman shift characteristic of chain segments having \( \lambda \) corresponding to the value of \( \lambda \) corresponding to an electronic excitation equal to the photon energy. Thus, red excitation provides only one line (at least for samples prepared via the usual Shirakawa route) because the most probable chain segments have an electronic excitation energy in the red, so that both component functions are peaked at the same Raman shift. As the excitation wavelength is decreased, the sparser population of chain segments having higher excitation energy are allowed to come into resonance, exhibiting their characteristic Raman frequencies as well; multiplication of the two component functions with different peaks provides a double-peaked function consistent with experiment. In this scenario, the interpretation of the Raman dispersion
is critically dependent upon the model used for electron-phonon coupling and the model used for the electronic excitation as a function of that coupling. One could, if desired, decorate this model with the assumption that the parameters $\lambda$ and $\lambda^*$ are primarily dependent upon some form of effective conjugation length. This approach allows a perhaps more easily rationalizable assumption of unimodal population distribution to explain the data.

Figure 3. Raman spectra between 1000-1700 cm$^{-1}$ of t-butyl capped polyenes, for $n=2-12$, as labelled. These spectra were recorded for materials as solids at room temperature with excitation wavelength 6470.9 Å.

At the present time, it is difficult to choose between these models; however, it is clear that both of them would benefit from calibration information: dependence of measured Raman spectra upon polyene segments with known conjugation length, or, through measurement of uv-visible absorption, of known electronic excitation energy. For this reason, we have measured the Raman spectra of these isolated compounds having known conjugation length and absorption energies. In figure 3, we show the the Raman spectra between 1000 and 1700 cm$^{-1}$, for excitation at 6470.9 Å, of the t-butyl capped polyenes for $n$ from 2 to 12. As noted above for polyacetylene, two bands are most prominent for the 12-ene, at the top of the figure. The "single bond stretch" is at 1120 cm$^{-1}$, while the "double bond stretch" is at 1501 cm$^{-1}$. As the conjugation length is decreased, moving down the figure, the shift of both bands are
apparent. The simpler behavior is that of the double bond stretch, which moves monotonically to higher energy as n decreases and is seen centered at 1654 cm\(^{-1}\) for the 2-ene. The single bond stretch similarly begins to increase in frequency as n decreases. It is also seen, however, that another band, which for the 12-ene is not visible on the scale of this figure but is found at 1167 cm\(^{-1}\), grows in magnitude as conjugation length is increased. This band is, in the 12-ene, attributed to the carbon-carbon single bond stretch of the capping t-butyl groups, and as the central portion of the molecule becomes shorter, containing fewer single bonds, the outer segments become relatively more significant. This band is also seen to monotonically increase in frequency. For n<5, however, the "chain" single bond band begins to decrease in frequency.

In fact, higher sensitivity observation of these spectra show that the situation is more complicated. The single bond region has between two and five bands, depending on the molecule, while the double band has between one and three. The number of bands, their position, and their relative intensities for each conjugation length, the correlation of these data with optical absorption energies, and the dependence of oscillator strengths upon excitation wavelength, will be reported in a following publication. Here we focus on the relevance of the conjugation behavior of the three most prominent bands.

Figure 4. Raman frequencies of the strongest band in the carbon-carbon double bond stretch region. The squares are the data for the t-butyl capped polyenes, the +'s are data reported for ethyl ester capped polyenes (Ref. 27) and the diamonds are data reported for unsubstituted polyenes (Ref. 28). The full line is the linear fit to our data for n=7-12, and the dashed line is given by the parameters reported in Ref. 21.
Figure 4 shows our measured values of the double bond stretch, along with similar values for polyenes either totally unsubstituted\textsuperscript{27} or terminated with ethyl ester groups,\textsuperscript{28} as a function of inverse conjugation length $1/n$. Good agreement between data sets for shorter conjugation is found; however, our data provide for the first time, an extension of molecular polyenes to a conjugation length that can support extrapolation to polyacyetylene. The full line is a linear (in inverse conjugation) fit to our data for $n \geq 7$. The dashed line is determined from the parameters as given above for $\nu_2$ as given in Ref. 21. In comparison to these values, we find $A_2 = 1430$ cm$^{-1}$ and $B_2 = 840$ cm$^{-1}$. The ultimate origin of the parameters quoted in Ref. 21 is as follows:\textsuperscript{19,20} the slope was determined by fitting of the values for $n$ between 4 and 7; as can be seen in the figure, this would provide a shallower slope than we have found. The intercept was set to mimic the value for trans-polyacyetylene under red excitation, upon the assumption that this corresponded to infinite conjugation. One can deduce from our determined fit, and the good linearity of the measured data for $n \geq 7$, that a measured Raman shift of $1460$ cm$^{-1}$ for polyacyetylene corresponds to a conjugation length of about 30 double bonds.

Figure 5 shows the dependence of the two most prominent single bond bands in the single bond region as a function of inverse conjugation. Also included

![Figure 5](image_url)

**Figure 5.** Raman frequencies of the two strongest bands in the carbon-carbon single bond region. The squares and +’s are data measured for t-butyl capped polyenes. The triangles are data reported for ethyl ester capped polyenes (Ref. 27) and the diamonds are data reported for unsubstituted polyenes (Ref. 28). The full line is the best fit to our data assuming the same slope as found for the double bond frequencies; the dashed line for comparison is given by the parameters reported in Ref. 21.
for comparison are values reported by other workers for unsubstituted poly-

enes 27 and for di-ethyl ester capped polyenes. 28 Attempts to fit the repul-
dedependent coupling parameter were unsuccessful. For $\nu$ at large $n$, our data
are not precise enough and the linear regime not extended enough for determi-
nation of the linear fit parameters $A_1$, $B_1$. To estimate them, we have assumed
$B_2 = B_1$, since both $\nu_1$ and $\nu_2$ contain strong admixture of single and double
bonds. With this assumption we find for the intercept $A_1 = 1045$ cm$^{-1}$. We
have shown this as a full line, and the line determined from the parameters of
Ref. 21 as a dashed line. The implications of these data for the second model
will be discussed with the full Raman data in a forthcoming publication.

V. Conclusions

In this paper we have described the optical and resonance Raman spectra of a
series of polyenes with the number of double bonds varying from 1 to 13.
These data serve to calibrate the conjugation length dependence of the elec-
tron properties of polyacetylene oligomers beyond the previously existing
data base. Extrapolation of these data to infinite conjugation length allows
comparison to the corresponding values in polyacetylene. This comparison
suggests that the longest conjugation lengths in polyacetylene are only about
30 double bonds. Alternative models, which would allow longer conjugation
lengths, are possible, but they require more elaborate relationships among
conjugation length, optical gap and resonance Raman spectrum, based on assum-
ing a form for the electron phonon coupling.

Acknowledgements: We thank Professor Bryan Kohler for many helpful discus-
sions. R. R. S. thanks the Director, Office of Basic Energy Research, Office of
Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of
Energy (Contract DE-FG02-86ER13564) for support. K. K. thanks the Deutscher
Akademischer Austauschdienst for a NATO fellowship. Part of this research was
funded by a grant from the NSF (to Silbey and Schrock), #DMR87-19217.

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