# Conformational disorder in long polyenes

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We have studied the temperature dependence of the absorption spectra of soluble, conjugated polymers of known chain length ($\sim$100–1000 double bonds), synthesized by Schattenmann *et al.* [Macromolecules **29**, 8990 (1996)] using living polymerization techniques. The polymer spectra show significant redshifts upon cooling from 300 to 80 K. To estimate the distributions of conjugated segments in these conformationally disordered samples, the spectra were fitted to a superposition of absorption spectra of conjugated segments of known lengths. These ''experimental'' distributions of conjugated segments then were compared to those predicted by theoretical models of conformational disorder. Although the low-temperature samples contain significant populations of long segments, the shortest polyene segments dominate all distributions. We compare these experimental results with distributions derived from the model of Yaliraki and Silbey [J. Chem. Phys. **104**, 1245 (1996)]. Adjustment of relevant energy parameters gives good qualitative agreement between the experimental and theoretical distributions in long polyenes. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1416871]

## I. INTRODUCTION

Conjugated polymers are an important class of materials from both the physical and technological standpoints. They are unique in combining semiconducting properties with ease of processing, thus lending themselves to many applications in light-emitting devices and molecular electronics.[1–4] Their electronic states lie in the regime between the relatively localized states of small molecules and the extended states of semiconductors. Linear polyenes in the form of carotenoids such as $\beta$-carotene (Fig. 1) convert light into chemical energy in photobiological processes such as vision and photosynthesis. Recent research on the excited states of these molecules has greatly improved our understanding of the photophysics and photochemistry of short, conjugated $\pi$–electron systems, and a great deal of detailed spectroscopic and theoretical information is now available on the electronic states of carotenoids and model polyenes.[5–8] However, much work remains in understanding the links between the optical properties of short polyenes and conjugated polymers of technological interest.

Polymers have enormous scope for conformational disorder. This can have a strong influence on the electronic and optical properties of conjugated polymers, as the degree of electronic delocalization is strongly dependent on the conformation of the polymer chain. It therefore is important to understand the processes involved in conformational disorder in order to understand fully the photophysics of these materials. Theoretical studies of the electronic states of polyenes[9–12] have concentrated on the room temperature properties of symmetric, short polyenes such as octatetraene (Fig. 1). However, an understanding of the behavior of polymer solutions and films is important both for fundamental science and for designing materials for technological applications. Here, we study the conformational disorder of conjugated polymers in solution as a function of temperature. The change in absorption as a function of temperature provides a critical test for models of conformational disorder.

The transition energy for the electronic origin [(0–0) vibronic band] of the symmetry-allowed ($1\,^1A_g\rightarrow1\,^1B_u$) absorption of short polyenes can be expressed by $E = A + B/N$, where $A$ and $B$ are constants and $N$ is the number of conjugated double bonds in the polyene.[13] This simple equation provides an excellent account of the spectra of model polyenes and carotenoids ($N < 15$). However, the absorptions of long conjugated polymers tend to lie at higher energies than predicted by this equation. This suggests that the polymers are disordered with the polymer chain breaking into shorter conjugated segments. The unresolved shapes of the polymer absorption spectra further implicate some form of conformational disorder. Shorter conjugated molecules, e.g., most carotenoids, exhibit vibronic structure, even in room temperature solutions.[14] The spectra of conjugated polymers can be explained by breaks into shorter segments of different conjugation lengths. The absorptions of these segments overlap, leading to broad, unresolved spectra.

Extrapolation of the empirical $A + B/N$ equation for the $S_0 \rightarrow S_2$ transition energy to $N = \infty$ indicates that an infinitely

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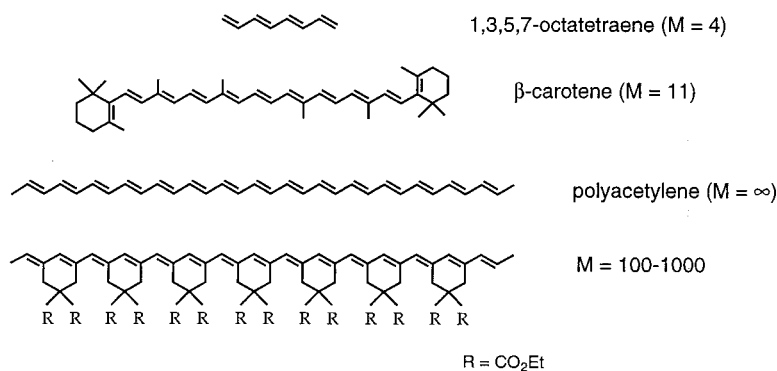
FIG. 1. The molecular structures of the polyenes and polymers referred to in this study. $M$ designates the number of double bonds.

long polyene should absorb ($E_{0-0}$) at about 14 400 cm$^{-1}$ ($\lambda \sim 700$ nm).[13] It was quickly appreciated that the absorption spectra of the majority of polyacetylene and polydiacetylene solutions typically fall well short of this limit, indicating conjugated segments that are substantially shorter than the chain lengths of these polymers. Baughman and Chance,[15,16] Exharos, Risen, and Baughman,[17] Shand *et al.*,[18] and Rossi, Chance, and Silbey[19] developed simple models that invoked a distribution of conjugated segments of different lengths within the polymer. These models explain the relatively broad, blue-shifted absorptions as being due to distributions of conjugated segments of different lengths, where the length of a conjugated segment is defined as the distance ($N$ double bonds) over which the planarity of the polyene backbone is maintained without interruption. This model also explains the dispersion of the vibrational frequencies of C–C and C$=$C symmetric stretches observed in resonance Raman photoselection experiments.[17] Spectra obtained by exciting different regions of the broad polymer absorptions give rise to different vibrational frequencies. The frequency of the C$=$C symmetric stretch also shows an $A + B/N$ dependence, reaching a long polyene limit of 1460 cm$^{-1}$.[18] As originally pointed out by Shand *et al.*[18] this should allow the distribution of conjugated segment lengths to be extracted from the distribution of vibrational frequencies.

More recently, Kohler and Samuel[20] revisited the effect of conformational disorder on the electronic properties of conjugated polymers by fitting absorption spectra of various long-chain polyene oligomers to a superposition of spectra of polyenes with known lengths.[21,22] These fits gave distributions that were dominated by the shortest polyene segments with probabilities rapidly decreasing with increasing segment length. These conclusions were reinforced by a simple model[23] in which each single bond had the same energy barrier for twisting out of the plane of conjugation. Statistical and entropic considerations then rationalize the apparent domination of the shortest segment lengths. Yaliraki and Silbey[24] later extended the earlier work of Rossi *et al.*,[19] to apply a more sophisticated theoretical approach, starting with a microscopic Hamiltonian that contained appropriate steric terms for the torsional motions that disrupt the conjugation. The resulting probability distributions for the lengths of conjugated segments show that short segments are the most probable. Yaliraki and Silbey[24] also used their model to explain the chain-length dependence of the third-order non-linearity observed by Samuel *et al.*[22,25]

The primary purpose of the work presented here is to investigate the temperature dependence of the conformation of conjugated polymers in solution and the validity of current conformational disorder models, especially that of Yaliraki and Silbey. This study also explores the connection between the optical properties of conjugated polymers and the relatively well-understood electronic spectra of short polyenes. We have studied the temperature dependence of the absorption spectra of soluble polyene oligomers of known chain length ($\sim 100$–1000 double bonds), synthesized by Schattenmann *et al.*[26] using living polymerization techniques (Fig. 1). By using conjugated oligomers of well-defined length, we reduce effects that arise from samples containing large variations in chain length. Unlike carotenoids and other simple polyenes, the absorption spectra of the polymers experience significant redshifts when their solutions are cooled. The analysis of these temperature shifts provides further support for conformational disorder in the polymers.

Estimates of conjugation length distributions were obtained by fitting the polymer absorption spectra to superpositions of spectra of conjugated polyene segments using a least-squares method. This extends the approach of Kohler and Samuel,[20] which assumed that the distribution of conjugated segments could be approximated by a sum of Gaussians centered at the shortest conjugation length ($N = 2$). Our approach does not impose any functional form on the distribution of conjugated segments. This yields experimental distributions that can be compared to the distributions predicted by the model of Yaliraki and Silbey.[24] The experimental determination of the distribution of conjugation lengths as a function of temperature provides a demanding test of the conformational disorder model. We find that the Yaliraki and Silbey model shows qualitative agreement with the experimental distributions, but there are some quantitative differences in the temperature dependence of the polymer absorption spectra.

## II. EXPERIMENT

The synthesis of the polymer samples (Fig. 1) has been described by Schattenmann and Schrock.[25–27] Our experi-

ments focused on two members of the series; **A**, which contains ~137 double bonds, with a polydispersity of 1.21 and **B**, which contains ~880 double bonds with a polydispersity of 1.62. These polymers appear as the "3mer" and the "65mer" in Table III of Ref. 25. **A** and **B** contain only 6-membered rings, whereas the samples used by Kohler and Samuel contained random mixtures of 5- and 6-membered rings. Molecular masses and chain lengths were estimated by GPC and matrix-assisted laser desorption ionization (MALDI) time-of-flight (TOF)[25] mass spectrometry. The molecular masses determined from MALDI TOF were approximately half those obtained by GPC. The conjugated polymers used in this study are more rigid than the polystyrene standard used in the GPC measurements, and they appear heavier than they actually are when compared to this standard. Although these molecules are considerably more stable than simple, unsubstituted polyenes such as octatetraene (Fig. 1), our samples showed evidence of degradation since their original synthesis. For example, the 476 nm room temperature absorption maximum of **A** in tetrahydrofuran compares with an original maximum of 480 nm, indicating irreversible breaks in conjugation, possibly due to oxidation of some double bonds.

Absorption spectra were obtained in 2-methyl tetrahydrofuran, a solvent that forms a glass at 135 K, permitting absorption measurements on the polymers over a wide range of temperatures. Absorption spectra were monitored in approximately 50 K intervals between 80 and 300 K, and the spectra were corrected for the absorption of 2-methyl tetrahydrofuran. Scattering effects and the subtraction of the low-temperature solvent absorptions introduce some errors in the 300–350 nm range.

We fit the polymer absorption spectra $[A(E)]$ to a linear superposition of the absorption spectra $[A_N(E)]$ of a set of conjugated segments with $N$ conjugated double bonds

$$A(E) = \sum_{N=1}^{M} a_N A_N(E). \qquad (1)$$

$M$ corresponds to the chain length (maximum possible length of a conjugated segment) of the polymer and $N$ is the length of a given conjugated segment. Since $a_N$ represents the probability of a given segment length, the least-squares fits were constrained to have $a_N \geq 0$. A program was written to perform these non-negative least-squares (NNLS) fits following an algorithm given by Lawson and Hanson.[28] This method has the advantage over those used by Shand *et al.*[18] and Kohler and Samuel[20] in not forcing the distribution of conjugated segments to assume any particular functional form. We also explored fits in which the probability of a given segment length ($a_N$) followed the form suggested by Kohler and Samuel, i.e., a sum of two Gaussians both centered on $N=2$, where the widths and relative amplitudes of the Gaussians were parameters in the least-squares fits.[20] Although the two methods yield similar qualitative results, the direct determination of the population coefficients using the NNLS procedure provided better fits and is the basis for the conclusions presented in this paper.

The mean conjugated segment length $\langle N \rangle$ was obtained from the $a_N$'s by taking a simple weighted average

$$\langle N \rangle = \frac{\sum_{i=1}^{M} i a_i}{\sum_{i=1}^{M} a_i}. \qquad (2)$$

Expressing the polymer absorption as the superposition of the absorptions of conjugated segments [Eq. (1)] requires a complete reference library of the absorption spectra of conjugated segments with $N$ double bonds $[A_N(E)]$. Three elements are required to generate such a library:[20] (i) how the energy of the $S_0 \rightarrow S_2$ absorption band varies with $N$; (ii) how the shape of the absorption spectra (relative Franck–Condon factors) changes with $N$; (iii) how the intensity of the absorption (i.e., the oscillator strength of the $S_0 \rightarrow S_2$ transition) scales with $N$.

To generate a library of absorption spectra, we have used the absorption profile of $\beta$-carotene in pentane as a template and shifted the position of the absorption according to appropriate models. Knoll and Schrock[13] have shown that the transition energies for the electronic origins [(0–0) bands] for $S_0 \rightarrow S_2$ polyene spectra $[E_{0-0}(N)]$ follow a simple empirical relationship: $E_{0-0}(N) = A + B/N$, where $A = 14\,400$ cm$^{-1}$ and $B = 75\,730$ cm$^{-1}$. Although these parameters only apply strictly to di-tert-butyl polyenes in room temperature $n$-pentane, they allow an estimate of the position of the electronic origin for any polyene in any solvent. For example, $E_{0-0} = 21\,300$ cm$^{-1}$ ($\lambda_{0-0} = 470$ nm) for $N = 11$, which is in reasonable agreement with the absorption spectrum of $\beta$-carotene ($\lambda_{0-0} = 483$ nm in room temperature $n$-pentane). We also assume that the Franck–Condon envelopes (relative vibronic intensities and linewidths) for the $S_0 \rightarrow S_2$ transition in $\beta$-carotene are appropriate for shorter and longer conjugated segments. This simplifying assumption probably underestimates the relative intensities of the $S_0 \rightarrow S_2(0-0)$ bands in longer conjugated systems.

If the oscillator strength and Franck–Condon factors were independent of $N$, the absorption of any conjugated segment containing $N$ double bonds at an energy $E$ could be expressed as

$$A_N(E) \propto A_{\text{olig}}(E - (E_N - E_{\text{olig}})), \qquad (3)$$

where $A_{\text{olig}}$ is the absorption of the oligomer template (e.g., $\beta$-carotene), $E_N = A + B/N$, i.e., the 0–0 transition energy predicted by the Knoll and Schrock equation,[13] and $E_{\text{olig}} = A + B/N_{\text{olig}}$, where $N_{\text{olig}}$ is the number of conjugated double bonds in the template used for the vibronic lineshapes. $N_{\text{olig}} = 11$ for $\beta$-carotene.

In order to estimate the change in the intensity of absorption with the number of conjugated double bonds ($N$), we use the squares of the transition dipole moments given by the Hückel spectrum simulator (HSS) model of Kohler.[29] In the HSS model the oscillator strength $[f(N)]$ increases with $N$, approaching a constant asymptote for large $N$.[30] The full expression for the absorption of a conjugated segment with $N$ double bonds at energy $E$ is given by

$$A_N(E) = f(N) A_{\text{olig}}(E - (E_N - E_{\text{olig}})), \qquad (4)$$

where $f(N)$ is the oscillator strength and all other symbols have the same meaning as in Eq. (3).

A library of absorption spectra of conjugated segments with $N = 5 - 100$ was calculated and then used to fit 500 lin-
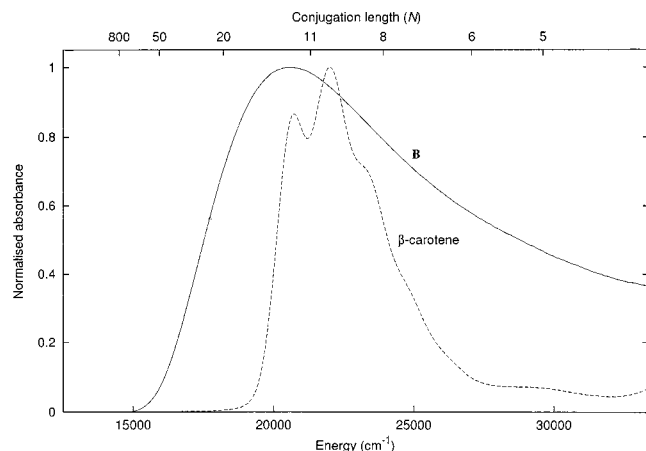
FIG. 2. Absorption spectra of $\beta$-carotene (dashed line) and **B** (solid line) in 2-methyl tetrahydrofuran at 300 K.



FIG. 3. The polyene absorption library used for the NNLS fits presented in this paper. Conjugation lengths are indicated.

early spaced points in the polymer spectrum between 12 500 and 33 333 cm$^{-1}$ (300 and 800 nm). The spectra of the polymers could not be obtained below 300 nm (above 33 333 cm$^{-1}$) due to the strong absorption of the 2-methyl tetrahydrofuran solvent. Within our fitting range, there is no significant overlap between the polymer absorptions and the spectra of conjugated segments with $N=1-4$. The segment lengths $(N)$ in Eq. (1) do not need to be restricted to integers, and improved fits can be obtained by using a finer grid $(\Delta N < 1)$ in the summations. However, the inclusion of nonintegral conjugated segment lengths in the NNLS fits does not appreciably change the distributions. Given the assumptions and approximations of this model, fits using integral conjugated segment lengths were deemed sufficient for analyzing the effects of disorder.

## III. RESULTS

Most of the basic issues involved in interpreting the solution absorption spectra of conjugated polymers in terms of conformational disorder are illustrated in Fig. 2. Polymer **B** exhibits a broad, room temperature absorption typical of many other conjugated polyenes, and its absorption maximum lies only slightly to the red of the $\beta$-carotene template. The upper $x$ axis in this figure shows the $S_0 \rightarrow S_2$ transition energies $(E_{0-0})$ for selected conjugation lengths, as predicted from the results of Knoll and Schrock.[13] While the absorption profile of **B** is somewhat lower in energy than that of $\beta$-carotene $(N=11)$, the electronic origin lies at a significantly higher energy than the $\sim 14\,500$ cm$^{-1}$ predicted by application of $E_{0-0}=A+B/N$ to $N=880$.[13] The room temperature absorption spectrum thus requires that the majority of the absorption of **B** must be ascribed to conjugated segments with $N<20$. The mean segment length clearly is much shorter than the chain length of this polymer.

Figure 3 shows part of the library of polymer absorption spectra that was generated from Eq. (4) and the absorption spectrum of $\beta$-carotene at 300 K. We see that the absorption spectra of short segments (small $N$) in the high-energy end
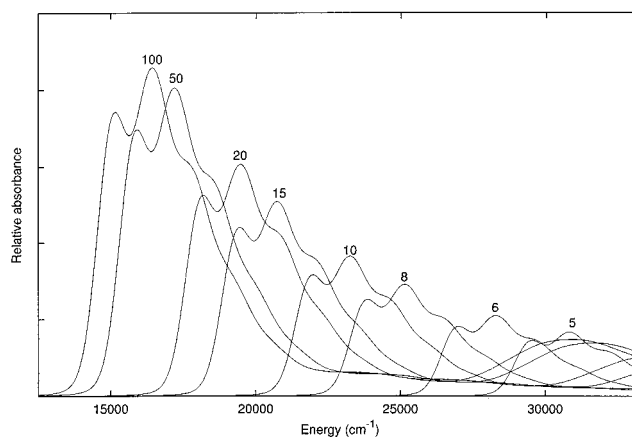
of our fitting range do not overlap very much. (Note that there is some overlap between the absorption of the long segments and the absorption of the short segments in the high-energy range.) As the length of the conjugated segment increases, the spectra move towards lower energies (longer wavelengths) and their $1/N$ dependence gives rise to considerable overlap in the spectra of segments with comparable lengths. In addition, the Kohler HSS model predicts an approximately sixfold increase in the absorptivity [proportional to $f(N)$] in changing from $N=5$ to $N=100$.

The NNLS fit [Eq. (1)] of the 300 K spectrum of **B** is given in Fig. 4(a). The fit is particularly good at low energies, and the inclusion of nonintegral conjugation lengths in the fits would reduce the deviations at higher energies. Figure 4(b) shows the distribution of conjugation lengths resulting from this fit. As previously noted in the work of Kohler and Samuel, the absorption spectrum of this polymer is dominated by contributions from the shortest conjugated segments.

Figure 4(b) also shows the distribution of conjugation lengths obtained from a fit of the spectrum in Fig. 2 to the model of Yaliraki and Silbey.[24] In this model the polymer chain is assumed to distort to form planar, noninteracting segments separated by local breaks in the conjugation. The effective torsional potential is modeled by

$$V(\phi) = -E_c \cos 2\phi - E_s \cos \phi, \tag{5}$$

where $\phi$ is the angle between neighboring segments. The first term represents the "conjugation" energy and the second term deals with "steric hindrance" for the twist of a polyene segment from its idealized planar $(\phi=0)$ geometry. To calculate the spectrum in this figure we use Eq. (10) in Ref. 24 to calculate the segment length distribution and then use our oligomer library to calculate the absorption spectrum. $E_s$ and $E_c$ were varied to get the best fit to the spectrum, giving $E_s=0.024$ eV $(0.92\,kT)$ and the $E_c=0.015$ eV $(0.58\,kT)$ at $T=300$ K. The Yaliraki and Silbey model leads to a continuous function for the distribution of all conjugated segment lengths. In contrast, the NNLS fits can be obtained only for discrete segment lengths with absorptions overlapping our fitting range, which starts at $N=5$ for our data set. We thus have normalized the two segment length distribu-
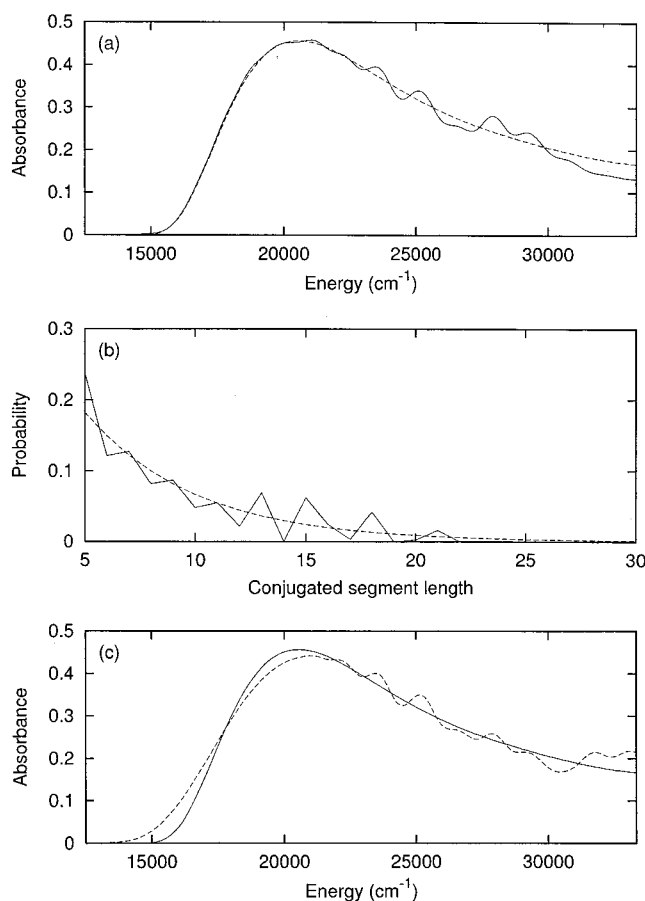
FIG. 4. (a) NNLS fit of the 300 K absorption spectrum of **B** to a superposition of spectra of polyene segments (solid line). Absorption spectrum of **B** at 300 K (dashed line). (b) Conjugated segment length distributions for NNLS fits in (a) (solid line) and fit using the model of Yaliraki and Silbey in (c) (dashed line). (c) Yaliraki and Silbey fit to the 300 K absorption spectrum of **B** (solid line). The absorption spectrum of **B** at 300 K (dashed line).
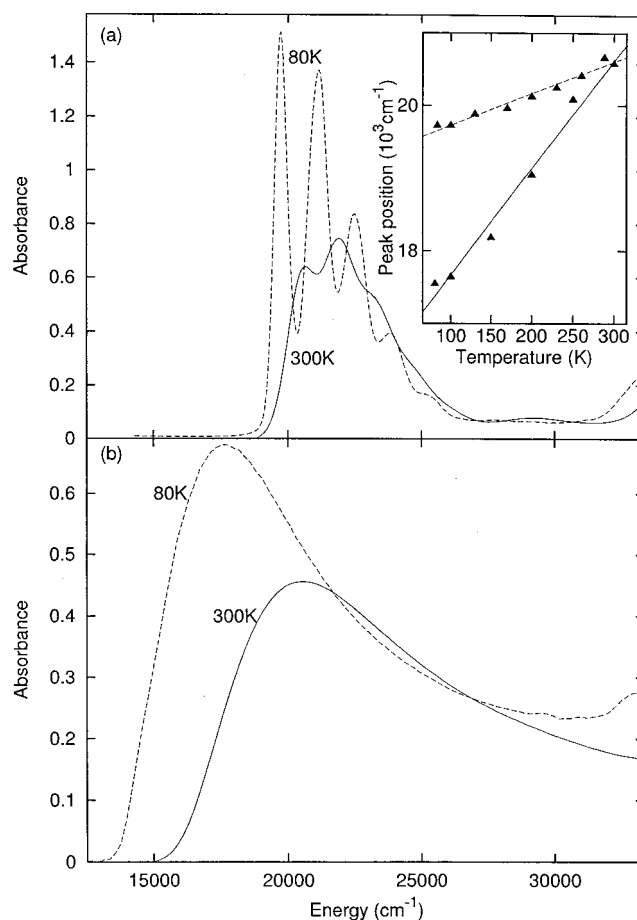


FIG. 5. (a) Absorption spectra of $\beta$-carotene at 80 K (dashed line) and 300 K (solid line) in 2-methyl tetrahydrofuran. (b) Absorption spectra of **B** at 80 K (dashed line) and 300 K (solid line) in 2-methyl tetrahydrofuran. Inset— the shift of absorption peak of **B** (solid line) and $\beta$-carotene (dashed line) with temperature.

tions in Fig. 4(b) such that the area under each is unity between $N=5$ and $N=100$. The two distributions are remarkably similar. The main difference is that the distribution predicted by the Yaliraki and Silbey model has a greater abundance of long conjugated segments ($N>20$). Figure 4(c) gives the absorption spectrum of **B** at 300 K, reconstructed by using Eq. (1) and the distribution [Fig. 4(b)] calculated from the model of Yaliraki and Silbey. The higher abundance of longer conjugated segments in this distribution accounts for the discrepancies between the experimental and theoretical spectra at low energies.

We have further probed the conformational disorder and the validity of the Yaliraki and Silbey model by investigating the temperature dependence of the polymer absorptions. Figure 5(b) shows the absorption of **B** at 300 and 80 K. There is a large redshift in the absorption upon cooling: reddish-orange solutions turn bluish-purple as they are cooled. The solid line in the inset of Fig. 5(a) shows the shift of the peak of absorption of **B** with temperature; the dashed line shows the shift in the lowest energy peak of absorption of $\beta$-carotene over the same temperature range. Figure 5(a) shows the absorption spectra of $\beta$-carotene at 300 and 80 K. Both samples exhibit smooth shifts in their absorption

maxima as the temperature is reduced, and we see no discontinuities near the glass transition temperature (135 K). The spectra of $\beta$-carotene show a much smaller shift ($\sim$one-third that of **B**) in the position of the absorption peak and a significant enhancement of the vibronic structure upon cooling. There are also significant increases in the integral of the intensity of the absorption with respect to energy as the temperature is reduced. $\int A(E) d \ln(E)$ increases by a factor of 1.7 when the solution of **B** is cooled from 300 to 80 K; for $\beta$-carotene the integrated absorption increases by a factor of 1.4 over the same temperature range.

We also have investigated the temperature dependence of the absorption of a shorter polymer (**A** with $\sim$137 double bonds) with the same monomer structure as **B** (Fig. 1). The 300 and 80 K absorption of this polymer are compared with the spectra of **B** in Fig. 6. As expected, the absorption spectra of **A** peak to the blue of **B**. The distributions are quite similar; the shortest segments dominate both; however, **B** has a slightly greater proportion of longer segments.

Figure 7 compares the 80 K absorption of **B** and the spectrum predicted from the model of Yaliraki and Silbey using the values for and $E_c$ and $E_s$ obtained from the room temperature fits that generated the distributions in Figs. 4(b)
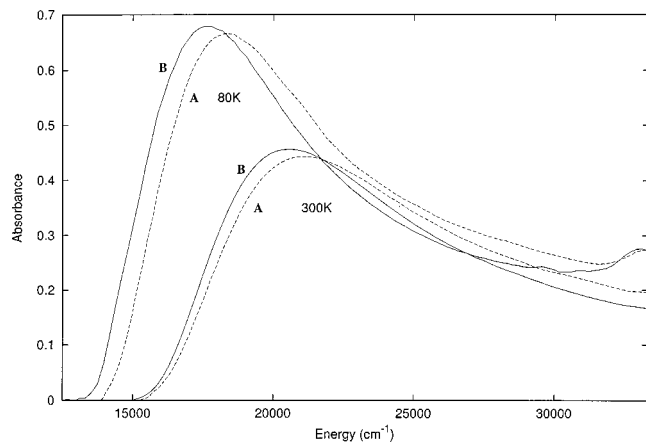
FIG. 6. Absorption spectra at 80 and 300 K of **B** (solid line) and **A** (dashed line) in 2-methyl tetrahydrofuran.

and 4(c). The inset in this figure compares the experimental shift with temperature of the absorption maximum of **B** with spectra calculated from the model of Yaliraki and Silbey, again using $E_c$ and $E_s$ from the room temperature fits. At 80 K the Yaliraki and Silbey distributions contain significant contributions from segments with more than 100 double bonds. However, the spectra used in this figure were generated using a library of segments with $N = 5 - 100$. Due to the convergence of the $S_0 \rightarrow S_2$ transition energy ($E_{0-0}$) at long segment lengths, the error introduced by using this restricted library underestimates the redshift by no more than 650 cm$^{-1}$. The spectra calculated from the model of Yaliraki and Silbey show a greater shift with temperature than the measured spectra. The experimental NNLS fits work well at all temperatures and show increases in the abundance of longer conjugated segments with cooling. This is illustrated in Table I, which shows the mean segment lengths calculated using Eq. (2) for both **A** and **B**. We see that the mean conjugation length ($\langle N \rangle$) for **A** is shorter than **B** and that $\langle N \rangle$ increases for both polymers as the temperature is reduced.
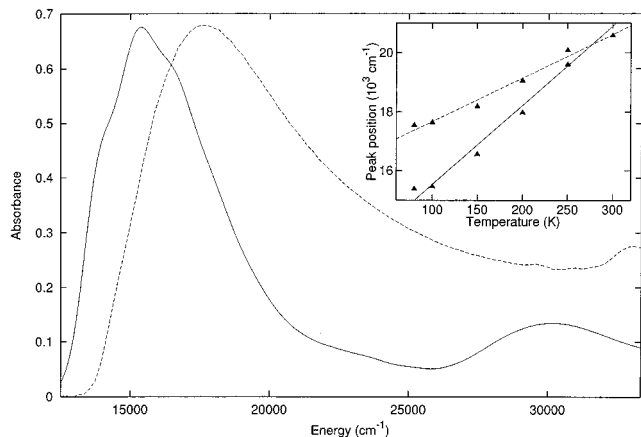


FIG. 7. Comparison of the Yaliraki and Silbey prediction (solid line) of the absorption spectrum of **B** at 80 K with experiment (dashed line). Inset— comparison of the temperature dependence of the peak of absorption of **B** given by the model of Yaliraki and Silbey (solid line) and experiment (dashed line).

TABLE I. Mean conjugation length $\langle N \rangle$ calculated using Eq. (2) for **A** and **B**.

| Temperature (K) | A | B |
| --- | --- | --- |
| 80 | 11.7 | 13.8 |
| 100 | 11.5 | 13.8 |
| 150 | 10.1 | 12.7 |
| 200 | 9.2 | 10.7 |
| 250 | 8.8 | 9.3 |
| 300 | 8.5 | 9 |

## IV. DISCUSSION

The fit to the absorption spectrum of **B** at 300 K [Fig. 4(a)] supports the notion that the absorption of these and other conjugated polymers can be described by a superposition of spectra of shorter conjugated segments. These fits are much better at low energies due to the $A + B/N$ dependence of polyene $S_0 \rightarrow S_2$ transition energies ($E_{0-0}$). For longer conjugated segments (larger values of $N$) there are a relatively large number of library members with similar, overlapping absorptions, leading to a smooth superposition at the low-energy end of our fitting range. Similarly, the relatively poor fits at high energies are the result of restricting the absorption library to integral $N$, giving a small number of widely spaced segment spectra at the high-energy end of our fitting range. Inclusion of nonintegral $N$s improves the fits but does not significantly change the distribution in Fig. 4(b) or the values of $\langle N \rangle$ in Table I. The dominance of short conjugated segments in the NNLS distribution [Fig. 4(b)] also was observed by Kohler and Samuel[20] for a different family of polymers. These distributions can be rationalized using a simple model in which the probability of a single bond twisting out of the plane of conjugation is independent of its position in the polyene chain.[23] The more sophisticated theoretical treatment of Yaliraki and Silbey[24] also predicts that the shortest conjugated segments should dominate the distribution of segment lengths in these polymers [see Fig. 4(b)]. However, the Yaliraki/Silbey model appears to overestimate the contributions of long polyene segments in the polymer solutions at 300 K.

By exploring the effect of temperature on polymer and carotenoid absorptions we are able to probe these models of conformational disorder and to better understand the torsional motions that disrupt conjugation. These measurements take advantage of the high solubilities of the polymers, even in low-temperature glasses. Cooling $\beta$-carotene solution from 300 to 80 K results in a significant narrowing of the vibronic structure and a modest ($\sim$950 cm$^{-1}$) redshift of its absorption [Fig. 5(a)]. The well-resolved vibronic structure implies that there is a narrow set of conformations, in which the 11 double bonds form a single, relatively planar conjugated segment. The redshift and narrowing of vibronic lines observed upon cooling can be explained by a combination of subtle conformational effects (e.g., the 11 double bonds become more planar) and stronger solvent interactions due to solvent contraction and the increased polarizability of 2-methyl-tetrahydrofuran at low temperatures. Cooling $\beta$-carotene to 80 K also results in an approximately 40%

increase in its integrated absorption spectrum. This change may be ascribed to the effects of solvent contraction and the increase in $f(N)$ in the more planar species.

In comparison with $\beta$-carotene, the spectrum of **B** shows a large ($\sim$3000 cm$^{-1}$) redshift and no narrowing upon cooling [Fig. 5(b)]. The redshift indicates that there is a greater abundance of longer segments, i.e., some of the conformational breaks are removed when the temperature is lowered. The smooth spectrum at low temperature indicates that conformational breaks are still present, even when the thermal energy is greatly reduced. The apparent shift to conformational distributions containing longer conjugated segments is consistent with estimates of a few $kT_{room}$ for the torsional barriers ($\sim E_c + E_s$) for breaking the planes of conjugation in these systems. Furthermore, as observed for $\beta$-carotene, the absorption maximum smoothly shifts to longer wavelengths as the temperature is lowered from 300 to 80 K. The absence of discontinuities indicates that the redshifted spectra cannot be ascribed to solvent phase changes or the effects of folding or aggregation. The low-temperature sample contains a small population of species that absorb at <15 000 cm$^{-1}$, suggesting a significant abundance of polymer segments with extremely long conjugation lengths. If this interpretation is correct, these low-temperature samples provide a unique opportunity to use photoselection techniques, e.g., resonance Raman spectroscopy and time-resolved optical spectroscopy, to study the properties of exceptionally long conjugated systems.

The temperature dependencies of the absorption spectra of **A** ($\sim$137 double bonds) and **B** ($\sim$880 double bonds) are compared in Fig. 6. The differences between the absorption spectra of **A** and **B** are more pronounced at low temperature with **B** containing a larger concentration of species absorbing at <15 000 cm$^{-1}$. The relative insensitivity of the absorption spectra to chain length is consistent with the model of Yaliraki and Silbey. For long chains, the model predicts that the distribution of segment lengths becomes relatively insensitive to the chain length. Also, it should be noted that the integrated absorption strengths, $\int A(E) d \ln(E)$, increase by a factor of 1.7 when the polymer solutions are cooled from 300 to 80 K, whereas they increase by a factor of 1.4 for $\beta$-carotene. While some of this change may be due to the $\sim$20% reduction in the solvent volume, the major part of this increase must be attributed to changes in the oscillator strength [$f(N)$] of the polyene $S_0 \rightarrow S_2$ transitions with increasing $N$.

The model of Yaliraki and Silbey appears to overestimate the redshift of the polymer absorptions with decreasing temperature (Fig. 7). Several explanations merit consideration: First, the assumption of this model simply may be unrealistic, leading to overestimates of the importance of long conjugated segments in the distributions. It also is possible that the increased viscosity of cooled solution increases the barriers to torsional motion ($\sim E_c + E_s$), partially locking the samples into their high temperature conformations. In addition to conformational breaks in conjugation, these samples may also contain irreversible chemical breaks due to defects in the original polymerizations or subsequent chemical degradation. The lengths of the conjugated segments then

would be limited by both chemical and conformational disruptions. It is important to note that the spectra reported by Schattenmann *et al.*[25] originally exhibited absorption maxima (in room temperature THF) at 480 nm for **A** and 507 nm for **B**. The spectra of solutions of **A** and **B** used in this study were significantly blueshifted with absorption maxima at 474 and 486 nm, indicating that our samples have additional chemical breaks in conjugation, e.g., due to oxidation. The spectral shifts induced by lowering the temperature are thus all the more remarkable, and we would expect even larger temperature-dependent effects in polymer samples without irreparable chemical breaks in conjugation. This also suggests that the Yaliraki and Silbey model should perform even better in accounting for the absorption spectra of fresh samples. In principle, the presence of permanent, random defects also could be incorporated into the calculations of the conjugation length distributions.

The results presented here support the original hypotheses of Exharos *et al.*,[17] Shand *et al.*,[18] and others concerning absorption maxima and vibrational frequencies that fall well short of those expected for extremely long conjugated systems. The simple theoretical models proposed by Kohler and Woehl[23] and by Yaliraki and Silbey[24] predict distributions of conjugated segment lengths that are similar at least qualitatively to those extracted from our empirical NNLS fits. Nevertheless, these models and the fits deserve careful scrutiny. Most problematic are the predictions that solutions of even relatively short conjugated systems also should have length distributions that are dominated by the shortest conjugation segments. However, the vibronically resolved absorption spectra of molecules such as $\beta$-carotene in Fig. 5(a) point to the absence of appreciable concentrations of conjugated segments with $N < 11$, and neither the Kohler/Woehl nor the Yaliraki/Silbey models account for the observation that conjugation lengths are equal to chain lengths in simple polyenes and carotenoids. More work will be needed to develop models that establish a smooth connection between the optical properties of short and long polyene systems.

It also is important to acknowledge the inherent simplifications of a linear superposition model [Eq. (1)], which assumes a collection of essentially orthogonal, noninteracting segments. Coupling between these segments could result in the transfer of electronic energy to neighboring sequences on very short time scales. This would lead to homogeneous broadening due to the extremely rapid dephasing of the $S_2$ excited states. One might then question whether the vibronic profiles and linewidths of molecules such as $\beta$-carotene are appropriate for describing the linewidths observed for the polymers. Resonance Raman excitation profiles have been used to differentiate between homogeneous and inhomogeneous components of vibronic linewidths.[31,32] Recent time-resolved experiments by Scholes *et al.*[33] indicate that inhomogeneous broadening plays an important role in the optical properties of substituted polyphenylenevinylenes (PPVs). If the polymer spectra are broadened beyond the $\sim$500–1000 cm$^{-1}$ of homogeneous and inhomogeneous broadening experienced by $\beta$-carotene and lycopene,[31,32] Eq. (1) will then overestimate the importance of long polyene segments in accounting for absorption on the long wavelength end of the

polymer solution spectra. However, given that short polyene segments already dominate our distributions, corrections for the effects of coupling would not significantly modify the conclusions presented in this paper.

In addition to making realistic choices for vibronic band shapes and intensities, any model that purports to extract population distributions from polymer absorption spectra also must accurately portray the dependence of the $S_0 \rightarrow S_2$ oscillator strengths on conjugation length. The spectra used in our library of polyene absorptions[9,20] conform to the experimental observation of an apparent leveling off of oscillator strengths for polyenes with 2–12 double bonds.[34,35] However, there is very little experimental or theoretical guidance on the behavior of oscillator strengths in the long polyene limit. It is tempting to ascribe the extra increase in the integrated absorption strength of **B** compared to $\beta$-carotene to the increase in the population of longer segments that carry larger $S_0 \rightarrow S_2$ oscillator strengths. However, the function we have used for $f(N)$ cannot rationalize the ~70% increase in absorption when cooling **B** from 300 to 80 K. As we have shown, understanding the origins of the absorption spectra of conjugated polymers is a challenging problem with many factors to take into account. However, even with the simplified approach presented here it is possible to gain considerable insight into the importance of conformational disorder in these systems.

## V. CONCLUSIONS

Previous research on polyacetylenes, polydiacetylenes, and other conjugated polymers indicates that conformational disorder has a profound effect on the photophysics of these systems. Conformational disorder explains the typically broad and blueshifted optical spectra of these polymers and the dispersion of their C=C vibrational frequencies in resonance Raman excitation experiments. We have shown that the absorption spectra may be expressed as the linear superposition of absorptions of shorter conjugated segments. Our fits yield distributions of conjugation lengths that are dominated by short polyene segments. The average conjugation length increases when the polymers are cooled from room temperature to 80 K, providing additional evidence for conformational disorder. In addition, the low-temperature samples show absorptions ($\lambda > 600$ nm) that can be attributed to a significant abundance of polyenes with extremely long conjugation lengths.

The temperature dependence of the polymer spectra allows a demanding test of the conformational disorder model of Yaliraki and Silbey, and we find qualitative agreement between experiment and theory. However, for our samples the Yaliraki and Silbey model overestimates both the importance of long polyene segments in the distributions and the redshift of the absorption profile upon cooling. Further refinement of the conjugated segment length distribution awaits a more accurate picture of how the transition energies, oscillator strengths, and vibronic intensities of polyene absorptions change with the length of conjugation. Current models of conformational disorder assume that the probability for twisting about a given single bond is independent of the geometry of adjacent bonds. The models also neglect the

possibility of chemical breaks in conjugation and the interactions between polyene segments. It is important to note that these simple models predict that short segments also should dominate the conformational distributions of short polyenes and carotenoids. However, these molecules show no evidence for species with conjugation lengths significantly different than the full chain lengths. A major challenge for theory thus is to account for polyene absorption spectra in both the short and long chain length limits.

## ACKNOWLEDGMENTS

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