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 ($\sim$

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

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

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 β-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 β-carotene ($N=11$), the electronic origin lies at a significantly higher energy than the ~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 β-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 ϕ is the angle between neighboring segments. The

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**

and 4(c). The inset in this figure compares the experimental shift with temperature of the absorption maximum of **B** with

increase in its integrated absorption spectrum. This change

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 β-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

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