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Optical Spectroscopy of Long Polyenes

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We have synthesized a homologous series of soluble, linearly conjugated oligomers and related polymers using molybdenum alkylidene catalysts. We have developed HPLC procedures to isolate the oligomers according to their chain lengths and have obtained the absorption spectra of the purified oligomers in room temperature solutions and in 77 K glasses. The oligomer absorption spectra are structured and remarkably similar to those of simple polyenes with comparable numbers of conjugated double bonds (N). Furthermore, the electronic origins of the low-energy, strongly allowed $1^1A_g^- \rightarrow 1^1B_u^+$ transitions follow the $E(0-0) = A + B/N$ behavior previously noted in simple polyenes and carotenoids. Extrapolation of data for oligomers with $N = 3-15$ suggests $E(0-0) \approx 14\,000$ cm^{-1} ($\lambda \approx 700$ nm) in the long polyene limit. The oligomer spectra exhibit modest red shifts on cooling, suggesting minimal conformational disorder in the room temperature samples. In contrast, the absorption spectrum of the longest soluble polymer ($N > 100$) in this series undergoes a significant red shift and sharpening upon cooling from 300 to 77 K. This indicates that the room temperature polymer is disordered due to relatively low thermal barriers for torsional motion about carbon−carbon single bonds. Unlike the longer oligomers, the low-temperature absorption of the polymer shows well-defined vibronic structure. The polymerization reactions lead to a distribution of conjugation lengths in the unpurified polymer sample. However, the vibronically resolved, red-shifted absorption at low temperature ($\lambda(0-0) = 630$ nm) indicates that this distribution is dominated by species with very long conjugation lengths. The resolution of the low-temperature spectrum argues that the absorption is due to the superposition of almost identical $1^1A_g^- \rightarrow 1^1B_u^+$ spectra and that all conjugated segments in this sample absorb near the asymptotic limit ($1/N \approx 0$).

Introduction

The electronic states of linear polyenes have been the objects of considerable experimental and theoretical scrutiny in recent years.[1−5] Simple, symmetrical linear polyenes such as *all-trans*-octatetraene (Figure 1) have been studied in low-temperature mixed crystals and in supersonic jets. One- and two-photon absorption, fluorescence, and fluorescence excitation experiments have allowed the mapping of polyene electronic, vibronic, and rovibronic states in considerable detail in these prototypical linearly conjugated systems.[6,7] This has led to a deeper understanding of the electronic properties of one-dimensional π-electron systems on a framework of alternating double and single bonds.[8] One of the most important outcomes of the work on simple polyenes was the discovery of a low-energy, symmetry-forbidden ($1^1A_g^- \rightarrow 2^1A_g^-$) transition that lies below the strongly allowed $1^1A_g^- \rightarrow 1^1B_u^+$ transitions associated with the elevation of an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) in simple versions of molecular orbital theory. The presence of the low-lying $2^1A_g^-$ state has important implications for the spectroscopy and photochemistry of these molecules. For example, the relatively long radiative lifetime of the $2^1A_g^-$ state leads to the dominance of nonradiative decay processes in long polyene systems.

Studies on the simple polyenes prompted interest in the spectroscopy and photochemistry of longer polyenes and an understanding of how the energetics and dynamics of polyene excited states change with the increase in the π-electron delocalization. Naturally occurring polyenes in the form of carotenoids (Figure 1)[7] play important roles in photobiology, for example, vision and photosynthesis, as well as lending their broad palette of colors to plants and animals.[4,9−11] Systematic extension of the optical studies carried out on model polyenes has provided a catalog of the energies of the $2^1A_g^-$ and $1^1B_u^+$ states in several homologous series of synthetic and naturally occurring carotenoids.[12−14] Transition energies shift to lower energy with increasing conjugation and often are expressed by $E(0-0) = A + B/N$, where N is the number of conjugated double bonds in the polyene. For the $1^1A_g^- \rightarrow 1^1B_u^+$ transitions, this empirical approximation finds support from simple models of $\pi\pi^*$ transitions in linear systems, both in the particle in a box model (for which $A \approx 0$) and in extensions that include

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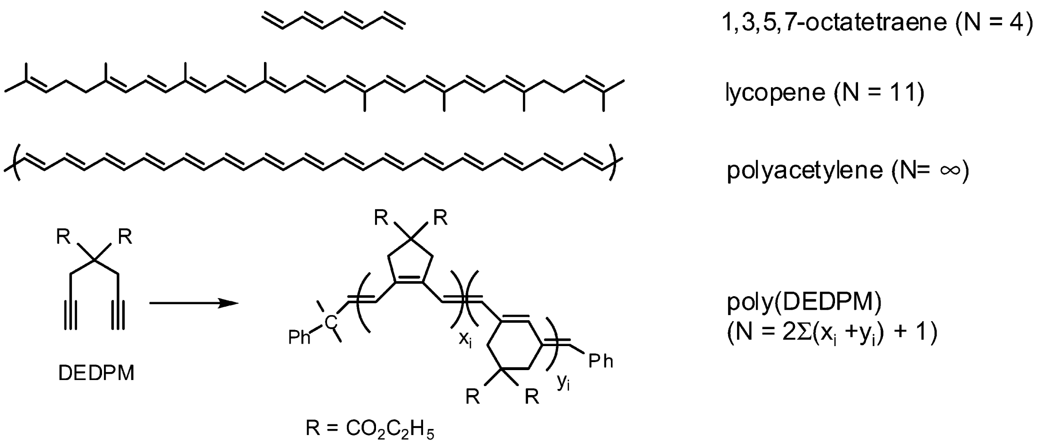

Figure 1. Structures of polyenes including octatetraene, lycopene, polyacetylene, and the generic poly(DEPDM) oligomer.

alternation in bond lengths along the carbon chain.[15,16] Inclusion of bond alternation, in fact, provided an early explanation of the asymptotic approach of the $1^1A_g^- \rightarrow 1^1B_u^+$ transitions to a long polyene limit ($E(0-0) \approx 14\,000$ cm^{-1}, $\lambda(0-0) \approx 700$ nm).[15,16]

The systematic study of "long" polyenes has been limited to molecules with less than ∼15 double bonds, due to the lack of suitable synthetic routes, including limitations on the biosynthesis of carotenoids.[9] At the other extreme, considerable progress has been made in the synthesis and optical characterization of long conjugated polymers such as polyacetylene (Figure 1). These studies have been motivated in large part by the semiconducting properties of such molecules and the advent of rational synthetic approaches toward the design of molecules for displays, lasers, photovoltaics, and nonlinear optical materials.[17,18] However, much work remains in understanding the bridge between the optical properties of the "short" ($N < 15$) and "long" ($N > 100$) polyenes. In a recent study we explored models of conformational disorder that rationalize the broad, blue-shifted absorption spectra (due to the strongly allowed $1^1A_g^- \rightarrow 1^1B_u^+$ transitions) of conjugated polymers in room temperature solutions.[19] These models account for the broad polymer absorptions as superpositions of spectra due to shorter polyene segments. The models also predict significant conformational disorder in short polyenes and carotenoids such as lycopene (Figure 1).[20,21] However, the vibronically resolved absorption spectra of simple polyenes and carotenoids indicate minimal conformational disorder with conjugation lengths being equal to the full chain lengths in these systems. The connections between the absorption spectra of short and long linearly conjugated systems thus deserve more detailed experimental and theoretical attention.

To develop improved theoretical descriptions that establish a smooth connection between the optical properties of short polyenes and conjugated polymers, we have initiated a study of the spectroscopy of oligomers of intermediate conjugation length. Here we address this issue in a new way, which combines living polymerization and HPLC techniques to obtain purified oligomers with a wide range of chain lengths. The targets of these initial investigations are obtained from the living cyclopolymerization of diethyldipropargylmalonate (DEDPM) (Figure 1), using the alkylidene complex $Mo(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)(CHCMe_2Ph)(OCMe(CF_3)_2)$ as a catalyst.[22] Varying the ratio of monomer to catalyst provides control over the distributions of chain lengths. HPLC techniques have been used to isolate oligomers with a specific number of monomers (x), providing conjugated polyenes with a given number of double bonds ($N = 2x + 1$). In principle, the syntheses allow the formation of a complicated distribution of oligomers with combinations of five- and six-membered rings and cis and trans isomers. However, the absorption spectra of chromatographic fractions exhibit vibronic structure, indicating the production of a narrow range of similar molecules with a given chain length. This allows a systematic comparison between the absorption spectra of simple polyenes[7] and oligomers[7] with identical conjugation lengths ($N = 5-13$). The spectra of the oligomers are remarkably similar to those of simple polyenes and carotenoids.[7] Using an effective number of conjugated double bonds to account for the terminal phenyl substituent in the oligomers gives excellent fits to $E = A + B/N$ with parameters comparable to those found for simple polyenes. These fits suggest that in the limit of infinite conjugation the electronic origin of the $1^1A_g^- \rightarrow 1^1B_u^+$ transition should approach ∼700 nm.

We also have obtained the room temperature and 77 K absorption spectra of a high molecular weight polymer of DEDPM. Lowering the temperature results in a red shift and a significant increase in vibronic structure, indicating that the room temperature sample is conformationally disordered. Despite the distribution of chain lengths and the wide range of structural variations allowed by the cyclopolymerizations, the low-temperature absorption spectrum of the polymer is extraordinarily simple. The low-temperature, $1^1A_g^- \rightarrow 1^1B_u^+$ spectrum is compared with that predicted from extrapolation of the oligomer spectra to $1/N = 0$. The red-shifted, vibronically resolved spectrum suggests the dominance of very long conjugation lengths in the low-temperature, polymer solution.

Experimental Section

Synthesis. Oligomer and polymer samples were synthesized by the living cyclopolymerization of diethyldipropargylmalonate (DEDPM, Figure 1), following the previous work of Fox et al.[22] A typical polymerization was carried out as follows: A solution of DEDPM (321 mg (1.36 mmol) in 3.5 mL of dimethoxyethane (DME)) was added to a solution of $Mo(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)(CHCMe_2\text{-}Ph)(OCMe(CF_3)_2)_2$ (35 mg (46 μmol) in 9 mL of DME). The deep purple reaction mixture was stirred for 90 min and then quenched by the addition of benzaldehyde (30 μL). The resulting mixture was stirred overnight and concentrated in vacuo. The solid residue was washed in pentane (4 × 5 mL) and the resulting orange solution evaporated to give an orange crystalline solid containing a mixture of short oligomers. The molybdenum impurities in the pentane-insoluble fraction were removed by dissolving the polymer in DME (1.5 mL) and precipitating into

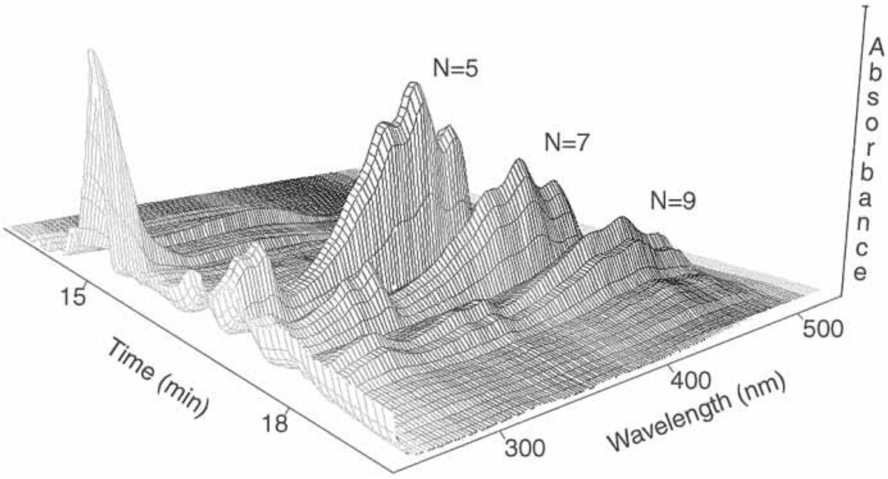

Figure 2. HPLC separation of a typical oligomer sample.

pentane (100 mL). The polymer was collected by filtration to give a deep purple powder. Varying the ratio of monomer to catalyst gave different proportions of oligomers (3−15 monomers) and very long polymers. This synthesis did not produce polymers with intermediate conjugation lengths.

Analysis and Purification of Samples. The polymer samples were analyzed by GPC/light scattering (690 nm) in THF. The polymer used for our optical measurements (whose synthesis is described above) had an average molar mass (M_n) of $\sim 3.9 \times 10^5$ with a polydispersity (M_w/M_n) of 1.05. These values translate into polymers with $\sim 1650 \pm 380$ (1σ) monomers and $\sim 3300 \pm 760$ (1σ) double bonds. There is a large discrepancy between the apparent size of these polymers and the shorter chain lengths expected from a living polymerization with a 30-fold excess of monomer over catalyst. This suggests that, for at least some fraction of the sample, the rate of propagation is significantly higher than the rate of initiation in these syntheses.[17]

Reactions carried out with low ratios of monomer to catalyst (<10:1) contained significant proportions of the shorter oligomers. The molecular mass distributions of these polyenes were analyzed with an IonSpec High-Resolution MALDI-ICR-FTMS. Samples were deposited on the sample probe and a 337-nm N_2 laser used for desorption. A variety of matrix/solvent combinations were explored. The most effective preparation method involved the use of a saturated solution of 2,5-dihydrobenzoic acid in acetone (10 μL) and 0.1 M solutions of alkali metal salts (1 μL). Cationized oligomers were most efficiently produced by applying the matrix to the probe tip and then adding the sample (in $CHCl_3$) to the dried matrix. This results in a MALDI spectrum dominated by monocations separated by the 236.2 mass of a single monomer. The oligomer distributions are influenced by the cation, for example, larger oligomers appeared to be more abundant for Cs^+-cationized oligomers than for Na^+- or Li^+-cationized oligomers.

The oligomers were purified on an Agilent 1100 series HPLC and 5 μm Waters YMC C_{30}-reverse-phase column (4.6 mm × 250 mm), employing a photodiode array as the detector. The mobile phase initially was 98:2 v/v methanol/water with a linear solvent gradient changing to 60:40 v/v methanol/ethyl acetate during the first 12 min. The HPLC then was run in isocratic mode for another 8 min when the solvent was changed to pure methanol. Collection of three-dimensional data files (absorption vs time vs wavelength) proved crucial in identifying chromatography peaks with oligomers with given conjugation lengths. Samples were collected from the HPLC, evaporated under a stream of nitrogen, and reconstituted into *n*-pentane or 2-methyl-THF for spectroscopic measurements. Solutions of purified samples (as well as the original oligomer/polymer solutions) appear to be relatively robust with respect to oxidation and other degradation processes compared with carotenoids and simple, unsubstituted polyenes.

Spectroscopic Methods. Absorption spectra at room temperature and at 77 K were recorded on a Cary 400 spectrophotometer. Low-temperature spectra were obtained from samples in a 1-cm Suprasil cryogenic cuvette (NSG) suspended in a copper holder within a flat-windowed (Suprasil) liquid-nitrogen cryostat. The liquid nitrogen was in contact with the copper cuvette holder but did not cover the optical path through the cuvette. The low-temperature spectra were corrected for the absorption and light scattering of the 2-methyl-THF glass and other optical components. Absorption spectra were converted to an energy scale and fitted to sums of Gaussians to establish the transition energies and bandwidths of the electronic origins and other vibronic bands. Line widths of the Gaussians were constrained to be less than 2500 cm^{-1}. For some fits to longer oligomers in room temperature solutions the number of Gaussians and their relative amplitudes were restricted based on the fits of the better resolved absorption spectra of the low-temperature glasses.

Results and Discussion

HPLC Analysis and Purification of Oligomers. A three-dimensional chromatogram of one of the pentane-soluble oligomer extracts is presented in Figure 2. The systematic shift in the $1^1A_g^- \rightarrow 1^1B_u^+$ spectrum to longer wavelengths with increasing retention time illustrates the ability of the C_{30}-reverse-phase column to partition the shorter oligomers according to their chain lengths. The absorption spectra are very similar to those of simple polyenes and carotenoids with comparable lengths of conjugation. The presence of well-resolved "cis-peaks" ($1^1A_g^- \rightarrow 1^1A_g^+$) at higher transition energies than the main absorption bands, a common signature in the spectra of polyenes and carotenoids,[9,10] has been used to confirm the presence of "cis" double bonds in the polyene chains. For the oligomers shown in Figure 1, true cis isomers would require the presence of five-membered rings. However, similar spectral features could arise from oligomers constructed from six-membered rings. Their unsymmetrical, disubstituted double bonds also would distort the center of symmetry associated with the trans bonds of simple, unsubstituted polyenes. For a given

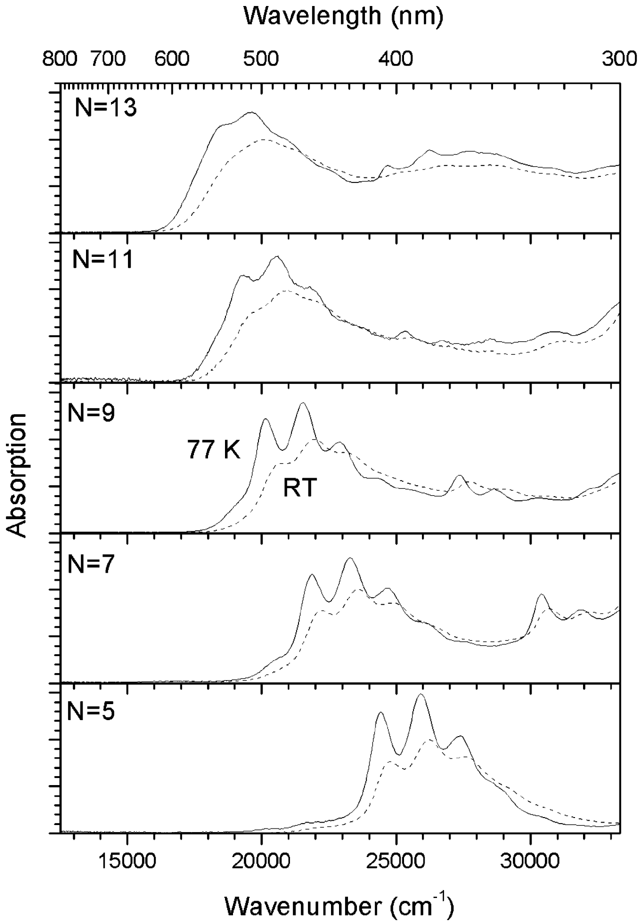

Figure 3. Room temperature (dashed lines) and 77 K absorption spectra (solid lines) of oligomers ($N = 5, 7, 9, 11, 13$) in 2-methyl-THF. Room temperature spectra are normalized.

number of monomers, the mechanism for cyclopolymerization allows the formation of many combinations of "cis" and "trans" isomers and mixtures of five- and six-membered rings. However, the relatively well-resolved vibronic features and the small variations in the absorption spectra across each HPLC peak (Figure 2) suggest that our samples contain a narrow range of oligomer structures.

Collection of individual bands from the HPLC allows more detailed spectroscopic studies of the absorptions of oligomers with a given N. The 300 K absorption spectra of oligomers with $N = 5-13$ are presented in Figure 3. The identification of a given sample with a particular conjugation length is based on comparisons with spectra of model polyenes[23] and greatly simplified by the fact that the polymerization method only produces oligomers with an odd number of double bonds. The absorption spectra show a systematic broadening with increasing N. This most likely is due to the larger number of permutations of molecular structures with a given number of monomers and our inability to resolve these components with current HPLC techniques. Subtle, but significant shifts due to variations in the number and position of "cis" double bonds and the number and position of the five- and six-membered rings would give rise to a more complicated superposition of spectra in these samples. In considering the effect of "cis" linkages on the spectra, it is interesting to note that the introduction of a central cis double bond in β-carotene ($N = 11$) shifts the (0−0) of its primary absorption band by ~500 cm^{-1} (from 496 to 484 nm).[9] An exhaustive study of almost 40 isomers of lycopene (also $N = 11$) showed that multiple cis bonds could shift the principle absorption band ($1^1A_g^- \rightarrow 1^1B_u^+$) by as much as 40 nm (~2000 cm^{-1}).[9] The resolution of our spectra indicates that the purified oligomers are dominated by a relatively small number of geometric isomers with almost identical spectra.

The absorption spectra of the oligomers are similar to those of simple all-trans and cis polyenes and carotenoids with comparable conjugation lengths. High-resolution absorption and emission spectra of short model polyenes are dominated by combinations of totally symmetric C−C and C═C stretching modes of ~1200 and ~1600 cm^{-1}.[1,24,25] These frequencies decrease with increasing conjugation. For example, ν(C═C) shows a $1/N$ dependence with a long polyene limit of 1440 cm^{-1}.[26−28] In low-resolution spectra, vibronic combinations of ν(C−C) and ν(C═C) coalesce into progressions of what appears to be a single, intermediate frequency of 1300−1400 cm^{-1}. For example, the absorption spectrum of the $N = 5$ oligomer shows vibronic intervals of ~1400 cm^{-1} (Figure 3). The spectra of the longer oligomers are systematically broader than those of simple polyenes but still allow the accurate determination of the electronic origins (Table 1) and other vibronic bands by fitting the absorption spectra to sums of Gaussians. We then identify the electronic origins as the average $1^1A_g^- \rightarrow 1^1B_u^+$ transition energy for the collection of oligomers with a given conjugation length.

The relative homogeneity of samples collected from the HPLC is reinforced by the well-resolved, low-temperature absorption spectra obtained in 77 K glasses (Figure 3). As with carotenoids and other polyenes, cooling the oligomer samples results in small red shifts (300−400 cm^{-1}) as well as significant enhancements in the vibronic resolution of the main absorption bands. The relatively small temperature-dependent shifts are comparable to those observed in the absorption spectra of simple, model polyenes, and a significant fraction of these shifts can be attributed to the higher polarizability of the low-temperature glasses. The room temperature oligomers thus show little evidence for conformational disorder, in contrast with their longer polymer relatives.[19] Theoretical models for conformational disorder in conjugated polymers[20,21] also predict significant disorder in the oligomers and other short polyenes, and the current work reinforces the need for improved models that account for the spectra of both short and long conjugated systems. This study also emphasizes the importance of the temperature dependence of absorption spectra as a probe of conformational disorder.

Comparison of Oligomer Absorption Transition Energies with Those of Simple Polyenes. The work of Knoll and Schrock on *all-trans-tert*-butyl-capped polyenes with $N = 2-15$ (also synthesized using living polymerization techniques) provides a canonical set of data for understanding the absorption spectra of the DEPDM oligomers.[23] In comparing spectra of molecules with the same conjugation lengths, we need to account for the effects of the terminal phenyl groups (Figure 1) on the oligomer spectra. We rely on the analysis presented by Kohler[29] of the differences between the $1^1A_g^- \rightarrow 1^1B_u^+$ transitions energies of a series of unsubstituted α,ω-dialkyl polyenes and corresponding α,ω-diphenyl polyenes. Comparison of the (0−0) bands for these two series led to an empirical "effective conjugation length" ($N_{\text{effective}} = N + 3.2$), reflecting the additional conjugation provided by the terminal phenyl substituents.[29] For the monophenyl-substituted oligomers, we assume $N_{\text{effective}} = N + 1.6$.

Figure 4 and Table 1 compare the energies of the electronic origins for the $1^1A_g^- \rightarrow 1^1B_u^+$ transitions in the two polyene series. Given the structural differences between the two series,

TABLE 1: Electronic Origins ($E(0-0)$) for $1^1A_g^- \rightarrow 1^1B_u^+$ Transitions in Di-*tert*-butyl Polyenes and Polyene Oligomers

	$E(0-0)$/cm^{-1}			
N	di-*tert*-butyl polyenes in 300 K *n*-pentane[a]	oligomers in 300 K *n*-pentane	oligomers in 300 K 2-Me-THF	oligomers in 77 K 2-Me-THF
5	29 155	25 010(10)[b]	24 730(10)	24 450(10)
7	25 240	22 430(10)	22 120(15)	21 880(10)
9	22 790	21 070(20)	20 560(10)	20 180(5)
11	21 330	19 970(280)	19 680(60)	19 280(50)
13	20 240		18 800(25)	18 350(45)
A[c]	14 400(100)	14 500(180)	14 000(140)	13 400(130)
B[c]	75 800(900)	69 300(1600)	70 700(1400)	73 000(1200)

[a] Knoll and Schrock, ref 23. [b] Estimated standard deviations are given in parentheses. [c] Parameters from fits to $E(0-0) = A + B/N_{\text{effective}}$. For the di-*tert*-butyl polyenes, $N_{\text{effective}} = N$, and the fit given for this series is for N =7, 8, 9, 10, 11, and 13.[23] For the oligomers, $N_{\text{effective}} = N + 1.6$.

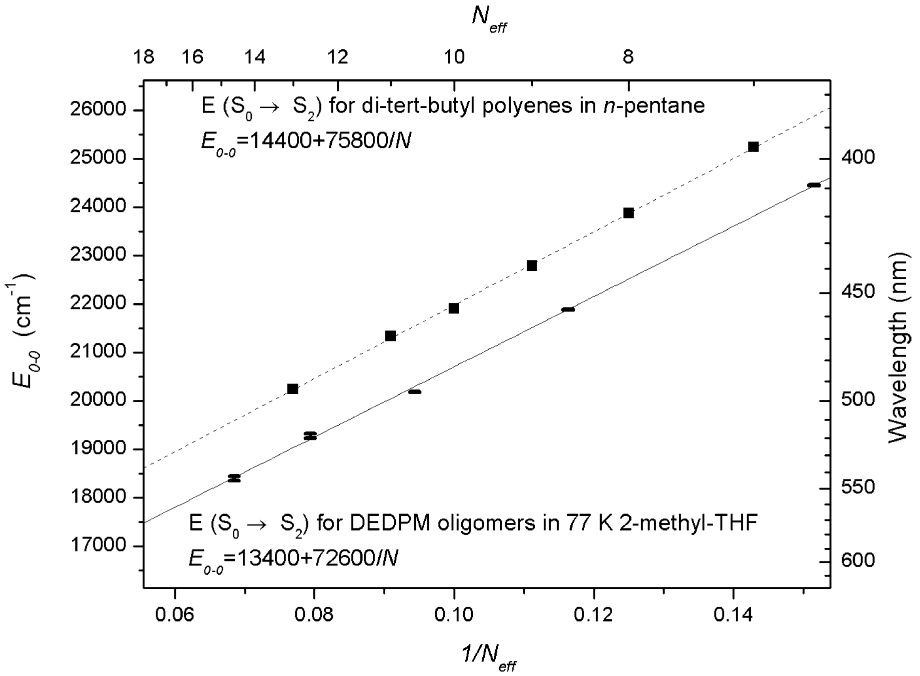

Figure 4. $E(0-0)$ versus $1/N_{\text{effective}}$ for $1^1A_g \rightarrow 1^1B_u$ absorptions of *all-trans-di-tert*-butyl polyenes (in room temperature *n*-pentane)[23] and of DEPDM oligomers (in 77 K 2-methyl-THF). For the *di-tert*-butyl polyenes, $N_{\text{effective}} = N$. For the monophenyl-substituted oligomers, $N_{\text{effective}} = N + 1.6$.

the $E(0-0)$ versus $1/N_{\text{effective}}$ plots are quite similar, indicating the fundamental importance of the conjugation length in determining the optical properties of these molecules. The relatively good agreement between the (0−0) energies of the two series confirms the assignments of oligomer lengths (number of monomers) based on the chromatograms and absorption data. The oligomers exhibit a small, but systematic red shift in transition energies for a given $N_{\text{effective}}$. Similar, though somewhat larger shifts are observed in the more highly substituted carotenoids[14] and can be ascribed to the relative stabilization of the $1^1B_u^+$ excited state by electron-withdrawing substituents along the polyene chains. In addition to these structural effects, the fits summarized in Table 1 also show that the spectra are systematically red shifted (~600−800 cm^{-1}) in changing the oligomer environment from 300 K *n*-pentane to 77 K 2-methyl-THF. Approximately half of this shift is due to the effects of cooling and half to the difference in solvents.

The Absorption Spectra of Long Polyenes. The $1^1A_g^- \rightarrow 1^1B_u^+$ transition energies of these oligomers, the *tert*-butyl-polyenes,[23] and a series of open-chain carotenoids[14] exhibit linear ($1/N_{\text{effective}}$) behavior over the range of conjugation lengths ($N \approx 5-15$) currently available from the syntheses and HPLC purification procedures. Extrapolation of these transition energies to $N_{\text{effective}} = \infty$ predicts $\lambda(0-0) \approx 700$ nm in the infinite polyene limit. The production of high molecular weight, soluble, conjugated polymers in the living polymerizations provides a unique opportunity to explore the accuracy of these extrapolations.

The room temperature and 77 K absorption spectra of one of our highest molecular weight polymers (molecular mass ~4 × 10^5) are presented in Figure 5. Lowering the temperature changes the color of the polymer solution from purple to blue. The red shift in absorption and the parallel enhancement in the vibronic resolution of this spectrum are most easily explained by a reduction in conformational disorder in this inhomogeneous collection of long polyene chains. Our previous analysis of similar temperature effects in related polymers (containing all six-member rings) provided an estimate of the changes in the distribution of conjugation lengths as a function of temperature.[19] Comparison of these distributions with the theoretical model of Yaliraki and Silbey[21] gave realistic energy parameters (~kT at room temperature) for the torsional motion of polyene single bonds from their idealized planar geometries. This model assumes that spectra are due to a linear superposition of spectra of noninteracting polyene segments. It does not include the effects of intersegment coupling which would lead to homogeneous broadening due to the dephasing of the 1^1B_u excited states.[30] Most likely, both heterogeneous and homogeneous

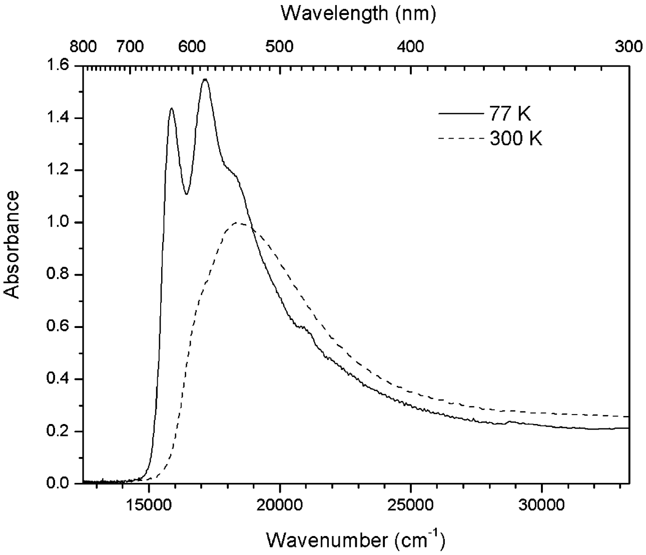

Figure 5. Room temperature and 77 K absorption spectra of DEPDM polymer in 2-methyl-THF.

effects are important in accounting for the transition energies and vibronic bandwidths in these systems.

Our discussion will focus on the low-temperature absorption spectrum of the polymer (Figure 5). The spectrum of this high molecular weight, polydisperse sample is exceptionally simple, with vibronic progressions (~1200 cm^{-1}, cf. ~1400 cm^{-1} for the $N = 5$ oligomer) and Franck−Condon factors very similar to those seen in the low-temperature optical spectra of the oligomers (Figure 3) and simple polyenes.[4] The apparent loss of resolution in the blue, asymmetric tail of the absorption may, in part, be due to the presence of shorter polyene impurities in the polymer sample. The well-resolved (0−0) band (631 nm, 15 800 cm^{-1}) approaches, but does not reach, the infinite polyene limit (746 nm, 13 400 cm^{-1}) predicted by extrapolation of the oligomer $1/N$ plots. The vibronic resolution observed in the spectrum (fwhm ~ 800 cm^{-1}) provides the strongest evidence that polyene segments with long conjugation lengths dominate the low-temperature spectrum. Light-scattering experiments indicate that the unpurified polymer has a ±20% deviation (1σ) in the distribution of chain lengths. This plus the effects of conformational disorder within a given polyene would give rise to a broad superposition of spectra unless all conjugated segments had very similar spectra. The simplest explanation for a homogeneous distribution of spectra in such a highly heterogeneous sample is that all of the polyene segments in the low-temperature sample are sufficiently long ($1/N \approx 0$) to have spectra very close to the long polyene limit.

Given the results of the GPC/light scattering experiments and the estimated size of the polymers ($N > 1000$), it might seem obvious that the polymer solution should absorb near the long polyene ($1/N = 0$) limit. However, the room temperature solution absorption spectra of almost all high molecular weight conjugated polymers tend to be unresolved and at significantly shorter wavelengths than predicted by extrapolations of spectra of shorter oligomers. As discussed above, this indicates that even in samples with no chemical defects, the polymers are disordered into collections of chains with relatively short conjugated segments.[20,21,27,28] We recently demonstrated that cooling overcomes at least some of this disorder and that the temperature dependence of the spectra is consistent with relatively small barriers for twisting about the carbon−carbon single bonds.[19] Room temperature solution spectra of shorter polyenes and carotenoids ($N = 5-15$), on the other hand, tend to be vibronically resolved and show smaller red shifts upon cooling. These molecules thus appear to be planar with minimal conformational disorder at room temperature, and their full conjugation lengths are manifested in their resolved spectra. The typically broad spectra of many conjugated polymers thus might be rationalized as an entropic/statistical effect, due to the higher probability of conformational breaks in conjugation in polyenes possessing a large number of carbon−carbon single bonds.[21,31,32]

We also can relate the low-temperature absorption spectrum of the polymer (Figure 5) to the variation in chain lengths ($\Delta(N)/N \approx 0.20$) derived from the polydispersity (1.05) determined from light-scattering experiments. If the $E = A + B/N$ approximation remained valid for large N and if sample polydispersity were the only source of spectral broadening, the range in transition energies (ΔE) due to the heterogeneity of conjugation lengths would be given by $\Delta E = B(\Delta(N)/N^2)$. This implies $\Delta E \approx 15\,000$ cm^{-1}/N, based on the B values given in Table 1. For shorter polymers and oligomers with comparable polydispersities, for example, $N = 10 \pm 2$, $\Delta E \approx 1500$ cm^{-1} and the range of transition energies would exceed the 1200−1300 cm^{-1} vibronic intervals observed in typical polyene spectra. This, plus additional sources of broadening, for example, heterogeneous solvent interactions, conformational disorder, vibrational congestion, and the effects of homogeneous coupling, would ensure broad absorption spectra in short polyenes with polydispersities similar to that of the polymer. However, for $N = 100 \pm 20$, $\Delta E \approx 150$ cm^{-1} and the heterogeneity in conjugation lengths would only be a minor contributor to the ~800 cm^{-1} vibronic line width of the (0−0) band in the low-temperature glass (Figure 5). It is important to note that this is less than the ~1150 cm^{-1} width observed in the low-temperature (0−0) band of the shortest, purified oligomer ($N = 5$, Figure 3). This further supports the notion that polydispersity and conformational disorder in the low-temperature polymer make negligible contributions to the observed line widths, which only can be the case if N is large for all components. Despite the broad range of conjugation lengths, all of the polyenes manifested in the polydisperse chain length distributions of the polymer sample absorb sufficiently close to the asymptotic limit that they exhibit almost identical spectra.

The significant sharpening of the low-temperature polymer absorption spectrum provides the strongest argument for the approach to a long polyene limit. The fact that the electronic origin of the polymer absorption ($E(0-0) = 15\,800$ cm^{-1} in 77 K 2-methyl-THF) approaches that predicted by extrapolation of the oligomer spectra (Figure 4) reinforces the analysis. However, the simple, linear extrapolation of the low-temperature oligomer transition energies ($A \approx 13\,400$ cm^{-1}) significantly underestimates the apparent asymptotic band gap for this polyene series. If the simple, inverse linear relationship between $E(0-0)$ and N is accurate for all N, $E(0-0) = 15\,800$ cm^{-1} requires $N \approx 30$. However, this leads to a ~500 cm^{-1} line width due to sample inhomogeneity. We then would expect the observed (homogeneous plus inhomogeneous) vibronic line widths to be even larger than those seen for the purified oligomers, for example, ~1150 cm^{-1} for the low-temperature (0−0) band of $N = 5$. The discrepancy between A and $E(0-0)$ for the low-temperature polymer, at least in part, may reflect the inadequacies of the $1/N$ fits to predict transition energies in the long polyene limit. There is little theoretical support for the simple $1/N$ dependence of the transition energies for large N and no experimental data for $N > 15$. It clearly would be helpful to extend the data on the oligomers to systems with significantly larger N to better understand the relationship between the number of monomers, conjugation lengths, and the absorption spectra of these and similar polyene systems.

It is useful to note other examples and experimental conditions under which the absorption spectra of conjugated polymer solutions approach similar asymptotic limits. For example, we recently observed comparable temperature effects in substituted polyphenylenevinylene (PPV) systems in which vinylene segments alternate with phenyl rings.[33] The lowest temperature spectra give a structured absorption with $E(0-0) \approx 17\,000$ cm^{-1} ($\approx$ 590 nm). In addition, the longest oligomers of a thienylenevinylene series[34] show a similar approach to a long wavelength limit ($\lambda \approx 600$ nm) that also is accompanied by an increase in vibronic resolution. This does not require cooling, presumably due to significantly less conformational disorder in these semirigid, planar polyene systems. A rather different example is the series of substituted polythiophenes, for which red-shifted, vibronically resolved spectra (($\lambda \approx 550$ nm) are observed at room temperature in solvents in which the polymer has a low solubility (e.g., a mixture of chloroform and toluene).[35] The authors attribute this to the formation of microcrystals dominated by long, planar, conjugated sections of the polymer, which are separated from each other by bulky side chains and not disrupted by strong interactions with solvent molecules. Finally, it is interesting to note the spectra of extended arrays of porphyrin rings (“porphyrin tapes”), which also approach asymptotic limits with increasing conjugation.[36] Although the long wavelength limits depend on the solvent environment, the chemical structures of the monomers, and the extent of bond alternation, there are many similarities in the spectra of these rather dissimilar, “one-dimensional” conjugated systems.

The absorption spectrum presented in Figure 5 provides no evidence for activity of “cis-band” peaks and the higher energy electronic transitions observed in the oligomers and other short polyenes. A possible explanation is found in the spectra of the *tert*-butyl-capped polyene series.[23] The cis peak ($1^1A_g^- \rightarrow 1^1A_g^+$) and a higher energy transition ($1^1A_g^- \rightarrow 2^1B_u^+$) also exhibit approximate $1/N$ behavior with both transition energies approaching long polyene limits that are comparable to the limit of the strongly allowed $1^1A_g^- \rightarrow 1^1B_u^+$ transition. If these three transitions converge to similar asymptotic limits, we then would expect the oligomer spectra to collapse into the single absorption band observed in Figure 5. The simplicity of the spectrum of the polymer also may be influenced by the relative enhancement of $1^1A_g^- \rightarrow 1^1B_u^+$ oscillator strength with increasing N. Very little is known about the behavior of polyene oscillator strengths as $N \rightarrow \infty$. Kohler predicted a saturation of the $1^1A_g^- \rightarrow 1^1B_u^+$ transition moment in the long polyene limit.[37,38] The extinction coefficients of short polyenes and carotenoids offer some experimental support,[10] but there are insufficient data available for sufficiently large N to confirm this hypothesis. In any event, there is no experimental or theoretical evidence for the notion that the polymer absorption spectrum (Figure 5) is dominated by a small fraction of very long polyenes with exceptionally high, $1^1A_g^- \rightarrow 1^1B_u^+$ oscillator strengths.

It is interesting to note the early theoretical work on simple, model polyenes by Tavan and Schulten,[39,40] who predicted a clustering of polyene electronic transitions as $N \rightarrow \infty$ according to the “pseudoparity” of their excited states. These pseudoparity designations derive from orbital pairing relationships among singly excited configurations.[41,42] The ground electronic state of a polyene is designated as $1^1A_g^-$ and all of the allowed, one-photon absorptions terminate in “+” states, for example, $1^1A_g^- \rightarrow 1^1B_u^+$ for the strongly allowed transition and $1^1A_g^- \rightarrow 1^1A_g^+$ for the cis peaks. The Tavan and Schulten calculations suggest that the $- \leftrightarrow +$ transition energies converge in the infinite polyene limit, in apparent agreement with the limited data available for the di-*tert*-butyl polyenes.[23] This clustering of excited states would account for the simplicity of the low-temperature spectrum of the polymer (Figure 5).

Finally, it should be recognized that the $1^1A_g^- \rightarrow 1^1B_u^+$ transition is not the lowest energy transition in polyenes. In addition to the well-studied, symmetry-forbidden, low-energy $1^1A_g^- \leftrightarrow 2^1A_g^-$ transition (most easily observed as fluorescence in shorter polyenes),[1,2,4] there also is evidence for additional low-lying $- \leftrightarrow -$ transitions in longer polyenes, for example, $1^1A_g^- \rightarrow 1^1B_u^-$.[43,44] These transitions are predicted to converge to the same energy in the long polyene limit with the $- \leftrightarrow -$ transition limit remaining below that of the $- \leftrightarrow +$ transitions.[39,40] Fluorescence and transient absorption measurements on purified oligomers and polymers will provide a better understanding of the energies and dynamics of these low-lying states both in the shorter polyenes and in the approach to the long polyene limit.

Conclusions

The vibronic resolution observed in our low-temperature spectra offers significant advantages in probing the electronic states of these conjugated systems. The living polymerizations apparently produce only a small fraction of the molecular combinations available from repeated cyclizations of the monomer. Although our current HPLC procedures are unable to resolve all components, the reverse-phase methods are capable of partitioning the oligomers according to their number of monomers. This results in a set of vibronically resolved spectra, particularly in 77 K glasses. Analysis of the vibronic details allows close comparisons with the spectra of simple polyenes and open-chain carotenoids and indicates that, despite significant structural differences, the spectra of the three series exhibit very similar $1^1A_g^- \rightarrow 1^1B_u^+$ transition energies and vibronic intensities. This confirms that the electronic properties of these systems are primarily determined by the number of conjugated double bonds and that simple polyenes serve as good starting points for understanding the electronic properties of a range of conjugated polymers and their oligomers.

The vibronic resolution seen in the low-temperature absorption spectrum of the high molecular mass polymer is the critical feature in interpreting the absorption of this system. GPC/light-scattering measurements establish that the unpurified polymer sample contains a broad distribution of conjugated chain lengths. The observation of oligomer-like vibronic resolution in the low-temperature spectrum of the unpurified polymer indicates a rather homogeneous distribution of transition energies in this highly heterogeneous sample. This can be rationalized by the asymptotic approach of the $1^1A_g^- \rightarrow 1^1B_u^+$ absorption to the long polyene limit. The low-temperature polymer absorption (630 nm) lies close to the asymptotic limit estimated by simple, linear ($1/N$) extrapolations of spectra of the oligomers, carotenoids, and simple polyenes. This reinforces the notion that the polymer solution is dominated by conjugated components with long conjugation lengths ($1/N \approx 0$). However, the strongest argument for long conjugation lengths is found in the resolved spectrum, which mimics the $1^1A_g^- \rightarrow 1^1B_u^+$ absorptions of the shortest oligomers. The convolution of a large number of almost identical spectra leads to the vibronically resolved polymer spectrum presented in Figure 5.

The low-temperature sample of the polymer offers further opportunities to explore the optical and electronic properties of linearly conjugated systems in the long polyene limit. Extension of optical studies on these systems also should lead to a better understanding of the electronic properties of both short and long polyenes and the connections between chain lengths and conformational disorder. A crucial advantage of the oligomers and the high molecular weight polymers is their relatively high solubility in a range of organic solvents. This allows their purification with standard chromatographic techniques and optical measurements on relatively concentrated solutions. Comparison of the oligomer absorption spectra with those of simple polyenes with comparable conjugation lengths demonstrates that the optical properties of these systems are remarkably similar in both the short and long polyene limits. A more detailed understanding of the electronic properties of the low-temperature polymer thus should be relevant to all long polyenes.

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