Optical Spectroscopy of Long Polyenes

Ronald L. Christensen,* Arij Faksh, and John A. Meyers

Department of Chemistry, Bowdoin College, Brunswick, Maine 04011

Ifor D. W. Samuel and Phillip Wood

School of Physics and Astronomy, Uni ersity of St. Andrews, North Haugh,
St. Andrews, Fife, KY16 9SS, United Kingdom

Richard R. Schrock and Kai C. Hultzsch

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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 $1^1A_g^-$ f $1^1B_u^+$ 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} (conjugation lengths. The resolution of the low-temperature spectrum argues that the absorption superposition of almost identical 1 $^1A_g^-$ f $1^1B_u^+$ 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 -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 ($1^1A_g^-$ f $2^1A_g^-$) transition that lies below the strongly allowed $1^1A_g^-$ f $1^1B_u^+$ 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 -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 $1^1A_g^-$ f $1^1B_u^+$ transitions, this empirical approximation finds support from simple models of * transitions in linear systems, both in the particle in a box

alternation in bond lengths alon9 54.563 pbhe.563 pcarb-242(in)chain.

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 ∼3.9 × 10^5 with a polydispersity (M_w/M_n) of 1.05. These values translate into polymers with ∼1650 ± 380 (1) monomers and ∼3300 ± 760 (1

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 (

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 (

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 ($\sim$1200 cm^{-1}, cf. $\sim$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 $\sim$ 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 $\pm$20% deviation (1) 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}

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} (≈ 590 nm). In addition, the longest oligomers of a thienylene-vinylene 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 ($1^1A_g^-$ f $1^1A_g^+$) and a higher energy transition ($1^1A_g^-$ f $2^1B_u^+$) also exhibit approximate $1/N$ behavior with both transition energies approaching long polyene limits that are comparable to the limit of the strongly allowed $1^1A_g^-$ f $1^1B_u^+$ transition. If these three transitions converge to similar asymptotic limits, we then would

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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"carotenoids" refers to naturally occurring, isoprenic polyenes such as lycopene; "oligomers" refers to the DEDPM oligomers; and "polymer" refers to the high molecular weight DEDPM polymer described in the Experimental Section.

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