COMMUNICATIONS

The surprising nonlinear optical properties of conjugated polyyne oligomers

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Polyynes represent a unique class of conjugated organic compounds. The third-order nonlinear optical response of polyynes has been extensively modeled theoretically, and it is generally believed that the increase in molecular second hyperpolarizability (γ) as a function of length for polyynes should be lower than that for polyenes. Experimental evidence to test this prediction, however, has been absent. We have synthesized conjugated polyynes that contain up to 20 consecutive sp-hybridized carbons, and we have determined their nonresonant γ-values as a function of the number of acetylene repeat units (n). These γ-values demonstrate a power-law behavior versus n($\gamma \sim n^{4.28 \pm 0.13}$), with an exponent that is both larger than theoretically predicted for polyynes and substantially higher than that observed for polyenes or polyenynes. Furthermore, no saturation of the linear or nonlinear optical properties is observed. © *2004 American Institute of Physics.*
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Conjugated oligomers play a vital role in the study and scaling of linear and nonlinear optical properties with respect to length, serving as models for predicting the properties of infinite-length systems.[1] Polyynes, i.e., sp-hybridized carbon chains, are perhaps the simplest and yet most intriguing of conjugated organic oligomers (Fig. 1).[1,2] As truly one-dimensional molecules, polyynes represent a unique model for probing electronic communication free of the configurational limitations often imposed by rotation about single bonds. This characteristic distinguishes polyynes from other typical organic oligomers and polymers, for which bond rotation can result in an interruption in conjugation along the molecular framework.[3,4] This is, for example, well documented in the case of polydiacetylenes, for which the electronic and optical properties are dependent on solution-state conformation.[5] A strong dependence of the nonlinear optical properties on bond configuration has also been shown for conjugated polyenes.[6]

Compared to other semiconducting organic compounds such as polyenes,[7] polydiacetylenes,[8] and polytriacetylenes,[9] polyynes remain the most synthetically challenging and difficult to study.[10–14] To date, formidable synthetic obstacles have limited the study of electronic, optical, and, in particular, third-order nonlinear optical properties of extended polyynes. In lieu of sufficient experimental data, the linear and nonlinear optical properties of extended polyyne carbon chains have been widely explored theoretically, often in comparison to other conjugated oligomeric structures.[1]

While the molecular structures of the systems vary, these reports consistently predict that the molecular second hyperpolarizability, γ, for polyynes will increase as a power-law with respect to length.[15–18] These same studies also suggest that this power-law relationship of γ versus length for polyynes will be inferior to that of polyenes and polyenynes. Experimentally, however, these predictions have been neither challenged nor confirmed.[19]

We have developed a synthetic route that allows for the realization of significant quantities of polyyne compounds,[20] and we have used this method to assemble the triisopropyl-silyl (TIPS) end-capped polyyne oligomers with up to 20 consecutive sp-hybridized carbons (Fig. 1). This has allowed for previously unfeasible or difficult spectroscopic characterization, including the study of their third-order nonlinear optical properties as a function of chain length. The results of these efforts are reported herein.

The linear absorption spectra of polyynes **3–10** are presented in Fig. 2(a). Unlike most other conjugated organic molecules, the high-energy region of the UV spectrum (220–270 nm) for the longest polyynes is, for the most part, transparent with only low intensity fine structure apparent. This interesting feature suggests a possible use for polyynes at high-energy wavelengths within this window of transparency. The most intriguing region of the spectrum, however, is the lower energy segment ($\geq$270 nm), which contains the highest occupied molecular orbital to lowest unoccupied molecular orbital (HOMO→LUMO) transition of the conjugated framework. The vibronic fine structure is clearly visible, appearing as a series of narrow absorption peaks with steadily increasing intensity toward the visible region. As the number of repeat units in the chain grows from $n = 3$ in the

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Polyenes   Polydiacetylenes   Polytriacetylenes   Polyynes

TIPS———TIPS
diyne, **2**

TIPS———TIPS
triyne, **3**

TIPS———TIPS
tetrayne, **4**

TIPS———TIPS
pentayne, **5**

TIPS———TIPS
hexayne, **6**

TIPS———TIPS
octayne, **8**

TIPS———TIPS
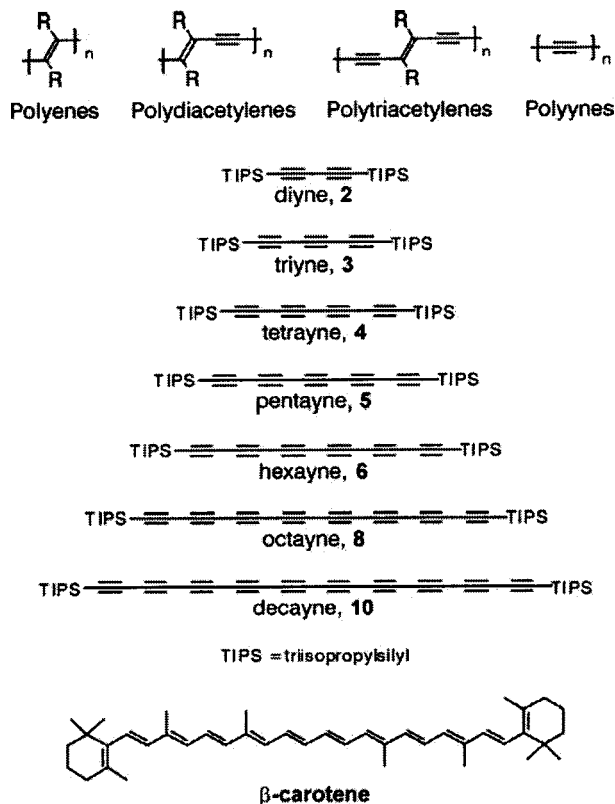decayne, **10**

TIPS = triisopropylsilyl

β-carotene

FIG. 1. Structural representation of the oligomeric compounds discussed in this work. The third-order nonlinear coefficients for polyyne samples **2–10** and β-carotene have been examined.

FIG. 2. (a) UV-vis absorption spectra for compounds **3–10** as measured in hexanes. The molar absorptivity (ε) at the lowest-energy wavelength of maximal absorption (λ_{max}) is shown for the decayne (compound **10**). Spectra have been shifted vertically for display. (b) Power-law plot of E_{max} versus n ($E_{max}=1/\lambda_{max}\times 10^7$), showing that saturation of λ_{max} has not begun. λ_{max}-values are given in parentheses next to the respective data points. The solid line represents the line-of-best-fit to the data.

triyne **3** to $n=10$ in the decayne **10**, there is a concurrent and dramatic increase in molar absorptivity, ε. The highest-wavelength absorption peak, λ_{max}, in each polyyne oligomer reflects a transition from the lowest energy vibrational level in the ground state to the lowest energy vibrational level in the excited state. A redshift in λ_{max} is clearly visible as the conjugation length of these carbon rods is increased, indicating a decrease in the HOMO→LUMO energy gap. It is expected that at a particular chain length, saturation of this effect will occur. Such saturation would represent the effective conjugation length of the oligomers, where the energy gap reaches a minimum and constant value representative of the theoretical carbon allotrope, carbyne.[21] This property is linked to the bond-order alternation, or electronic homogeneity of the conjugated backbone.[22,23] Theoretical studies have predicted various degrees of bond-order alternation in carbyne chains, from sizable values,[24] through extremely small,[22] or even zero.[25] For example, Chaquin and co-workers have predicted on the basis of semi-empirical calculations (ZINDO) that saturation ($\Delta\lambda_{max}/\Delta n=0$) for a polyyne chain will occur at 400 nm.[21] This value is lower than 565 nm (Ref. 13) and 569 nm (Ref. 12) predicted by previous experimental studies. If electron correlation effects are taken into consideration, the empirical power-law $1/\lambda_{max}=E_{max}\sim n^{-x}$ best describes the relationship between E_{max}, λ_{max}, and n.[1] This relationship is well represented in Fig. 2(b), and portrays the power-law decrease in E_{max} as a function of chain length through at least C_{20}. Overall, the TIPS-protected polyyne oligomers yield a fit of E_{max}
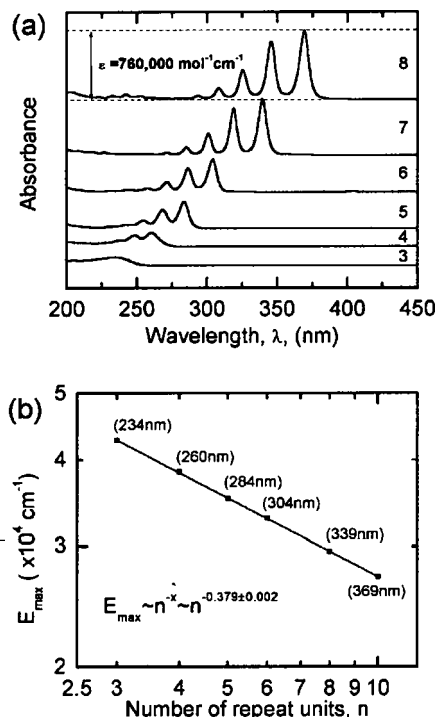
$\sim n^{-0.379\pm 0.002}$ to high precision. This result contrasts that of Gladysz and co-workers who observed a relationship of $E_{max}\sim n^{-1}$.[13] It is, however, close to the well-established relationship of $E_{max}\sim n^{-0.5}$ observed for many polyenic materials.[26,27] Since the high-precision fit for polyynes **3–10** includes the longer oligomers, no indication of saturation of the HOMO–LUMO energy is yet observed, as would be indicated by the leveling of E_{max} values as n increased. Thus, a prediction regarding saturation in λ_{max} cannot be made on the basis of these UV-vis results. This trend is mirrored in the nonlinear optical behavior of the polyyne oligomers, as discussed below.

We have determined the molecular second hyperpolarizabilities, γ, of polyynes **2–10** using a differential optical Kerr effect (DOKE) detection setup described elsewhere.[28] In this time-resolved pump-probe technique, we utilized amplified, 100 fs, 800 nm laser pulses at a 1 kHz repetition rate for nonresonant γ measurements of dilute polyynes in tetrahydrofuran (THF) solutions. A THF nonlinearity of $\gamma_{THF}=5.2\times 10^{-37}$ esu was used as a reference for the samples. All polyyne γ-values represent an average measurement from at least three individual experiments.

The third-order response for polyynes **2–10** is dominated by an ultrafast (<100 fs) electronic hyperpolarizability, with a negligible contribution from either multiphoton absorption or vibrational hyperpolarizabilities.[29] Our results [Fig. 3(a)] show that, while the second hyperpolarizabilities for shorter polyynes ($n\leq 6$) display only moderate values,
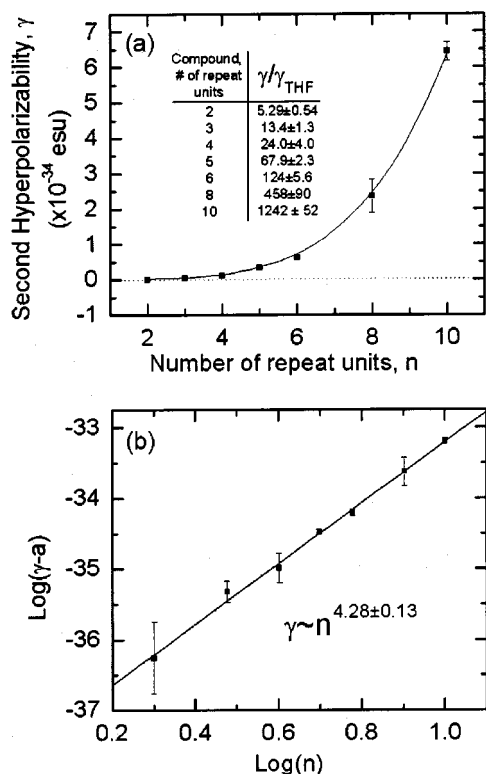
FIG. 3. (a) Polyyne molecular second hyperpolarizability (γ) as a function of the number of repeat units (n) in the oligomer chain. The solid line is a fit of the form $\gamma = a + bn^c$, where a is an offset due to the end-group effect, b is a constant, and c is the power-law exponent. The relative γ-values for the polyyne series are shown in the inset table. (b) log–log plot of ($\gamma - a$) vs n, yielding a power-law exponent (slope of the solid line) of $c = 4.28 \pm 0.13$ for the polyynes.

hyperpolarizabilities of the longest polyynes (e.g., **10**: $\gamma = 6.5 \pm 0.3 \times 10^{-34}$ esu) are substantial for relatively small molecules.[30,31] By way of comparison, the conjugated polyene molecule β-carotene, which has 11 consecutive single-double bonds, has a γ-value of $(7.9 \pm 0.8) \times 10^{-34}$ esu, as measured in THF with the DOKE set-up. The similar values measured under the same experimental conditions for the decayne and β-carotene contrast theoretical studies on oligomers of analogous length that predict substantially smaller ratios for $\gamma_{\text{polyyne}} / \gamma_{\text{polyene}}$ (calculated at zero frequency).[16,32]

Various mathematical approaches have been established to explain the relationship between the molecular hyperpolarizability and conjugation length for conjugated oligomers and show that γ-values generally increase superlinearly as a function of length for a series of structurally similar molecules.[1,23,33] For linear conjugated oligomers shorter than the effective conjugation length, such theoretical models invariably predict a power-law dependence of $\gamma \sim L^c \sim n^c$, where L is the length of the molecule (in nm) and n is the number of repeat units. Both theoretically and experimentally, the exponent c remains the most commonly used figure of merit for the comparison of different oligomer series.[1] A constant c-value is expected in small or medium chain lengths. As the chain length approaches the effective conjugation length, the onset of saturation will be manifested as a decreasing c-value that becomes length-dependent. Finally, for oligomers longer than the effective conjugation length,

where saturation has been reached, γ will vary linearly with length (i.e., $c = 1$).[7] For oligomers shorter than the effective conjugation length, the value of c can vary dramatically depending on the theoretical model used to calculate γ, ranging from $c = 5$ for both the "free electron in a box" and the one-electron Hückel models, to $c = 3.2$ for more complex approximations that account for electron-correlation effects.[1,30] Most computational models predict an exponent around $c = 4$.[1] Theoretical studies specifically addressing γ-values for polyyne chains predict exponents that range from $c = 1.26$ to 3.3.[16,18,34] Although reconciling the various power-law predictions is challenging, a consistent trend is common to studies that compare the hyperpolarizabilities of polyenes and polyynes, that is, they predict power-law exponents for polyenes superior to those for polyynes.[16,18,30] Our experimental results (discussed below) challenge these well-established predictions.

The nonlinear optical behavior of polyyne samples **2–10** fits well with the relationship $\gamma = a + bn^c$ and gives a value of $c = 4.28 \pm 0.13$, as shown in Fig. 3, where the coefficient a reflects the contribution from the terminal silyl groups of each oligomer to the overall hyperpolarizability.[35] This trend is continuous to the longest polyyne studied, the C_{20} chain **10**, and shows no indication of saturation of the second hyperpolarizability, consistent with the linear absorption data [Fig. 2(b)]. To the best of our knowledge, the exponent $c = 4.28 \pm 0.13$ is the highest nonresonant exponent observed for a series of nonaromatic, conjugated oligomers.[36] Unlike comparisons of absolute γ-values, comparisons of power-law exponents are less sensitive to the experimental method used. The third-order optical nonlinearities of various substituted and unsubstituted polyenes have been investigated by other groups, with experimental power-law exponents ranging from $c = 2.3$ to 3.6.[7,30,37] The third-order NLO response of polytriacetylenes, the closest structural relative to polyynes, shows power-law behavior with a reported exponent ($c = 2.5$)[9] that is substantially smaller than that reported herein for polyynes. Conjugated oligomers such as oligo(1,4-phenyleneethynylene)s also show an exponent of $c = 2.5$,[38] whereas values as high as $c = 4.05$ have been reported for polythiophenes.[39]

The extended sp-hybridized π-electron system of polyynes gives rise to significant nonresonant γ-values that show a superlinear increase as a function of molecular length. The magnitude of this power-law relationship for polyynes is surprisingly high in comparison to that of other conjugated materials, and several factors may account for this observation. The major component to molecular hyperpolarizability in organic molecules arises from electron delocalization along the conjugated backbone (longitudinal hyperpolarizability).[1,30] Since a linear polyyne molecule exhibits minimal conformational distortion in solution, orbital overlap along the conjugated framework is better maintained. This would ultimately enhance experimental γ-values in comparison to other structures. This effect is potentially amplified by the two π-electron systems of the sp-hybridized structure for a polyyne, which provide an approximately cylindrical electronic delocalization along the conjugated framework.[11] In comparison to an sp^2-hybridized oligomer

with an essentially planar π-electron system, the longitudinal hyperpolarizability of a polyyne would be less dependent on solution state orientation with respect to the electric field of the incident light source, which would also enhance γ-values.

The experimentally determined power-law exponent $c = 4.28$ is higher than the theoretically predicted polyyne values of $c = 1.26$ to 3.3.[16,18,34] This may result from the fact that the effect of electron-correlation has been identified as more significant for the molecular hyperpolarizabilities of polyynes than other conjugated oligomers, and the effect increases with the length of the polyyne chain.[40] Thus, the role of electron correlation effects in polyynes may hold the key to bridging the experimental and theoretical third-order NLO results.[40–42] In addition to electron correlation effects, frequency dispersion and changes in geometry also impact calculated NLO properties of linear π-systems.[42] For example, a recent report demonstrates that the MP2/6-31G* method can provide geometrical data in good agreement with experiments,[43] but γ-values have not yet been computed with these most relevant geometries.

Comparing the hyperpolarizabilities of our polyynes with sum-rules-derived predictions on the upper bound γ-values of 1-D π-systems also proves interesting. Recently, Kuzyk has identified $\gamma_{xxxx} < 4e^4\hbar^4 m^{-2} N^2 E^{-5}$, as a theoretical upper bound for linear conjugated systems, where N is the number of electrons and E is the first excited state transition energy.[44] Using the power-law behavior of $E \sim n^{-0.379}$ from Fig. 2(b), and assuming that the number of delocalized electrons scales linearly with the number of multiple bonds, we get $\gamma \sim n^{3.90}$ as the predicted upper bound on γ. This value is very close to the measured value of $\gamma \sim n^{4.28}$. To date, polyynes are the first 1-D system to experimentally exhibit hyperpolarizabilities that approach this predicted limit.[44]

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