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POLYDIACETYLENE: THE IDEAL LOW DIMENSIONAL ORGANIC MATERIAL

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Abstract. Polydiacetylenes, owing to their unique backbone structure and crystalline organization, can be considered to be the prototype one dimensional systems. We have developed techniques to engineer the diacetylene monomer in a manner that polydiacetylene is grown in the form of a large area-oriented film with controlled thickness and optical qualities. Linear and nonlinear optical properties of these systems have been investigated.

Polymers have often been considered model 1-D systems due to the stronger bonded interactions along the backbone and weaker, usually van der Waals nonbonded interactions between the individual polymer chains or widely separated segments of the same chain. However, due to the rotational freedom about relevant backbone bonds, most polymers adopt a multitude of conformations and, as a result, all long range order and anisotropy is lost. Even when the symmetry of the chain repeating unit permits crystalline organization, a helical intrachain conformation is often preferred. In a few polymers, however, the extended chain conformation is the preferred conformation and, depending upon the electronic structure of the backbone, interesting phenomena are manifested. These include unusual and highly anisotropic electronic and optical as well as thermal and mechanical properties.

For crystalline polymers where an extended chain conformation is preferred (2_1 helix), the overall morphologies can still be very complex. Unless all other conformations are virtually ruled out from structural or energetic consideration, kinks, jogs, folds, and other conformational defects drastically affect the extended chain geometries. These interruptions usually occur at typical distances of ≃100A or less along the chain direction and are often dictated by entropic considerations. There are several approaches of post synthetic processing that can alleviate this problem, such as stress induced alignment, melt spinning and stretching, etc. Simultaneous synthesis and co-crystallization can also lead to extended chain geometries over several hundred angstroms. Polyacetylene is a case in point. Using a Ziegler-Natta catalyst, Shirakawa and coworkers were able to synthesize polyacetylene which simultaneously crystallized in an extended chain conformation to form long interconnected fibrils. This polymer with a conjugated backbone has since been extensively investigated. Strong interaction of backbone conformation and electronic structure is a fundamental property of conjugated polymers and it is very important to explore ways to fabricate macroscopic organization of polyconjugated systems in a desired conformation.

The polydiacetylenes provide an unique opportunity to achieve this by suitable "molecular engineering" and solid state polymerization techniques. Monomer single crystals of diacetylenes can be grown by a variety of approaches in desired macroscopic forms. The side groups R and R' (Fig. 1) can be suitably designed to make the monomer amenable to specific crystal growth techniques. Additionally, the size and electronic structure of the side groups can be manipulated to control the separation of the diacetylene backbones and subtly influence their electronic properties as well.

The polydiacetylene chains in the solid state polymerized system adopt an all-trans chain conformation. Thus, polydiacetylenes in these structures can be considered prototype one dimensional materials and have been extensively studied for their structural,[1] electronic[2] and optical properties.[3] These materials become even more attractive when one considers the possibilities of manipulating their molecular architecture to "tailor" specific property aspects.

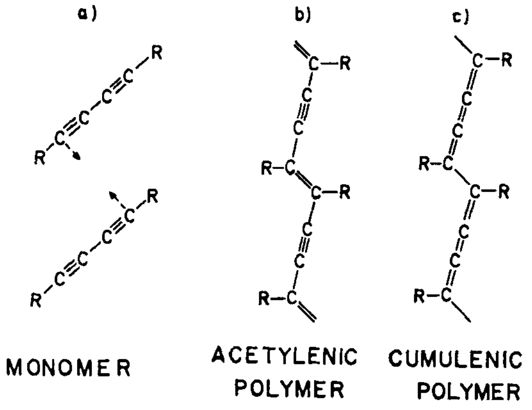

FIGURE 1 Diacetylene Reaction Scheme

(a) Diacetylene monomers regularly arranged in a single crystal

(b) Polydiacetylene in the acetylenic form

(c) Polydiacetylene in the cumulenic form

One class of polydiacetylenes where this structural modification can be introduced with ease and, additionally, controlled thickness macroscopic organizations are possible, has R and R' as a long alkyl chain and an alkyl chain with a terminal acid group, respectively. This permits growth of these materials in the form of multilayer assemblies using a Langmuir-Blodgett film balance. Additionally, by altering the lengths of the alkyl groups, one can alter the packing of the diacetylene backbones. We have carried out detailed investigation of structural and linear and nonlinear optical properties of polydiacetylenes belonging to this class. The polydiacetylenes were grown as a multilayer assembly on a silver grating to act as a waveguide structure. This permitted the investigation of the third order nonlinear susceptibility $\chi^{(3)}(\omega)$ of these materials fabricated in a technologically relevant form. Polydiacetylene as a prototype 1-D semiconductor was shown to have a large $\chi^{(3)}(\omega)$ over a range of wavelengths in the nonabsorptive region, a property considered important to realize concepts of all optical signal processing.[4] The measurements were carried out by a technique developed in our laboratory. These results have been communicated.[5]

Additionally, details of synthesis of several new monomers, their fabrication and processing aspects, and the investigation of their linear and nonlinear optical properties are being presently investigated. Apart from the use of the Langmuir-Blodgett technique to grow controlled thickness multilayer assemblies, approaches such as vapor and liquid phase epitaxy and pressure induced crystallization are being pursued. Of particular interest is the investigation of optical nonlinearities in the time domain and preliminary experiments have been initiated. In this communication we will detail the results of some of these investigations.

EXPERIMENTAL

Multilayer Fabrication

The nonacosa-10,12 diynoic acid monomer with chemical structure $CH_3-(CH_2)_{15}-C\equiv C-C\equiv C-(CH_2)_8-COOH$ is synthesized following the Cadiot-Chodkiewicz coupling reaction outlined in an earlier communication.[6] The monomer is purified by repeated crystallization from petroleum ether. Monolayers are spread at the gas-water interface from dilute solution of the monomer in chloroform. Lauda film balance is used to monitor the film pressure and polymerization (reaction scheme, Fig. 1) is achieved by using UV radiation at the appropriate film pressure. Multilayer assemblies of polydiacetylenes can be built up from this monolayer by consecutive dipping of a substrate, following the Langmuir-Blodgett technique.[7]

Growth of Oriented Thin Films by Other Techniques

The thin film fabrication technique has been perfected to the extent that it is possible to make a multilayer assembly with precise control of layer thickness. Fabrication of a large area assembly of several thousand angstrom thickness film is still a very laborious and time-consuming operation. Additionally, the detailed morphology and microstructure of each layer has to be precisely controlled. Apart from these operational difficulties, one is further limited by the specific side groups (R and R' in Fig. 1) one must build to make the monomer suitable for Langmuir-Blodgett growth. This has prompted us to explore the crystal growth of other diacetylene systems by judicious use of such conventional techniques as liquid and vapour phase epitaxy and other parallel approaches normally employed for small molecular and atomic systems. The systems of choice have been these materials, where the monomers are melt stable and radiation polymerizable. This provides a great deal of flexibility in manipulating the organization of the monomer crystals.

TCDU (R is $\leftarrow CH_2)_4OCONHC_6H_5$) is a case in point. Large area ($\approx$.5cm x .5cm), thin ($\approx 1\mu$) and optical quality single crystals of TCDU have been grown in our laboratory. The radiation polymerized TCDU retains the integrity of the monomer single crystals and polymerization microscopy reveals a uniform thickness optical quality single crystalline polyTCDU film. The observed absorption spectrum for two different directions of polarization (parallel and perpendicular to the chain axis) is given in Fig. 2. It should be noted that the visible spectrum of polyTCDU heretofore has been obtained only in the reflection mode for lack of large area single crystals that would be thin enough for investigation under transmission mode.

Several features of this spectrum (Fig. 2) are noteworthy. The principal excitonic peak is at 605nm, until now unobserved for any of the known phases of polyTCDU.[8] Detailed structural characterization and the evolution of

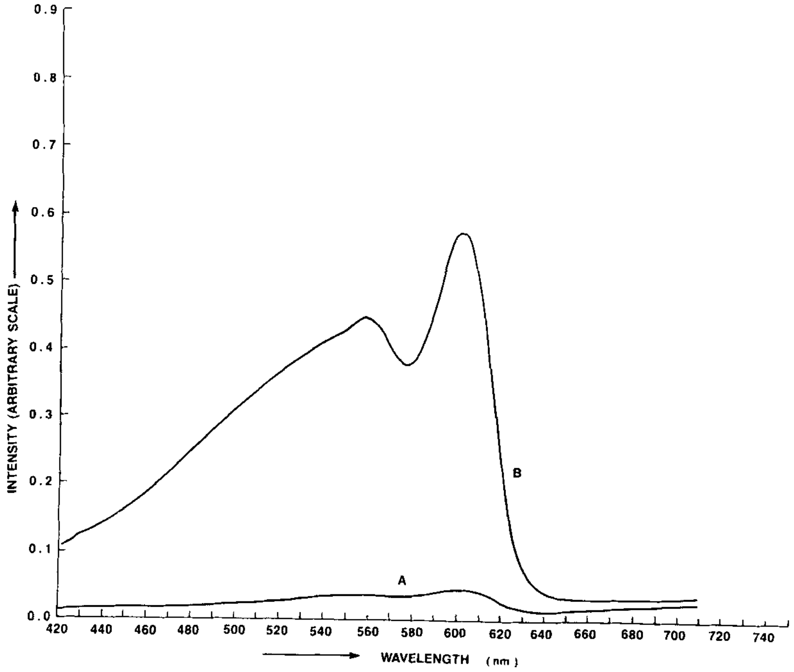

FIGURE 2 (a) Visible absorption spectrum of TCDU for polarization parallel to the chain axis

(b) Absorption spectrum for polarization perpendicular to the chain axis the characteristic absorption spectrum will be discussed in a forthcoming publication. Other important features of the spectrum are the sharpness of the absorption edge as well as the degree of anisotropy.

Since the alignment of the polarizers could not be perfectly controlled in our spectrophotometer setup, the *spectrum under polarized light, while indicative of the* excellent orientation of the polymer chains in the crystal, may not be totally quantitative.

Linear and Nonlinear Optical Measurements in the Polydiacetylene Multilayer

Although we have reported both linear[6] and nonlinear[5] optical measurements in a multilayer of the polydiacetylene film, we review the technique and provide a discussion of the results in terms of modeling the nonlinear processes. First, a 5000Å multilayer polydiacetylene film is deposited (monolayer by monolayer) upon a metalized grating (5000Å period).[6] This structure forms a planar waveguide which can be coupled via the grating. For our case, the effective index of refraction for the guided wave mode, n_g is such that $1<n_g<n_f$ where n_f is the index of polydiacetylene film. By observing the direct reflection of a laser beam from the sample, we measure the change in reflectivity as a function of incident angle θ_i (measured with respect to the plane normal). Near a waveguide mode resonance a characteristic resonance "dip" is observed indicating a loss energy from the incident beam, and hence a gain in the energy in the guided wave mode. For our case, the angle (θ_c) corresponding to the minimum in reflectivity (maximum in power transferred to the guided wave mode) is given by $n_g = \lambda/\Lambda - \sin\theta_c$, where λ and Λ are the wavelength and grating spacing, respectively. By measuring n_g as a function of λ, one can deduce n_f, the index of the polydiacetylene film.

The nonlinear optical property of the polydiacetylene film that is of interest to us is the nonlinear index of refraction n_2, where n_2 is proportional to $\chi^{(3)}(\omega)$. n_2 can easily be measured by our coupling scheme because a change in optical intensity (ΔI) in the film causes a change in film index, $\Delta n_f = n_2\Delta I$. This leads simply to a change in coupling angle $\Delta\theta_c$ which is proportional to $n_2\Delta I$ (since Δn_g is proportional to Δn_f). By using a pulsed ($\simeq$10 nsec duration) dye laser, we measured $\Delta\theta_c$, and hence

n_2 from .67 - 1.04μm by changing the intensity at each wavelength.[5] We observed that, throughout the range, n_2 was negative in contrast to the positive sign predicted by the one dimensional semiconductor band model.[9] Further, the value of n_2 for $\lambda \geq 7500\text{Å}$ (the transparent region of our film) was $\simeq 10^{-6}/(\text{MW}(\text{cm}^2))$, in good agreement with data (both sign and magnitude) taken on a PTS (R is $-CH_2-O-SO_2-C_6H_5-CH_3$) crystal at $\lambda = 1.89\mu m$.[10,11]

The observation that the sign of $\chi^{(3)}(\omega)$ is negative at both long ($\lambda = 1.89\mu m$)[11] and short ($\lambda \leq 1\mu m$)[5] wavelengths provides some insight into the models of the electronic states contributing to the optical nonlinearity. A one dimensional semiconductor model for the polydiacetylenes predicts a positive $\chi^{(3)}(\omega)$ in the limit $\lambda \rightarrow \infty$.[9] This is primarily due to the predominance of intraband contributions to the nonlinearity.[12,13] It should be further pointed out that a discrete three-state model has been used to explain two-photon absorption in the polydiacetylenes in solution.[14] Such a model yields two contributions to $\chi^{(3)}$;[15] one positive with a two-photon resonant denominator, the other negative with only single-photon resonant denominators. The two-photon contribution changes sign and becomes negative when the wavelength is above the two-photon resonance. We estimate from the results in Ref. 14 that such a resonance should occur for $7000\text{Å} \leq \lambda \leq 9000\text{Å}$ in our polydiacetylenes. Thus, if such a discrete model holds, the term with a two-photon resonant denominator is a small contribution of the observed $\chi^{(3)}$, especially since we observe no drastic negative jump in $\chi^{(3)}(\omega)$ near the expected two-photon resonance. In fact, we observe that within experimental error $\chi^{(3)}(\omega)$ is nearly constant until the wavelength reaches the one-photon absorption edge.[5]

We are continuing our experiments in an attempt to find the response time of the observed n_2, both in the absorptive and transparent region of the polydiacetylenes, using a psec dye laser. Two co-linear beams delayed in time will be incident on our grating waveguide sample. By observing the coupling angle θ_c as a function of time delay between the two pulses, in principle we should be able to determine the response time of the optical nonlinearity.

Additionally, parallel experiments have been initiated to investigate the optical properties of several other polydiacetylene systems that can be grown in large area (several mm by several mm) single crystals of controlled thickness by techniques that have been perfected in our laboratory. The myriads of structural variations that can be introduced in this class of material and the richness of the properties make this area of research a very fascinating as well as challenging one.

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