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# Photoluminescence, absorption, and Raman spectra of a polydiacetylene monolayer

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Optical properties of a single layer of polydiacetylene [poly-(heptacosa-10,12-diynoic acid)] have been studied. The morphology of the sample does not affect the optical properties. However, the exciton peak energy depends on the monolayer orientation with respect to the substrate. We tentatively ascribe the effect to stress variation in the first layer on the substrate.

Long-chain conjugated $\pi$-electron systems have attracted much attention recently[1] because their unique electronic properties are of fundamental interest and also because they may be exploited to realize the so-called molecular devices.[2] Among the polymer conjugated $\pi$-electron systems, polydiacetylenes (PDA's) are unique in that they can be prepared in large single crystals by the topochemical reaction of the monomer crystals.[3] Many measurements have already been reported on these polymer crystals.[4] Amphiphilic diacetylene derivatives can be spread on water as well, which upon the topochemical reaction transforms into a polymer monolayer. Many experiments have also been performed on the multilayer samples of PDA's which are prepared by the layer-by-layer deposition technique, the so-called Langmuir-Blodgett method.[5] However, measurements on single-layer films are scarce, although circumstantial evidence exists[5] that the first layer next to the substrate has a different character than the other part in the multilayer system. It is thought that this difference results from the difference in the stress environment: substrate-film adhesion versus film-film adhesion. Because it has been found that the electronic structure of some polydiacetylenes is very sensitive to the backbone-chain deformation,[6,7] it is particularly interesting to see if there is a corresponding effect of the stress on the first monolayer. In this Communication, we would like to report what we believe to be the first measurement of a set of optical properties (photoluminescence, absorption, and resonance Raman scattering) of single-layer PDA films on a glass substrate.

The amphiphilic diacetylene derivative, heptacosa-10,12-diynoic acid ($C_{14}H_{29}—C{\equiv}C—C{\equiv}C—C_8H_{16}—COOH$), was dissolved in benzene and spread on water containing $10^{-3}M$ of LiOH.[8] Benzene was chosen because larger domains result with this solvent.[9] The temperature of the water was in the range of 7–10 °C and was kept constant within 0.1 °C during one set of experiments. The trough was enclosed in a box which was purged of air by pure argon gas. Polymerization was done by irradiating the compressed monolayer on water with the uv light from a low-pressure Hg lamp for 20–30 min. The polymerization was monitored by observing the pressure drop (for the constant-area polymerization) or the decrease in area (for the constant-pressure process). The polymerized film was transferred onto a cover glass ($18\times18\times0.17$ mm$^3$) by the horizontal lift-off technique[8,10] from above the film (when the glass surface was hydrophobic) or from below the film (when the surface was hydrophilic). The hydrophilic surface was prepared by cleaning the glass in a detergent solution and then rinsing with a copious amount of running water. The hydrophobic surface was obtained by the adsorption of cetyltrimethylammonium bromide from chloroform solution onto the cleaned glass prepared in the above-described manner [see the inset of Fig. 1(b)].

The samples show a variety of morphologies[8] which can easily be observed under a polarizing microscope. Good-quality films have spherulitic domains as large as 1 mm in diameter. Mosaic structures with domain size of the order of 50 $\mu$m have also been found. These films do not have macroscopic voids. Films of poorer quality showed filamentary fragments with vacant areas which were probably introduce during the transfer process. Although we have not performed an in-depth study, no simple relation between the morphology and the sample-preparation process seems to exist; various kinds of morphology coexist in a single preparation.

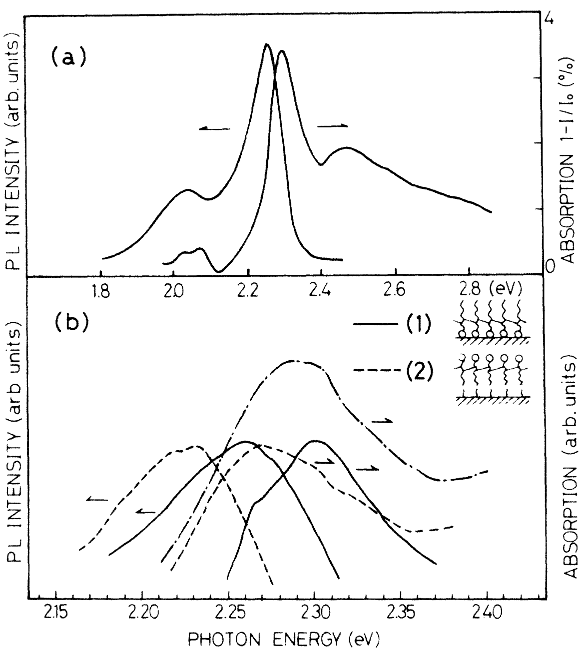

FIG. 1. (a) Absorption and photoluminescence spectra of a PDA monolayer on a hydrophilic glass surface. (b) Exciton peaks of absorption and photoluminescence of a PDA monolayer on a hydrophilic glass surface (inset 1) and on a hydrophobic surface (inset 2). In the inset, circles stand for the hydrophilic head group while the wiggly lines for the alkyl chains. The dot and chain curve is for a tail-to-tail bilayer.

The absorption and photoluminescence (PL) spectra of a PDA monolayer on the hydrophilic glass are shown in Fig. 1(a). The spectra exhibit the exciton peak and the phonon sideband. In terms of the molar extinction coefficient, 1% absorption here corresponds to $0.6\times10^4$ l/mol cm, if a mole is measured per monomer unit. The PL spectra were obtained by illuminating the sample with Ar-laser light of wavelength in the range between 4579 and 5145 Å. Typically, 20 mW of the laser light was focused onto an area of $0.05\times4$ mm$^2$. Quenching of the luminescence did not occur at this intensity. The spectra were independent of the excitation photon energy. Taking the overall efficiency of the measuring system into account, the quantum yield of the photoluminescence was estimated to be of the order of $1\times10^{-4}$.

The spectral features remain the same as in Fig. 1(a) regardless of the morphology of the sample, as long as the hydrophilic glass slides are used, i.e., the film adheres to the substrate by the polar head. This is surprising in view of the wide variety of morphology. The spectra, however, do depend on the orientation of the monolayer with respect to the glass substrate. The spectra from the monolayers prepared on a hydrophobic surface are uniformly shifted downward by about 30 meV from those shown in Fig. 1(a). Although the phonon sideband is too broad to see the shift clearly, it is resolved at the narrower exciton peak [see Fig. 1(b)]. It is reasonable to assume that the shift of the exciton energy parallels the shift of the $\pi^*$ band edge which the exciton is associated with. Therefore, our observation suggests that a slight modification of the electronic states of the $\pi$ electron occurs, depending on the film orientation. It is unlikely, however, that the interfacial electronic environment varies so much that it causes the shift of the energy gap of the PDA backbone. We, therefore, attribute the observed exciton-peak shift to the varying stress (hence, the strain) states in the first monolayer on a solid substrate. In fact, a stress-induced shift of the peak energy has been seen in a PDA crystal,[11] where a shift of 37 meV per percent of strain was found along the backbone-chain direction. If we assume a similar value for our samples, the strain difference, depending on the film orientation, is about 1%.

The width of the exciton peak in a crystalline sample is about 50 meV,[12] whereas the corresponding width in Fig. 1 is about 100 meV. The broadening may be due to the sample inhomogeneity, but, since the width does not depend very much on the sample preparation, it could have an origin inherent to the monolayer.

In a bilayer sample, where two types of arrangements are possible as shown in Fig. 2, the first layer acts as a substrate for the second one. In the tail-to-tail arrangement [Fig. 2(a)], the stress in the outer layer is not expected to be much different from that in the monolayer on a hydrophobic glass surface [inset (1) in Fig. 1(b)], because in both cases the interaction is weak between the alkyl chain sheets. By the same argument, the stress in the first layer would also be similar to that in the monolayer on a hydrophilic glass surface. In fact, the absorption peak of a bilayer in the tail-to-tail arrangement is a simple sum of the two peaks as shown in Fig. 1(b). On the other hand, the exciton-peak shape for a bilayer in the head-to-head arrangement varies from sample to sample. Some samples produce a shape similar to that of the tail-to-tail bilayer while others show a narrower peak (but broader than the monolayer peak). In any case, the peaks are within the two bounds of the monolayer peaks. This phenomenon can be understood by considering that the head-to-head interaction is stronger, and hence, the stress of both layers would be modified. The registration of the head groups of the upper and lower layers, which cannot be controlled in our experiment, may be a factor in determining the stress variation.

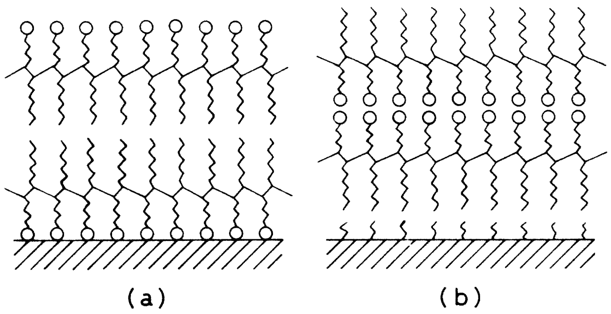

FIG. 2. Two types of bilayer arrangement: (a) tail to tail and (b) head to head.

Resonance Raman (RR) scattering from PDA crystals has previously been studied in detail.[12] The resonance enhancement is such that the Raman spectra can be easily obtained from a monolayer on glass without any additional enhancement mechanism.[13] Typical Raman spectra are shown in Fig. 3. Three peaks are clearly seen at $\nu_1=2116$ cm$^{-1}$, $\nu_2=1517$ cm$^{-1}$, and $\nu_3=1072$ cm$^{-1}$. No features were observed below 800 cm$^{-1}$ down to 40 cm$^{-1}$. No Raman or fluorescent peaks from the substrate were observed either. Since the number of PDA molecules in the scattering volume is extremely low, it is clear that only those vibrations which are strongly coupled with the backbone electronic states are observable. Normal-mode analysis shows three such vibrations (i.e., dominantly of stretching character) in the PDA backbone, $\nu_1$ through $\nu_3$ being in reasonable agreement with the previously observed RR data.[6] In contrast with the RR result from polyacetylenes,[14] no shift of the Raman peaks was found within an accuracy of ±6 cm$^{-1}$ nor was there a change of the line shape when the incident laser wavelength was varied from 4579–4880 Å. It is thus expected that no significantly broad distribution of con-

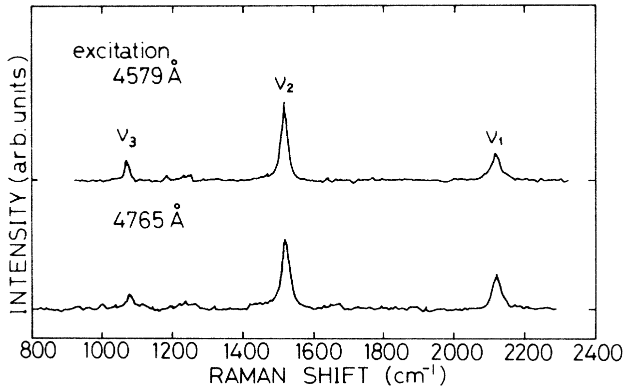

FIG. 3. Resonance Raman spectra of a PDA monolayer at two laser excitation wavelengths. Slowly varying fluorescence background is subtracted.

jugation lengths exist. (The Raman spectra excited at 5145 Å were swamped by the fluorescence and reliable measurements were not possible.) The Raman frequencies were also independent of the morphology or the orientation of the monolayer within our resolution. The dependence of the Raman frequencies on the external stress is not very large,[15] and their change for 1% strain is likely to be below our resolution. However, the relative intensity of the three peaks depends on the excitation photon energy (Fig. 3). The resonance Raman excitation profiles (RREP's) of a PDA crystal have been studied both experimentally and theoretically.[12] The RREP in a PDA crystal is distorted very much because of the extremely large variation of the absorption coefficient and the index of refraction in the wavelength range of interest. This does not cause any problem in a monolayer sample since it is optically thin, and hence, it could be an ideal system to study the RREP. Unfortunately, the scope of the current investigation does not warrant going further into the RREP investigation because the exciton peak was rather broad, and also because the available excitation frequencies were limited.

Finally, a word about the type of conjugation of our sample is in order. In a PDA backbone, two extreme types of conjugation are possible, i.e., the acetylene structure $(=RC-C\equiv C-CR'=)_n$ (type $A$) and the butatriene structure $(-RC=C=C=CR'-)_n$ (type $B$), where side branches of alkyl chains, aromatic groups, etc. are represented by $R$ and $R'$. It has been suggested that by choosing the side groups $R$ and $R'$ and the temperature, pressure, or other external factors and thereby changing the stress on the backbone, one can obtain either type;[4,6,7] although accompanying x-ray crystallographic measurements have rarely been done to verify the structure directly. Usually the assignment is based on measurements of the exciton energy or the lattice vibrational frequencies; an exciton energy of $\simeq 2.0$ eV is attributed to the type $A$ structure while that of $\simeq 2.3$ eV is due to the type $B$.[7] According to this scheme, our sample is of type $B$. However, from an electron diffraction experiment of a homologous PDA sample, it has been suggested otherwise.[16] Nevertheless, we consider this still an open question because the structure within the unit cell is not well known for monolayer PDA's, on the one hand, and because a different opinion exists, on the other, as to the interpretation of the exciton-peak energy with respect to the conjugation type.[1,17] According to this latter viewpoint, the difference in the exciton-peak energy does not reflect the backbone conjugation alteration. Further systematic studies are needed to settle the question.

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