

Stability of hydrogen bonds upon polymerization and color transition of diacetylenes: An FTIR spectroscopy study



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ABSTRACT

FTIR spectra (400–7500 cm⁻¹) have been recorded for polycrystalline films and single crystals of the diacetylene 4BCMU in the monomer, blue and red polymer states, and of 3BCMU monomer. Particular attention was paid to the amide bands associated to the urethanes in the side groups, which form one-dimensional H-bond linear chains quite similar to those found in peptides and proteins. The positions and strengths of these absorptions are practically unchanged by polymerization or blue to red polymer color transition. This suggests that the H-bond linear chains are the main constitutive interactions in these crystals, and that the conjugated parts must and do “adapt” to the unchanged H-bond lines. No evidence of side group disordering was observed at the irreversible blue to red transition in poly-4BCMU crystal.

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1. Introduction

Diacetylenes (DA) R–C≡C–C≡C–R' where the so-called “side groups” R and R' may be diverse chemical entities, form a very large family of molecules. The polymer (PDA) can be prepared by UV or γ irradiation of self assembled DA (crystal, LB film, vesicles), through a topochemical reaction (Fig. 1). Most often the polymerization leads to long conjugated blue PDA (maximum absorption $\lambda_{\max} \approx 640$ nm).

Blue PDA can undergo a transition to red PDA ($\lambda_{\max} \approx 550$ nm) under various stimuli: temperature, pressure, pH, etc. This blue to red transition corresponds to a change of electronic structure without chemical modification of the chain. Such transitions are observed in Langmuir film or vesicle-forming PDA and are being used to develop biological sensors [1–5]. This is presently an active research area.

Another important past motivation has been that PDA chains in crystal have very regular periodic geometries, so they could be used as a model conjugated polymer in which the effects of disorder on electronic properties are minimized or altogether eliminated [6,7]. In an important class of reactive DA, the side groups contain urethanes OCONH forming linear chains of hydrogen bonds running parallel to the direction of chain propagation in polymerization. This arrangement may induce reactivity, since it favors an optimal stacking of the C≡C–C≡C groups for chain initiation. Such H-bond

lines between side-groups containing urethane or analogs such as urea have been shown to be good “organizers” able to promote reactivity in diacetylene crystals [8].

The urethane-containing DAs chosen for this study are 4BCMU and to a lesser extent 3BCMU (abbreviated below 4B and 3B), which have been most intensively studied. Their side group formulae are R = R' = $-(\text{CH}_2)_n-\text{OCONH}-\text{CH}_2-\text{COOC}_4\text{H}_9$ with $n = 4$ in 4B and $n = 3$ in 3B. Side group formulae and acronyms of these and other DA and PDA, and of other molecules mentioned in this work are given in Supplementary Data (SD) §1.

A blue to red irreversible transition is observed in poly-4B similarly to LB films or vesicles, so the blue state is metastable [9,10], and is considered to be related to the breaking of H-bonds and to the onset of side group disordering unlike the case of reversible blue to red transition [11–14]. The problem of H-bond network changes in the reversible color transition in single crystals has been addressed in previous work using IR, mostly on poly-ETCD [15], poly-IPUDO [16] or other PDA which side groups contain an urethane and terminal alkyl groups up to decyl [13]. It was concluded that the IR absorptions associated to the urethane groups were barely affected by the reversible transition, but the irreversible transition in 4B was considered different.

It will be shown that in 4B the H-bonds are unaffected by polymerization and by the irreversible color transition, which therefore cannot be triggered by a disordering due to H-bond breaking in side groups.

In the course of this study, it became apparent that the IR properties of H-bonds in the materials here studied are very similar to those in polypeptides and proteins. Force fields for protein

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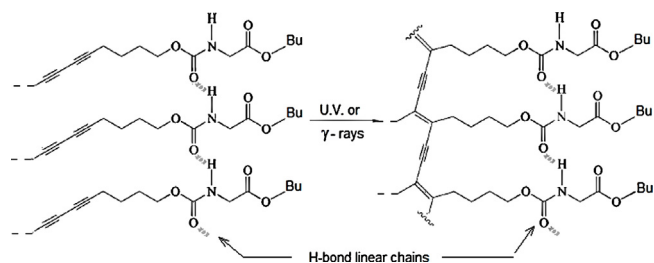


Fig. 1. 4BCMU topochemical polymerization, for clarity only a half molecule has been sketched.

studies have been built using model molecules such as N-methylacetamide (NMA) [17]. 4B and 3B might be used for improving these force fields. Moreover the possible existence in polypeptides and proteins of vibrational solitons or polarons on H-bond chains, and their possible role in the transport of vibrational energy at relatively long distance in proteins have been widely discussed [18]. These problems are not the main theme of this paper but a short discussion is given in SD §5.

This paper is organized as follows. In Section 2 the experimental methods, the reasons for using them and the different types of samples used are described. In Section 3 the experimental results are presented separately for the different regions of interest in the overall spectrum, together with discussion concerning specifically a given region, the main emphasis being on absorptions related to the urethane groups. Section 4 is a more general discussion of two problems related to this study: correlations between H-bond geometry and vibrational frequencies; geometrical changes upon polymerization (this is further discussed in SD §7). The range of the evanescent field is calculated in SD §2. Absorptions related to the conjugated parts of DA and PDA, and those in the overtone region ($4000\text{--}7500\text{ cm}^{-1}$) are presented in SD §3 and 4, respectively. Vibrational exciton interaction energies are discussed in SD §6, comparison between monomer, blue and red polymer in the CH region in SD §8 and crystallographic data in SD §9.

2. Experimental methods

Infrared (IR) spectra were recorded using a Fourier-transform infrared spectrometer (FTIRS) Magna-IR Nicolet 860 equipped with MCT and DTGS detectors. All spectra shown have been obtained with a resolution of 4 cm^{-1} . This spectrometer is particularly stable, enabling to study ultra thin films.

The choice of the IR methods used and of the samples studied was motivated by 2 reasons:

- absorption intensities may be vastly different: between the highest peak absorbance, that of the amide I band, and those of the weakest bands of interest to us (the overtones around 6500 cm^{-1}), there are at least 5 orders of magnitude. So, samples of very different thicknesses were needed,
- we are dealing with crystalline materials so the absorptions are polarized, hence the interest of polarized spectra and determination of the dichroism. The determination of polarization directions relative to the common direction of both the polymer chain axis and the H-bond lines will be of interest. This study can only be done on single crystal samples. This leads us to use two IR spectroscopic methods, and several types of samples.

2.1. Spectroscopic methods

2.1.1. Attenuated total reflection in multiple internal reflection (ATR/MIR)

$920\text{ }\mu\text{m}$ thick undoped semi-insulating single crystal GaAs wafers with orientation (100) were acquired from Geo

Semiconductors Ltd. $500\text{ }\mu\text{m}$ thick intrinsic silicon single crystal wafers with orientation (100) were purchased from Siltronix. ATR/MIR elements were cut from double-side polished wafers in $40\text{ mm} \times 15\text{ mm}$ rectangles and optically polished in 45° beveled edges in an isosceles trapezoidal shape. The studied films are deposited onto one surface of the ATR/MIR element and the IR beam is attenuated by absorption of the evanescent wave by the organic film [19]. The beam path in the wafer is long, and the substrate absorbs below 1200 cm^{-1} for Si and 650 cm^{-1} for GaAs, so useful ATR/MIR spectra are therefore limited to higher wavenumbers.

2.1.2. Direct transmission

Direct transmission spectra were recorded using two types of samples.

First on bulk single crystals, which are self supported and were not deposited on a substrate to study the polarization. A KRS5 polarizer was used since it is transparent up to 7500 cm^{-1} , our upper frequency limit.

Second on a $\approx 250\text{ nm}$ thick evaporated films in unpolarized light to check that MIR and transmission spectra are identical. No effect of polarization of light due to multireflexion can be noticed.

In this geometry all wavenumbers down to 650 cm^{-1} were accessible since Si absorption between 1150 and 650 cm^{-1} remains weak enough due to the much shorter light path.

2.2. Types of samples, their preparation and characterization

4B and 3B monomers were synthesized in the laboratory using standard methods [20] and purified by column chromatography. The shape of DSC melting endotherms indicates the high purity of the materials.

Two types of samples were studied:

(1) Polycrystalline 4B or 3B monomer films, with average thickness from $\approx 3\text{ nm}$ to 250 nm , were prepared by evaporation of monomer powders onto Si or in some cases GaAs ATR elements at room temperature. For such thickness the irradiation can be assumed homogeneous (see SD §2). Si wafers were cleaned ultrasonically in detergent then in acetone and dried in an oven just before use. GaAs wafers were cleaned in acetone only.

Film crystallinity was checked on a polymerized (blue) 4B film on Si, in a grazing incidence X-ray diffraction experiment using a Rigaku Smartlab diffractometer. The reflectivity shows well defined peaks, showing that the film is indeed composed of layers parallel to the substrate surface; the peaks positions correspond to a layer thickness of 2.7 nm in excellent agreement with the polymer crystal value [21]; and several Kiessig fringes corresponding to a total film thickness of 120 nm , in agreement with the nominal thickness. The latter observation shows that the film has a fairly homogeneous constant thickness (number of layers). In-plane diffraction shows several Bragg peaks, still with a poor signal to noise ratio. Therefore, the layers themselves are crystalline as well. The corresponding figures are shown in SD §9

Polymerization was carried out by irradiation of the films by polychromatic UV light ($230\text{--}270\text{ nm}$) as described elsewhere [22]. The polymerizability of these films, including the 3 nm thick ones, proves their crystallinity since the reaction is topochemical and strictly controlled by the relative positions of the molecules, and AFM images show crystallite sizes $\approx 400\text{ nm}$ [22]. 3B and 4B crystals are lamellar, and AFM also shows that lamellae are parallel to the substrate surface since steps with heights equal to a lamella thickness $\approx 2.7\text{ nm}$ or a small multiple of it are observed. Film thicknesses were determined by monitoring during evaporation using a calibrated quartz, and also, for thicknesses $\geq 30\text{ nm}$ by direct measurement using Nuclear Reaction Analysis (NRA) as described elsewhere [22]. Films on glass, identical to those used for our

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