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Investigation of the structure of polymer diacetylene Langmuir–Blodgett films

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The structure of Langmuir–Blodgett (LB) diacetylene films CH_3–$(CH_2)_{11}$–$C\equiv C$–$C\equiv C$–$(CH_2)_8$–$COOCd_{1/2}$ (DA1) and CH_3–$(CH_2)_{20}$–CO_2–CH_2–$C\equiv C$–$C\equiv CH_2OH$ (DA2) was studied by X-ray small angle scattering and electron diffraction methods prior to and upon their polymerization. It has been established that Langmuir films have layer packing. The periods of the constituent layers were determined as 58 Å (for DA1) and 69 Å (for DA2). This indicates the existence of a vertical bilayered packing of molecules. It has also been established that polymerization of LB diacetylene films due to the action of UV irradiation does not change the layer thickness appreciably and the structural rearrangement reduces to a slight redistribution of the electron density along the molecules which is explained by a break of the triple bonds during the UV irradiation.

1. Introduction

Because of ever increasing interest in the practical application of superthin polymer films a great importance is acquired by polydiacetylenes (DA)—polymers based on disubstituted diacetylenes with the conjugated triple bonds having the structure R–$C\equiv C$–$C\equiv C$–R''. They possess non-linear optical properties, high mobility of current carriers, high mechanical strength and thermal stability, etc. [1, 2]. It is well known that DA are easily polymerizable crytals having multilayers of various morphology. The solid phase polymerization of DA can be initiated by various external factors including UV irradiation, and therefore is classified as a topochemical reacton. Distinct from the growth of single crystals, the formation of LB films is associated with problems caused by the fact that LB layers are formed by amphiphilic molecules. Also, the presence of a hydrophobic hydrocarbon tail can substantially change the crystallization process in the layer thus hindering polymerization.

The present study is devoted to the LB films of diacetylene polymers of two types:

$$\text{DA-salts}\quad CH_3\text{–}(CH_2)_{11}\text{–}C\equiv C\text{–}C\equiv C\text{–}(CH_2)_8\text{–}COOCd_{1/2} \qquad \text{(DA1)}$$

and

$$\text{DA-alcohols}\quad CH_3\text{–}(CH_2)_{20}\text{–}CO_2\text{–}CH_2\text{–}C\equiv C\text{–}C\equiv CH_2OH \qquad \text{(DA2)}$$

with the aim of comparing the film quality, layer ordering, possible packings, and the character of the polymerization process.

2. Experimental

As a subphase for applying films a $3\times10^{-4}\,\mathrm{mol\,l^{-1}}$ $CdCl_2\cdot2\cdot5H_2O$ solution with pH = 7 and deionized water filtered through 0·3 μm Vladipor membranes were

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used for DA1 and DA2, respectively. The DA1 films were transferred on to silicon substrates by the method of vertical lift at a rate of 10–15 mm min^{-1} under pressures of 30 mH m^{-1} for DA1 and 35 mH m^{-1} for DA2. Thus 34 monolayers were deposited on to silicon substrates. Film polymerization was performed in an argon flow-in Teflon chamber with the aid of a quartz lead DLR-250 valve for 3, 6, 9, or 12 min [3].

The quality of the layer packing was controlled by an X-ray small angle scattering method with the use of a small angle reflection diffractometer with a position-sensitive AMUR-K detector and BSV-22 X-ray tube with a copper anode and nickel filter, the voltage being 30 kV. The angular resolution was 0·02° [4].

The arrangement of molecules in the layer plane was studied by reflection (RED) and transmission (TED) electron diffraction techniques in an electron diffraction camera with an accelerated voltage of 75 kV.

3. Results and discussion

The integral intensities from the obtained X-ray patterns were determined for Bragg reflections of up to the tenth order. This provided the determination of the periods of the films ($D = 58$ Å for DA1 and $D = 69$ Å for DA2) that are in good agreement with the ellipsometry measurements of the total thickness of films containing 34 layers, namely, 1000 Å and 1200 Å for DA1 and DA2, respectively. This indicates a Y-type bilayer packing with the correlation radius $R = 650$ Å.

Upon UV irradiation, the periods of the layer packings for both DA1 (see figure 1) and DA2 (see figure 2) films remained constant within the measurement error (2 Å), but the polymerization of the DA2 films resulted in a noticeable rearrangement of the relative intensities of the Bragg peaks that was observed after 3 min of the UV irradiation but then remained unchanged.

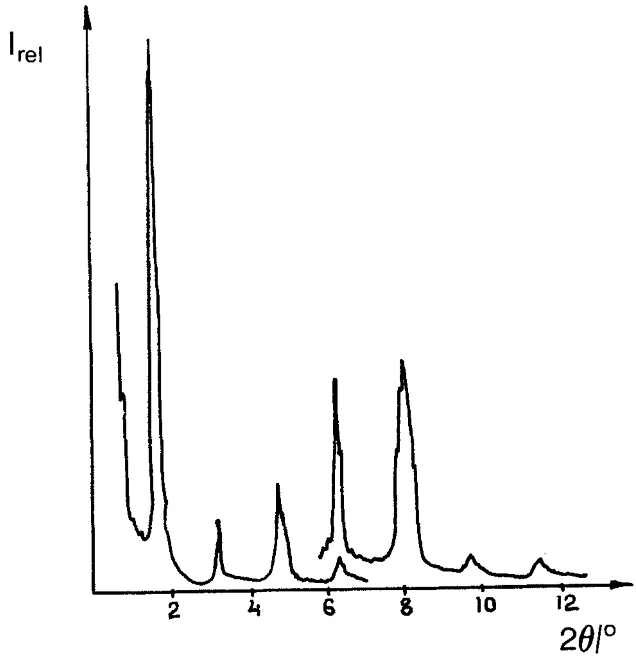

Figure 1. X-ray small angle pattern from 34 DA1 monolayers on Si (the same curve obtained before and after UV irradiation). $d = 5·8$ nm.

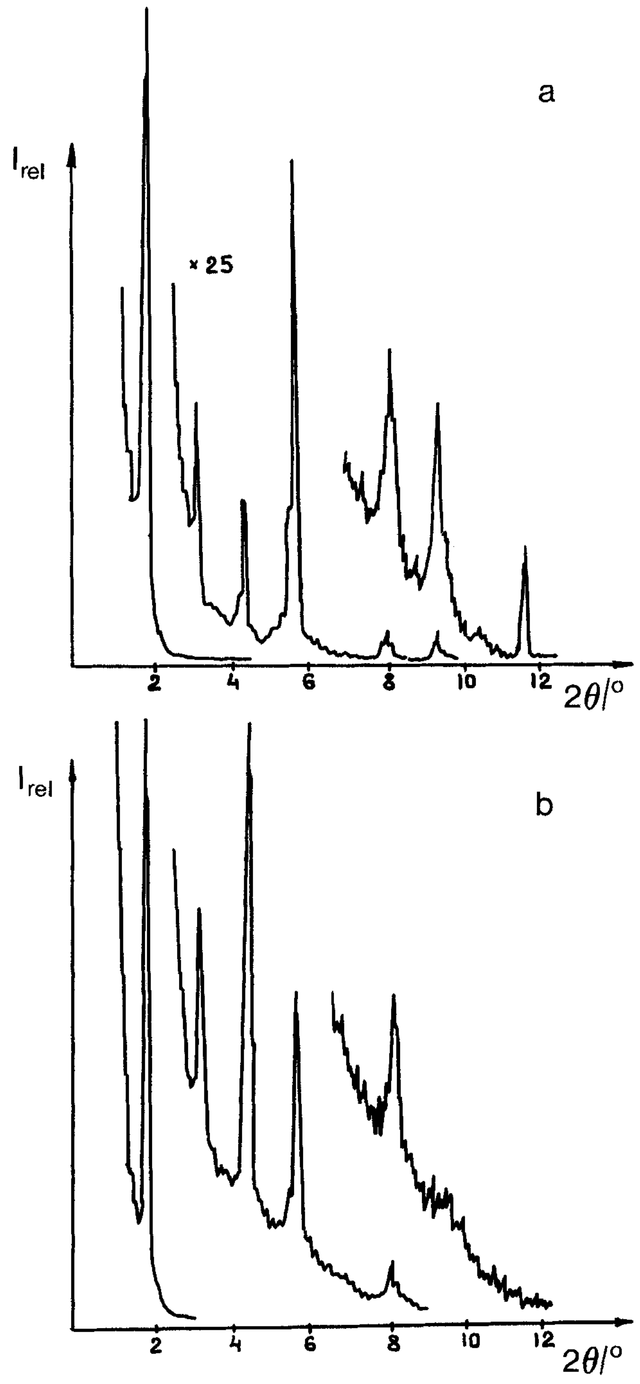

Figure 2. X-ray small angle pattern from 34 DA2 monolayers on Si (*a*) before UV irradiation, and (*b*) after UV irradiation. $d = 6{\cdot}9\,\mathrm{nm}$.

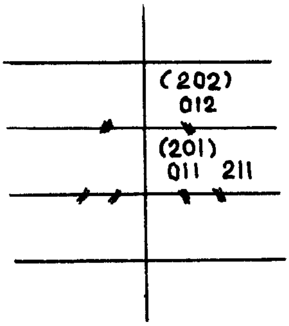

Figure 3. Schematic reflection electron diffraction pattern from a DA2 LB film.

The reflection electron diffraction patterns from the DA2 films have continuous layer lines with well-distinguishable but rather broad reflections on them (see figure 3). The distances between the layer lines correspond to a subperiod $c = 2{\cdot}6$ Å characteristic of a zigzag hydrocarbon chain. Electron diffraction patterns of the DA1 films are more diffuse but nevertheless provide a qualitative conclusion to a certain ordering of the molecules in the layers. Upon UV irradiation both types of film yielded electron diffraction patterns typical of the amorphous state.

Transmission electron diffraction patterns of the DA1 films had only diffuse rings, those obtained for the DA2 films normal to the electron beam showed the presence of a ring consisting of four sharp reflections with five diffuse rings of a larger diameter that degenerated into ellipses as the sample was tilted relative to the electron beam (see figure 4).

The analysis of the reflection arrangement and spacings from the electron diffraction patterns of DA2 yielded the unit cell dimensions in the layer plane: $a = 4{\cdot}9$ Å and $b = 7{\cdot}4$ Å.

The reconstruction of the molecule configurations in DA1 and DA2 was based on the model of atom–atom potentials [5] and the use of the FORCE FIELD MM2 program written by Allinger (see figure 5). The calculated size of the DA2 molecule equal to 34 Å corresponds to the known data for the LB film structure with the period 69 Å.

Electron diffraction studies indicate that DA1 molecules in monolayers that build LB films are only slightly ordered probably because of the complicated shape of the molecule tail. 'Heavy' Cd atoms in the heads of the molecules decrease the sensitivity of the X-ray technique to possible small electron density variations during polymerization.

The analysis of the electron diffraction data [6] from DA2 LB films shows that they contain very small (50 Å) ordered regions. The comparison of the lattice periods

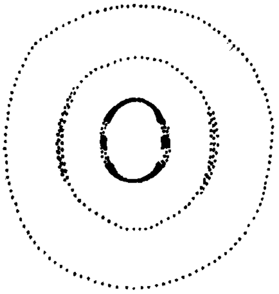

Figure 4. Schematic transmission electron diffraction pattern from a DA2 LB film.

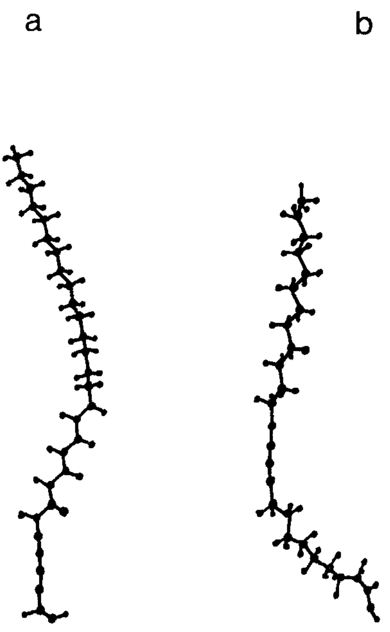

Figure 5. Reconstructed molecular configurations for DA2 (*a*) and DA1 (*b*) calculated by Allinger's FORCE FIELD program.

calculated by the electron diffraction and small angle X-ray scattering data with the known literature data for various types of aliphatic hydrocarbon chain packings [7] brought us to the conclusion that in such inclusions the 'tails' should interact, and the most probable packing for such crystalline islands in DA2 films is orthorhombic with periods $a = 4{\cdot}9$ Å, $b = 7{\cdot}4$ Å, and $c = 69$ Å (see figure 6).

The disappearance of reflections on the layer lines of the electron diffraction patterns from UV irradiated samples indicate the changes in the molecule arrangement occurring during polymerization. This may be explained by the fact that the interaction between the molecule heads in polymerized samples after the break of triple bonds turns out to be much stronger than the tail attraction, which, in turn, can give rise to structural changes in the heads, rotation of some molecules to positions although energetically advantageous for the polymer, but breaking the crystallographic packings.

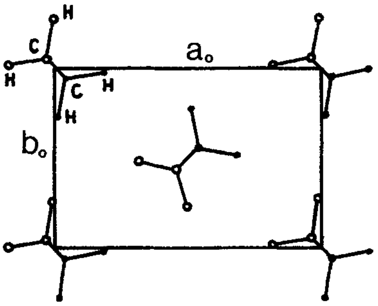

Figure 6. Suggested packing for aliphatic hydrocarbon chains in diacetylenes.

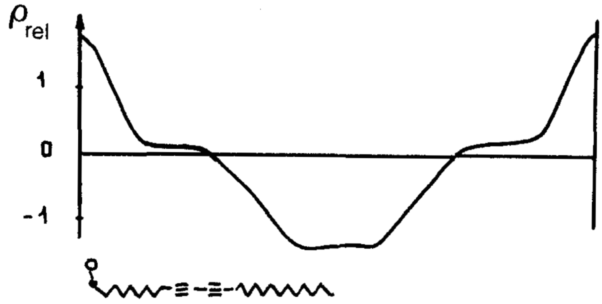

Figure 7. Electron density profiles calculated for a DA1 LB film.

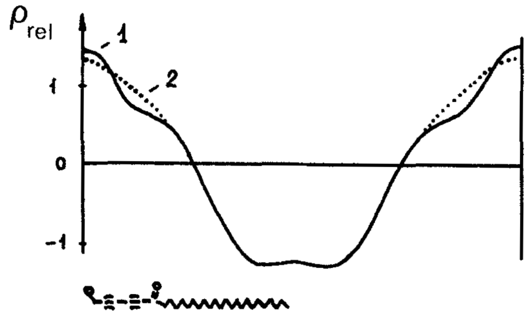

Figure 8. Electron density profiles calculated for a DA2 LB film (1) before UV irradiation, and (2) after UV irradiation.

The electron density profiles of the initial and irradiated samples (see figures 7 and 8) restored from the X-ray data by the inverse Fourier transformation technique [8] show some differences in the region of diacetylene heads of the molecules and confirm indirectly the assumption that the observed structural changes are associated with the break of triple bonds in molecules during polymerization. But the attained 7 Å resolution does not allow us to model the expected structural rearrangement in detail. Thus further detailed investigations of the films are necessary.

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