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Single Sheet of a Quasi-Planar Macromolecule Prepared by Photopolymerization at a Solid Surface

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When vapor deposited onto a cleavage plane of graphite is cooled adequately, a planar or linear organic compound having considerable molecular weight forms a monolayer in which the molecules are oriented with the carbon skeleton plane parallel to the substrate surface.[2−7] Further, the monolayers of the same[2] or differernt compound(s)[3] can be piled up layer-by-layer. The molecules are liable, however, to be desorbed[3,4] as well as disordered in aggregation[2,5] since they are gathered by weak van der Waals interactions. Therefore, a stronger interaction must be introduced among them to prepare a new material by utilizing unique aggregation in an extrathin film. A surface reaction has an advantage over a bulk reaction in that it can be confined to a certain place or direction. For example, monomer molecules in the outermost surface layer can be selectively combined because they are not sandwiched between the molecules of neighboring layers; hence, they are liable to take an orientation suitable for polymerization reactions.[4] In addition, donor and acceptor molecules can be connected by charge transfer reactions between donor and acceptor monolayers deposited alternately.[3] In this study, we have tried to form a quasi-planar macromolecule by joining monolayer molecules with covalent bonds, using Penning ionization electron spectroscopy[8] as a probe for the molecular orientation and electronic structure.[6,7]

For the preparation of a network of carbon atoms arranged in a single plane, a topochemical reaction[9] must occur in the monolayer of flat-lying and closely-packed molecules without desorption. A monolayer of dialkyldiacetylene seems to be appropriate here because diacetylene groups, which are known to undergo topochemical polymerization in the bulk,[10] are expected to be held close together and arranged regularly with the dense monolayer packing of slender alkyl chains, as shown in Figure 1a.[7,11] This arrangement maximizes van der Waals interactions among molecules and the substrate and enables molecules to undergo the intramonolayer reaction. The estimated stacking distance, $d = 4.7$ Å, and the angle, $\gamma = 56°$, between the diacetylene rod and the stacking axis are for the case of reactive diacetylenes.[9] As the first step to unite molecules two-dimensionally, we thus plan to stitch up a row of flat-lying alkyl chains with a polydiacetylene chain one-dimensionally in each column and form a sashlike macromolecule (see Figure 1b). Since the molecular packing does not depend on the length of the alkyl chain, 17,19-hexatriacontadiyne (HTDY) was used to make the vapor pressure suitable for monolayer preparation.

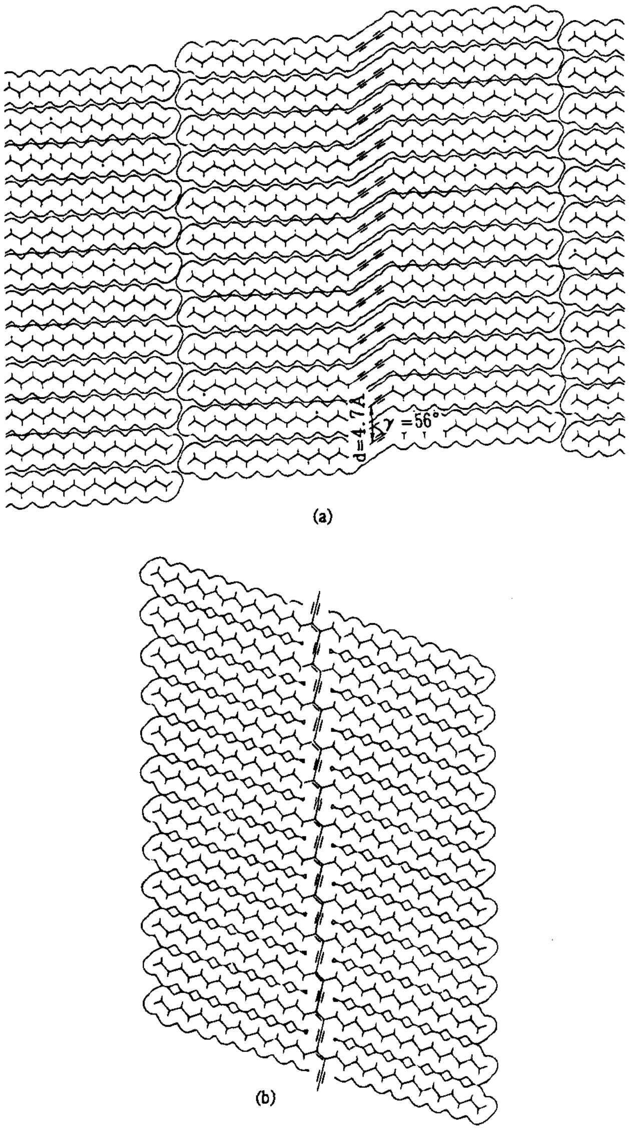

Figure 1. Schematic diagrams for (a) a monolayer of 17,19-hexatriacontadiyne (HTDY, $C_{16}H_{33}C{\equiv}CC{\equiv}CC_{16}H_{33}$) molecules laid flat in *all-trans* conformation and (b) a single sheet of a quasi-planar macromolecule produced by polymerizing HTDY molecules in each column of (a). These diagrams are for an ideal case; all the HTDY molecules in each column are not necessarily linked to form an infinite sash.

In Figure 2A, the He* (2 ^{3}S, 19.82 eV) Penning ionization electron spectrum (PIES) of a graphite substrate held at 173 K and that of an HTDY monolayer formed on the graphite substrate are shown as curves a and b; the deposited amount was controlled precisely at 1 *monolayer equivalence* (MLE),[7] the number of HTDY molecules required to cover the substrate surface with the arrangement shown in Figure 1a. The signal to be ascribed to graphite is hardly detectable for curve b because metastables cannot penetrate into the solid; instead they interact with the monolayer, which indicates that HTDY molecules lie flat uniformly (note that the surface cannot be covered with 1 MLE of HTDY in other orientations). Bands *P* and *S* are

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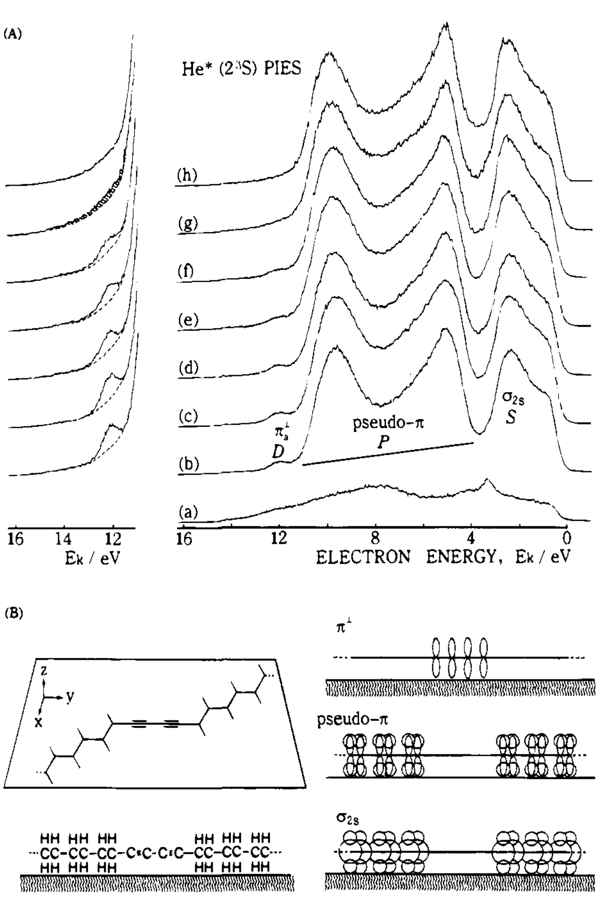

Figure 2. (A) He* ($2\,^3S$, 19.82 eV) Penning ionization electron spectra of a graphite substrate held at 173 K (curve a) and an HTDY monolayer prepared on it (curves b–g). The deposited amount was 1 MLE,[7] the number of HTDY molecules required to cover the substrate with the arrangement shown in Figure 1a. Curve b was obtained fresh at 173 K; curve c at 223 K; curves d–f during UV irradiation at 223 K (irradiation times, 2, 8, and 16 h, respectively); and curve g after the substrate temperature was raised slowly to 293 K with 12 h of UV irradiation. The PIES of a zinc stearate ($C_{17}H_{35}COOZnOCOC_{17}H_{35}$) monolayer on graphite[4] is shown as curve h for comparison. In the left, the high E_k parts of magnified curves b–h are shown; broken curves h are superimposed on curves b–g. (B) Schematic diagrams of an HTDY molecule laid flat on a substrate surface (a top and a side view) and the three types of MOs responsible for bands *D*, *P*, and *S*. The pseudo-π and σ_{2s} MOs mainly consist of the alkyl C $2p_z$ and H 1s atomic orbitals, and the alkyl C 2s and H 1s atomic orbitals, respectively.

assigned to the pseudo-π and σ_{2s} molecular orbitals (MOs) of alkyl chains,[7] respectively (see the right of Figure 2B). Selective detection of these alkyl MOs extending normal to the zigzag carbon plane also indicates that the molecule orients with the plane parallel to the substrate surface to make these MOs interact with metastables effectively. Bands *P* and *S* with similar shapes are observed for a monolayer of zinc stearate ($ZnSt_2$) as well (curve h) because of the structural similarity and flat orientation of $ZnSt_2$ and HTDY molecules.[4] The assignment of band *D* is as follows.

Bonding and antibonding interactions between the highest occupied acetylene π MOs, perpendicular ($\pi^{\perp}$) or parallel ($\pi^{\parallel}$) to the zigzag plane, afford diacetylene π MOs, $\pi_b^{\perp}$ and $\pi_a^{\perp}$ MOs or $\pi_b^{\parallel}$ and $\pi_a^{\parallel}$ MOs.[4] In the flat molecular orientation, however, the $\pi_b^{\parallel}$ and $\pi_a^{\parallel}$ MOs are scarcely attacked by metastables and do not contribute to the PIES. Moreover, since the $\pi_b^{\perp}$ MO is buried in the high density of states of the pseudo-π MOs, the corresponding band is smeared out by the overwhelmingly strong band (*P*) around $E_k = 9.5$ eV. Therefore, the $\pi_a^{\perp}$ MO alone, with sufficiently low ionization potential compared to those of the pseudo-π MOs, provides a well-separated band *D*.

Since 173 K is too low to carry out photopolymerization according to our preliminary experiment, the substrate temperature was raised to 223 K (curve c) before UV irradiation to provide the molecules with adequate mobility necessary for the reaction. Curve c shows that the monolayer does not evaporate at this temperature. The PIES changes (curves d–f) during UV irradiation with a deuterium lamp (maximum intensity at 190 nm) at 223 K: the peak of band *D* becomes lower, and both the sides upheave little by little.[12] Further irradiation while heating the substrate slowly to 293 K (curve g) leaves band *D* stretched and monotonous. These changes indicate that the conjugation of the $\pi^{\perp}$ MOs becomes elongated, their energies being split and spread over the shadowed region in Figure 2A to form broad-band structures. Since no significant change, however, is observed in the shapes of bands *P* and *S*, we can confirm that the flat orientation of the alkyl chains is essentially maintained during polymerization. In contrast to this result, an unirradiated HTDY monolayer easily sublimes upon heating to room temperature. These observations are fully consistent with a model in which the diacetylene units in each column are polymerized to stitch up the rows of the flat-lying alkyl chains and yield a sashlike single sheet of a planar carbon network.

The present study demonstrates that a monolayer comprising flat-lying chains is available for the formation of a single sheet of a quasi-planar macromolecule. A sheet spreading two-dimensionally will also be obtained if the alkyl ends of neighboring sashes are bridged; this can be effectuated with a compound having terminal polymerizable groups, which is now under investigation. In addition, intra- and interlayer interactions could be investigated separately, if changes in the electronic structure were observed upon layer-by-layer piling of macromolecular sheets.

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[12] Since the PIES of the $ZnSt_2$ monolayer lacks features at $E_k > 11$ eV[4] and has bands *P* and *S* very similar to those for HTDY, the high E_k part of curve h can be used as a background line for band *D*.