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[32] Metallization schemes other than Pt do not tolerate this latter step.
[33] We used a large area base electrode to which a connection could be made by stripping a portion of the three-layer assembly.

Adjacent Reentry of Folded Polydimethylsilane Polymer Chains**

By *Robert D. Boyd* and *Jas Pal S. Badyal**

The growth of polymer single crystals from dilute solutions has been known for a long time.[1] These generally tend to grow as thin lamellae with lateral dimensions of micrometers and nanometer-scale thickness.[2,3] At the molecular level, polymer chains align themselves perpendicular to the lamella surface via chain folding.[4,5] Because of the very small thickness of the crystallites along the chain direction, a single polymer chain must traverse the crystallite from which it originates many times. Two types of model can potentially describe this polymer chain folding:[6] a random (switchboard) model, where the polymer chains give rise to an amorphous overlayer, or, alternatively, the polymer chains are regularly folded, making hairpin turns at the surface, which is known as the adjacent reentry model (Fig. 1).[7] Indirect measurements based on neutron scattering[8] and infrared absorption[9] studies tend to support the latter description. In addition, physically adsorbed polymer material[9] and defects[10] can be present at the surface.

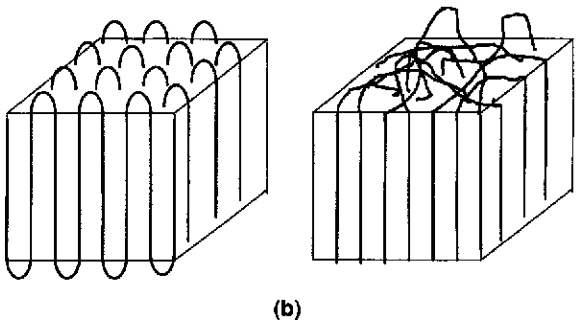

Fig. 1. Schematic representation of chain folds in a polymer single crystal: a) regular adjacent reentry model, and b) random switchboard model.

The surface morphology of polymer single crystals has previously been studied using electron microscopy[11,12] and atomic force microscopy (AFM).[3,13–16] Molecular scale resolution has been mainly hampered as a result of the small size of the polymer backbone carbon atoms and also the presence of an amorphous surface overlayer.[17–20] Here, we investigate the surface structure of polydimethylsilane ($[-Si(CH_3)_2-]_n$) crystals using AFM. Polydimethylsilane is a highly crystalline polymer that adopts an all-*trans* packing arrangement in the solid state.[21] A distinct advantage of silicon-containing polymer backbones over their carbon counterparts is that they crystallize with larger lattice parameters (due to the greater size of silicon atoms), thereby making it easier in principle to image the polymer backbone using AFM.

A 0.001 % w/v dilute solution of polydimethylsilane (ABCR) in toluene was heated to 100 °C and maintained at this temperature for 30 min and then allowed to slowly cool down to room temperature. A few drops of the suspension were then deposited onto freshly cleaved mica, and the solvent was allowed to evaporate prior to AFM analysis. These experiments were repeated using a flat glass substrate in order to check that there were no artifacts in the obtained AFM images due to the mica substrate. All AFM images were acquired using a Digital Instruments Nanoscope III atomic force microscope operating in the contact mode. 200 μm cantilevers were used with a spring constant of 0.06 N m^{-1}, which resulted in an applied force of 3 nN. Micrometer-scale and molecular resolution images were obtained on a number of polydimethylsilane crystals using 100 μm and 1 μm piezoelectric scanner heads, respectively.

Crystallite thickness was measured to be of the order of 5 nm (Fig. 2). This is in good agreement with previous electron microscopy thickness measurements of polydimethyl-

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[**] R.D.B. thanks ICI for financial support and EPSRC for provision of instrumentation during the course of this work.

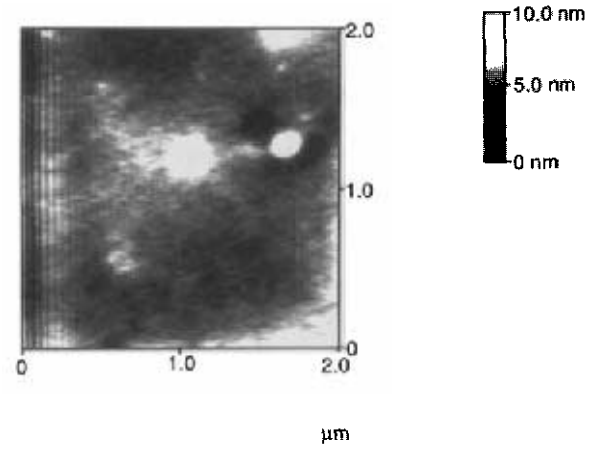

Fig. 2. Low resolution AFM image of lamellar polydimethylsilane crystals (light regions).

silane single crystals.[22] Molecular scale resolution AFM of polydimethylsilane revealed rows of rod-like features (Fig. 3); these rod-like features cannot be associated with the polymer repeat units since they are much longer than

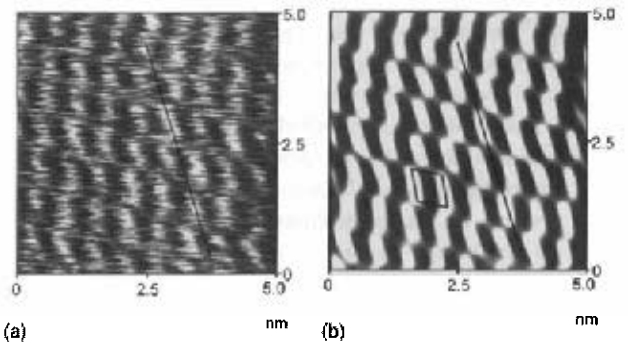

Fig. 3. Molecular resolution AFM image of a polydimethylsilane single crystal surface: a) before filtering, and b) after filtering. The drawn straight line represents the top view of a folded polymer chain.

the Si–Si bond length contained along the polymer backbone of polydimethylsilane (which is reported to be 0.4 nm[21]). It is more likely that the rod-like features correspond to chain folds at the single crystal surface, as expected for the regular adjacent reentry model (Fig. 1). The dimensions of the unit cell are 0.80 ± 0.05 nm and 0.62 ± 0.03 nm, with a lattice angle of $95 \pm 5°$. These results are consistent with electron and X-ray diffraction studies of polydimethylsilane, which report the unit cell dimensions as being a = 0.80 nm, b = 1.22 nm, and γ = 91°, where b corresponds to twice the interchain lattice spacing.[21]

Hence it can be concluded that the folding of polymer chains at the surface of polydimethylsilane single crystals can be seen at molecular scale resolution by atomic force microscopy. Comparison with previous electron and X-ray diffraction data indicates that polymer chain folding at the surface is consistent with the regular adjacent reentry model.

Received: March 3, 1997
Final version: May 21, 1997

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β_{CO}-$(ET)_2I_3$: Non-electrochemical Synthesis and Structural and Physical Properties of an Organic Superconductor with 7.1 K ≤ T_c ≤ 7.9 K

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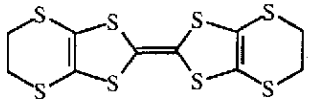
Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET for short, see Scheme 1) and iodine form a plethora of polymorphic phases, denoted by small Greek letters, the electrical conductivities of which range from semiconducting to metallic to superconducting.[1] β-$(ET)_2I_3$,[2–4] θ-$(ET)_2I_3$,[5] κ-$(ET)_2I_3$,[6] and γ-$(ET)_3(I_3)_{2.5}$[7] are superconductors at ambient pressure, with transition temperatures T_c of 1.4 K, 3.6 K, 3.6 K and 2.5 K, respectively. A superconducting product ($T_c \approx$ 7–8 K),[8] generally referred to as α_t-$(ET)_2I_3$, is obtained by thermal conversion of the organ-



Scheme 1. BEDT-TTF (the abbreviation ET is used in this communication).

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