17. Epitaxial Polymerization of Polyester as Studied by Scanning Tunneling Microscopy

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Abstract: \(\varepsilon\)-Caprolactone was epitaxially polymerized on the basal plane of graphite by the conventional ring-opening reaction. An ultra-thin polymer film remained upon washing the bulk polymer away as confirmed by Infrared and X-ray photoelectron spectroscopies. Direct observation by scanning tunneling microscopy revealed the chain packing of poly(\(\varepsilon\)-caprolactone) as well as its epitaxial orientation in atomic detail.

Key words: Epitaxial polymerization; poly(\(\varepsilon\)-caprolactone); scanning tunneling microscopy.

Epitaxial polymerization is a newly found process where macromolecules are polymerized on the solid surface in such a way that the resulting structure reflect the atomic arrangement of the solid surface. Ultra-thin polymeric films can be obtained by washing the bulk materials away with good solvents. The alignment of individual macromolecules, whose monomeric units are regularly linked along the chain backbone, imparts two dimensional structural order to the ultra-thin film. This method appears to be applicable to various types of polymer molecules with a possibility that their two dimensional structures may be pre-designed.

Here, we present a study of epitaxial structures of a polyester film on the graphite surface. Scanning tunneling microscopy (STM) is used to observe the resulting epitaxial film in atomic resolution, exhibiting the intra- and inter-molecular structures as well as the epitaxial orientations with respect to the substrate atomic lattice. Cationic ring-opening polymerization of \(\varepsilon\)-caprolactone was conducted by diethylzinc catalyst in benzene as reported earlier. Freshly cleaved highly oriented pyrolytic graphite (HOPG) was placed in the reaction mixture at the early stage of polymerization. After 44 hours of reaction time at 60°C, HOPG was taken out of the mixture and washed thoroughly with benzene, ethanol, THF, acetic acid, and water. The number averaged molecular weight of the bulk polymer was 8300.

Formation of a poly(\(\varepsilon\)-caprolactone) film on the HOPG surface was evidenced by Fourier transform infrared spectroscopy (FTIR, Nicolet 710) and X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5300 ESCA system). FTIR peaks at ca. 2930 and 2850 cm\(^{-1}\) and a considerable increase in the O1s peak in an XPS spectrum suggested that a polymer film remained on the HOPG surface even after washing with good solvents of the bulk polymer. No XPS peak for Zn2p3/2 was found.

STM was operated in air at room temperature in the variable current mode. Similar to the polyether\(^{(1),(2)}\) or polyamide\(^{(3)}\) studies, we have made the following assumptions for interpreting the STM images. (1) It is well known that, on bare graphite, every other carbon atom on the hexagonal lattice is the predominant tunneling site and appears brighter on STM images. The adsorbate atom in the vicinity of this bright graphite carbon appears brighter than others that are away from it. (2) There are four major types of...
atomic species on the polymer molecule besides hydrogen; an aliphatic carbon, an alkoxy oxygen, a carbonyl carbon, and a carbonyl oxygen. Consistent with the previous studies, the alkoxy oxygen and the carbonyl group are assumed to be the enhanced current sites on a polymer chain.

While polyethers produced numerous types of STM images, the images of poly(ε-caprolactone) were dominated by the one shown in Fig. 1. The bright discs form straight lines whose perpendicular separation is 11.3 Å. A model that is associated with this image is schematically shown in Fig. 2. This is not the only model for the STM image, since the

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**Fig. 1.** STM image of poly(ε-caprolactone) on HOPG, taken at a current of 200 pA with a bias of 0.8 V. The darker contrast toward left is caused by the tilted baselines.

**Fig. 2.** Schematic drawing of an epitaxial orientation of poly(ε-caprolactone) on HOPG. A small circle on the graphite hexagonal lattice represents the predominant tunneling site. The atom shown in the bold, italic character lies in the neighborhood of the bright graphite carbon.
chain direction or the direction of the carbonyl group can be inverted to give an STM image indistinguishable from that of Fig. 1, depending upon the relative current strength of the alkoxy oxygen and the carbonyl group. In any event, each macromolecule has a planar zigzag structure. Due to the all trans conformation of the chain, as shown in Fig. 2, the relevant repeat unit is given by every other ester group. The repeating distance of 17.2 Å as measured by the graphite hexagonal cells (7×2.46 Å) is in complete agreement with the length of the two repeat units of the polymer (17.1~17.2 Å) obtained from bulk structural studies.6,7

As demonstrated in the polyether study,1,2 various interchain structures can be constructed by mutual shifts of the adjacent chain by integer multiples of the graphite hexagonal cell along the chain backbone direction. Assuming that the carbonyl group corresponds to the brighter region of the image, the mutual shift of 0, 1, 2, and 3 hexagonal cells produce the perpendicular distances between the bright lines of 17.2, 14.9, 11.3, and 8.6 Å, respectively. The proposed model of Fig. 2 is strongly supported by the complete agreement between the distance measured on the image and the calculated distance of the mutual shift of 2 hexagonal cells. An analogous relative orientation of the carbonyl group is also seen in the bulk structures.6,7

On the other hand, it is not correct to assign each brighter disc to the individual carbonyl group. According to the epitaxial structure shown in Fig. 2, each polymer chain is separated by 4.3 Å, equal to the distance between every other graphite hexagonal cell. However, the corresponding distance measured on the STM image amounts to less than 3 Å as indicated in Fig. 1. This is the only case where these distances disagree, since similarly constructed structures have explained the observed STM images quite well in the case of polyethers and polyamide. Thus, the spatial extent of electronic interaction between the ester group and the graphite hexagonal lattice need to be considered in order to predict the detailed feature of STM images.

In conclusion, an ultra-thin film of two dimensionally oriented poly(e-caprolactone) is synthesized by epitaxial polymerization. The dipolar carbonyl group appears to regulate the two dimensional structure of the epitaxial film. This process offers a novel approach to produce new composite materials for electro-optical or quantum-electronic devices and for biotechnological applications.

References

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