Epitaxial Growth of Polymers Induced by Cationic Ring-Opening Polymerization below the Equilibrium Monomer Concentration

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Polymerization-induced epitaxy (PIE) refers to epitaxial growth of polymers on a substrate surface during solution polymerization of monomers.[1] Many crystalline polymers have been shown to form epitaxial films on graphite, during cationic and anionic ring-opening polymerization,[2−4] radical polymerization,[5] and polycondensation and polyaddition.[6] Despite its generality, however, the growth mechanism is not well understood. This paper is the first report of PIE kinetic studies, comparing the polymer growth in solution with the film growth on the surface when the initial monomer concentration is varied. Here, we show that it is possible to have epitaxial growth even below the equilibrium monomer concentration in solution. This result implies that the PIE process is not an adsorption of the polymer which has formed in solution.

Reaction kinetics of cationic ring-opening polymerization of tetrahydrofuran (THF) is one of the most well-known systems.[7−10] We have shown previously that this polymerization induces epitaxial growth of a poly(THF) monolayer on the basal plane of graphite.[2] Local structures within a single domain of the PIE film have been studied in detail. Here, we controlled the solution polymerization kinetics by the initial THF concentration and observed the growth of the poly(THF) PIE film by atomic force microscopy (AFM).[11] In particular, we focus on the size of each crystalline island as well as the surface coverage by all islands.

Cationic ring-opening polymerization involving oxonium ions is usually treated as an equilibrium polymerization without termination and is known to possess ceiling temperatures.[9] This means that an equilibrium monomer concentration (C_{emc}) exists for a given ceiling temperature. The monomer concentration must be greater than C_{emc} for polymerization to proceed, and the value of C_{emc} is determined uniquely by reaction thermodynamics. In the present reaction conditions of initiation by the $BF_3O(C_2H_5)_2$/epichlorohydrin system at 0 °C in CH_2Cl_2, no polymer was formed below $C_{emc} \cong 3$ mol/L in solution.[12] This value is close to C_{emc} taken by other cationic initiators.[7,8,10]

Figure 1 displays an AFM image of the PIE film of poly-(THF). At all THF concentrations, the film exhibits flat rectangular islands having a uniform AFM height of approximately 0.5 nm. These islands intersect each other with
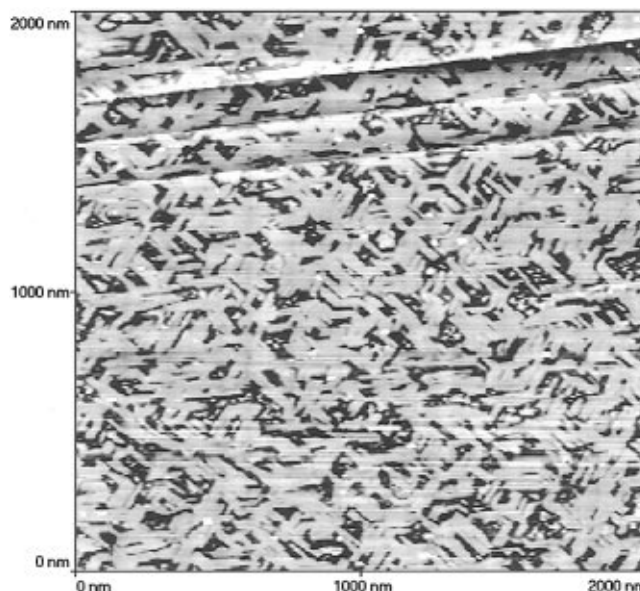

Figure 1. An AFM image of the poly(THF) PIE film on graphite formed at [THF] = 1.85 mol/L. The rectangular islands have a height of 0.5 nm uniformly over the entire area.
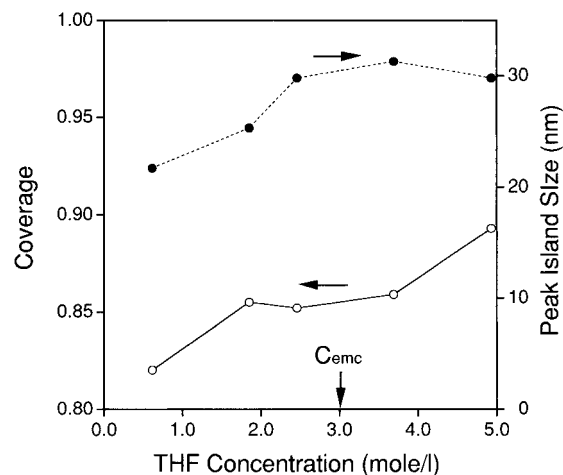

Figure 2. Surface coverage (the solid line, in units of monolayers) and average island sizes (the dotted line) measured from AFM images around the solution C_{emc} of 3 mol/L. Each average (peak) island size is given as the smallest mean value of Gaussian-shaped distributions of the island width.

an angle of 120°. This is consistent with the monolayer model of chains lying flat with its fiber axis parallel to the surface and orienting epitaxially on the graphite hexagonal lattice.[2] This unique feature is one of the characteristics of poly(THF) PIE films and is used advantageously to differentiate it from other types of surface features.

The surface coverage is calculated by measuring the fractional area occupied by all islands in a given frame. We have found that the coverage increases almost monotonically with the initial THF concentration except at very high concentrations. Figure 2 displays the coverage at low concentrations. The PIE film is formed even below C_{emc} of solution polymerization, and the coverage reaches over 0.8 already at 0.62 mol/L.

Since the islands have different sizes and various orientations, statistical analyses of island size distributions are required to quantify the island size at a given monomer concentration.[13] At low THF concentrations, however, the distributions are relatively simple and give well-defined average sizes. Below C_{emc}, the average width and length are approximately 30 nm (Figure 2) and 100 nm (not shown), respectively. These values

(1) Sano, M.; Lvov, Y.; Kunitake, T. *Annu. Rev. Mater. Sci.* **1996,** *26,* 153−187.
(2) Sano, M.; Sasaki, D. Y.; Kunitake, T. *Macromolecules* **1992,** *25,* 6961−6969.
(3) Sano, M.; Sasaki, D. Y.; Kunitake, T. *Science* **1992,** *258,* 441−443.
(4) Sano, M.; Sandberg, M. O.; Yoshimura, S. *Langmuir* **1994,** *10,* 3815−3819.
(5) Sano, M.; Sasaki, D. Y.; Kunitake, T. *Langmuir* **1993,** *9,* 629−631.
(6) Sano, M.; Sandberg, M. O.; Yamada, N.; Yoshimura, S. *Macromolecules* **1995,** *28,* 1925−1937.
(7) (a) Dreyfuss, P.; Dreyfuss, M. P. *Adv. Polym. Sci.* **1967,** *4,* 528−590. (b) Dreyfuss, P.; Dreyfuss, M. P. In *Ring-Opening Polymerization*; Frisch, K. C., Reegen, S. L., Eds.; Marcel Dekker: New York, 1969; Vol. 2, pp 111−158.
(8) Saegusa, T.; Kimura, Y.; Fujii, H.; Kobayashi, S. *Macromolecules* **1973,** *6,* 657−660.
(9) For example, Odian, G. *Principles of Polymerization*, 2nd ed.; John Wiley & Sons: New York, 1981; pp 268−270, 524−528.
(10) Vofsi, D.; Tobolsky, A. V. *J. Polym. Sci., A* **1965,** *3,* 3261.
(11) AFM observation was made in air at ambient temperature in the noncontact mode, using Si cantilevers with resonance frequencies of ca. 150 kHz. No image processing has been performed other than flat leveling.

are equivalent to those of ideally extended straight chains of poly(THF) having molecular weights of 3500 and 12 000. A previous study suggests that a chain extends continuously from one edge of the island to the opposite edge.[14] Thus, the length of a chain in the film may be considerably longer than these values. Regardless of the direction of the chain axes with respect to the island edge, these equivalent molecular weights indicate that the polymerization near the surface has proceeded significantly even below C_{emc}.

These results clearly show that the PIE film was formed when polymerization was not allowed to proceed in solution and the

(12) Highly oriented pyrolytic graphite was immersed in a solution containing controlled amounts of THF in CH_2Cl_2. Polymerization was initiated by 0.093 mmol of $BF_3O(C_2H_5)_2$ with a small amount of epichlorohydrin at 0 °C and was continued without strong stirring. It was allowed to react for 24 h before being quenched with methanol. The graphite was taken out of the mixture and rinsed repeatedly with THF, chloroform, ethanol, and water over a few days at room temperature. The molecular weight of the polymer isolated from solution was measured by GPC with polystyrene standards.

(13) Because of the increasing difficulty in recognizing an individual island from a group of closely lying islands as the surface coverage becomes larger, only the narrower width of each island could be measured at higher concentrations. The island size distributions are well approximated by a single Gaussian at lower concentrations, but multi-Gaussian curves are needed to fit the distributions above 2 mol/L. The peak sizes plotted in Figure 2 are the smallest mean values at the given concentrations.

(14) Observations of the same film in molecular resolutions by scanning tunneling microscopy (STM) have shown only a few point defects within a single domain of the film. Since the chain end is structurally different from the rest, any chain end should be detectable by STM if it exists. This suggests that a chain extends continuously from one end to another within an island. On the other hand, the STM images of the region around the island edge were too complex to analyze. The state of chains at the edge, including possible folds and loops, remains unknown.

reaction responsible for PIE took place far more efficient than one in solution. This implies that the PIE process is not an adsorption of polymer which has formed in solution. Instead, it supports a model of the segmental adsorption (with a crystallographic ordering) taking place at the same time as polymerization.[6]

Within the frame work of known polymerization kinetics, there are several possibilities to explain the present result, such as enhancement of THF concentration near the surface and lowering of the free energy due to the substrate−reagent interactions. Here, we propose another model based on a positive feedback between polymerization and epitaxial adsorption. Consider a reactive chain segment extending into the solution phase with the body of the polymer being adsorbed to the graphite as a crystalline film. Since the crystalline body is chemically inactive, the extending segment can be considered as a propagating chain with a reactive end. Then, incorporation of a part of the segment into the body by epitaxial adsorption implies shortening of the propagating chain. This effective depolymerization by epitaxial adsorption shifts the reaction equilibrium of the propagating segment toward polymerization. As the length of the segment increases by polymerization, more parts of the segment become available for epitaxial adsorption. Self-accelerating growth is entropically regulated and infinite growth of islands is avoided by the graphite defects and the island itself (with respect to neighboring islands). The feedback model with these control parameters will be discussed in more detail in the forthcoming paper.