# Kinetic Studies of Poly(tetrahydrofuran) Epitaxial Film Formed by Polymerization-Induced Epitaxy Using Atomic Force Microscopy

**Masahito Sano*,†** and **Momoyo Wada**

*Contribution from the Pi-Electron Materials Project—JST 43, Miyukigaoka, Tsukuba, Ibaraki 305 Japan*

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**Abstract:** To understand the mechanism of polymer epitaxy during solution polymerization (polymerization-induced epitaxy, PIE), the kinetics of the epitaxial film growth was compared with that of polymerization in solution. The surface coverage and the domain size of epitaxial films as well as the molecular weight of the polymer formed in solution were examined as functions of the reaction time, the monomer concentration, and the initiator concentration. Atomic force microscopy was used to evaluate the coverage and the apparent island size distribution. Cationic ring-opening polymerization of tetrahydrofuran (THF) in dichloromethane at 0 °C on a graphite substrate in the reaction mixture induces an epitaxial film of poly(THF), consisting of 0.5 nm thick, flat, rectangular islands. The reaction time dependence indicates that the film has developed much faster than the polymer growth in solution. When the monomer concentration was varied, no polymer was formed in solution below 3 mol/L, corresponding to the equilibrium monomer concentration. The well-developed PIE film was formed even below this concentration. This result proves that PIE is not an adsorption of the polymers that have first formed in solution. At low initiator concentrations, the polymerization in solution was significantly disturbed due to side reactions, while the PIE film developed well at all concentrations without noticeable dependence on the initiator concentration. This shows that the polymerization reaction responsible for PIE is minimally affected by termination or chain transfer reactions. The kinetics suggests a possibility of the monomer concentration enhancement near the surface. On the basis of these results, a positive feedback model of polymerization with epitaxial adsorption through conformational constraint is proposed as a PIE mechanism.

## Introduction

Ordinary solution polymerization may induce epitaxial growth of synthesized polymers on a solid substrate that has been immersed in the reaction mixture.[1] The resulting epitaxial films often take the form of monolayers with the chain backbone running parallel to the substrate surface.[2] Because polymerization is a necessary condition for epitaxial adsorption to take place, this process is named polymerization-induced epitaxy (PIE). Epitaxial growth of many kinds of polymers has been induced by various methods including cationic and anionic ring-opening polymerization,[2,3] radical polymerization,[4] polycondensation, and polyaddition.[5]

Despite its wide applicability,[6] the PIE mechanism is not well understood. Technically, it is difficult to access the substrate surface in solution when the reaction is in progress. We do not know if the reaction occurring near the substrate surface proceeds in the identical way as the same reaction continuing in solution. Several experimental observations have been made that are not in accord with the known crystallization or adsorption processes of polymers in solution or melt.[1,5] For instance, PIE films can be obtained regardless of whether growing polymers precipitate during polymerization or all products stay soluble until the end.[5]

This paper is concerned with the PIE kinetics, in an attempt to understand why ordinary polymerization reactions can induce epitaxial growth of polymer. Cationic ring-opening polymerization of tetrahydrofuran (THF) is used as a model system, since this polymerization has been found to produce the PIE film of poly(THF) on graphite and the precise epitaxial structures are known.[2] In addition, this is one of the most well-studied polymerization reactions in solution.[7−10] Atomic force microscopy (AFM) has revealed that the poly(THF) epitaxial film consists of 0.5 nm thick, rectangular islands (domains). The detailed account of island morphology is given elsewhere.[11] We have found that the crystallites nucleate homogeneously on the graphite surface and develop monomolecular thick, crystalline islands. The graphite steps and the island itself are found to terminate the growth of neighboring islands.

Here, both the size of crystalline islands and the coverage by all islands measured from AFM images are considered in order to characterize the state of film growth. The experiment consists of comparison of the film growth with the polymer formation in solution when the duration of reaction, the

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[†] Present address: JST, 2432 Aikawa, Kurume, Fukuoka 839 Japan.

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monomer concentration, and the initiator concentration are varied, respectively. Although changing the reaction period does not follow temporal growth of a particular crystal domain, the reaction time dependence indicates how fast the average domain grows in comparison with the polymer growth in solution. The results indicate a much faster rate of film growth than of polymerization in solution. The monomer concentration dependence is the primary interest here, since the THF polymerization is an equilibrium reaction that possesses the equilibrium monomer concentration. We show that the film has developed quite well even below the equilibrium monomer concentration where no polymerization can occur in solution.[12] The initiator concentration dependence was investigated in reference to termination and chain transfer reactions. It shows that the polymerization responsible for the film growth is minimally affected by these side reactions while the polymerization in solution is significantly disturbed. On the basis of the results of three experiments, we propose that the monomer concentration enhancement near the surface and a positive feedback between polymerization and epitaxial adsorption through conformational constraint are the important factors in the PIE mechanism.

## Experimental Sections

A general procedure for a polymerization is given below. Highly oriented pyrolytic graphite (Union Carbide, typically 10 × 25 × 2 mm) was cleaved by peeling off the top layers with adhesive tape in air. This graphite was placed in a 10 mL round-bottom flask and kept in an oven at 150 °C for at least 1 h. The hot flask was quickly attached to a reaction assembly where the following steps could be performed in $N_2$ atmosphere. To this flask were introduced freshly purified, dry THF and dry $CH_2Cl_2$.[13] The total volume was adjusted so that the graphite substrate was completely covered by the reaction mixture. Polymerization was initiated by adding $BF_3O(C_2H_5)_2$ and dry epichlorohydrin at 0 °C without strong stirring.[14] After a predetermined time, methanol was added to quench the reaction.

For the reaction time study, 9.25 mol of THF and 0.093 mol of $BF_3O(C_2H_5)_2$ were used. Only one graphite sample was obtained from each reacting mixture, instead of all graphite samples reacted for different times from a single batch of the reacting mixture.

For the monomer concentration study, 0.093 mol of $BF_3O(C_2H_5)_2$ was used to initiate the polymerization which was allowed to react for 24 h.

For the initiator concentration study, 9.25 mol of THF was used and reacted for 24 h.

In all cases, after the reaction was quenched, the graphite was taken out of the mixture and rinsed repeatedly with THF, $CH_2Cl_2$, ethanol, and water at room temperature over a few days. The polymer formed in solution was collected in methanol from chloroform solution. The reaction mixtures that did not precipitate were simply concentrated by evaporating the solvent under vacuum. The number average molecular weight was measured by GPC using polystyrene as standards.

The graphite samples with the similar conditions have been analyzed previously by Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy to verify that the film on graphite is poly(THF) and that no element from the initiator products is present on graphite.[2] Since the poly(THF) epitaxial film has its own characteristic morphology, we confirm the presence of poly(THF) film from AFM observations rather than by taking a spectrum of every sample. When the reaction had proceeded successfully, we always found the epitaxial film on graphite.

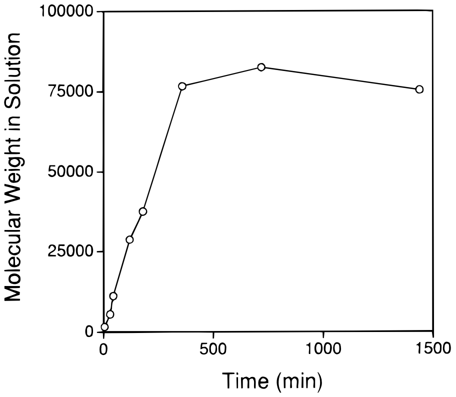

**Figure 1.** Molecular weights of poly(THF) formed in solution at various reaction times.

AFM (TopoMetrix) was performed in the noncontact mode in air at room temperature. We used Si cantilevers with resonance frequencies of either approximately 170 or 300 kHz. Flat leveling was the only process performed on the images. Over 20 images were collected for a given sample using different scan ranges (200−2500 nm) to minimize finite resolution effects.

## Results

**Reaction Time Dependence.** Figure 1 shows the molecular weight of the polymer formed in solution at various reaction times. The molecular weight increases almost linearly with time until about 400 min and then levels off to a constant value. This is in accord with poly(THF) polymerization using other catalysts.[9,10] If we scale the molecular weight of solution grown polymer by its maximum value, the initial growth line gives a slope of 0.0026 $min^{-1}$.

Figure 2 displays the AFM images of poly(THF) on graphite at two different reaction times. The PIE film is characterized by nearly rectangular, 0.5 nm thick, flat islands, intersecting each other with an angle of 60 or 120° that is in accord with epitaxy on the graphite hexagonal lattice. As the mixture is reacted longer, the islands grow to cover the entire graphite surface.

Because the islands have the same height and no multilayers have formed, the surface coverage is calculated, as a function of time, from averaging the fractional area of all islands appearing in each image frame (Figure 3). Each data point is an average from several independent polymerizations quenched after a controlled time. Due to the finite tip size of AFM cantilevers and the signal noise, the imaged island area may be larger than the true size, although the difference should be small for these very thin films.

The coverage increases very steeply at first and then levels off to 0.93 after 200 min of polymerization. The solid line is the best fit curve to the Langmuir-type equation of a form

$$\text{coverage} = \frac{0.125t}{(1 + 0.134t)}$$

where $t$ is time in minutes. Because the change of coverage is rather small, other forms of mathematical expressions may be used to fit the data. However, the Langmuir-type equation fits much better than Freundlich form. This is consistent with a monolayer formation as evidenced by the AFM observations.

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[12] Sano, M.; Wada, M. *J. Am. Chem. Soc.* **1997**, *119*, 4793−4794. The discussion of the positive feedback model given in this reference is not exact, and the refined model is presented here.

[13] Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: New York, 1988.

[14] (a) Although most reagents are freshly distilled for each reaction, the as-purchased initiator was used as a stock solution for a single series of experiments. This gave more reproducible and consistent results than distilling the initiator each time, especially for the polymerization in solution. Thus, the absolute concentrations of the active initiator species would be smaller than ones actually introduced (the reported values). (b) There is an indication that shearing of the reaction mixture during polymerization causes the polymer to be adsorbed strongly.

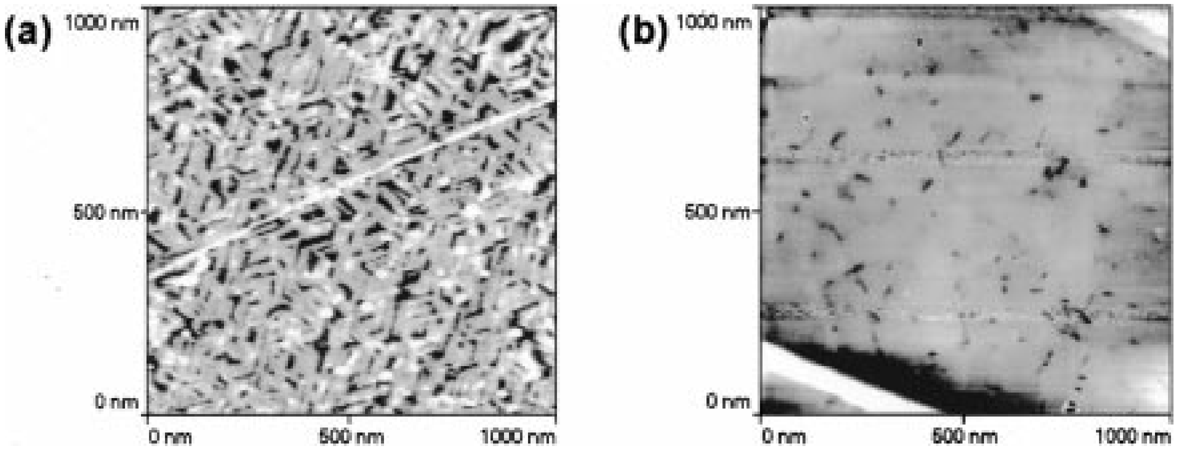

**Figure 2.** AMF images of poly(THF) PIE film on graphite reacted for (a) 5 min and (b) 360 min. The dark region corresponds to the bare graphite surface, and several straight lines running diagonally are the graphite steps. The rectangular islands have a uniform thickness of 0.5 nm.

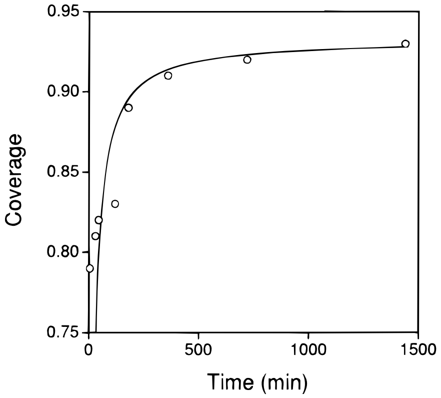

**Figure 3.** Surface coverage in a unit of monolayers as a function of the reaction time. The solid line is the best fit to Langmuir equation.

A comparison with the initial growth rate in solution shows that the coverage reaches the maximum value approximately 50 times faster than the molecular weight of polymer in solution.

Observations of the island features with different magnifications show that there are numerous sizes of islands existing on the same surface. Since these islands have nearly rectangular shape with 0.5 nm height, both width and length are needed to specify the island size. Because it was difficult to differentiate an individual island from a group of closely lying islands on AFM images, and there are more regions of the spaces without neighbors along the long axis, only the narrower width of each rectangular island were measured. To characterize the island size and also to evaluate possible artifacts, the histograms of measured widths are constructed to give apparent island width distributions.

Figure 4 exhibits the histograms of measured widths for the selected reaction times. At short reaction times, each distribution has a symmetric shape and the maximum simply shifts to the right as the polymerization continues. After about 180 min, the distribution starts to disperse. While the larger widths are emerging, the smaller width remains to be observed. Because of the recognition problem discussed earlier, the apparent distribution may contain instrumental effects. To see these characteristics of the island size distributions better, each distribution is fitted with the smallest number of Gaussian curves.

We show the maxima of Gaussian curves, or the peak island sizes, at each reaction time in Figure 5. Until about 180 min, only one Gaussian is required to characterize the distributions and the peak island size increases monotonically. As the polymerization continues, multi-Gaussian curves are needed to fit the distributions. We note that, in these multivalue cases, the larger peak island sizes are roughly integer multiples of the smallest peak island size. This suggests a possibility that the larger peak values are the results of two or three similar-sized

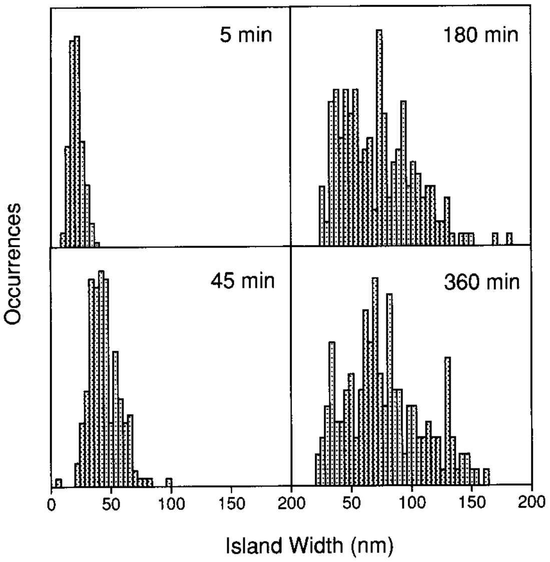

**Figure 4.** Histograms of the island widths for selected reaction times.

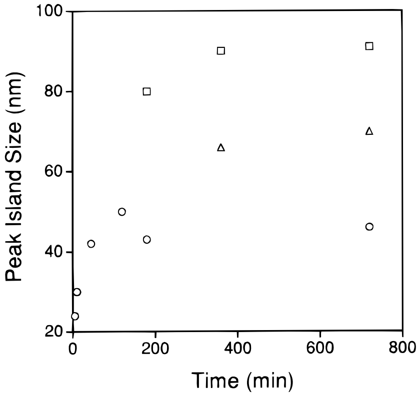

**Figure 5.** The maxima of Gaussian curves, or the peak island sizes, at each reaction time. These are obtained by fitting each island size distribution by the smallest number of Gaussian curves. Circle, triangle, and square marks are used to differentiate the maxima in descending magnitudes in order to show that the larger values are close to the integer multiples of the smallest value and that the island size within the same order increases with the time.

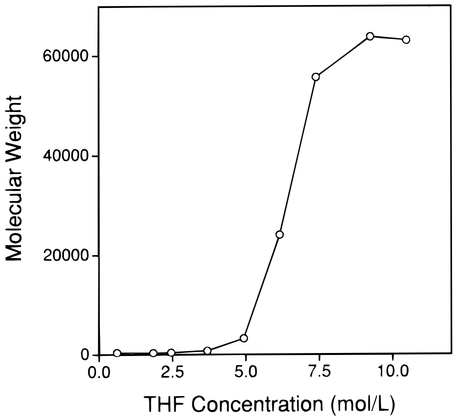

**Figure 6.** Molecular weights of poly(THF) formed in solution at various initial THF concentration. Polymerization occurs only if the THF concentration exceeds 3 mol/L, corresponding to the equilibrium monomer concentration.

islands lying so close together that AFM could not distinguish them. In this case, the peak island size increases fast at the beginning and then levels off to 45−50 nm after 200 min of reaction. On the other hand, we can define a curve that connects the largest peak island size at each reaction time. This curve is an envelope that follows the development of the fastest growing group.

Because of the possible instrumental effect on the island size distributions, we are unable to discuss how the true island size changes with the reaction time. However, at shorter reaction times, the excellent fitting to single Gaussian suggests that a mean value reflects the average size of island widths. Similarly at the early stage of polymerization, the longer length of each rectangular island could be measured in the same way as the width. After 5 min of the reaction, the average width and length are 24 and 70 nm, respectively. The previous study of the same system by scanning tunneling microscopy indicates that a single crystallographic domain contains only a few point defects.[2] This suggests that a single chain extends continuously from one edge to the opposite edge in the direction of either the narrower or the longer side. A chain may hold at the edge to make a lamella. In this case, the chain length within an island is longer than on either side of the island, and 24 and 70 nm are the minimum lengths of chains in the film. At the same reaction time in solution, the length of ideally extended poly(THF) chain estimated from the molecular weight is less than 14 nm.

It is clear from both the surface coverage and the island size that the film growth is much faster than the polymer synthesis in solution. This result offers an explanation to the solubility problem. During the present THF polymerization, all solution-grown products including poly(THF) stayed soluble in the reaction mixture. In other cases of different monomers, some polymers were observed to precipitate in the course of polymerization, although PIE films were successfully formed.[5] The present result implies that by the time the polymer becomes long enough to be insoluble in a reaction mixture, the PIE film has been already formed. Thus, as long as oligomers can stay soluble, epitaxial films can grow.

**Monomer Concentration Dependence.** Figure 6 shows the molecular weight of the polymer formed in solution at various initial THF concentrations. Polymerization has occurred only when the THF concentration exceeds about 3 mol/L. The molecular weight increases almost linearly until about 7 mol/L and then levels off at high concentrations. Cationic ring-opening polymerization of THF involving oxonium ions is an equilibrium polymerization with very slow termination and is known to possess ceiling temperatures.[8] This means that an equilibrium monomer concentration ($C_{\mathrm{emc}}$) exists for a given ceiling temperature. Under ordinary conditions, the THF concentration must be greater than $C_{\mathrm{emc}}$ for polymerization to proceed. The present result indicates that $C_{\mathrm{emc}}$ is approximately 3 mol/L, which is close to $C_{\mathrm{emc}}$ taken by other cationic initiators.[9,10]

Figure 7 displays AFM images of poly(THF) PIE films obtained at different initial THF concentrations. As the THF concentration is varied, the coverage and the island size change, but morphology stays the same.

The surface coverage is presented in Figure 8 as a function of the THF concentration. The coverage is already over 0.8 at very low concentration of 0.62 mol/L. It increases monotonically until 9.3 mol/L, although the magnitude of change is too small to claim that the coverage is linear in the monomer concentration. The sharp drop at higher concentrations measures more than an experimental error and has been reproduced by a number of independently repeated experiments.

We have constructed the apparent island size distributions from these AFM images. At low concentrations, the distributions are well approximated by single Gaussian to give the mean island width of about 25 nm. As the concentration increases, more than one Gaussian are required to fit a distribution. Figure 9 summarizes the peak values of these Gaussian functions. We notice that the larger peak values at a given concentration are roughly 2 or 4 times the smallest peak value, suggesting a possibility of AFM artifacts as in the reaction time study. In this case, the peak island size remains approximately 30 nm over most of the concentrations. On the other hand, we cannot reject a possibility that there exist certain values of the widths that the islands become stabilized as suggested by the peak values. A curve that envelopes the largest peak values (not shown) then indicates that the island size increases with the THF concentration and drops at the high concentration.

Having known that poly(THF) chain has all-trans, planer zigzag conformation on graphite,[2] the minimum molecular weight of the polymer within an island at 0.62 mol/L is calculated to be 3500. The minimum molecular weight for higher concentrations are correspondingly larger than this value. Therefore, both the surface coverage and the island size indicate that the well developed PIE film has formed even below $C_{\mathrm{emc}}$ in solution.

**Initiator Concentration Dependence.** Figure 10 shows the molecular weight of the polymer formed in solution at various initiator concentrations. Other than the low concentration range, the molecular weight decreases with increasing concentrations, as expected with the equilibrium reaction.[8] The sharp decrease in molecular weights at low concentrations is most likely due to termination and transfer reactions frequently observed in the cationic ring-opening polymerization of cyclic ethers.[15]

The PIE films grown at various initiator concentrations are displayed in a series of AFM images in Figure 11. The film morphology did not change with the initiator concentration.

The surface coverage stays nearly constant over the entire range as shown in Figure 12. Most noticeably, the coverage at low concentrations remains high, even slightly larger than the rest of the concentrations, despite the poor polymer growth in solution.

At all concentrations, the island size distributions are non-symmetric, maximizing at smaller widths than the center position. As in the previous cases, we approximate each

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(15) Saegusa, T.; Matsumoto, S. *J. Macromol. Sci.* **1970**, *A4*, 873.

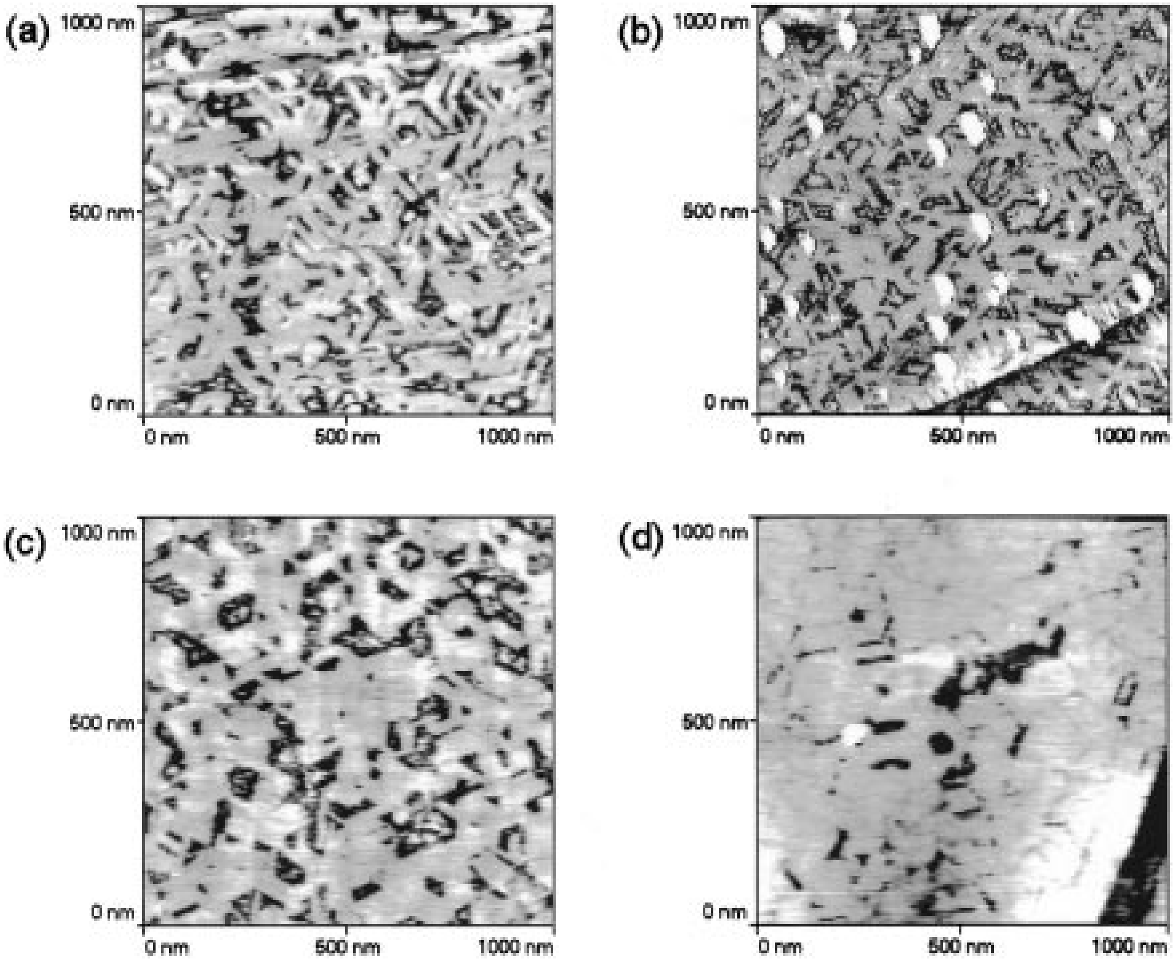

**Figure 7.** AMF images of poly(THF) PIE film on graphite formed at the THF concentrations of (a) 1.85, (b) 2.46, (c) 6.16, and (d) 9.25 mol/L. The dark regions are the bare graphite surface, and the straight lines running diagonally are the graphite steps. The rectangular islands have a uniform thickness of 0.5 nm.

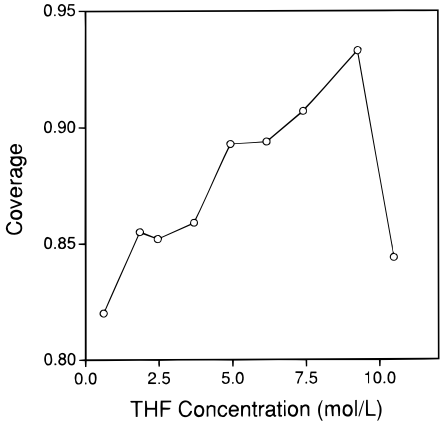

**Figure 8.** Surface coverage as a function of the THF concentration.

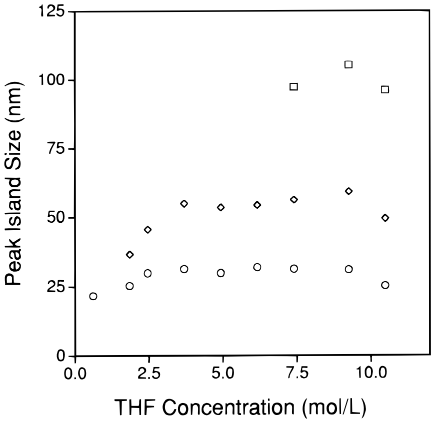

**Figure 9.** The maxima (or the peak island sizes) of Gaussian functions at each initial THF concentration. Circle, triangle, and square marks are used to differentiate the maxima in descending magnitudes in order to show that the larger values are close to the integer multiples of the smallest value and that the island size within the same order increases with the THF concentration.

distribution by the smallest number of Gaussian curves and indicate their peaks in Figure 13. There are two observations to be noted. First, all maxima hardly change over the entire concentration range. They stay the same even at the low concentration region. Second, the larger peak island size of about 120 or 60 nm are roughly integer multiples of the smallest peak island size of 30 to 40 nm. The same comment made previously for the AFM artifacts applies here also.

Both the coverage and the island size suggest that the nucleation density of islands, relating to the initiator concentration of the polymerization responsible for PIE, is already saturated at the smallest bulk concentration investigated. If there is a possibility of the initiator being adsorbed on the graphite surface, the surface excess concentration is already maximized at the smallest bulk concentration. More importantly, within the same concentration range examined, the polymerization in solution has suffered from side reactions. Thus, the present study indicates that termination and chain transfer reactions are suppressed for the polymerization reaction responsible for PIE.

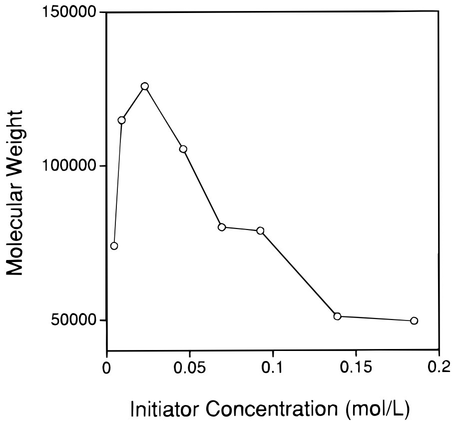

**Figure 10.** A plot of the molecular weight of poly(THF) formed in solution at various initiator concentrations.

## Discussion

**Kinetics.** The reaction time dependence study clearly indicate that the film growth is much faster than one expected from the polymer synthesis in solution. In solution, it is known that the initial reaction rate is the first order in the monomer and initiator concentrations, respectively.[7,10] Thus, if either of these species has high affinity for the graphite surface and produces a concentration enhancement near surface, it may result in an increase in the reaction rate. The present study indicates that the smallest initiator concentration used in this study is quite large on the surface, probably exceeding the maximum allowed number of initiating sites on the surface. On the other hand, THF is known to intercalate into graphite when it forms complexes with certain metals.[16] This suggests a possibility of a local increase in the THF concentration near the graphite surface, which may cause an increase in the polymerization rate and consequently results in the faster film growth.

Similarly, the monomer concentration study indicates that the PIE film has formed at the monomer concentration below $C_{\mathrm{emc}}$, where no solution polymerization has occurred. This leads to an important conclusion that PIE is not a process of adsorption of the polymer that has formed in solution. According to the known mechanism of equilibrium polymerization, $C_{\mathrm{emc}}$ is a thermodynamically determined function of the monomer concentration only.[8] We must then conclude that either the monomer concentration near the graphite surface is significantly higher than $C_{\mathrm{emc}}$ of the solution polymerization or the polymerization responsible for PIE possesses much smaller $C_{\mathrm{emc}}$. The former possibility is consistent with the increased reaction rate.

These kinetic results strongly suggest that the local THF concentration near the graphite surface is an important factor in the PIE process. If this is the only factor in the PIE kinetics, we estimate from the present results that the THF concentration near surface is at least 5−7 times greater the bulk value. However, as for the PIE mechanism, it is not clear how the high monomer concentration near the surface alone causes regular alignments of the polymerized chain. In the following, we discuss other possibilities that make $C_{\mathrm{emc}}$ smaller on the surface.

**Reaction Mechanism.** We have shown that the film growth is hardly affected by the initiator concentration, while the polymerization in solution has suffered from termination and chain transfer reactions. At this point, a brief review of cationic ring-opening polymerization of THF is helpful.[7,8] It is an equilibrium polymerization, and the propagating species is the tertiary oxonium ion. Propagation occurs by nucleophilic attack of monomer oxygen on a carbon adjacent to the positive oxygen (carbon 2 or 3 in Figure 14), and depropagation takes place by a similar nucleophilic back attack of the penultimate oxygen (oxygen 4) on the backbone carbon next to the positive oxygen (carbon 1). Equilibrium is established by the propagation and depropagation kinetics and is determined thermodynamically by the remaining monomer concentration for a given temperature. Termination or chain transfer may occur by the impurities, such as water and acid. It may also be induced by the gegenion. Tetrafluoroborate is known to be stable at 0 °C within the monomer and initiator concentration ranges investigated and is not relevant for the present case.[10] Chain transfer by an ether oxygen of a polymer chain reacting with the oxonium ion causes an alkyl exchange and a redistribution of molecular weights, but it does not lead to termination. An intramolecular backbiting reaction (oxygen 4 attacks carbon 2 or 3) together with displacement results in formation of cyclic oligomers and shortening of the propagating chain.

Among those factors that affect molecular weights, the reaction with water, the nucleophilic back attack of depropagation, and backbiting are relevant for the present study. Since graphite is highly hydrophobic, we expect less water on the graphite surface than in the bulk of solution. On the other hand, the reacting mixture could contain extremely small amount of residual water. Considering both that water mixes with THF more readily than with dichloromethane and that there is a possibility of higher THF concentration near the surface, the difference in the water concentration between the surface and the solution should be quite small. Thus, water should affect the polymerization near the surface as much as in the solution. This leaves the nucleophilic back attack and backbiting to be the important factors making the reaction near the surface different from the one in solution.

**PIE Mechanism.** We have stated that the kinetics suggests the monomer concentration enhancement near surface, but it is not clear how the high monomer concentration relates to the epitaxial growth. This led us to look for other mechanisms, and we now proceed to discuss a positive feedback model between polymerization and epitaxial adsorption, based on the known reaction mechanism and the present results.

We now consider a polymer chain that forms a crystalline island adsorbed on the surface and has its terminal segment extending into the solution phase. The solution end of the segment is an active propagating oxonium ion, while the part close to the crystalline domain is to be adsorbed epitaxially. The previous study has shown that epitaxy requires the poly(THF) chain to take an all-trans, planar zigzag conformation on graphite.[2] Because the segment needs to be adsorbed in an oriented fashion to satisfy crystalline attachment of its atomic species, the part close to the adsorbing end of the segment has severe structural restrictions in order to make the exact point of adsorption into a planar zigzag. On the other hand, to achieve either the nucleophilic back attack or backbiting, the monomer unit next to the oxonium ion needs to take a conformation that allows ring closure. Thus, if the length of terminal segment is short enough so that the structural restriction of the adsorbing part affects the propagating end, ring closure is significantly blocked. This results in a suppression of the depropagating nucleophilic back attack. Since the propagation reaction does not require ring closure and therefore is unaffected, the reaction is shifted toward propagation. As the propagation continues, the segment available for epitaxial adsorption becomes longer.

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[16] Schmidt, C.; Rosen, M. E.; Caplan, D. F.; Pines, A.; Quinton, M. F. *J. Phys. Chem.* **1995**, *99*, 10565−10572.

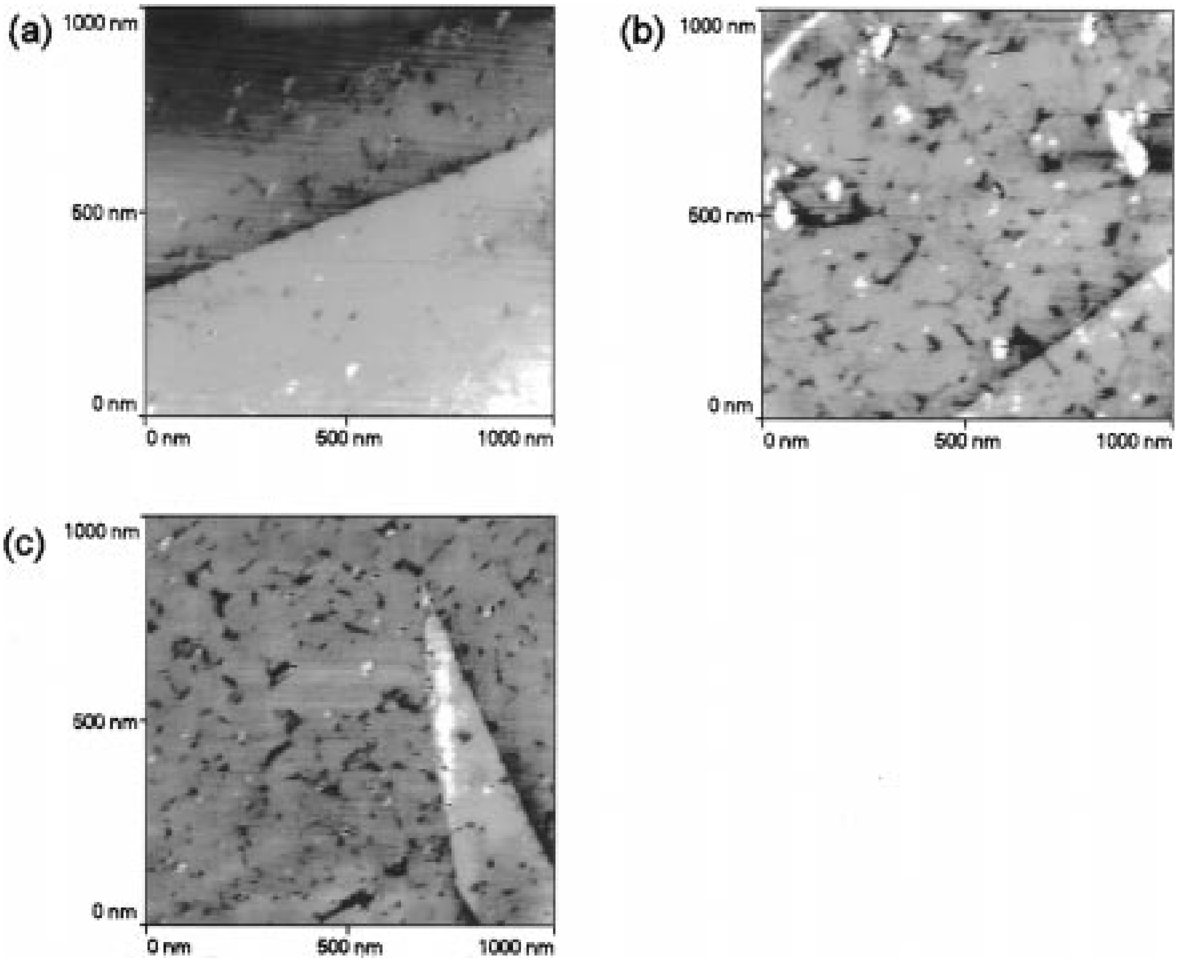

**Figure 11.** AMF images of poly(THF) PIE film on graphite at the initiator concentrations of (a) 4.63, (b) 46.3, and (c) 92.5 mmol/L. The dark regions are the bare graphite surface, and the straight lines running diagonally are the graphite steps. A sharp knife edge region in c is a graphite terrace situated on top of the rest of the plane.

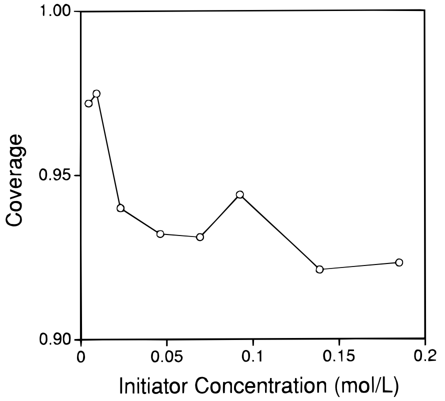

**Figure 12.** Surface coverage as a function of the initiator concentrations in a unit of monolayers. The coverage stays constant within an experimental error of 0.03.

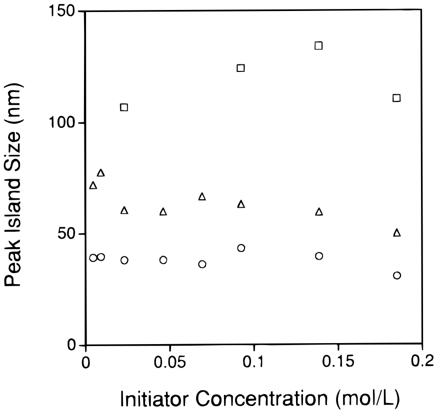

**Figure 13.** The maxima (or the peak island sizes) of Gaussian functions at each initiator concentration. Circle, triangle, and square marks are used to differentiate the maxima in descending magnitudes in order to show that the larger values are close to the integer multiples of the smallest value and that the island size stays nearly constant within the same series.

Enthalpy of epitaxial adsorption drives more of the segment to undergo crystalline attachment to the domain body and the surface.[17,18] As long as the segment is not a long polymer chain, the entropic penalty stays small. This adsorption causes shortening of the segment, which again leads to a suppression of the depropagating reaction, and the process repeats.

This model is consistent with the experimental results. Since the depropagation reaction is suppressed while the propagation reaction is not affected and no delay process is included in the feedback, the total polymerization reaction is shifted forward. Therefore, it results in faster growth and a smaller $C_{\mathrm{emc}}$ than in an ordinary polymerization in solution.

The model as given above alone predicts infinite growth and self-acceleration. Infinite growth of a crystalline domain is avoided by the presence of substrate defects and the collision with the neighboring domains, as they are experimentally

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(17) Groszek, A. J. *Proc. R. Soc. London* **1970**, *A314*, 473−498.

(18) Baukema, P. R.; Hopfinger, A. J. *J. Polym. Sci., Polym. Phys. Educ.* **1982**, *20*, 399−409.

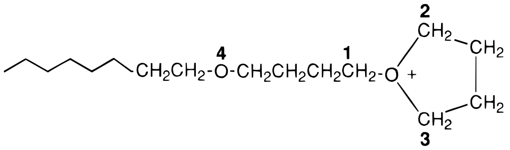

**Figure 14.** Chemical structure of the propagating end of poly(THF) segment. Propagation by an intermolecular nucleophilic attack of THF oxygen on carbon 2 or 3 casts no major constraints on the backbone conformation. Depropagating intramolecular nucleophilic back attack by oxygen 4 on carbon 1 and backbiting by oxygen 4 on carbon 2 or 3 require bending of the backbone to achieve ring closure.

confirmed to be the terminators of epitaxial adsorption.[11] Self-accelerating growth is regulated by the propagation rate and the maximum adsorption rate. If the propagation rate is very large compared with the adsorption rate, the segment may become too long to be attached with a crystalline order. Even in the case of a large adsorption rate, all parts of the segment cannot be adsorbed since the terminal oxonium ion does not satisfy the lattice matching with the graphite surface for epitaxy. Thus, the propagating end must remain free of crystalline attachment and await further polymerization before adsorption.

## Conclusions

The PIE mechanism was investigated by observing kinetics of the film growth in comparison with the polymer growth in solution. Both the size of each island and the surface coverage by all islands indicate that the film has formed much faster than the polymer synthesis in solution, that the film could grow even below the equilibrium monomer concentration, and that the nucleophilic back attack reaction is suppressed for PIE polymerization. These results suggest a possibility of the local monomer concentration enhancement near surface. Additionally, we propose a positive feedback model between polymerization and epitaxial adsorption as a PIE mechanism.

The feedback model depends fundamentally on the assumption that the cause for the suppression of depropagation is the structural constraint on the propagating segment due to an adsorption process accompanied by precise molecular orientation. In this case, the length of the terminal segment is a controlling factor for the feedback loop. These points remain to be examined by both experiments and numerical simulations.

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