# Polymerization-Induced Epitaxy. Highly Ordered Ultrathin Films of Poly(phenyloxazoline) on Graphite

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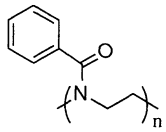
Ultrathin films of poly(N-benzoylethyleneimine) were grown on the basal plane of graphite by the method of polymerization-induced epitaxy. Scanning tunneling microscopy of the thin films showed periodic structures which indicate formation of crystalline layers.

Polymerization in presence of freshly cleaved graphite can produce an ultrathin polymer film containing crystalline regions on the basal plane of the graphite surface. This phenomenon, called polymerization-induced epitaxy (PIE), has been demonstrated previously for a number of unsubstituted polymers.[1] Films prepared by this method, here referred to as PIE-films, have been prepared by stereoregular polymerization of amino acid N-carboxy anhydrides,[2] while synthesis of atactic polymers have failed to produce PIE-films.[3] This indicates that a symmetric polymer structure is crucial for film growth by PIE. In preparation of PIE-films of polymers with side groups, alternatives to stereoregular polymerization are desirable. Here we have investigated possibilities of preparing PIE-films of polymers where side groups are connected to amide nitrogen atoms in the polymer backbone. Polymers of this type can be prepared by polymerization of 2-substituted oxazolines, for example. Specifically, synthesis of poly(benzoylethyleneimine) (PBEI) was carried out in presence of freshly cleaved graphite.



PBEI

PBEI was prepared by the method of Kagiya.[4] 2-Phenyl-oxazoline (15.2 mmole), purified according to the method of Tanaka,[5] 2-phenyloxazolinium tosylate[4] (59 μmole), and 2 ml of o-dichlorobenzene[6] was put in flask with a piece of freshly cleaved highly oriented pyrolytic graphite (HOPG, XYA-grade, Union Carbide). After a few freeze thaw cycles, the flask was heated to 135 °C. After 20 min, the reaction flask was allowed to reach room temperature. The graphite piece was liberated from visible bulk material by washing in chloroform. Copious washing in water, ethanol, acetone and chloroform ensured removal of soluble material. After a final washing in hexane, the sample was dried and analyzed. The STM was operated in air at ambient conditions with a mechanically sharpened Pt/Ir tip[1].

Three types of regions on the sample surface can be distinguished by STM. One region type produces images representing bare graphite. The second region type produces featureless STM images, and the third region type produces molecular images with periodic contrast patterns. The contrast patterns consists of parallel rows of bright spots, in which every second row appear brighter than the other. Image patterns with various appearances were observed. Images of the most commonly appearing type have repeating distances of 4.3 and 11.5 Å as illustrated in Figure 1. Knowledge of bulk structures of the studied polymer, or similar polymers is very helpful in the interpretation of STM images.[1] A crystalline structure of PBEI is, however, not known. The crystalline structure of other aroyl- and acyl substituted polyethyleneimines have been investigated.[7] It has been found that many polymers of this type have similar structure parameters with values for the c axis typically close to 6.5 Å. The periodic distances observed in the STM images of PBEI are not in accord with structural parameters observed for other aroyl- and acyl substituted polyethyleneimines. Although we cannot specify the molecular structures from the STM images directly, we can conclude, from the periodic feature of the images, that a film of PBEI with crystalline order is formed on the graphite surface.

A control experiment in which a graphite substrate was immersed in a solution of a prefabricated polymer under conditions similar to the polymerization conditions failed to produce an ordered film structure. This shows that the polymerization process is necessary for the formation of the highly ordered films.

The present study shows that PIE-films can be prepared of a polymer having side groups attached to amide nitrogen atoms on the polymer backbone. This widens possibilities of preparing PIE-films of polymers with functional side groups.

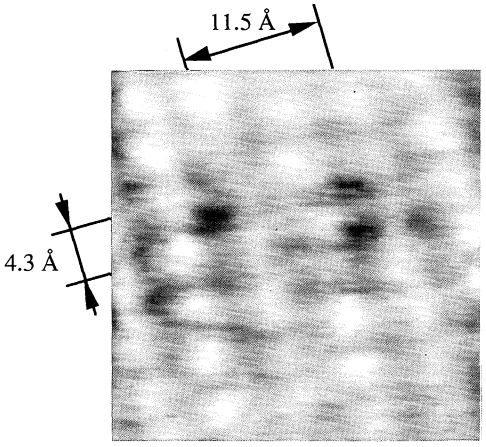



**Figure 1.** An STM image of a PIE-film of PBEI on HOPG.

**References and Notes**

1 M. Sano, D. Y. Sasaki, and T. Kunitake, *Macromolecules*, **25**, 6961 (1992).
2 M. Sano, M. Sandberg, and S. Yoshimura, *Langmuir*, **10**, 3815 (1994).
3 Synthesis of polymers with asymmetric structures as atactic polyvinylchloride, polypropyleneoxide etc., fails to produce highly ordered ultrathin films by PIE. M. Sano, unpublished results.
4 T. Kagiya and T. Matsuda, *J. Macromol. Sci., Chem.*, **A5**, 1265 (1971).
5 R. Tanaka, I. Ueoka, Y. Takaki, K. Kataoka, and S. Saito, *Macromolecules*, **16**, 849 (1983).
6 o-Dichlorobenzene was added as a softener to the mixture in order to prevent destruction of the graphite sample when the formed solid polymer as the temperature is lowered to ambient temperature.
7 M. Litt, F. Rahl, and L. G. Roldan, *J. Polym. Sci.*, **A-2**, 7, 463 (1969).