J|A|C|S
COMMUNICATIONS

Published on Web 11/21/2002

What Is the Mechanism of Oriented Crystal Growth on Rubbed Polymer Substrates? Topography vs Epitaxy

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Received June 3, 2002

Physicochemical self-assembly has generated new methods of fabricating materials,[1] from the organic crystals commonly used as nucleating agents in the manufacturing of polymers[2] to complex DNA structures.[3] The structure of self-assembled systems is usually governed by weak intermolecular forces at interfaces. For instance, crystal formation during biomineralization is usually controlled in all its aspects: orientation, size, and shape, through specialized proteins that recognize specific surfaces during the growth of the crystals.[4] Understanding the limit and capabilities of self-assembly to tailor materials via the formation of weak interactions is therefore a real challenge.

This Communication describes new experimental results giving a deeper insight into the growth mechanism of oriented crystals on polymer substrates. Our strategy is based on the use of rubbed amorphous polymer films. By choosing appropriate polymers and preparation techniques, we obtain substrates suitable for crystal growth with independently varying surface topography (i.e., rough or smooth) and degree of order for the chains at the air/polymer interface (i.e., disordered−amorphous or ordered−crystalline).

Since the seminal work of J.-C. Wittmann and P. Smith,[5] a large number of experimental and theoretical works have been dedicated to studying the oriented growth of various crystals on friction-transfer polymer substrates.[6−11] Whatever the details of the nucleation/growth mechanism, the ability of orienting crystals is directly related to the surface of the polymer substrate (at various length scales). Numerous mechanisms such as direct condensation/nucleation[6−8] and droplets coalescence[9] have been proposed in the literature. Nevertheless, *the equilibrium crystalline orientations* actually reflect the crystal/substrate interface energetics.[12,13] With respect to this, two main models have emerged:

Epitaxy model (molecular scale), the orientation is achieved via the formation of specific intermolecular interactions between the polymer surface and that of the growing crystals. The nature and quality of the orientation are fully determined by the chain order at the polymer surface.

Topography model (mesoscopic scale), the crystals specifically grow along surface features. The spatial distribution of these features determines the nature and the quality of the overlayer orientation.

The origin of the controversy and the difficulty to solve it arise from the structure of the rubbed polymer thin films. Various studies, using AFM,[14] X-ray,[15] and electron diffraction[5,16,17] have evidenced two major features of these polymer substrates: (i) a single-crystal-like orientation of the polymer chains parallel to the rubbing direction (e.g., a single crystallographic plane is observed in the diffraction patterns); (ii) a well-defined topography characterized by a large number of surface mesoscopic features, the symmetry of their spatial distribution reflecting the unidirectional rubbing (i.e., the terraces and fibers exhibit an axial symmetry).

Since both the molecular and the mesoscopic features have the same axial symmetry (parallel to the rubbing direction), it is rather difficult to assess the relative importance of each contribution in the overall crystallization of the deposited material. For instance, the crystallization of rodlike molecules on poly(tetrafluoroethylene) substrates usually yields crystalline orientations with the molecular axis parallel to the chain/rubbing direction.[6,11]

To separate the molecular and mesoscopic contributions, we have crystallized *p*-nitroaniline (PNA) on polymer substrates prepared by rubbing with a velvet cloth poly(ethylene terephthalate) (PET) or atactic polystyrene (aPS) amorphous films ~1 μm thick. In a previous publication, we have shown that rubbing "crystallizable" polymers such as PET induces the ordering of the polymer chains within the outer surface layer (the crystallized domain depth is a few tens of nanometers).[18] Due to the lack of regularity expected for atactic chains, the use of aPS substrates allows us to investigate selectively the contribution of the surface topography, while rubbed PET substrates are in principle able to induce crystal orientation via the epitaxy and the topography mechanisms. A typical AFM image of a rubbed PET substrate is shown in Figure 1; it reveals the surface morphology made of flat "terraces" separated by grooves parallel to the rubbing direction (this morphology is similar to those observed for friction-transfer PTFE substrates).

It should be noted that PET and aPS rubbed films have similar surface topography and roughness: 3.6 and 2.4 nm (for a 20 × 20 μm^2 surface area), respectively. In addition, these rubbed thin films undergo a complete relaxation of the surface topography above the glass transition temperature, yielding smooth films with a very low roughness around 0.5 nm (Figure 1b).[18−20] For "crystallizable" polymers, such as PET, cold crystallization experiments have also shown that the chain orientation is maintained within the surface region after the relaxation.[18] Therefore, we can obtain disordered (amorphous) or ordered (crystalline) substrates with contrasting surface topography (i.e., rough or smooth).

The crystallization of PNA molecules was performed in a vacuum by direct condensation of the vapor onto the polymer substrates, according to the previously reported method.[6] After crystal growth, the average orientation was estimated from IR dichroism measurements. The assignment of the PNA IR bands to normal modes was reported in ref 6b. The absorption spectra recorded with an IR beam polarized either parallel or perpendicular to the rubbing direction illustrate the quality of the axial orientation (see Figure 2).

A more quantitative analysis of the average crystal orientation has been made using Hermans' orientation function,[21] $f = (3\langle\cos^2\theta\rangle -1)/2$ directly computed from the dichroic ratios. Table 1

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10.1021/ja027145l CCC: $22.00

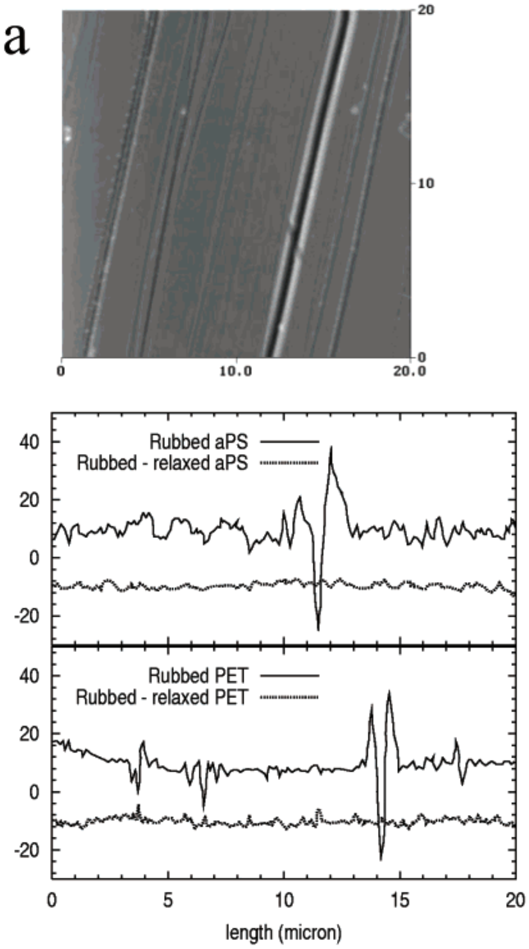

Figure 1. (a) AFM topographic image of a rubbed amorphous PET surface. (b) Typical section profiles from topographic images of PET and aPS surfaces, rubbed or relaxed (as indicated).

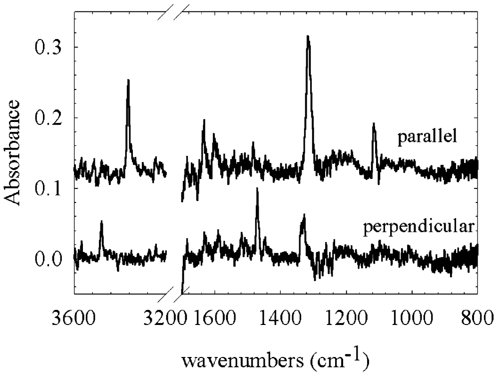

Figure 2. FTIR polarized difference spectra recorded for PNA layers crystallized from the vapor phase on smooth rubbed PET (relaxed at the glass transition). The polarizer was set either parallel or perpendicular to the rubbing direction, as indicated. The difference spectra were obtained by subtracting the IR absorption spectrum of the PET substrate from the IR absorption spectrum of PNA-substrate overlayers.

summarizes our observations and gives the average values of the Hermans' function, *f*, for the different substrates.

Even if a small effect could be observed for rough rubbed aPS substrates, it is very clear that the quality of the orientation is dramatically better with both rough and smooth PET thin films.

These observations therefore indicate the great significance of the molecular order of the polymer chains located within the top surface in promoting the oriented growth of crystals. The oriented nucleation of PNA on PET can be accounted for by considering the structure of both surfaces. In fact, there is an almost perfect fit between the (100) PET and (101) PNA dense crystallographic planes, the polar axis of PNA molecules being parallel to the PET chain axis (the 2D lattice mismatch is lower than 3%).

Table 1. Summary of the Observed Orientations for PNA Crystals Grown on PET or aPS Substrates. The Values of the Orientation Function, *f*, Are Given in Parentheses

	rough (~3 nm)[a]	smooth (~0.5 nm)[a]
ordered (PET)	$++$ ($f \sim 1$)	$++$ ($f \sim 1$)
disordered (aPS)	$-$ ($f \sim 0.2$)	$--$ ($f \sim 0$)

[a] The RMS roughness was measured for a 20 × 20 μm^2 AFM surface area.

Although we do not exclude kinetic mechanisms giving transient orientations which very likely disappear or transform after annealing (~ equilibrium conditions), we can conclude that the observation of a nearly perfect crystalline orientation is a real indicator of the formation of specific intermolecular interactions between the overlayer and the substrate crystal planes.

Acknowledgment. This work was supported by the Belgian National Fund for Scientific Research (FNRS) and by the Belgian Federal Government Service des Affaires Scientifiques, Techniques et Culturelles (SSTC) in the framework of the Pôle d'Attraction Interuniversitaire en Chimie Supramoléculaire et Catalyse Supramoléculaire (PAI 5/3). P. Damman and R. Lazzaroni are Research Associate and Research Director of the FNRS, respectively.

References

(1) Whitesides, G. M.; Grzybowski, B. *Science* **2002**, *295*, 2418.
(2) Wittmann, J. C.; Lotz B. *Prog. Polym. Sci.* **1990**, *15*, 909.
(3) Winfree E.; Liu F.; Wenzler L. A.; Seeman N. C. *Nature* **1998**, *394*, 539.
(4) Addadi, L.; Weiner, S. *Nature* **2001**, *411*, 753.
(5) Wittmann, J. C.; Smith, P. *Nature* **1990**, *352*, 414.
(6) (a) Damman, P.; Dosière, M.; Smith, P.; Wittmann, J. C. *J. Am. Chem. Soc.* **1995**, *117*, 1117. (b) Damman, P.; Dosière, M.; Brunel, M.; Wittmann, J. C. *J. Am. Chem. Soc.* **1997**, *119*, 4633. (c) Vallée, R.; Damman, P.; Dosière, M.; Toussaere, E.; Zyss, J. *J. Am. Chem. Soc.* **2000**, *122*, 6701.
(7) Tanaka, T.; Matsuoka, M. *Thin Solid Films* **2001**, *393*, 148.
(8) Tanaka, T.; Ishitobi, M. *J. Phys. Chem. B* **2002**, *106*, 564.
(9) Brinkmann, M.; Wittmann, J. C.; Barthel, M.; Hanack, M.; Chaumont, C. *Chem. Mater.* **2002**, *14*, 904.
(10) Moulin, J. F.; Brinkmann, M.; Thierry, A.; Wittmann, J. C. *Adv. Mater.* **2002**, *14*, 436.
(11) Damman, P.; Fisher, C.; Krüger, J. K. *J. Chem. Phys.* **2001**, *114*, 8196.
(12) Hooks, D. E.; Fritz, T.; Ward, M. D. *Adv. Mater.* **2001**, *13*, 227.
(13) Tiller, W. A. *The Science of Crystallization, Microscopic Interfacial Phenomena*; Cambridge University Press: Cambridge, 1991.
(14) Hansma, H.; Motamedi, F.; Smith, P.; Hansma, P.; Wittmann, J. C. *Polymer* **1992**, *33*, 647.
(15) Tanigaki, N.; Yoshida, Y.; Kaito, A.; Yase, K. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 432.
(16) Makinson, K. R.; Tabor, D. *Proc. R. Soc. London Sect. A* **1964**, *281*, 49.
(17) Pooly, C. M.; Tabor, D. *Proc. R. Soc. London Sect. A* **1972**, *329*, 251.
(18) Damman, P.; Zolotukhin, M. G.; Villers, D.; Geskin, V. M.; Lazzaroni, R. *Macromolecules* **2002**, *35*, 2.
(19) Kerle, T.; Lin, Z.; Kim, H. C., Russell, T. P. *Macromolecules* **2001**, *34*, 3484.
(20) Pu, Y.; White, H.; Rafailovich, M. H.; Sokolov, J.; Schwarz, S. A.; Dhinojwala, A.; Agra, D. M. G.; Kumar, S. *Macromolecules* **2001**, *34*, 4972.
(21) Gedde, U. W. *Polymer Physics*; Kluwer Academic Publishers: Dordrecht, 1995.

JA027145L