

AppNote: High resolution AFM imaging

High resolution imaging of single PTFE molecules on Teflon surface

Vladimir Korolkov¹

¹Park Systems UK Ltd, MediCity, Nottingham, United Kingdom

Introduction

The structural studies of polymers are of high importance in material sciences since polymeric materials are widely used across a broad range of applications. From micelles for drug carriers to car tyres and bulletproof vests, and many more. This versatility stems from their unique structure composed of very long polymeric chains that fold, pack and assemble together. That exquisite molecular architecture that often combines both, highly ordered and amorphous regions, provides a wide range of tunable properties. Hence, understanding the very packing of polymer chains, the way they form and their dynamic behavior under external stimuli is arguably the final goal of structural studies of polymers. Historically, such studies have been carried out with diffraction or spectroscopy-based techniques that can only provide average structural information. Furthermore, they always rely on a certain model for data interpretation. On the other hand, they lack in providing real-space imaging capabilities, i.e. they are not able to see individual molecules. The only technique that can perform real-space imaging in almost any environment and temperature range is Atomic Force Microscopy (AFM).

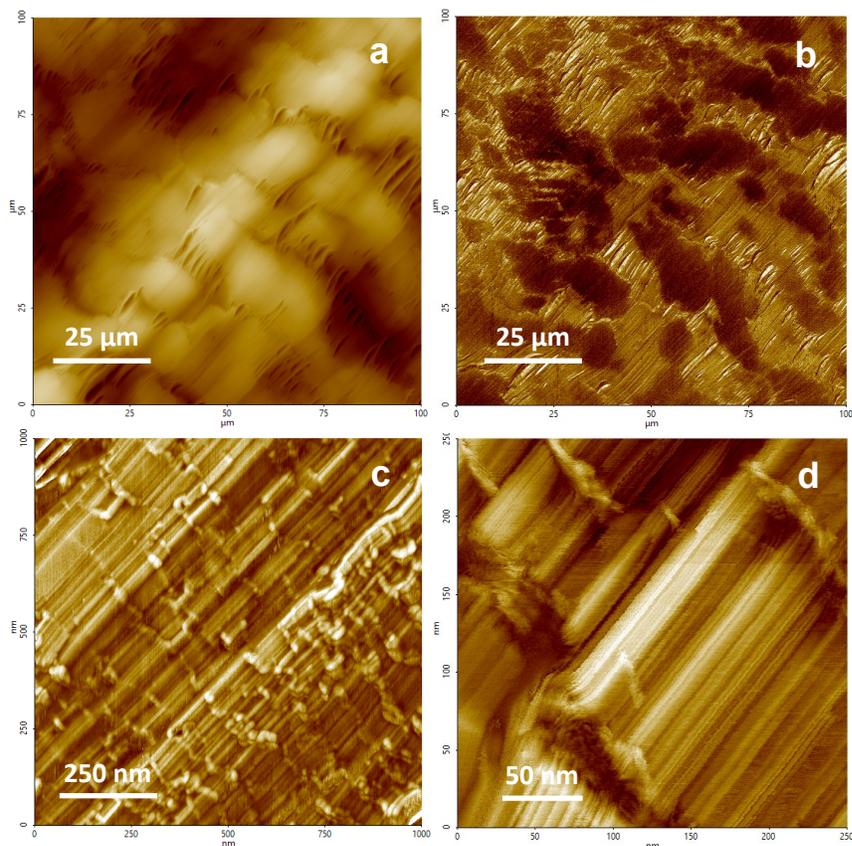
AFM was developed more than three decades¹. However, it took a long time to utilise AFM to obtain high resolution images of polymers. We can certainly mention the development of torsional tapping to observe single polyethylene molecules by Hobbs and Mullin^{2,3}, bimodal tapping by Proksch⁴ and higher eigenmode imaging by Korolkov⁵. The latter technique, unlike others, does not require any special cantilevers or custom-modified AFM components. In this work, we have implemented this technique on a commercial AFM – Park Systems NX20 – to achieve molecular resolution on a real-world sample of Teflon.

AFM Imaging on Polytetrafluoroethylene (PTFE)

Polytetrafluoroethylene (PTFE), commonly known as Teflon, is a fluorocarbon solid that has one of the lowest coefficients of friction. Therefore, it is widely used as a material with low adhesion or as an inert coating. Despite its chemical simplicity, PTFE exists in four different crystalline phases that have been studied with electron diffraction techniques^{6,7}. Interestingly, no high resolution AFM data of Teflon have been published to date.

Teflon is known to be a semi-crystalline polymer⁷. Figure 1 shows a set of large scale images of a Teflon surface. A 100 μm x 100 μm image (Fig. 1 a and b) already shows two distinctive areas: large 20 μm domains and rope-like areas connecting them. A closer look at domain areas reveals their highly directional nature. A high resolution phase image (Fig. 1d) shows predominantly crystalline regions separated by smaller amorphous regions on the surface of the polymer. These crystalline domains exhibit flat terraces as observed in Figure 1c and d.

On the following height and phase images (Figure 2), we examine these flat terraces a bit closer. A 100 nm x 100 nm height image (Fig. 2a) shows $\sim 5\text{\AA}$ steps with sharp edges. Corresponding phase images (Fig. 2b and c) reveal true molecular nature of these flat steps – we can clearly resolve single molecules with a period of 5.6\AA . A cross-section (Fig. 2d) gives a clear periodic structure of the terrace. From this cross-section, we can also measure the width of a single line at full width at half maximum being 3.5\AA . This determines the maximum resolution achieved on this sample. When comparing the observed period of 5.6\AA to the reported diffraction data of PTFE unit cell $a = 5.66\text{\AA}$ ⁷, we can note a remarkable agreement.



Conclusion

To conclude, we have demonstrated a straightforward practical approach for high-resolution imaging using higher eigenmodes of a standard cantilever in tapping mode on a commercial large-scale NX20 Park Systems AFM achieving molecular resolution of a Teflon sample. AFM, a surface sensitive technique which is always confined to the utmost/outermost surface layer, is able to accurately reproduce results obtained from volume average techniques. Thus, proving that AFM is an important tool in the investigation of the molecular structure of polymers. In fact, AFM is able to provide more structural

Figure 1. Large-scale height and phase tapping mode images of a Teflon surface. a – height image, 512 x 512 px, scan rate 0.5 Hz. b – phase image acquired simultaneously with image A. c – phase image, 512 x 512 px, scan rate 4 Hz. d – high resolution phase image showing both crystalline and amorphous regions, 512 x 512 px, scan rate 4 Hz. Captured by Park NX20 Large Sample AFM.

information by shining a light onto the amorphous regions of Teflon – something that diffraction techniques cannot easily achieve. For instance, a phase image (Fig. 2b) shows that PTFE molecules extend from well-ordered crystalline regions further into the amorphous region of the polymer. The highly localized and high resolution nature of AFM places it in a unique position to investigate the structure of polymers in real space.

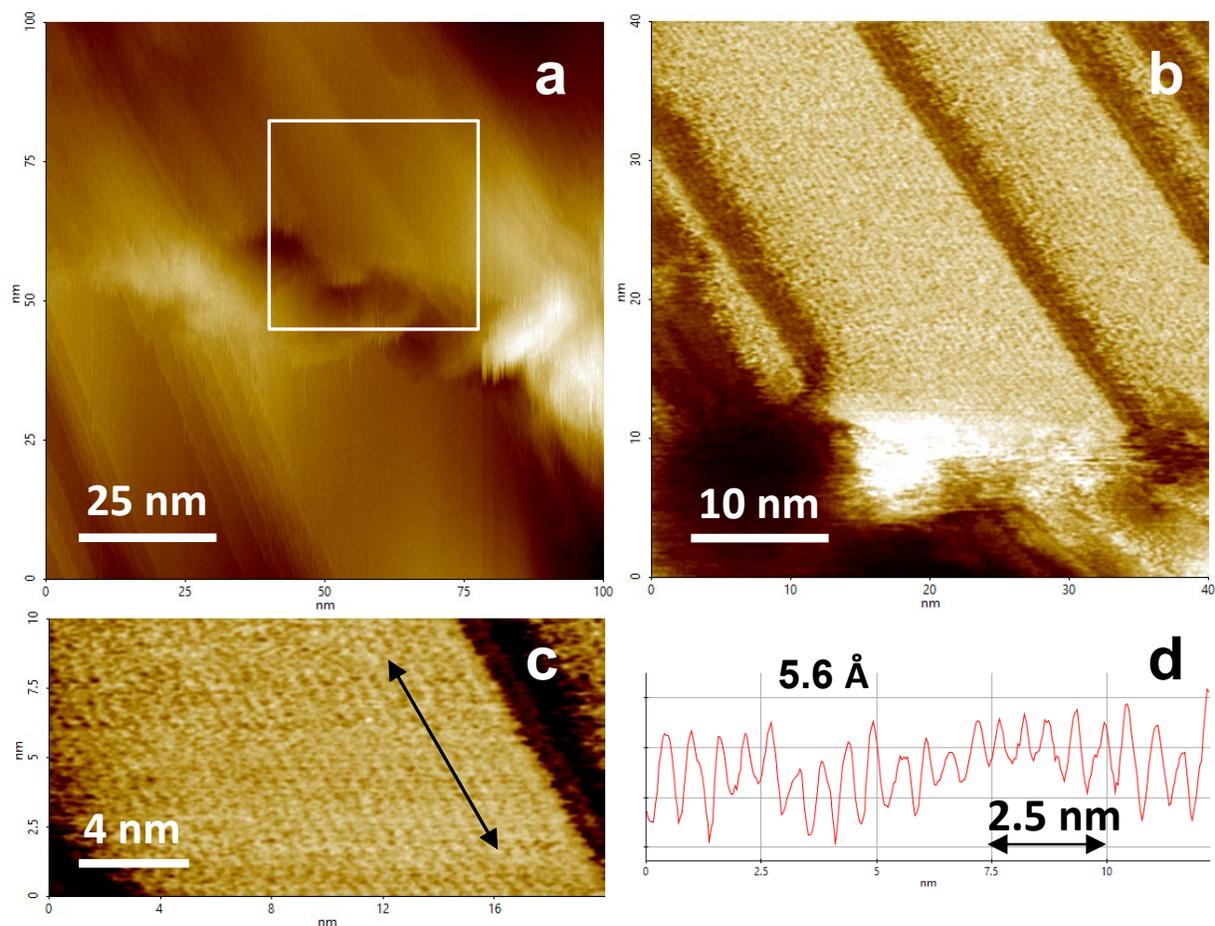


Figure 2. High resolution AFM images of a Teflon surface showing single PTFE molecules. **a** – height image, 512 x 512 px, scan rate 2Hz. **b** – phase image, 512 x 512 px, scan rate 4Hz. **c** – phase image, 512 x 512 px, scan rate 6Hz. All images were acquired using a 3rd eigenmode of Multi75Al-G cantilever at 1.1Mhz and set point of 1.15nm. **d** – a cross-section illustrates the periodicity of the terraced surface. Captured by Park NX20 Large Sample AFM.

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Contact:

Vladimir Korolkov

Park Systems UK Ltd, MediCity, Nottingham, UK.

pse@parksystems.com

www.parksystems.com