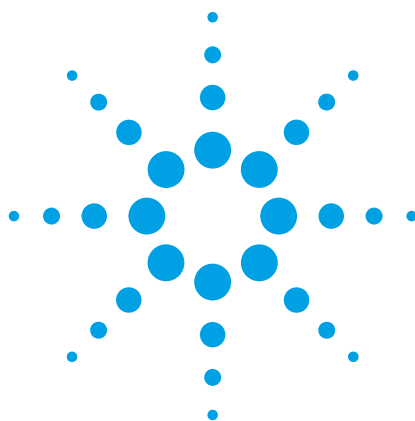


# Application of Atomic Force Microscopy (AFM) in Polymer Materials



## Application Note

### Introduction

Atomic force microscopy (AFM) is a powerful characterization tool for polymer science, capable of revealing surface structures with superior spatial resolution. AFM is extremely useful for studying the local surface molecular composition and mechanical properties of a broad range of polymer materials, including block copolymers, bulk polymers, thin-film polymers, polymer composites, and polymer blends.

### Instrumentation

The Agilent 5400 AFM/SPM microscope is an easy-to-use, high-precision instrument that delivers atomic resolution at a remarkably affordable price. The standard Agilent 5400 includes contact mode, acoustic AC mode, and phase imaging. Agilent's patented magnetic AC mode (MAC<sup>®</sup> Mode) is offered as a system option. Switching imaging modes with the Agilent 5400 AFM/SPM microscope is quick and convenient, thanks to the scanner's interchangeable, easy-to-load nose cones. For a lower mechanical noise floor, the Agilent 5400 is

built with rigid materials and a rigid frame. The compact, open-loop X-Y & Z scanner employs a patented balanced-pendulum design to minimize X-Y coupling, significantly reducing creep and hysteresis. Furthermore, the scanner can be repositioned in Z to accommodate larger samples.

A state-of-the-art temperature controller (-30°C to 250°C) and sample plates are also available. The controller enables observation of structural and mechanical property changes of polymers induced by temperature and phase transitions. Finally, to keep pace with the evolving requirements of researchers and educators alike, the modular Agilent 5400 provides a simple upgrade path to the sophisticated Agilent 5500 microscope, which offers more comprehensive environmental controls.

### High-resolution Imaging of Polymer Structures

High-resolution visualization of a sample's morphology, which is a key feature of AFM, defines most of its applications. Contact mode imaging originates from the introduction of AFM and is still one of

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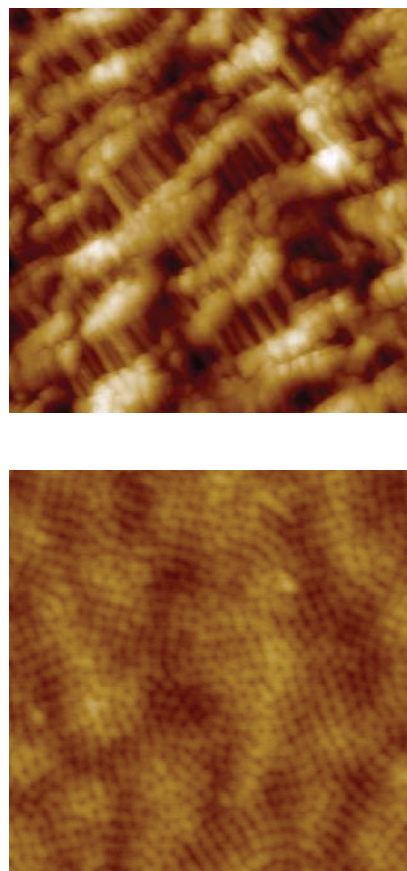
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the most widely used imaging modes. Although molecular resolution (e.g. 1 Å) has been demonstrated with crystalline structures such as calcite (0001), AFM imaging of polymers under contact mode has some intrinsic challenges. The major difficulties of achieving the ultimate high resolution arise from the soft nature of the specimen and strong adhesion of tip-sample contact. The lateral force may cause the transient stick-and-slip between the tip and sample during the scan and may lead to sample damage. All these can usually manifest into spikes in the image (along the scanning direction) and dramatically sacrifice the resolution. The introduction of oscillatory AFM imaging modes, for example, Acoustic AC (AAC) mode, provides a solution to this problem. In AAC mode, a transducer attached to cantilever housing is used to excite a cantilever into oscillation near its resonant frequency. The cantilever amplitude will decrease as the tip approaches the sample surface. The system monitors the amplitude of the cantilever oscillation and keeps it constant by a feedback circuit that moves the scanner up and down. The tip-sample interactions are predominately vertical, and thus dramatically eliminate the lateral forces. Consequently, the tip or sample degradation effects, which usually occur in multiple scanning of soft materials in contact mode AFM, are not common for AAC.

Therefore, this is a good technique for imaging of polymer and rubbery samples. Shown below are two examples that demonstrate the AFM capability of direct and high-resolution visualization of polymer surface structures.

Polypropylene (PP) is one of the non-foam plastics of the most common resins and it has the lowest density of plastics used in packaging. More specifically, the first sample is microporous membrane Celgard™ made of isotactic polypropylene. This material is prepared by alternative stretching and annealing procedures. As a result, the material exhibits surface features corresponding to fibrillar and lamellar regions. These features are clearly seen in topography image, in which stacks of lamellae are  $\sim 10\text{-}15$  nm higher than the surrounding fibrillar regions (Figure 1, top). In addition, one can see individual fibers of  $\sim 20$  nm in diameter, which are uniaxially oriented and separated by nanometer-scale gaps that serve as pores for filtration purposes.

The self-assembly of block copolymers has attracted tremendous attention recently because they offer simple and versatile means to produce nano-structured materials which has led to the development of block copolymer lithography. The second sample used here is a triblock copolymer of poly(ethylene oxide-*b*-methyl methacrylate-*b*-styrene)



**Figure 1.** AFM topographic images of polymer isotactic polypropylene with a scan size of  $1.5\ \mu\text{m} \times 1.5\ \mu\text{m}$  (top) and triblock copolymer poly(ethylene oxide-*b*-methyl methacrylate-*b*-styrene) with a scan size of  $1\ \mu\text{m} \times 1\ \mu\text{m}$  (bottom).

(PEO-b-PMMA-b-PS), where PS is the major component and PMMA and PEO are minor ones. This system provides a promising route to form surfaces of highly-ordered nanoporous arrays because the use of PMMA as a photodegradable mid-block may lead to nanoporous structures with an unprecedented degree of lateral order. The exact surface morphology of thin films made of these block copolymers can be characterized using AFM imaging. The example of AFM images of the block copolymer surface is shown in Figure 1, bottom. This topography image shows that surface morphology with highly-ordered cylindrical pores ranges from 10 to 15 nm in diameter.

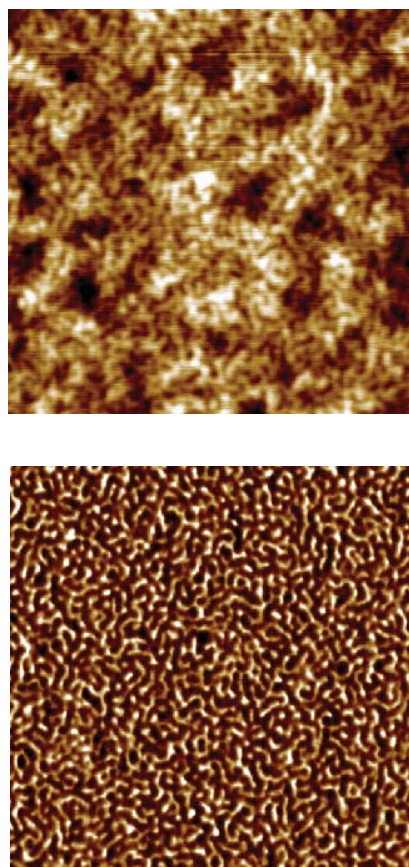
The lateral dimensions of some typical surface structures of the two chosen polymer samples such as the nanofibril width and nanopore size are only at the order of tens of nanometers. Therefore, high-resolution imaging of polymer or plastic samples with sub-100 nm spatial resolution can be readily achieved.

### **Differentiation of Heterogeneous Polymer Systems Using Phase Imaging**

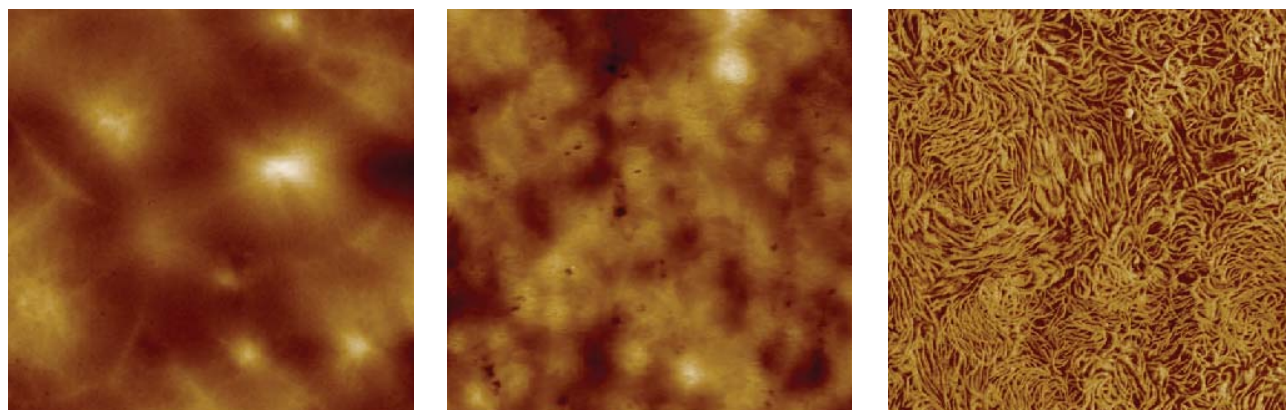
In addition to the unprecedented high spatial resolution, another key advantage of AFM is the simultaneous multi-channel data acquisition. In AAC mode, tip-sample force interactions cause

changes in amplitude, phase and the resonance frequency of the oscillating cantilever. The spatial variation of the change can be presented in height (topography) or interaction (amplitude or phase) images. Also, a feed-back system monitors the oscillating amplitude of the cantilever at each sample location and tries to maintain that to a set value (set-point) by moving the scanner up or down based on the surface morphology. While those vertical motions of the scanner are used to generate a topographic image, the actual oscillation amplitudes and the phase lag between the AC drive input and the cantilever oscillation output can also be collected simultaneously to produce the corresponding amplitude and phase image, respectively. It has been demonstrated by many research groups that phase contrast is very sensitive to the differences in material properties such as variation of the mechanical (stiffness, friction) and adhesive properties.

Visualization of different components of heterogeneous polymer materials in phase images will be demonstrated by examples taken from studies of block copolymers, semicrystalline and mesomorphic polymers.



**Figure 2. AFM topography(top) and phase (bottom) images of copolymer PS-b-PB-b-PS. Scan size: 1.5  $\mu$ m x1.5  $\mu$ m.**



**Figure 3.** AFM topography images of LDPE (left) and LLDPE (center) with a scan size of  $18\ \mu\text{m} \times 18\ \mu\text{m}$  and the phase image of LLDPE (right) with a scan size of  $8\ \mu\text{m} \times 8\ \mu\text{m}$ .

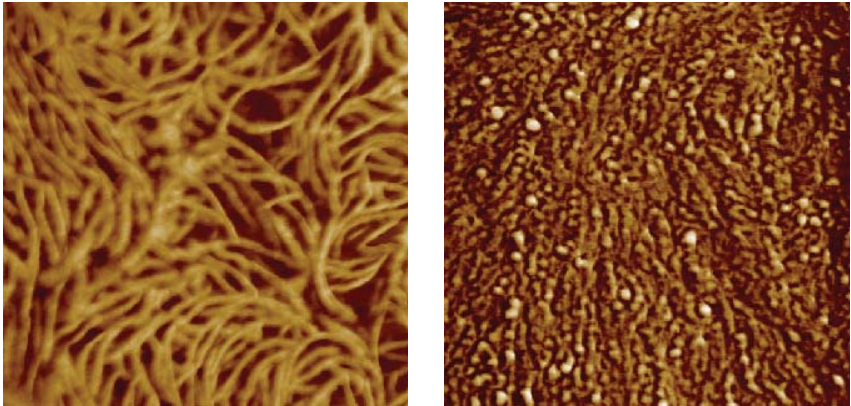
### Block copolymers

Compositional mapping with AFM is often used for observations of microphase separation of block copolymers, which occurs at the sub-100 nm scale. This is seen clearly in height and phase images of a triblock copolymer polystyrene-*b*-polybutadiene-*b*-polystyrene (PS-*b*-PB-*b*-PS) film. A microphase separation pattern of this material, which is mostly pronounced in the phase image, is characterized by structural parameter  $\sim 35\ \text{nm}$ . The phase contrast is related to the fact that at room temperature, PS is in a glassy state while PB is in a rubber-like state. Consequently, the brighter areas in the phase image (corresponding higher areas in topographic image) can be attributed to stiff lamellae of PS.

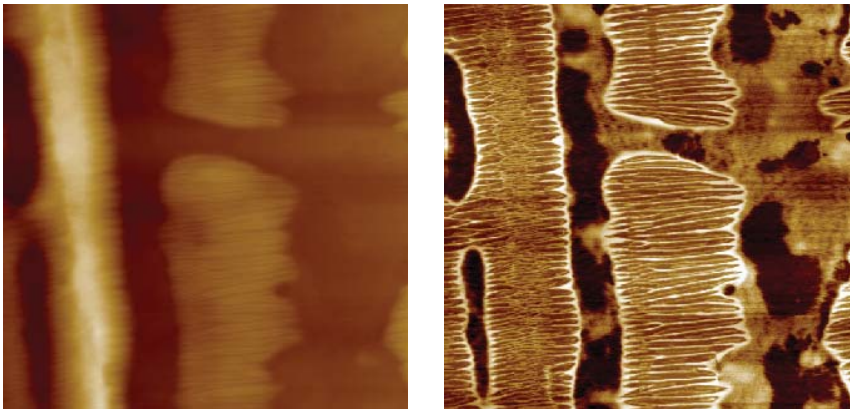
### Semicrystalline polymers

Structural heterogeneity is a common feature even for most crystalline polymers in which amorphous materials is a necessary component. In addition to the compositional imaging of multi-component polymer samples, visualization of amorphous and crystalline components is another important application of phase imaging. The examples of such polymers are linear low density polyethylene (LLDPE) and low density polyethylene (LDPE). Samples of both polymers, which are prepared from melt, exhibit morphology common for semicrystalline materials. In large scales AFM topography images of LDPE and LLDPE one can see spherulites (Figures 3, left and center). In LDPE, the spherulites are  $\sim 5\text{-}10$  micron in diameter with elevated centers and borders. Spherulites are smaller tightly packed in LLDPE samples, Figure 3, center. At higher magnification, phase images revealed lamellar structures, which are embedded in amorphous surrounding. This is demonstrated by  $8\ \mu\text{m}$  phase image of LLDPE, which shows bundles of lamellae (brighter contrast) separated by amorphous





**Figure 4.** AFM phase images of LLDPE (left) and LDPE(right). Scan size: 2  $\mu\text{m}$  x 2  $\mu\text{m}$ .



**Figure 5.** AFM topography (left) and phase (right) images of PDES at room temperatures. Scan size: 8  $\mu\text{m}$  x 8  $\mu\text{m}$ .

polymer (darker regions). Some of the lamellae are oriented edge-on; others are tilted to expose the larger surface of the platelets. The latter are seen as wider bright strips. Differences in lamellar structures of LLDPE and LDPE are evident in the 2  $\mu\text{m}$  phase images in Figure 4, where lamellae exhibit brighter contrast. The LLDPE sample is populated with edge-on lamellae, many of them being curved. Tiny lamellae with grainy overgrowth dominate on the surface of LDPE sample. It is worth noting that compositional imaging of semicrystalline materials is efficient when AFM experiment is performed at temperature

above glass transition of amorphous component, which is well below RT for LDPE and LLDPE. Compositional imaging is usually performed at elevated forces (large free oscillating amplitude and set-point amplitude around half of the free amplitude) to get a most pronounced phase contrast. Also during imaging at elevated forces the probe can penetrate through the topmost rubbery layer and reveal the subsurface structures.

### Mesomorphic polymer

Besides amorphous and crystalline forms, many liquid crystalline polymers such as poly(diethylsiloxane)(PDES) usually exist in a partially ordered or mesomorphic form, which can also be characterized by phase imaging. Rubbing of PDES on Si substrate leads to patches of the polymer as seen in height image in Figure 5. The rubbing was performed in the direction from bottom to top of the image. The phase image, which was acquired simultaneously with the height image, revealed a complex morphology of this sample. The main polymer material is in several stretched patches at the left and in the center of the image. Arrays of cigar-type structures, which are oriented perpendicular to the rubbing direction, are distinguished by their darker contrast. These lamellar-like aggregates, which are embedded in amorphous material, are visible due to its brighter contrast. In the phase image, besides the patches, one can also see substrate areas, which are partially covered by thin layer of polymer. The corresponding areas in the height image do not show any pronounced features.

### Examination of Polymer Thermal Transitions

Polymer or plastic materials can be divided into two major groups: thermoplastic ones or thermosetting ones based on their heat response. Therefore, knowledge of polymer behavior at different temperatures is essential for many practical applications. Although quite a few macroscopic techniques such as differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and thermal mechanical analysis (TMA) are usually employed to probe the temperature changes of polymers. Direct and nanometer-scale visualization of polymers at different temperatures are still highly desired. With the development of both heating and cooling accessories, the scope of AFM application on polymer materials can be extended from ambient temperature to temperatures where polymer phase transitions occur. High-resolution AFM temperature studies can provide unique microscopic insight on polymer thermal behavior. One practical example, which describes sub-RT AFM studies on polymers, is in Figure 6.

Cooling of PDES sample, which was deposited on Si substrate, has induced crystallization of material inside the lamellar-like aggregates. This transformation is monitored by AFM images obtained at 23°C, -10°C and 15°C, which are shown in Figure 6. After the sample temperature drops below 0°C, phase image pattern differentiating the ordered aggregates and their amorphous surrounding, become homogeneous and darker in contrast. The change is consistent with densification of the material caused by its crystallization. The described process is largely reversible, shown by the re-appearance of the lamellar-like aggregates and their surroundings in the phase image recorded at 15°C. Yet the fine details of the aggregates, which are distinguished in the initial image, are different from those that appear after the cooling-heating cycle.

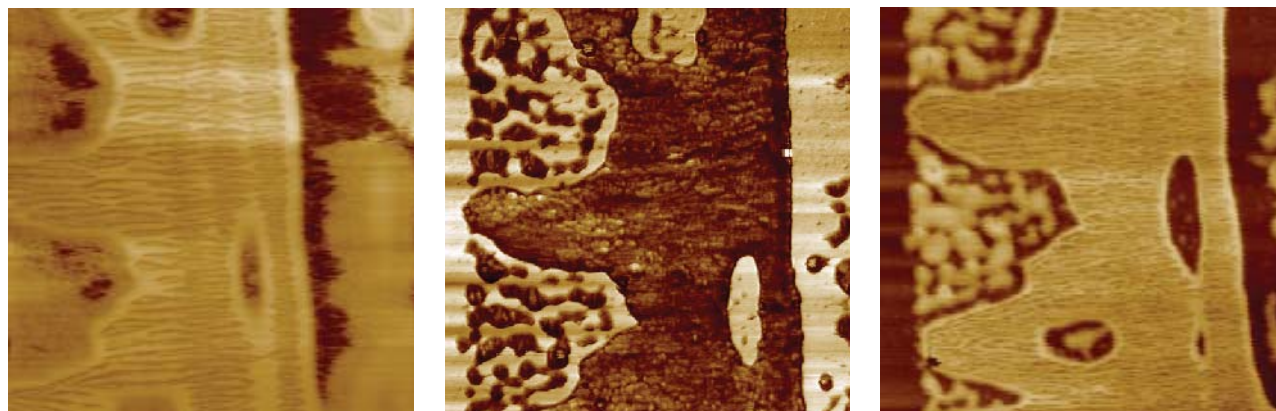


Figure 6. In situ AFM phase images of PDES at 23°C (left), -10°C (center) and 15°C (right), respectively. Scan size: 8  $\mu\text{m}$  x 8  $\mu\text{m}$ .

## **Summary**

Practical examples of imaging of different polymer samples with the Agilent 5400 microscope demonstrate the capabilities for visualizing important polymer nanostructures and monitoring of structural changes caused by thermal transitions. The outstanding thermal control is a rare feature for economically priced microscopes and the additional advantage of MAC Mode compatibility provides direct drive imaging in oscillatory mode in liquid and air.

## AFM Instrumentation from Agilent Technologies

Agilent Technologies offers high-precision, modular AFM solutions for research, industry, and education. Exceptional worldwide support is provided by experienced application scientists and technical service personnel. Agilent's leading-edge R&D laboratories ensure the continued, timely introduction and optimization of innovative, easy-to-use AFM technologies.

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