Tapping-Mode AFM Studies Using Phase Detection for Resolution of Nanophases in Segmented Polyurethanes and Other Block Copolymers

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ABSTRACT: The nanophase separated hard segment domains in solvent cast films of a segmented polyurethane and a segmented polyamide elastomer were imaged in real space using phase and topographical information from tapping-mode AFM techniques. A styrene triblock copolymer was used as a control to demonstrate the contrast mechanisms. For the segmented polyurethane and polyamide elastomers, contrast results from local stiffness variations of hard domains beneath a ca. 1 nm thick soft segment overlayer. Domain sizes and dispersity, shape, orientation, spacing, and uniformity in space are uniquely extracted from these real space AFM data. The ca. 7 nm diameter domains were relatively symmetric and uniformly space filling in the polyurethane. They were lamellar or sheetlike in the segmented polyamide elastomer, with a high aspect ratio and no curvature. There was no obvious correlation of lamellae orientation with macrocrystal aggregate (spherulite) position in the polyamide copolymer, while no such aggregates exist in the polyurethane.

Introduction

The use of AFM for polymer surface morphology is well established.[1,2] New developments of AFM include lateral friction and local stiffness sensitivity, all of which have many variations.[1,2] For glassy polymers, damage in contact mode AFM is well studied and difficult to avoid.[1−5] For elastomers the problem is even worse. Even when damage is minimized, the true surface topography of typical solvent cast multiphase films is ambiguous because of the contribution of elastic deformation of soft regions. Tapping-mode AFM with simultaneous topographical and phase detection is another relatively new variation[6−12] which has subnanometer surface chemical resolution via mechanical differences of the different domains. “Phase” information is obtained by detecting the phase shift between the driving and actual tip response oscillation signals at ca. 300 kHz. The phase shifts are due to different interactions of the tip with the surface, and show complicated variations depending on the magnitude of the applied forces.[10] In tapping mode, the rapid tip oscillation normal to the surface allows one to circumvent the water meniscus[13] and adhesion forces which cause uncontrollably high tip forces in contact mode. It also reduces the duration of tip−sample contact, leading to less deformation. Although the forces are low for tapping mode AFM, they are still finite and for soft elastomers this is a serious concern.[6,8] The forces for contact AFM[2] are ca. 5−500 nN vs maximum forces per oscillation of 0.1−1 nN for tapping-mode AFM.[2] These low forces combined with intermittent contact lead to very low lateral drag forces, and for soft polymers these low lateral forces may be even more important than the force normal to the surface. For contact AFM under liquid immersion the forces are ca. 0.01−1 nN.[2,14−16] For highly crystalline polymers and related materials atomic resolution has been demonstrated in liquid immersion studies,[2,14−16] but for elastomers swelling and softening of the surface by the solvent is a serious concern, so we have not attempted such experiments. Although permanent or plastic deformation is easy to check for and to avoid in tapping-mode AFM, elastic(recoverable) deformation effects are more subtle and are important in contributing to contrast in the topographical mode, as will be discussed here.

To our knowledge, there are no reports of scanning probe studies of segmented copolymers with true nanometer scale phase separated domains. The type of segmented polyurethanes studied here are phase separated on a length scale of a few nanometers, typical of this type of polymer.[17−19] Another segmented polymer with slightly larger domains was chosen to expand the study to elastomers with different morphologies, and a standard amorphous triblock copolymer was chosen in order to verify our experimental conditions and to contrast the tapping-mode data with contact AFM literature.[5]

Experimental Section

The triblock copolymer poly(styrene-*block*-ethylene/butylene-*block*-styrene)(SEBS, 15/70/15 weight ratio, $M_w = 55\,000$) was supplied by Dr. M. Motomatsu.[5] Thin optical quality films were prepared by solvent casting onto Si wafer from a 1% solution in toluene and drying overnight.

The polyurethane sample was Pelethane 70A from Dow Chemical. It is a segmented block copolymer consisting of about 80% by volume poly(tetramethylene oxide) (PTMeO, $T_g = -70$ °C). It is made from a pre-polymer of PTMeO 2000 g/mol of glycol reacted with 4,4′-diphenylmethane diisocyanate-(MDI), and then extended with butanediol. The aromatic urethane linked hard blocks are composed of MDI and butanediol. Pelethane samples are soluble in dimethylacetamide (DMAc) or dimethylformamide (DMF). Films were cast from 2−20% solutions at 60 °C, and the AFM results were independent of concentration.

Pebax 3533 from AtoChem, Inc. is a segmented copolymer made with 75% by weight PTMeO glycol ($M_w = 2000$), 21% nylon 11, and 4% adipic acid. Thus, it has a PTMeO soft segment and a polyamide hard segment. It is soluble in DMAc at elevated temperatures and was cast from a 0.5% solution at 70 °C.

Tapping-mode AFM was used to obtain height and phase imaging data simultaneously on a Nanoscope IIIa AFM from Digital Instruments, Santa Barbara, CA., Microfabricated cantilevers or silicon probes (Nanoprobes, Digital Instruments) with 125 μm long cantilevers were used at their fundamental resonance frequencies which typically varied from 270 to 350

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kHz depending on the cantilever. Cantilevers had a very small tip radius of 5–10 nm. The AFM was operated in ambient with a double vibration isolation system. Extender electronics were used to obtain height and phase information simultaneously. The lateral scan frequency was about 1.5 Hz. The images presented here are not filtered.

In tapping mode, the level of force applied to the surface can dramatically change the data, especially the phase data. These forces are roughly adjusted by the ratio of the engaged or set point amplitude to the free air amplitude.[10] It is not possible at present to exactly define the tip forces because of many unknowns including the tip contact area and the energy dissipated in the sample. This set point amplitude, which is used in feedback control, was adjusted to 10-25% of the free air amplitude for "high force" imaging and to 40–70% or 75–90% of the amplitude for moderate and low force imaging, respectively.[8,10] Some discussion is given below regarding the contribution of these different forces to the magnitude of the apparent topographical differences that are detected. Unless otherwise indicated, data presented here were obtained in moderate force mode. In this mode, the high phase corresponds to high modulus, and the low phase to low modulus.[8,10] This is a powerful tool for chemical assignment, and many controls in our lab were performed on patchy layers of polymers such as hard (polystyrene), soft (poly(vinylmethyl ether)), and also monolayers on Si to confirm that the high modulus regions (Si) were always high phase in this mode. Under moderate tapping conditions, hydrophilicity of the surfaces is not important, and local stiffness seems to govern the results.

No damage was seen on any of the polymer films studied here, while some damage was seen on the SEBS triblock polymer films in previous *contact* mode AFM studies on the SEBS copolymers in the weak repulsive mode, especially for the higher magnification scans.[5] Damage in our studies was monitored by rescanning at different magnifications in the same regions.

We also performed AFM in the contact mode in order to collect simultaneous topographical and lateral friction data. A triangular cantilever (from Digital) with a larger tip radius-(Si3N4) of about 20–60 nm. The scan frequency was about 1.5 Hz. The measurements were made in the weakest repulsive mode possible, without causing lifting off of the tip.

Results

Triblock Copolymer. To compare with previous literature using contact mode on the same material,[5] and to improve the interpretation of tapping mode AFM, a system with relatively distinct surface morphology was first studied. The topographical images (Figure 1A) for the triblock copolymer, SEBS-15/70/15, are qualitatively similar to published results taken using contact AFM.[5] Our results were independent of film thickness from 500 to 5000 nm. The phase differences are quite large resulting in excellent contrast. The peak to valley differences are on the order of 16–22° for moderate and high force tapping, and about 7–11° for light tapping (see below). For these very smooth surfaces, the phase background depends on compositions and not on topography, so it is very consistent across the scanned regions. It provides excellent "surface" chemical contrast through local mechanical differences.

At this styrene volume fraction (~27%) one would expect cylindrical domains of polystyrene (PS),[5,20] consistent with the data in Figure 1A. With AFM alone, there is no way to rule out a lamellar structure (Figure 1A), except maybe with cross section AFM studies. The repeat period determined from the power spectrum of the AFM data in Figure 1 is 25 ± 2 nm, consistent with the value from the Bragg peak of small-angle X-ray (SAXS) of 25 nm[21] for a solvent cast film. We have obtained water advancing and receding contact angles which suggest a high but not complete surface coverage of the soft component, consistent with TEM studies of Hasegawa et al.,[22] who show that the low surface energy component dominates the free surface on many systems. Some of the imaging may be done through the low surface energy ethylene–butylene soft segment layer, and would explain why we could not image the domain structure of SEBS with contact mode friction force microscopy.[7] During solvent removal, the large rods orient parallel to the surface (Figure 1 and ref 5), apparently driven by the surface activity of one of the components.[22]

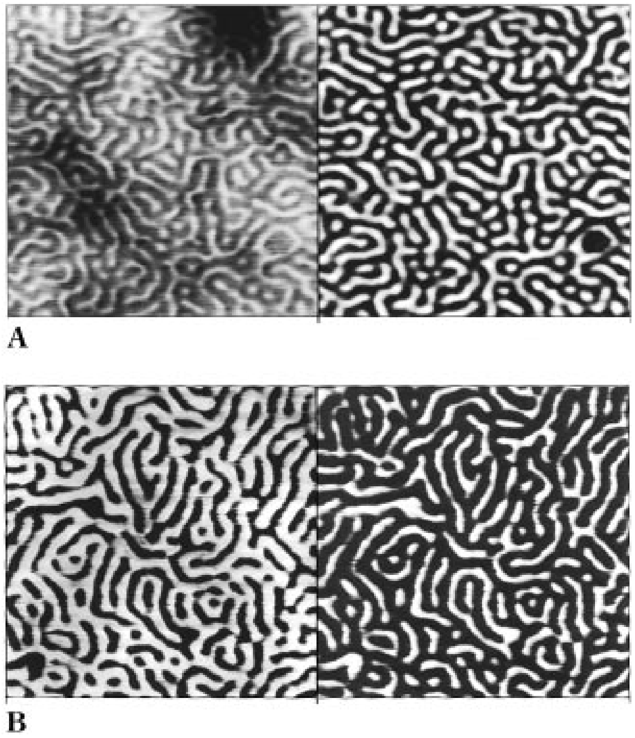

Figure 1. (A) Left: moderate force tapping mode topographical data (scale is 0–10 nm). Right: phase data (scale is 0–50°) taken simultaneously for the SEBS 15/70/15 triblock copolymer film. The scan box is 500 × 500 nm, and, the scan direction is from side to side. (B) Data taken in high force tapping mode to flip the topographical data (see text). E.g., low topographical points are high phase.

For moderate force tapping, "high spots" correspond to the high phase, and from our controls (Experimental Section) and other recent literature[8,10] we know that high phase corresponds to the harder material in this mode, which would be polystyrene in Figure 1A. This consistent with the assignment by Motomatsu et al.,[5] who provided direct evidence that the high spots in SEBS were the hard phase by AFM force-distance curves on separate domains. In other tapping mode literature on related block copolymers, the hard domains were assigned to the low spots.[6,11] As was discussed by van Dijk et al,[6] *apparent* topographies are measured in tapping AFM by feedback control where the tip distance is varied in order to keep the oscillation amplitude constant. When we use high tip forces we can reproduce the trend (Figure 1B) found by van Dijk et al. where hard domains are low spots; in other words the topography in Figure 1B is flipped compared to Figure 1A. At high forces and high penetrations into the polymer, the qualitative explanation is that the amplitude is reduced by higher interactions with the soft phase,[6] and as the tip feedback compensates for this, the soft domains contribute to apparent high spots.

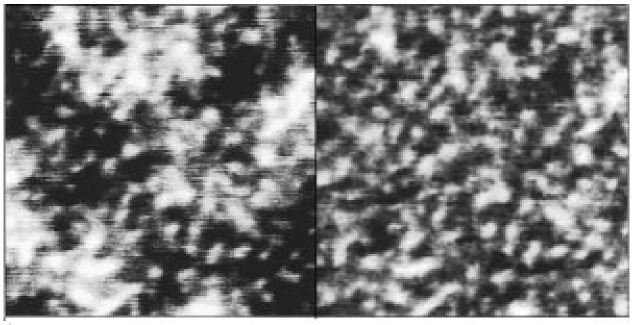

Figure 2. Topographical (left, vertical scale 0−5 nm) and phase (right, scale 0−20°) data for a 2000 nm thick Pellethane film surface showing that the "high" spots are high phase. The nanophase separated hard segment domains are resolved as the small (5−10 nm) in diameter structures. Longer range roughness contributes to the broader (but still very flat) depressions and hills with widths on the order of 50−100 nm in the topographical data. The scan width is 250 nm.

The data emphasize the importantance of understanding and recording tip forces with these new techniques.

For scanning probe studies of polymers in general, it is important to know whether there truly are height variations or whether the contrast is due to higher penetration of the tip into the softer regions due to the small but finite forces applied in tapping mode. The peak to valley height variations on the same SEBS triblock are on the order of 10 nm in the previous contact AFM literature[5] where the applied forces are many times higher. Here in moderate force tapping, height variations are equal to 1.6 nm from Figure 1A, and these are obviously many times smaller. Furthermore in light and heavy tapping, the apparent heights are 0.5 nm and 2−2.5 nm, respectively. Thus, the trend indicates that the roughness in topographical mode may actually be zero if a zero force measurement were possible. Contrary to this, for different scan boxes (all at 1.5 Hz lateral scan frequencies) of 250 × 250, 500 × 500, and 1000 × 1000 nm, the height variations are 1.1−1.3, 1.5−1.9, and 0.9−1.4 nm, respectively. One would expect considerably greater deformation for the 250 × 250 scan due to the time the tip interacts with each area of the surface, but this is apparently not the case. Thus, there is still more to learn, but the above results suggest that the true topographical contrast for a noninteracting probe is less than a few angstroms or possibly zero.

Nanoscale Hard Segment Domains. Moderate force tapping data are given in Figure 2 for Pellethane. The contrast is quite good in both topographical and phase modes (Figure 2), and the nanophase separated hard segment domains are the light areas. Computer analysis of the percent coverage of the high phase domains (Figure 2) gives about 20%, roughly consistent with the fraction of hard segment in the bulk. The size, dispersity, shape, and spacing of domains are characterized in real space. Furthermore, one can see that the hard segment domains fill space relatively uniformly with no gross regions free of hard segment domains. Much of this information is novel because techniques such as SAXS only characterize the coherently scattering objects and are insensitive to the nonperiodic structures. Standard[23] electron microscopy (TEM) procedures fail for segmented polyurethanes because of low contrast even with staining, but element-specific TEM has been used to resolve hard segment domains in polyurethanes,[24] but is limited to ultrathin films.

To see these structures with AFM, we must image through a thin soft segment layer which covers the first few angstroms of the surface[25] because of its low surface energy relative to the hard segments.[22] The contamination layer of water and other organics from the ambient air operation, presumably contribute negligibly relative to this soft segment excess layer. Consistent with the SEBS studies, as tapping forces are lowered the height variations for the Pellethane samples approach zero. Unlike SEBS, the phase variations between hard and soft domains also approach zero at lower tapping forces. The decrease in phase contrast is apparently because of the soft segment overlayer, e.g., if the forces are not high enough AFM cannot sense the underlying domains even in the phase mode. Analyzing the data (Figure 2) gives hard segment domain widths on the order of 9 ± 4 nm. An approximate repeat period from the AFM data converted to a power spectrum is 18 nm, which can be compared to the small-angle X-ray (SAXS) long period of about 12 nm for similar polyurethanes.[19] It should be noted that SAXS gives broad and sometimes poorly resolved diffraction peaks in these types of systems,[19] consistent with the heterogeneous structures detected by AFM. The small hard segment block sizes and their polydispersity contribute to the higher heterogeneity in Pellethane relative to the well defined structures in SEBS.

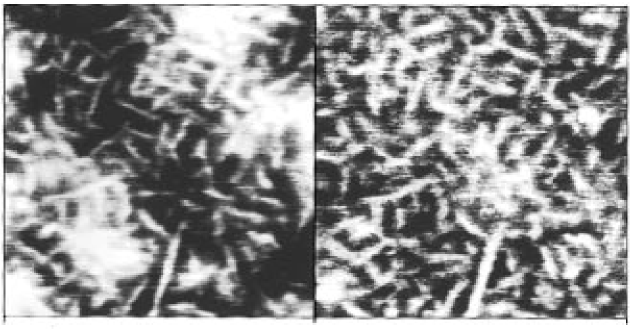

Figure 3. Topographical (left, scale 0−5 nm) and phase (right, scale 0−20°) data for a ca. 200 nm thick Pebax film. The nanophase separated hard segment crystals are resolved as the narrow (5−10 nm) wide structures, and these "high" spots are high in phase. Longer range roughness contributes to the broader (but very flat) depressions and hills with widths on the order of 50−100 nm in the topographical data. The scan width is 250 nm.

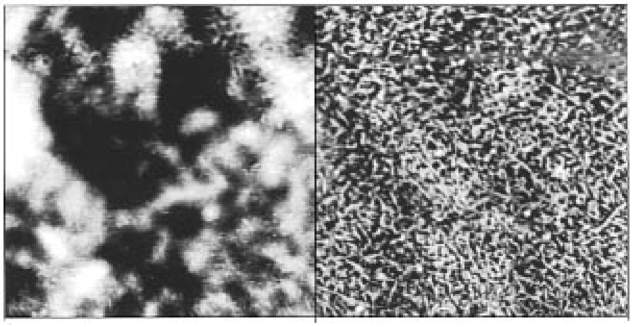

Figure 4. Lower magnification topographical (left, scale 0−10 nm) and phase (right, scale 0−50°) data for a ca. 200 nm thick Pebax film. Longer range roughness contributes to the broader (but quite flat) depressions and hills with widths on the order of 50−100 nm in the topographical data. These hills dominate the gray scale of the topographical data, but do not affect the phase data. The scan width is 1000 nm.

Figures 3 and 4 show topographical and phase data for Pebax. Good correlation is seen between the two, with lamellar or possibly rodlike crystals oriented perpendicular to the surface. These high spots (white) correlate with the high phase regions as expected for harder domains.[8,10] Details such as orientation, size distribution, and spatial distribution are novel to these real space techniques. Like Pellethane, Pebax also presumably has a soft segment overlayer. The film surface is generally much rougher because of macrocrystal structures (spherulites), especially in thicker samples. In Figures 3 and 4, very thin films (200 nm) cast from dilute solutions were used to minimize this, yet one can still see the broad but smooth low frequency peaks and valleys (50−200 nm wide and 0.5−1.5 nm high) in topographical but not phase data. The same lamellar crystals were seen in phase data on thicker and rougher films, so they are not unique to thin films.

Figure 4 shows the height and phase data at lower magnification where the lower frequency peaks and valleys are seen to dominate the gray scale for the topographical data, while the phase data have a more uniform background. This is an important advantage of the phase technique[11] and is found for almost every film system that we have studied. Even on relatively rough and/or thick films, the nano resolution of domains is possible using phase, in cases where it is not possible in topography. The peaks and valleys are not correlated with any unusual structure or orientation of the lamellar crystals. The crystals are typically 4−10 nm wide and 40 nm long with a long period determined from the power spectrum of 18 ± 2 nm. In the figures, the peak to valley height and phase differences are about 1.2 nm and 8°, respectively. The SAXS pattern[21] on solvent cast Pebax is very broad as would be expected for such misoriented crystals, and the Bragg spacing gives a 17 nm long period.

Contrasting the two systems, Pebax has larger crystals because crystallization drives “phase separation”,[26] even under conditions where solvent is still present. Since nucleation is limited, perfected lamellae and macrostructures such as spherulites are able to grow. In Pellethane and related segmented polyurethanes phase separation occurs first in the “liquid” or melt region, with subsequent crystallization after the domains have already formed. The blocks are frozen into small domains because of the high glass transition of the polyurethane hard segments even under slow solvent removal conditions, so large crystals and spherulites of hard segment are prohibited. Because of the lack of spherulites, the urethane materials are transparent and allow us to make very smooth films. In Pebax, spherulites grow as in the case of pure nylon 11 making rougher films. Of course the lamellar crystal morphology in Pebax is different relative to pure nylon 11 where in Pebax the soft segment is trapped between nylon 11 lamellae. Obviously, much more detailed information on the nano- and microscale[27] structures will be obtained in the future with these new AFM techniques.

To summarize, high resolution images of morphological structures at or near surfaces were obtained for three different systems, including one “control” triblock copolymer. For the segmented polyurethane and polyamide elastomers, contrast results from local stiffness variations of hard domains beneath a ca. 1 nm thick soft segment overlayer. Domain sizes and dispersity, shape, orientation, spacing, and uniformity in space are uniquely derived from these real space AFM data. The ca. 7 nm diameter hard segment domains were relatively symmetric and filled the entire space uniformly in the segmented polyurethane. They were lamellar or sheetlike in the segmented polyamide elastomer, with a high aspect ratio and no curvature. There was no obvious correlation of lamellae orientation with microcrystal aggregate (spherulite) position in the polyamide copolymer, while no such aggregates exist in the polyurethane. All domain spacings are consistent with independent small-angle X-ray data.

In addition to its ability to resolve nano-structures on smooth surfaces, tapping-mode AFM in the topographical and phase modes holds great promise for resolution of nanophases in “rough “ systems including sectioned samples, interfaces, thick layers, fibers, deformed samples, melt-processed samples, and various cross sections.

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