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Microdomain Morphology of Poly(urethane urea) Multiblock Copolymers

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ABSTRACT: As part of our continuing study of the solid-state morphology of poly(urethane urea) segmented block copolymers, we focus in the current paper on the use of atomic force microscopy to visualize the structure of phase-separated microdomains. Free surface and bulk images were obtained from two series of PUU films, for copolymers varying in hard segment content from 14 to 47 wt %. Using a progression of AFM tapping forces, the morphology of the hard domains at the free surfaces was found to be in the form of randomly oriented cylinders with additional spherical domains, both having lateral dimensions on the order of 5−10 nm. At higher tapping forces, phase images of microtomed surfaces of relatively high hard segment content PUU copolymers appear to exhibit hard segment-rich domains at two size scales. However, images of surfaces of specimens freeze-fractured at liquid N_2 temperatures (and acquired at relatively low tapping forces) reveal the larger structures to be aggregates of smaller hard microdomains.

Introduction

Microphase separation of multiblock polyurethane copolymers into “soft” and “hard” domains is well-known to be responsible for the versatile properties of this broad class of materials. However, real space characterization of the dimensions and organization of the dispersed hard phases is a challenging task due to their nanometer size scale. Transmission electron microscopy (TEM) studies on stained films[1,2] or using element specific TEM[3] have yielded some insight into the micromorphology of segmented polyurethanes, but the experiments are limited by the possibility of beam damage and, for the former approach, the efficacy of the staining. In recent years, atomic force microscopy (AFM), in particular tapping mode AFM, has been used to image the microphase-separated structure of a variety of block copolymers,[4−7] including some polyurethanes.[8−10]

Poly(urethane urea)s [PUU] are a subclass of the broad family of polyurethanes and are of interest in biomedical and other applications. Various PUU’s have been studied over the years, but until very recently, there has been no comprehensive examination of the microphase-separated morphology of these materials. In a recent paper, we described the synthesis of two series of well-defined segmented PUUs [prepared from 4,4′-methylene di(*p*-phenyl isocyanate) (MDI), poly(tetramethylene oxide), and ethylenediamine (and a diamine mixture)] and the subsequent investigation of their microdomain morphology using small-angle-X-ray scattering (SAXS).[11] Specimens cast from the typical solvent for these copolymers (dimethylacetamide) were found to exhibit relatively low overall degrees of phase separation [ranging from about 20% for the lowest hard segment content copolymers to about 40%], contrary to the common notion that PUU’s are well-phase-separated materials. In a recent paper, we demonstrate the sensitivity of phase segregation to preparation conditions, in particular for copolymers with higher hard segment concentrations.[12] As part of our continuing study, we focus in the current paper on the use of tapping mode atomic force microscopy to elucidate the microdomain morphology of the same two series of segmented PUU copolymers as noted above.

Experimental Section

Materials. Two series of poly(urethane urea) multiblock copolymers were synthesized via a two-step polycondensation reaction. They were prepared using a 2000 g/mol poly(tetramethylene oxide) (PTMO), end-capped with 4,4′-methylene di(*p*-phenyl isocyanate), and chain extended by ethylenediamine (EDA) [or a diamine mixture [EDA and 1,4 diaminocyclohexane (DACH)]]. The reactions were carried out in solution in *N*,*N*-dimethylacetamide (DMAc, 99+%, anhydrous). The details of the synthesis are provided in a previous paper.[11] Only EDA was used as the chain extender in the first group of copolymers, which consists of seven polymers with hard segment concentrations ranging from 14 to 47 wt %, and is referred to as series I. All copolymers in series II have the same hard segment weight fraction (22%), but some EDA was replaced with DACH in order to partially disrupt hydrogen bonding in the hard phase. There are five copolymers in series II, with DACH contents ranging from 0 to 35 mol % of the diamine. The series I copolymers are identified by “PUU” followed by a number denoting the hard segment weight fraction, which is calculated by assigning all MDI and EDA units to the hard segment. For the copolymers synthesized with mixed diamines, the hard segment weight fraction appears first, followed by the percentage of total diamine that is DACH. Molecular weights of the copolymers (determined by gel permeation chromatography) are typical for condensation polymers and are summarized in ref 11.

Sample Preparation. Samples used in the free surface experiments were prepared by solution casting relatively thin films from 1% DMAc solutions. Several drops of the polymer solution were placed onto round coverslips and dried in a vacuum oven under “full vacuum” (i.e., a mechanical pump) at 70 °C. No residual solvent was detected by FT-IR in similarly prepared films. Solution casting in this fashion produced films ~1 μm thick and an RMS surface roughness <0.5 nm over a 500 nm × 500 nm scan area, more than an

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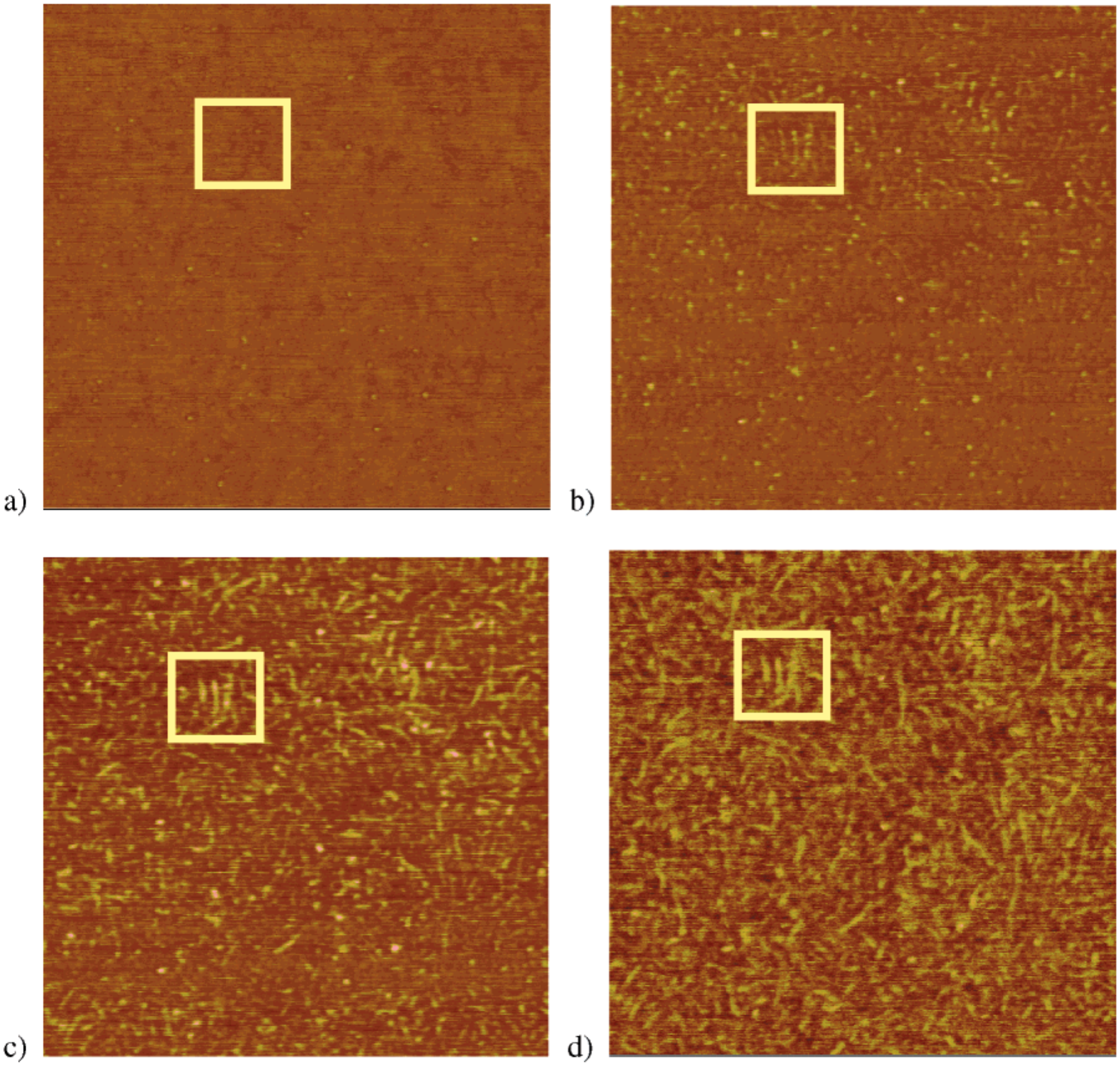


Figure 1. AFM tapping mode phase images of the as-cast surface of PUU 22 with force variation. The images are 500 nm × 500 nm, and the phase scale is 0−25°. The box indicates a reference feature common in all images. Key: (a) $r_{sp} = 0.90$; (b) $r_{sp} = 0.85$; (c) $r_{sp} = 0.80$; (d) $r_{sp} = 0.70$.

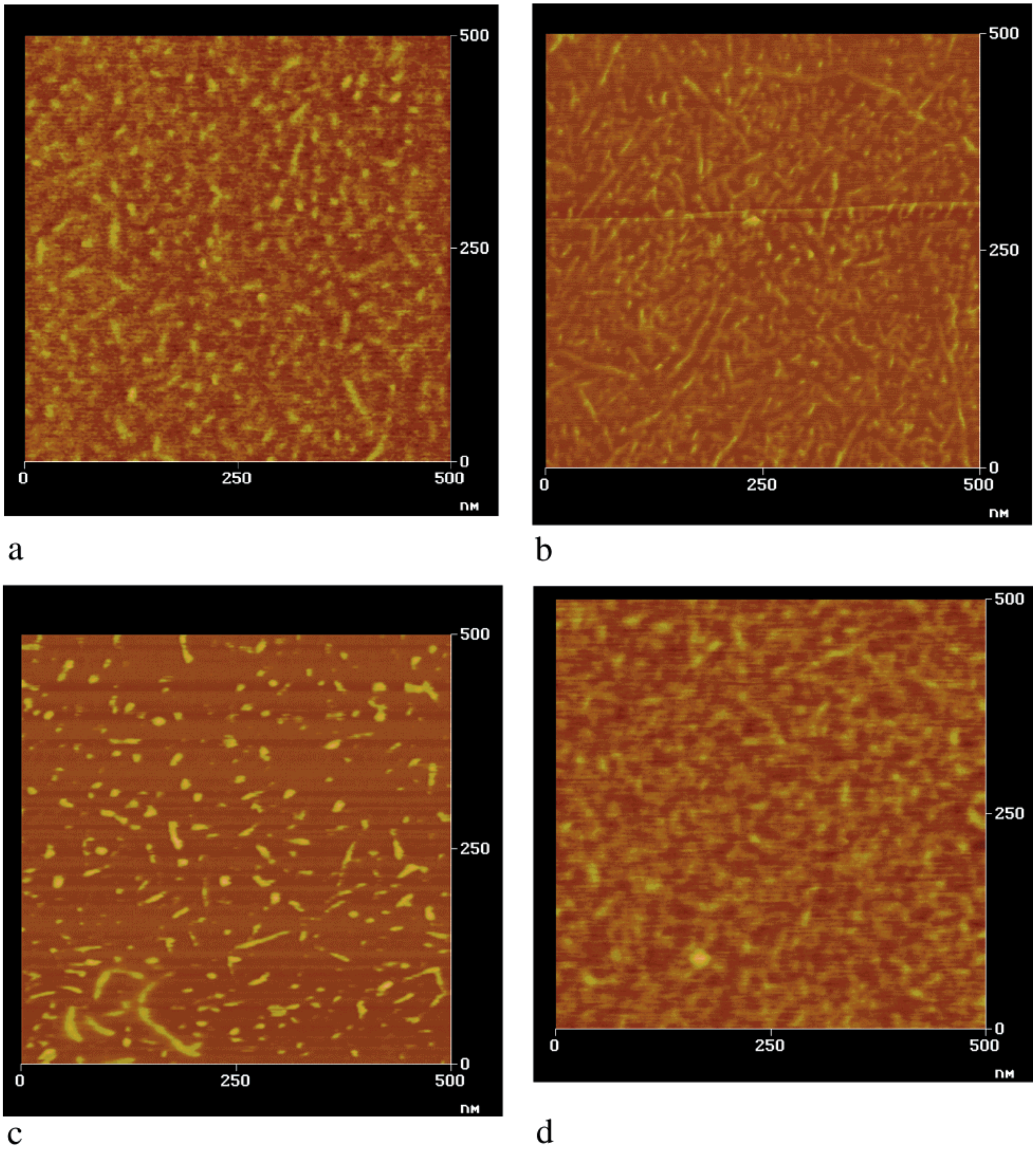
order of magnitude less than those that were spun cast from 1 to 3% solutions between 1000 and 3000 rpm. All films were dried under vacuum for 24 h at 70 °C. The coated coverslips were then mounted on steel AFM sample disks for imaging.

The bulk morphology was evaluated by imaging cross sections of thicker solution cast films. They were prepared from a more concentrated solution (~3%) and dried for 24 h under vacuum at room temperature followed by 24 h at 70 °C. The slower drying process was necessary to ensure continuous films. The films were on the order of 100−200 μm thick. Initially, cross sections of selected films were prepared by cryotoming the sample at LN_2 temperatures, but the surfaces of the cross sections of those samples consistently showed knife markings that dominated the nanoscale morphology. Microtoming normal to the surface on a Leica CM1850 Cryostat at −25 °C was found to produce samples that were much more suitable for imaging. Then, 20 μm thick sections were removed from a small square of the polymer film until the cross section was level. This method resulted in relatively smooth specimens. The roughness was somewhat greater than the solution cast films, but still less than spun cast films. RMS roughness values ranged from 1.1 nm for the PUU 22 cross section to 3.7 nm for the PUU 43 cross section. The remaining sample block was mounted cut-edge up on an AFM sample disk and imaged. Cross sections were also prepared by freeze-fracturing selected copolymer films at liquid N_2 temperatures. A small cut was made in the specimens and propagated through the samples while submerged in liquid N_2. The morphology of all freeze-fractured samples is consistent with that of those microtomed at −25 °C.

Instrumentation. The samples were imaged with a Digital Instruments multimode AFM using tapping mode and phase imaging. The images were acquired under ambient conditions using light to moderate tapping, $r_{sp} = 0.95$ to 0.50, where $r_{sp} = A/A_o$ (set point amplitude/free amplitude of oscillation). Unless otherwise indicated, the amplitude of free oscillation was 18 nm. Topographic and phase data were recorded simultaneously with a standard silicon tapping tip on a beam cantilever. The spring constant of the cantilever is between 20 and 100 N/m, and the nominal radius of curvature of a new tip is between 5 and 10 nm. The cantilever length is 125 μm, and the resonance frequency is 200−400 kHz. The data were analyzed with Nanoscope III software.

Results and Discussion

AFM Imaging of PUU Free Surfaces. A series of images was obtained for all series I and II copolymers at various values of r_{sp}. Samples were initially imaged at low tapping forces and the force was increased incrementally to obtain each subsequent image.[5] A series of such images is shown in Figure 1 for PUU 22. The highlighted box in each image indicates a landmark



a b c d

Figure 2. AFM tapping mode phase images of the as-cast surfaces of (a) PUU 17, $r_{sp} = 0.85$; (b) PUU 37, $r_{sp} = 0.95$; (c) PUU 47, $r_{sp} = 0.70$; and (d) PUU 22−35, $r_{sp} = 0.95$.

(three parallel domains), verifying that each was acquired from the same area of the specimen.

At low tapping forces (Figure 1a), the phase image shows a single uniform phase. In light of this and subsequent images, we believe that this top layer consists predominately of the soft phase. A similar observation has been made on a segmented polyurethane (Pellethane) containing ∼80 vol % soft segments[8] and is consistent with the results of previous X-ray photoelectron spectroscopy experiments on polyurethane block copolymers.[13] As the tapping force is increased, hard domains become visible. Small bright regions are visible in the phase image in Figure 1b, and some of these "stretch" into cylinders in Figure 1c. Sampling depth increases as tapping force increases and more hard domains subsequently appear in the images. At higher tapping forces, Figure 1d, the image is almost completely covered by hard domains because most data points are composed of contributions from both hard and soft domains. This domain overlap, which results from the three-dimensional sampling projected into two-dimensions, is similar to that observed in TEM images of films that are thick relative to the domain size.[2,14]

The same procedure was followed for all copolymers in series I and II. Figure 2 shows phase images from several representative copolymers at low or moderate tapping forces. [Note that images in Figure 1 are of 1 μm × 1 μm regions, while those in Figure 2 and all subsequent figures are from 500 nm × 500 nm areas.] All images indicate a morphology consisting of both

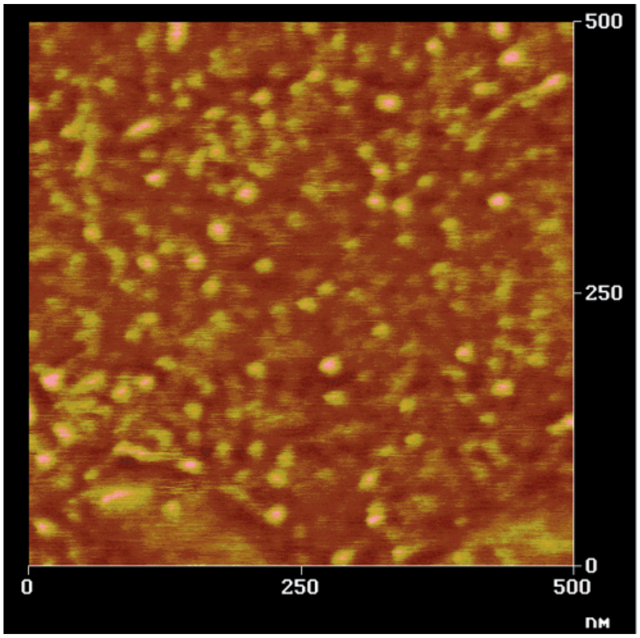


Figure 3. AFM tapping mode phase image of the cross section (−25 °C, microtomed) of PUU 22, $r_{sp} = 0.90$.

randomly oriented cylinders and domains that appear more or less spherical. These "spheres" are most likely a combination of spherical domains and portions of cylindrical domains. The hard domains have lateral dimensions on the order of 5−10 nm, and the lengths of the cylinders can exceed 100 nm. The widths of the hard domains are comparable to the average domain sizes reported for other solution cast segmented polyurethanes: ~9 nm by AFM[8] and ~13 nm by TEM.[1] However, because apparent domain sizes can depend on tapping force and the images of the domains broadened by tip−sample interactions,[15] we are not able to distinguish modest changes in domain size with copolymer composition.

AFM Imaging of PUU Cross Sections. In addition to free surfaces, microtomed cross sections were analyzed to investigate the bulk morphology of the PUU copolymers. The free surfaces of these thicker films were also investigated but we were unable to image hard domains, presumably as a result of a thicker soft phase overlayer. The cross section of PUU 22 is shown in Figure 3. The hard domains are apparent at very low tapping forces, in contrast to the surface images, presumably because of the absence of a soft phase overlayer. This allows immediate and direct imaging of the hard domains. For this reason, only a single, low tapping force image is displayed. In the PUU 22 cross sectional image many domains are nearly spherical in shape, while others are modestly elongated. The domains in Figure 3 are generally somewhat larger (10−15 nm in diameter) than comparable structures observed in the surface images in Figure 1. The overall morphology is similar to the microphase-separated structure seen with TEM of microtomed sections of relatively low hard segment content segmented polyurethane films[1] and poly(urethane urea) foams.[14,16]

The two-dimensional power spectral densities (PSD) of the largely isotropic PUU 22 cross sectional images were analyzed to extract information about domain spacing. The PSD of images acquired at four different tapping forces (from $r_{sp} = 0.85$ to $r_{sp} = 0.70$ in increments of 0.05) were analyzed to ensure that the indicated interdomain spacing was not simply a function of sampling depth. All PSDs indicated an average interdomain spacing of 11−12 nm, in excellent agreement with an interdomain spacing of 13 nm derived from SAXS experiments on the identical copolymer.[11]

As hard segment content in the series I copolymers increases, it appears that phase separation occurs at a second, larger size scale. As an example, Figure 4 shows images of both the −25 °C microtomed (Figure 4a) and liquid N_2 freeze-fractured (Figure 4b) cross sections of PUU 30. These larger structures are also seen in Figure 5a, the image of the freeze-fractured cross section of PUU 47, acquired at $r_{sp} = 0.75$. These structures are reminiscent of the larger domains observed in poly(urethane urea) foams[14,16] and polyurethane elastomers synthesized in one step reactions,[17,18] as well as very recently in a segmented polyurethane prepared in a two-step process similar to that used here.[19] However, imaging at lower tapping forces (see Figure 5b) reveals the larger structures to be aggregates of much smaller domains. In fact, the domains in Figure 5b are similar

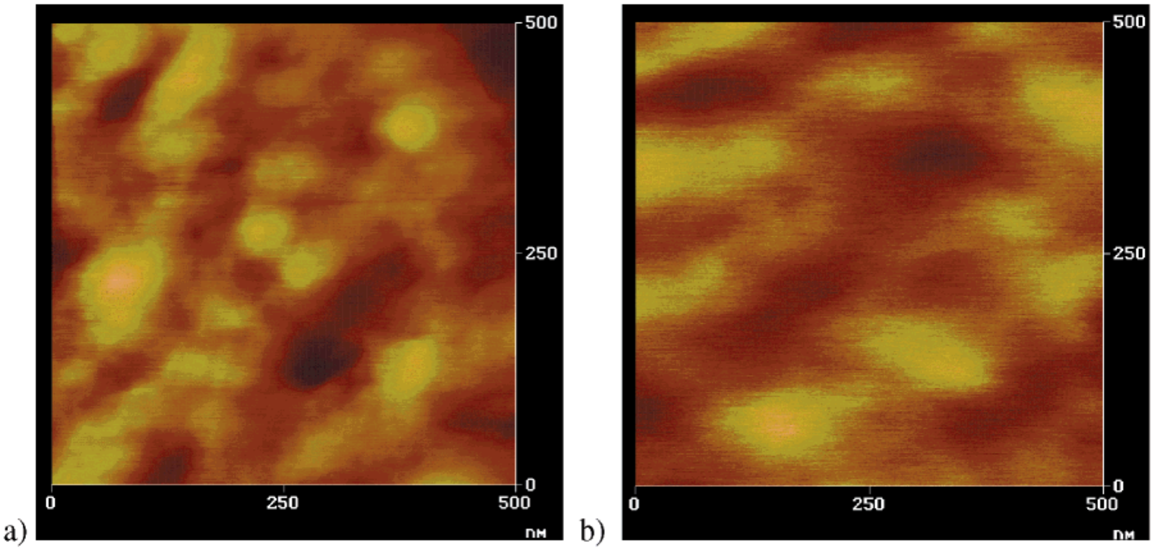


Figure 4. AFM tapping mode phase image of the cross section of PUU 30: (a) microtomed cross section (−25 °C), $r_{sp} = 0.95$; (b) freeze-fractured cross section (liquid N_2), $r_{sp} = 0.90$.

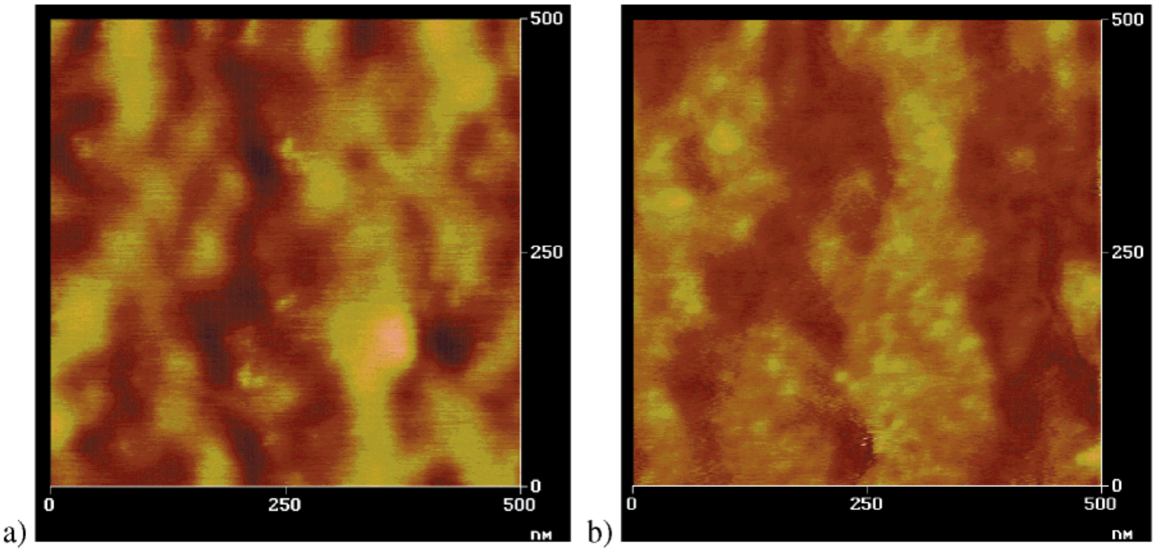


Figure 5. AFM tapping mode phase image of the cross section of PUU 47 obtained by freeze-fracturing in liquid N_2: (a) $r_{sp} = 0.75$; (b) $r_{sp} = 0.95$.

in size and distribution to those observed for PUU 22 (see Figure 4). At higher tapping forces, the projection of the three-dimensional sampling into two-dimensions apparently prevents the smaller domains from being resolved.

Conclusions

The microdomain morphology of two series of segmented poly(urethane urea) block copolymers varying in hard segment content and diamine composition was investigated using tapping mode AFM. Two types of films were analyzed: the free surfaces of solution cast films (~1 μm thick), and cross sections of thicker (100−200 μm) films which are representative of the bulk structure. The free surface morphology of all PUU copolymers was identified as largely cylindrical in nature; the cylinders are on the order of 5−10 nm in width (and up to ca. 100 nm in length) with additional spherical domains ~10 nm in diameter. Changes in the "surface" morphology or domain dimensions with copolymer composition were not detected in our experiments.

The bulk morphology (determined from cross sectional images) consists of approximately spherical domains, on the order of 10−15 nm in diameter. Quantitative analysis of the PUU 22 cross sectional image indicates an interdomain spacing of 11−12 nm, in excellent agreement with the mean interdomain spacing determined from a SAXS experiment on the same copolymer. As hard segment content increases, it appears from images acquired at higher tapping forces that phase separation also occurs at a second, much larger length scale. However, images acquired at lower tapping forces reveal the larger structures to be aggregates of much smaller domains, similar in size to those observed for lower hard segment content copolymers.

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