The Effects of Varied Imidization Conditions on Rubbed Polyimide Film Surface Morphology

C. L. H. Devlin,* S. Chiang, T. P. Russell

Department of Physics, University of California, Davis, California 95616
Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003

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ABSTRACT: The thermal histories of polyimide films were varied to study the effect of the extent of imidization on the response of films to rubbing. Films rubbed prior to imidization formed tears that extended to the substrate; tears in these films formed at smaller film thicknesses than in films imidized prior to rubbing. Aligned nanoscopic islands were also seen. The alignment of these islands disappeared upon imidization. Films imidized at a low temperature showed less alignment of islands than conventionally prepared films. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1192–1197, 2004

Key words: atomic force microscopy (AFM); curing of polymers; thin polymer films; rubbing; polyimide

INTRODUCTION

In recent years, there has been much attention placed on rubbed polyimides, which are used to align liquid crystals in displays. Many studies have focused on the mechanism of liquid crystal alignment. The major factor affecting liquid crystal alignment is the molecular interaction between the liquid crystal and the polyimide molecules.[1,2] Rubbing has been shown to align the polyimide chains near the surface along the rubbing direction.[3–7] Consequently, the orientation of the polyimide molecules at the surface is crucial. In addition, the extent of order of the rubbed polymer films has been found to appreciably affect the orientation of the liquid crystal.[8] The degree to which the surface layer of the film is ordered depends on the imidization temperature and subsequent heat treatments.[9]

Various alterations to the normal processing routine for heat-cured, rubbed polyimide films have been investigated to examine their influence on the ordering of the polyimide molecules and the ability to align liquid crystals. Experiments involving heating *after* rubbing have been shown to increase the order of the polyimide molecules at the surface, along the rubbing direction.[10] Higher temperatures *during* rubbing have also resulted in increased orientation of the polyimide films.[11] Kim et al.[12] have shown morphological relaxation in scratches in the polyimide surface due to low-temperature annealing, after which the scratched areas retained their ability to align liquid crystals. Kikuchi et al.[1] have found that BPDA-PDA, the polyimide used in this study, will even align smectic liquid crystals when imidized or cured at low temperatures. All of these studies show that the thermal history of a polyimide film can markedly influence its surface properties, and that heating during or after the rubbing process can increase the molecular orientation effects of rubbing.

In this study, atomic force microscopy (AFM) has been used to elucidate the effect of heating subsequent to rubbing and imidization. Many researchers have previously used AFM to study rubbed polyimide surfaces.[1,13–16] Since only ~ 10 nm of the film near the surface is aligned by the rubbing process,[3,5,7] our studies have focused on films with thicknesses just above and below 10 nm so as to understand the alignment mechanism. Previous studies have revealed two characteristics of rubbing that are unique to these very thin films: tears in the film, terminated by a large bolus, that extend to the substrate, and alignment of nanometer-scale polyimide islands along the rubbing direction.[16] Understanding the dependence of these on the thermal history of the film may lead to routes to enhance surface order.

EXPERIMENTAL

The poly(amic dialkyl ester) of biphenyltetracarboxylic dianhydride-*p*-phenylenediamine (BPDA-PDA)

Correspondence to: S. Chiang (chiang@physics.ucdavis.edu).
* *Present address:* Sensors Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH 45433.

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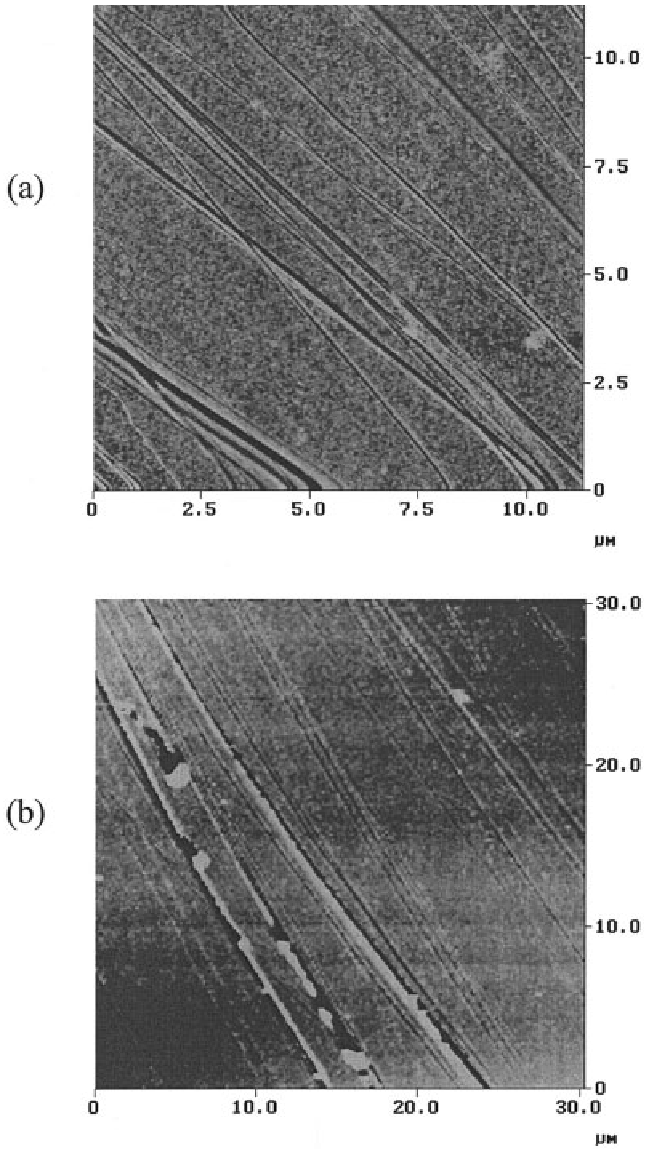

Figure 1 TMAFM images of tears and scratches on a 5 nm thick polyimide film on mica, which was rubbed before imidization. (a) After rubbing and before imidization. (b) A different region of the same film, after imidization. In both images, the deep scratches across the lower right hand corner extend to the substrate beneath. No discernible effect due to imidization on the tears or scratches can be seen. Note that tears tend to be long and narrow on these samples, often lacking the large terminating bolus of material seen on samples rubbed after imidization. The height difference between white and black areas is 10 nm. The rubbing direction is from upper left to lower right.

with a molecular weight of approximately 30,000 g/mol was spin-coated from 1-methyl-2-pyrrolidinone (NMP) solutions onto mica substrates. The film thickness was controlled by changing the solution concentration and/or spinning speed. Some films were then heated to 80°C (to remove excess solvent) and subsequently rubbed before imidization. Other films were imidized in an oven where the temperature was increased to the desired imidization temperature, either 200°C or 300°C at a rate of 1°C/min under flowing N_2. The samples were kept at the imidization temperature for 1 h and then cooled to room temperature at a rate of 1°C/min. The films were then rubbed by first placing them face down on a velour cloth. A known weight was applied to exert a laterally uniform load between the surface of the polyimide and the cloth. The cloth was pulled unidirectionally beneath the film at a rate of 30 cm/min for a distance of 30 cm. Some films, subsequent to imidization at 300°C and rubbing, were reheated to either 200°C or 300°C, using the method described above.

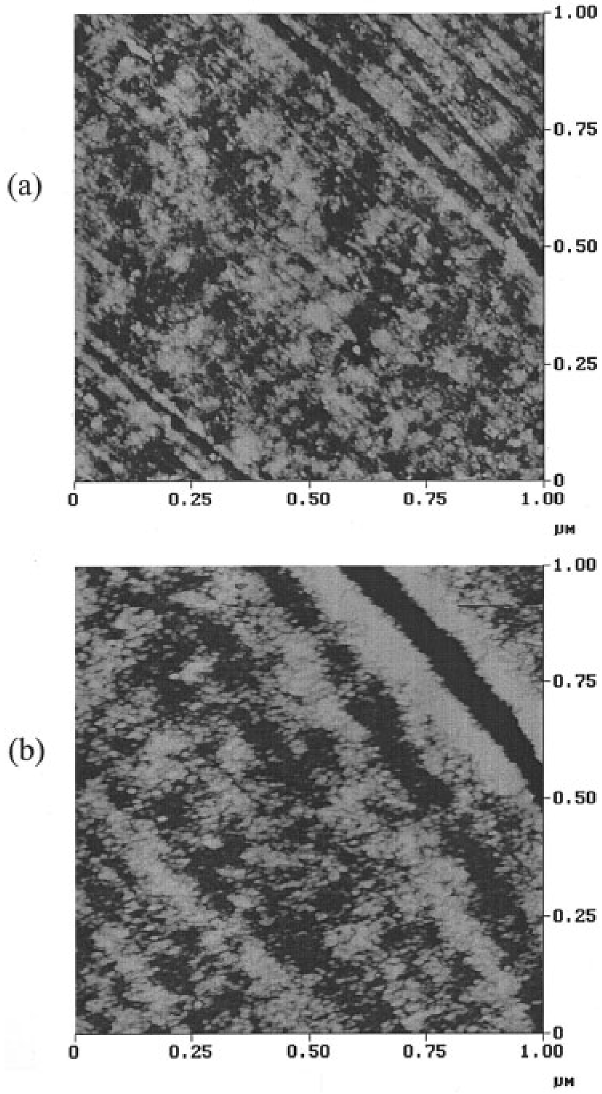

Figure 2 TMAFM images of two different regions of polyimide film on mica, showing nanometer-scale islands on a 35 nm thick film, rubbed while the film was in the precursor state. (a) After rubbing and before imidization; (b) after imidization. Note that while the islands are aligned into long chains along the rubbing axis (shown by the deeper scratches in the upper right of both images) in (a), alignment is lost after imidization in (b). The height difference between white and black areas is 3 nm.

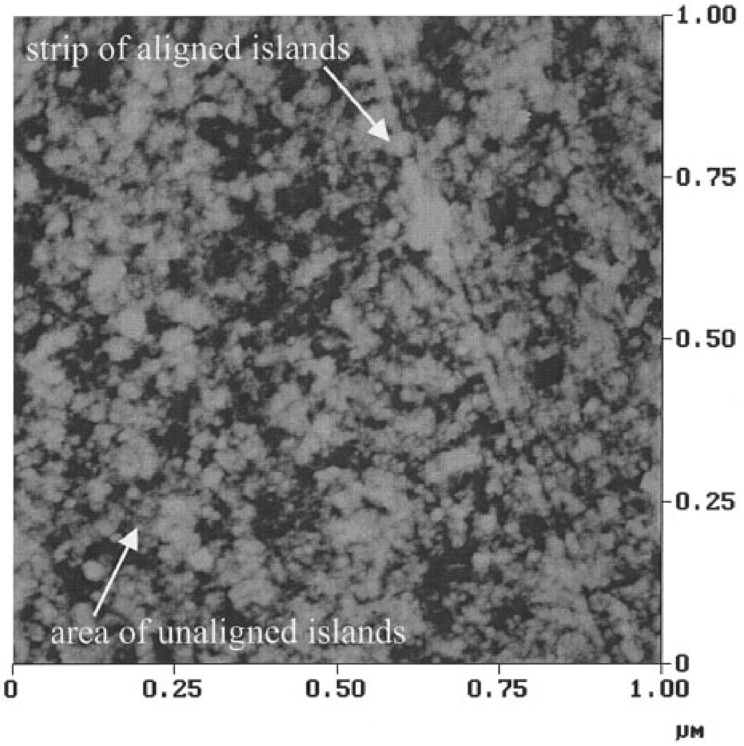

Figure 3 TMAFM image of nanometer scale islands on a rubbed 35 nm thick film, imidized at 200°C. Note the strips of islands aligned into chains on the right side of the image, while other areas remain unaligned. The height difference between white and black areas is 3 nm. The rubbing direction is from upper left to lower right.

The film thicknesses reported here were measured by optical ellipsometry on a parallel set of films spun onto silicon. A variation in the film thickness of ~ 10% was found laterally across the film. AFM measurements of tear depths in the film that reached to the substrate were averaged over a single sample to give an independent measure of film thickness. Average tear depths, however, were found to be larger than the ellipsometric thickness, possibly due to removal of substrate material within the tear. (This effect is discussed in previous work.[16])

Films were prepared on mica substrates since the atomically flat surface of the mica allowed any surface features to be attributed to the polyimide film alone. The bare mica surfaces, as prepared for film deposition, are step-free over areas of at least (40 μm)^2. Films on silicon and glass substrates were also observed, to study the effects of possible substrate specific interactions. AFM studies were performed in tapping mode (TMAFM) using a Digital Instruments Nanoscope IIIa (Santa Barbara, CA).

RESULTS AND DISCUSSION

Rubbing before imidization

Films of 5, 10, and 35 nm thickness were imaged in the precursor state after rubbing with a 4 g/cm^2 load. These films exhibited the same features as films rubbed after imidization: scratches, flat-bottomed tears in the film, and alignment of the nanometer-scale islands along the rubbing axis. Only 5 nm films exhibited tears. For the 5 nm film, an average of only 0.7% of the area imaged was within the boundaries of a tear, as compared to nearly 4% in films with comparable thickness and rubbing load that were imidized before rubbing. As seen in Figure 1, the tears tend to be long and narrow, often lacking the large terminating bolus of material seen on samples rubbed after imidization. The interisland spacing was found to be 10 to 40 nm, and the depth of the troughs between island chains was 0.5 to 1 nm.

With imidization, the micron-scale features of these films were unchanged, but the alignment of nanometer-scale islands induced by rubbing was mostly destroyed (Fig. 2). The much larger-scale morphological relaxation of the surface scratches seen by Kim et al.[12] with low-temperature annealing shows that significant relaxation occurs at the surface with heating. The relaxation seen here, though at a much smaller scale, may be of a similar origin.

Grooves on the surface, similar to those found in this study, were found by Kikuchi et al.[1] only after imidizing the precursor. The spacing and depth of the grooves in that study, however, were two or more

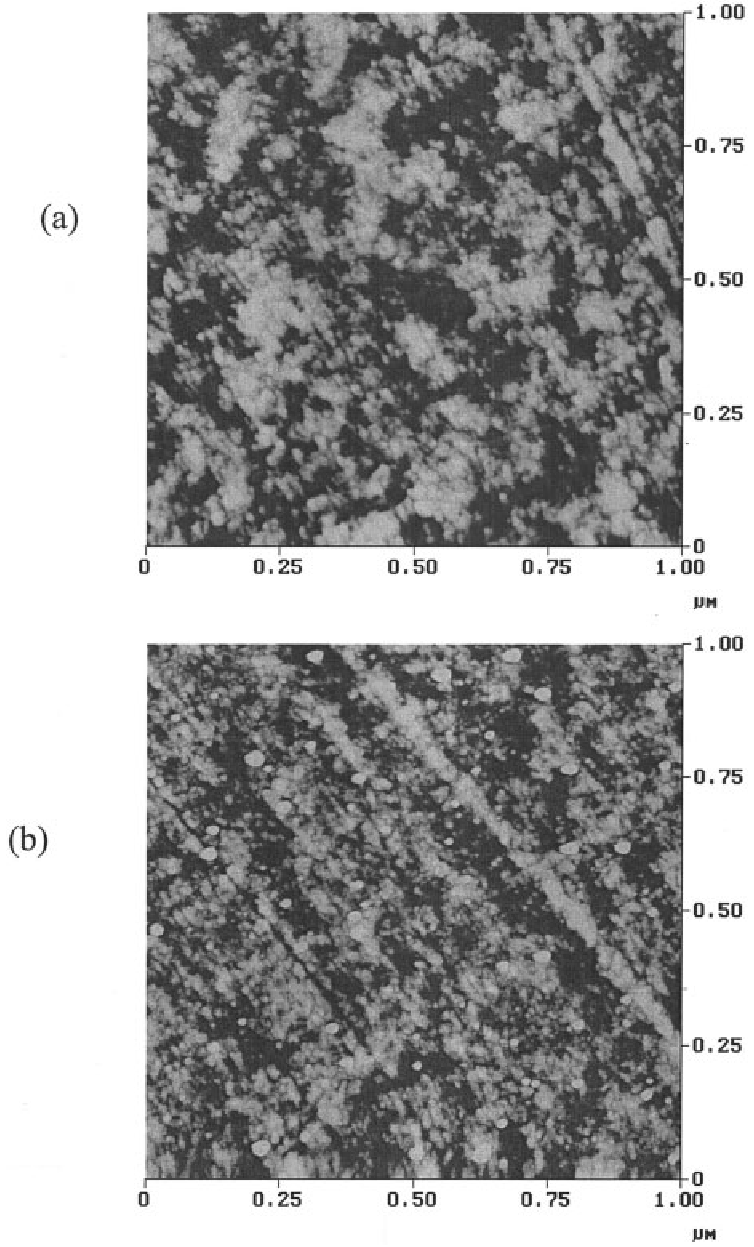

Figure 4 TMAFM images of nanometer-scale islands on polyimide films, rubbed from upper left to lower right. (a) 10 nm thick film, after being imidized and then rubbed. (b) Different region of the same film after being reheated to 200°C. Notice that the alignment of islands into chains along the rubbing axis can still be seen after reheating to 200°C. (c) 5 nm thick film, after being normally imidized, rubbed, and then reheated to 300°C. The previous alignment of islands is now lost. The height difference between white and black is 3 nm.

times larger than that found here. It is important to note that a poly(amic acid) precursor was used in the study of Kikuchi et al., whereas the poly(amic dialkyl ester) of BPDA-PDA was used here. While the BPDA-PDA that results from imidization of these different precursors is chemically identical, it is known that the amic acid precursor retains a substantial fraction of the casting solvent prior to curing. Amic dialkyl ester films, however, do not retain as much solvent and therefore exhibit different residual film stress and other properties.[17] In addition, the films used in Kikuchi's study were imidized at ~ 400°C, whereas the films used here were imidized at 300°C. Since the order and density of the unrubbed film increases with imidization temperature,[9,18] the film morphology and mechanical properties will be markedly altered upon heating subsequent to rubbing.

Lower imidization temperature

Samples imidized at 200°C and then rubbed also exhibited the features seen in films imidized at 300°C.

(c)

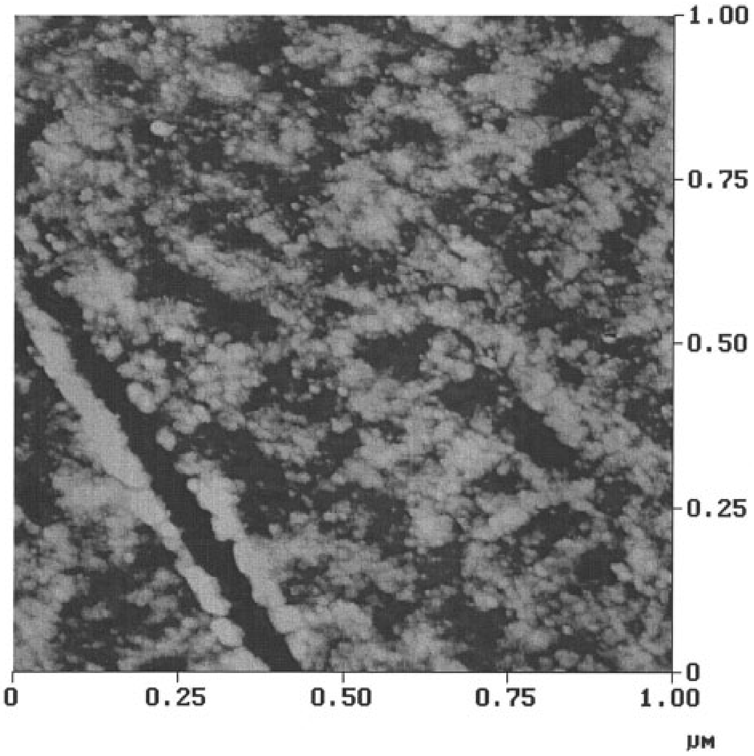

Figure 4 (*Continued from the previous page*)

For samples of various thickness rubbed with a 1 g/cm^2 load, troughs are observed at the same thickness as for other samples cured at 300°C. The alignment of nanometer scale islands was also present for these films, though not as distinct as for films cured at the higher temperature. The alignment found with these films also tended to be found only in narrow strips (Fig. 3). Films imidized at 300°C tended to exhibit a more distinct, uniform alignment, covering the entire area imaged (usually 1 μm^2).

Sands found that films imidized at 200°C show markedly lower packing efficiency than those imidized at 300°C.[18] Also, better ordering of the molecules in the unrubbed films is seen for higher imidization temperatures. Kikuchi et al., however, found that BPDA-PDA films imidized at close to 200°C were capable of aligning smectic liquid crystals, whereas films imidized at higher temperatures were not. The fact that these films have less distinct alignment of islands on the surface may influence the alignment of the smectic liquid crystals.

Reheating conventionally imidized and rubbed samples

Some samples, after being imidized at 300°C and then rubbed, were reheated to 300°C. No changes in the larger, micron-scale features (scratches and tears) of the film were seen. The alignment of nanometer-scale islands along the rubbing direction, however, was mostly destroyed (Fig. 4). Prior to reheating, most films showed marked alignment of islands over at least part of the imaged area. After reheating, few films exhibited this behavior. If the sample is reheated to only 200°C, however, the alignment of the nanoislands did not change. Subsequent heating to 300°C destroyed the alignment.

Since 300°C is close to the glass transition for BPDA-PDA films,[17] the loss of alignment along the rubbing direction arises from a relaxation of the chains. The loss of orientation can be directly linked to the increase in ordering with increasing temperature. With ordering there is a density increase and a corresponding volume contraction. This volume change can occur only if molecular motions occur that are accompanied by a relaxation of the chains. Since the state of order is dictated by the highest temperature, annealing the film at a lower temperature results in less ordering and no molecular relaxation.

CONCLUSIONS

It has been shown that different thermal histories can influence the response of the surface of polyimide films to rubbing. Thin nonimidized films begin to exhibit tears upon rubbing that extend to the substrate at a smaller film thickness than films rubbed after imidization. Imidization of the film randomizes the alignment of nanoislands found in both nonimidized and imidized polyimide films directly after rubbing.

Films imidized at a low temperature (200°C) and subsequently rubbed showed the same qualitative features as those imidized at 300°C, though the appearance of aligned chains of nanoislands was markedly less prevalent. Heating films to temperatures at or above the imidization temperature destroyed the alignment of nanoislands along the rubbing axis. This results from a local relaxation of the chains due to the proximity of the glass transition temperature. The loss of alignment can be attributed to a relaxation of the polymer brought about by a volume contraction associated with ordering.

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