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Studies of photosensitive alignment layer based on ladder-like polysilsequioxane liquid-crystal devices using atomic force microscopy/force curve

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Atomic force microscopy (AFM)/force curve measurements were used to study the photochemical process of UV-treated (0, 10, 20, 30 and 60 min) organic thin films that were prepared from azobenzene and cinnamate side-chain co-grafted ladder-like polysilsequioxanes (LPS). The morphological data of the thin films describe the changing process on the surface of the thin film. The statistical results of the adhesion force of the thin films further demonstrate the intermolecular characteristics of the thin films. A photosensitive thin film after UV exposure for 20 min would be a better material with a preferred orientation that can be used to make liquid-crystal devices. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: photosensitive thin film; adhesion force

INTRODUCTION

Liquid-crystal (LC) alignment films have been investigated widely by scientists and technologists in recent years.[1–7] The orientation of LCs plays a very important role in the performance of liquid-crystal displays (LCDs), and the orientation depends strongly on the nature of the substrate surface.[1] In particular, the pre-tilt angle between the LC director and the substrate plane significantly influences the optical properties and the dynamic behaviour of LCDs.[8–10] A photosensitive alignment organic layer with a high pre-tilt angle should be chosen. Furthermore, the above characteristics depend on the structure and composition of the LC alignment films.

The most promising aspect of the measurement of adhesion force using atomic force microscopy (AFM) is its capability for sampling small areas of a substrate; the limiting parameter for resolution is the radius of the AFM tip. Furthermore, the combination of the high spatial resolution of AFM coupled with its scanning capability affords a great potential for mapping adhesion forces across a surface. The data, which were presented as 'force slices', i.e. a map of the deflection of the cantilever at set distances into the force curve, were qualitative in that they contained information about the spatial distribution of adhesion, but this property was not deconvoluted from sample topography. Kawai *et al.* measured the adhesion force between a standard silicon nitride tip and several inorganic materials.[11,12]

Recently, and as part of our work on five thin films with the LC alignment layer UV-treated for different times (0, 10, 20, 30 and 60 min), we obtained a relationship between the data from the adhesion force in contact mode by AFM. We found that by applying the method of adhesion force we could map the composition and configuration changes in photochemical thin films. The recognized ability of the adhesion force is interesting for the study of organic materials.

MATERIALS AND EXPERIMENTS

An organic solution was prepared from azobenzene and cinnamate units grafted onto ladder-like polysilsequioxanes(LPS) (see Fig. 1).[13] The solution was spin-coated on a freshly cleaved mica surface. After annealing, the surface of the thin films was rubbed by a velvet plane along a certain direction. Then the thin films were treated for 0, 10, 20, 30 and 60 min under a 500 w high-pressure Hg lamp, which provided an ultraviolet light intensity of 15 MW cm^{-2} at 365 nm on the surface.

The AFM/force curve measurements were completed in contact mode using a Nano IIIa scanning probe microscope (Digital Instruments, USA) in air at a given temperature. The length of the cantilever is 200 μm, with a spring constant of 0.58 N m^{-1}. All images are obtained in height mode. We recorded multiple force curves for each film with the same tip.

RESULTS AND DISCUSSION

The data from images of the photochemical organic thin films were collected and analysed. In particular, the chemical composition of the thin films was studied using the force

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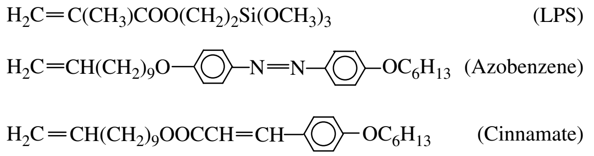

Figure 1. The structures of LPS, azobenzene and cinnamate.

curve statistic method. The different structural characteristics are listed in Table 1. The data illustrate that the diameter sizes of the nano particles (convex region) gradually decrease in the photochemical thin films after irradiation for 0–20 min but their average height gradually increases. The average height of the surface of convex regions also increases from the original 1.2 to 2.0 nm after irradiation for 0–20 min. There is a better photoresult experimentally.[13] The results are attributed mainly to good photoisomerization of azobenzene and cinnamate side-chains crosslinking the LPS layer. In particular, the two kinds of side-chains achieve the preferred orientation in the thin film UV-treated for 20 min The data of Table 1 also give information on the thin film UV-treated for 30 min. The nanoparticles (convex region) have a diameter of 30–100 nm and the homogeneous surface is destroyed in the thin film. The good state of both molecules (azobenzene and cinnamate) is changed in the LPS layer. Furthermore, after exposure for 60 min there are island-like structures in the thin film due to the more complex reaction of the photochemical process.

The photochemical process of the photosensitive thin film is described by using information on five thin films that underwent photoisomerization → photodesolvation (photopolymerization). The thin film after UV exposure for 20 min could be a new organic material with a preferred orientation that can be used to make LC devices.

Changes in chemical composition are further studied by the statistical results of adhesion force for the five organic thin films. The hysteresis in the force curves corresponds to the adhesive force between the AFM tip and the photochemical thin film. The statistical data of adhesion force between the tip and the five films are plotted in Fig. 2, illustrating the intermolecular state and the properties of the thin films. Because five lots of data for the adhesion force are obtained under the same conditions, the influence of system deviation is removed. The maximum value of the adhesion force (41.5 ± 2.0 nN) is shown in the frequency distribution for the thin film rubbed without UV treatment and the thin films UV-treated for 10 min (70.5 ± 6.6 nN) and for 20 min (113.8 ± 11.3 nN). The data on adhesion force were carefully assayed to find that the maximum value of the adhesion force gradually increased, as would be assumed from the molecular orientation in the three thin films. The configuration of the azobenzene molecule is different in the three thin films: cis-isomerized(rubbed); partly trans-isomerized (UV-treated for 10 min); and fully trans-isomerized (UV-treated for 20 min). The cinnamate molecule would be in parity with one of these configurations and photocrosslinking of cinnamate molecules in the thin film is reinforced according to the irradiation time (0–20 min).

Table 1. Statistical data on the morphology of the photosensitive thin films with UV irradiation for 0, 10, 20, 30 and 60 min

UV irradiation time (min)	Diameter (nm)	Height (nm)
0	55.5 ± 0.08	1.4 ± 0.08
10	45.5 ± 0.05	1.5 ± 0.08
20	38.9 ± 0.13	2.0 ± 0.28
30	30–100	
60	Disorder	

The character of the adhesion force reflects the intermolecular characteristics of the three thin films and their chemical compositions. Azobenzene and cinnamate side-chains with a smaller angle could display the natural states of the rubbed thin film. Rubbing makes the side-chains lie on the surface of the LPS at a smaller angle. The smaller height value could be shown in the thin film. A smaller adhesion force is presented when the tip approaches the surface of the rubbed thin film, as illustrated in Fig. 2. The low pre-tilt angle of the rubbed thin film is 1–3°.[13] The maximum value of the adhesion force is to the right of centre in the distribution plot for the thin film UV-treated for 10 min. The peak area becomes larger in the distribution and the azobenzene side-chains would be partly photoisomerized under this condition: the ends of the side-chains could be partly warped because the N = N bond could be photoinduced to broken and the surface character of the photosensitive thin film could be partly changed. Perhaps some of the cinnamate molecules could be crosslinked under a lower exposure energy. The order formation at a smaller angle will be changed onto the LPS layer.

The compositions of the thin film also start to vary. The frequency distribution of the adhesion force is shown as basically a symmetric triangle in the thin film UV-treated for 20 min. The value of the highest point is 113.8 ± 11.3 nN, which is larger than that of the thin film UV-treated for 10 min. Under this condition, the azobenzene molecules on the LPS layer are fully isomerized, i.e. the free terminal ends make the N = N bond and the photochemical reaction is fully completed. Also, the crosslinking reaction of cinnamate derivatives starts. In the meantime, the ideal configuration of the nematic LC on the LPS layer is maintained. The plane of the photosensitive thin film with the alignment layer is formed and the results agree well with the high pre-tilt angle of the thin film (the pre-tilt angle is 8–10°).[13] When the tip approaches the surface of the thin film, the adhesion force becomes larger. On further analysis, we find that this could be mainly the influence of the varying geometric configuration of both molecules.

The composition of the thin films can still be changed. There are two peaks in the frequency distribution of the adhesion force of the thin film UV-treated for 30 min. The area of distribution is further increased and the distance between the centre of the two peaks is 26.6 nN. This is obviously different from the frequency distribution for the thin film UV-treated for 20 min, and while the tip approaches the surfaces of the thin film both different adhesion forces exist. This demonstrates that the configuration of azobenzene

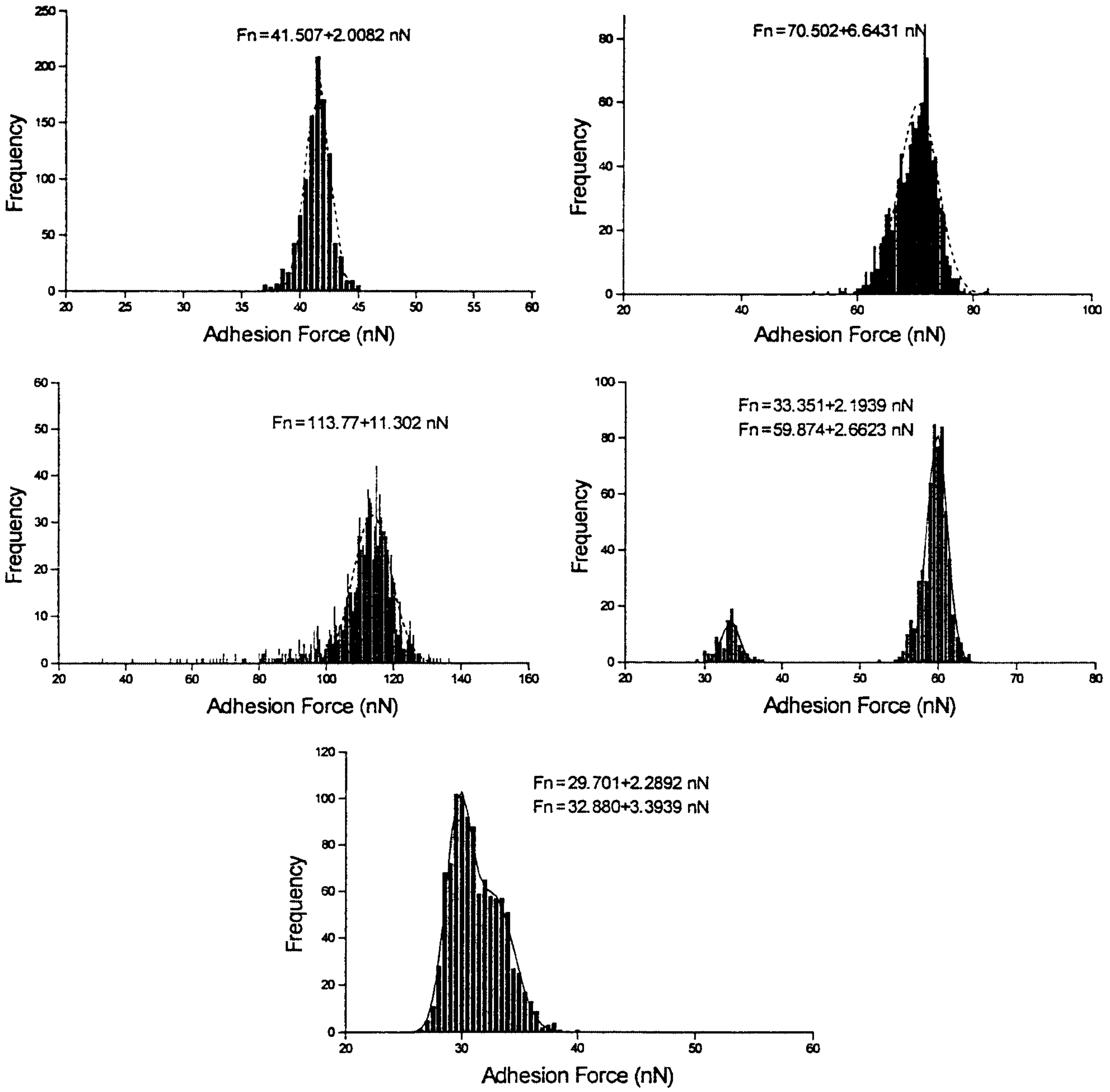

Figure 2. Statistics of adhesion force of the photosensitive thin films with UV irradiation for 0, 10, 20, 30 and 60 min.

side-chains is changed and the surface of the LPS layer is destroyed, consistent with the data of Table 1.

The statistics of the adhesion force with UV treatment for 60 min demonstrate that the highest point of the adhesion force in the frequency distribution map is located to the left of centre of the peak. The values of the adhesion force are 29.8 and 32.9 nN, both of which are smaller than that with UV treatment for 10 min. We know that a component of the photosensitive thin film would be varied completely and it could contain a more complex photochemical reaction. According to the results from UV treatment for 30 and 60 min, we know that photo polymerization or photodesolvation could be produced after UV irradiation and the composition of the thin films would be changed to differing degrees. If a good UV light source is chosen for the photochemical thin films and the UV exposure time is controlled, then a good LC alignment layer onto the (LPS) will occur. The photosensitive thin film after UV exposure for 20 min would be a better material with a preferred orientation that can be used to make LC devices.

Figure 3 shows the maximum values of the adhesion force in five organic thin films. It illustrates that a photochemical process takes place in the photosensitive thin films, with circles and squares showing the possible chemical compositions of the rubbed and photoinduced thin films, respectively. We found two distinct adhesion forces between the tip and the film when the film was exposed for 30 min, i.e. there are two components in the thin film. The top adhesion force is presented after UV exposure for 20 min. The alignment layer with ideal height was maintained. These results agree well with those in Fig. 2.

CONCLUSION

The morphological information and statistical results of adhesion force in photochemical thin films with UV

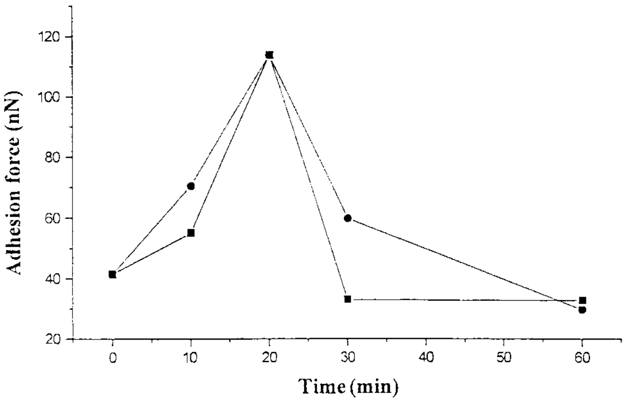

Figure 3. Maximum value of adhesion force of the photosensitive thin films with UV irradiation for 0, 10, 20, 30 and 60 min.

irradiation agree very well and verify each other. The morphological data of the thin films described the changing process onto the surface of the thin film. The statistical results of the adhesion force further demonstrated the characteristics of the interior of the thin films. The statistical results of the thin films UV-treated for 0–20 min mainly described the influence from the geometric configuration of both molecules in the LPS layer, whereas the statistical results of the thin films UV-treated for 30 and 60 min demonstrated the changing in composition of the thin films. The results suggest that under UV irradiation the photochemical process could undergo photoisomerization and photodesolvation of azobenzene side-chains and photocrosslinking and photodesolvation of cinnamate side-chains.

These results further prove that AFM combined with the force curve method is a useful analytical tool for observing the *in situ* chemical process. The recognization ability related to the adhesion force method is interesting to study new organic materials. The photo sensitive thin film after UV exposure for 20 min would be a better material with a preferred orientation that can be used to make LC devices.

Acknowledgements

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