

Structural Analysis of Aromatic Polyimide Ultrathin Films with Different Amounts of Fluorine

YUN-JI KANG, YOURI HA, EUNJU KIM, AND CHANG-SIK HA*

Department of Polymer Science and Engineering, Pusan National University,
Busan, Korea (*E-mail*: csha@pusan.ac.kr)

The monolayer behavior and structural difference of polyimide Langmuir-Blodgett(LB) films with different fluorine contents are studied. Three types of polyamic acid (PAA) were produced from polymerization of biphenyl dianhydride (BPDA) / 4,4'-Oxydianiline (ODA) (F0), BPDA / 2,2'-Bis(trifluoromethyl)benzidine (TFDB) (F6) and 4,4'-(Hexafluoro isopropylidene)-diphthalic anhydride (6FDA) / TFDB (F12) in N,N-dimethylacetamide (DMAc). The three type of polyamic acid alkyl salts (PAAS) using *O,O',O''*-trihexadecanoyl-triethanolamine formed stable monolayers and transferred to solid substrates to prepare the LB film. The PAAS LB films were converted to Polyimide (PI) LB films using thermal treatment. The behaviors of PAAS monolayers at air/water interface depend on the fluorine contents. As there is more fluorine in the main chain, the area per molecules of each monolayer is increased. Due to larger area per molecule, the hydrophobic alkyl chains leaned gradually and the thickness of each monolayer decreased from 2.5 nm to 2.0 nm. All monolayers came from gathering of small domains which consist of particles and showed different collapse behaviors.

Introduction

Polyimide(PI) is one of important heat and chemical resistant polymers. General polyimide shows yellowish color due to charge transfer complex formation and has limited application for optical purposes. Thus there are many researches about colorless polyimide by introducing fluorine or sulfone groups into polymer main chain. On the other hand, formation of the ultrathin film is an important part of nanotechnology. The films prepared using Langmuir-Blodgett (LB) method are usually ultrathin and defect-free with controlled thickness.

In this study, we synthesized and characterized polyimide LB films with different fluorine contents. We discuss the effect of fluorine contents on the formation of monolayer and their structural differences.

Experimental

O,O',O''-Trihexadecanoyl-triethanolamine was synthesized by the reported methods [1]. The polyamic acid was synthesized by adding equimolar quantities of diamine and dianhydride. 4 mmol of ODA was dissolved in DMAc to give a clear and colorless solution. 4 mmol of the BPDA was then added to the solution while stirring vigorously. The solution was stirred at room temperature under a dry nitrogen atmosphere for 4 hours and the PAA solution (10 wt %) was obtained. Other series of PAA as BPDA-TFDB and 6FDA-TFDB were also synthesized by the same process [2, 3].

LB films were deposited by using computer-controlled type 611 Langmuir trough (NIMA tech., UK). The spreading solution for LB deposition was prepared by the method of Kakimoto et al. [4]. The spreading solution which is 2:1 volume mixture of PAA and alkylchain in benzene and DMAc was prepared immediately prior to LB deposition. After spreading the solution on the subphase, the solvent was allowed to evaporate within 20 min from the subphase. The LB films were prepared by the vertical deposition method. The monolayers were transferred on to an appropriate substrate at constant surface pressure. The first layer was deposited at a speed of 2 mm/min and subsequent layer at 5 mm/min. The obtained LB films of polyamic acid alkyl salt (PAAS) were imidized with a thermal treatment to 300 °C.

Results and discussion

The π -A isotherms of F0, F6 and F12 PAAS monolayers are shown in Figure 1. All monolayers show condensed state at around 30 mN/m. The zero – pressure molecular area (A_0), which can be obtained by extrapolating the slope of the condensed state to zero pressure, shows the hypothetical area occupied by one molecule in the condensed state. The A_0 of F0, F6 and F12 monolayers are 150, 164 and 200 mN/m, respectively. The monolayer with more fluorine contents showed larger surface area due to the repulsion between fluorine groups. The Brewster angle microscopy (BAM) images showed the behaviors of each monolayer at air-water interface. All monolayers come from gathering of small domains consisting of particles and the F0 shows bright island as a probe of collapsed monolayer whereas F6 and F12 show bright band as a probe of collapsed monolayer. By repeating compression and relaxation cycles, we can check the monolayer stability. In hysteresis isotherms, All monolayers showed stable behaviors, where F12 showed the best stabilities.

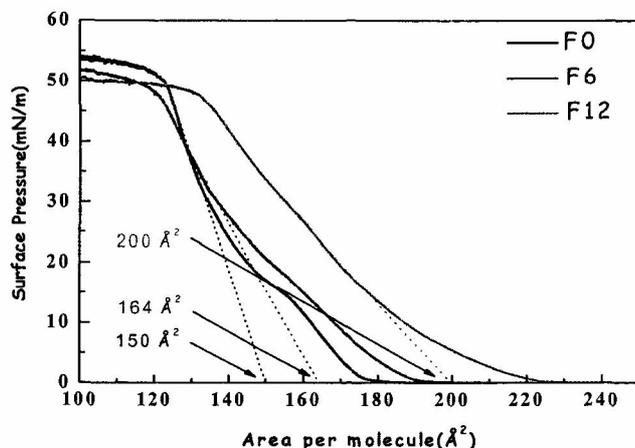


Figure 1. π -A isotherms of three type of PAAS monolayers

Three types of PAAS monolayer deposited onto a quartz with 10, 20, 30 and 40 layers were characterized by UV-Vis spectra. The absorption between 200 and 400 nm may be attributed to $n-\pi^*$ and $\pi-\pi^*$ transition of phenyl and carbonyl conjugation system. A linear relationship was observed between the intensity of the band and the number of monolayers at the maximum absorption wavelengths. It indicates the ordered structure of the multilayer.

After deposited monolayer onto a silicon wafer with 40 layers, films were characterized by XRD. All their patterns showed strong 001 peak, indicating that the films have uniform thickness. The d-spacings of three types PAAS LB film were 5.0, 4.3, 3.9 nm, respectively. They are corresponding to the length of two hydrocarbon chains. It suggests that the three PAAS LB films have Y-type structures. The monolayer with more fluorine contents had smaller d-spacing. Due to fluorine atoms the monolayer has larger area, the long alkyl chains incline, and the LB films show smaller d-spacing. In X-ray reflectivity, the number of fringe formed depends on the film thickness as well as the quality of the sample. For the case of F6 and F12 PAAS LB films, they showed less fringe number and no clear fringe. Due to rigidity and hydrophobicity of fluorine containing polymers, the F6 and F12 PAAS LB films have rougher surfaces and show less clear fringes. After thermal treatment, PAAS LB films were converted to PI LB film. The imidization can be confirmed by IR peaks' changes. After thermal treatment, C-H stretch peaks and ester group peak were disappeared in all cases. It means that long alkyl amine chains are burn out by thermal treatment. The carboxylic acid ion group and amide group peaks also disappeared and carbonyl and C-N-C peaks appeared, indicating the formation of imide ring.

The film thicknesses were measured by the ellipsometer. The thickness of one monolayer of F0 PAAS and PI LB films are 2.3 and 0.38 nm, respectively. The thicknesses of one monolayer of F6

PAAS and PI LB film could be 1.9 and 0.4 nm. The thickness of one monolayer of F12 PAAS and PI LB film is 2.1 and 0.45 nm, respectively. The thickness of the monolayer of F0, F6 and F12 PI LB films were almost same as 0.4 nm and, which is in good agreement with that reported previously [5].

AFM images of three PI LB films deposited on silicon wafer showed similar roughness but the film with more fluorine contents showed little higher roughness. All films showed small domains which have a diameter in range from 20 nm to 50 nm.

Conclusions

Three LB films of aromatic polyimide (BPDA-ODA PI, BPDA-TFDBV PI and 6FDA-TFDB PI) were prepared by precursor method using multi alkyl chains. The samples contained different fluorine contents and showed different properties. The monolayer with more fluorine contents had larger area per molecules. Three PAAS LB films had y-type structures and showed the controlled film deposition. They converted PI LB films was prepared successfully by thermal step treatment and the PI LB films had 0.4 nm thickness of one layer. And these results show that the formation of ultrathin PI films with multi chain was successful and this method using the multi chain can be applied for the nanodevice as insulting layer with ultra thin thickness.

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