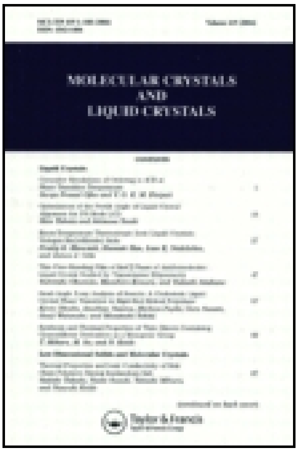

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THE PREPARATION AND TRANSFER CHARACTERISTICS OF POLYIMIDE LANGMUIR-BLODGETT FILM FOR LIQUID CRYSTAL ALIGNMENT

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Abstract The monolayer stability of polyamic acid salts (PAAS) increases as the chain length of salts increases and the hysteresis of the π-A isotherms is found when compressed and expanded. The transferabilities of the monolayers were sharply influenced by the stability at the interface, but not affected by the dipping conditions. In a well-balanced condition, the Langmuir film is transferred as a Y-type on various substrates. The thickness of PAAS was found to be 16.7 Å. After imidization, it was reduced to 5.6 Å per layer, but some ordered structures sustained.

INTRODUCTION

In spite of the good advantages of the Langmuir-Blodgett (LB) method, the inherent thermal instability and fragility of the layered assemblies restricted the applicability of the LB films. The use of polymers also has the limitation from the melting range of the side-chain segments (long alkyl chains) of the polymers[1]. However, polyimides do not have any pendent long alkyl chain, and can eliminate the instability from the side chains.

In this paper, we report the conditions for producing stable and homogeneous PAAS LB films.

EXPERIMENTAL

In order to form the monolayers of polyamic acid (PAA), which is soluble, alkylamines are added to form polyamic acid salts (PAAS). Two kinds of polyamic acids were primarily used, one is PMDA-3,3'-ODA, and the other is SE-150 (Nissan Co.). Three kinds of alkylamines, N,N-dimethyl tridecylamine (DMC 13) from Fluka Chemicals, N,N-dimethyl hexadecylamine (DMC 16), and N,N-dimethyl octadecylamine (DMC 18) from Tokyo Kasei Kogyo Co. were tested. PAA was prepared as a solution of 2 mmol/L, diluted with a mixed solvent of benzene and N,N-dimethyl formamide for PMDA-3,3'-ODA and N,Ndimethylacetamide for SE-150. The PAA solution was adjusted with alkyamine to produce 1 mmol/L solution of PAAS.

The prepared films were examined by FT-IR (Bomem FT-IR), ellipsometrer (Rudolph research/Auto E (II), $\lambda = 638$ nm), α-step (Tencor, α-step 200), and X-ray diffraction (Thin film X-ray diffracter, Rigaku, a Cu Kα X-ray source, $\lambda = 1.54$ Å)

RESULTS

π-A isotherms of PAAS

For the PAAS of SE-150, three different situations were selected (Figure 1). When PAA is mixed with DMC 16 in 1:2 (stoichiometric ratio) (solid line), its collapse pressure is about 40 mN/m, and its limiting area from tangent line is 164 Å^2/repeat unit. The excess amounts of DMC (1:4) (long dashed line) result in no improvement in the stability of the monolayer, but rather adverse effects since no changes in collapse pressure are observed, but the limiting area increases to 175 Å^2/repeat unit with a little gentle slope. In the case of using DMC 18, however, the increase of the collapse pressure up to 51 mN/m, but no limiting area changes occur. So, using DMC 18 in 1:2 ratio is the optimum condition in the available choices.

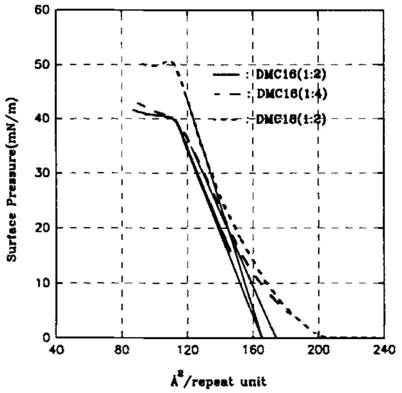

FIGURE 1 π-A isotherms of PAAS(SE-150)

Figure 2 represents the area changes of monolayers of SE-150 with DMC 18 for various setting surface pressures. The larger the surface pressure is, the more rapid change of area occurs. It is of course since the two causes for the area change (the dissolution into subphase and the rearrangement of molecules) are all more intensified by increasing the surface pressure. And, the smoother line of area change is obtained as the surface pressure increases; at lower surface pressure such as 10 or 15 mN/m, the discontinuous and abrupt changes of area are frequent. So, at lower surface pressure, the interface may not be covered uniformly, but there are coarse spots between boundaries of these patches.

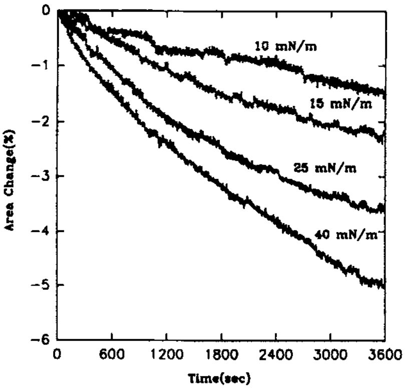

FIGURE 2 Area changes of PAAS (SE-150) with DMC 18 for different surface pressure

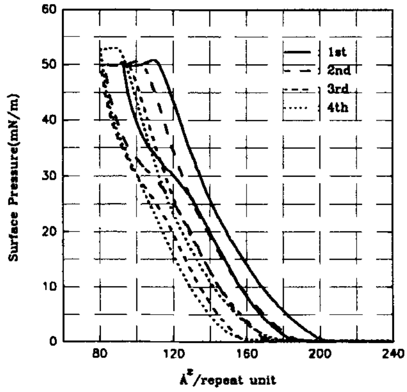

FIGURE 3 The cyclic operation in π-A isotherms of PAAS of SE-150 (1-3 : succesive operation, 4 : after overnight)

Figure 3 displays the cyclic operation in π-A isotherm measurements. From the 1st to the 3rd trial, the experiments were carried out consecutively with no pause time, but after the 3rd trial there was overnight leaving before starting the 4th trial. Up to the 3rd trial, there was hysteresis upon compression and release of the monolayer. The compression curve nearly retraces the expansion curve of the former trial.. These results indicate that the kinetic control of molecular relaxation is dominant compared to the equilibrium process and that the molecules strongly aggregate and only slowly spread, once they have compressed[3]. After the overnight interval, the 4th trial curve did not retraces the 3rd trial curve, so some release of aggregated molecules happened, but the curve did not restore to the original shape (1st trial).

Transfer of PAAS monolayer to multilayers

As shown earlier, the longer the alkylchain up to 18, the more stable monolayer is formed in the case of PMDA-3,3'-ODA. This stability at the air-water interface directly affects the transferability of this L film onto the substrate (Figure 4). The prevailing tendency of transfer is the Z-type like characteristics. So, the first deposition was carried out in the upward direction for all cases. One of the key factors to determine the transferability is the well-balanced amphiphilic ratio of the molecules. So, the improved stability, makes the transferability better. If the first layer was deposited in the upward direction, the transfer was better compared to that of the downward direction. This was valid regardless of the length of the dimethylalkylamine. It may be because in the case of downward-first deposition, the first layer is less uniform (the smaller amount of molecules are transferred), affecting the following layers.

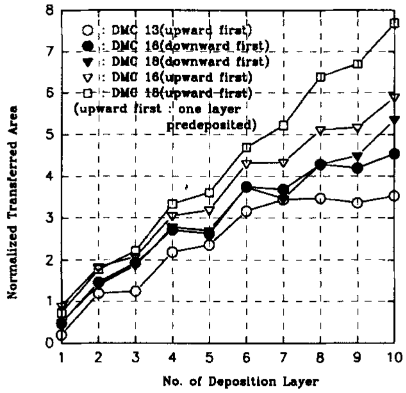

FIGURE 4 The change of transferred area of PAAS(PMDA-3,3'-ODA) according to the length of alkyamine (D.S.=10mm/min)

Another factor affecting the transferability is the water molecules entrapped during deposition[2]. To improve the vaporization of the entrapped water molecules, vacuum drying was applied after first layer deposition (Figure 5). The longer vacuum drying time was up to 60 min, the better the transfer was acquired. So, nearly a Z-type deposition could be ameliorated into a Y-type deposition through vacuum drying process.

When the dipping pressure was increased the transferability of PAAS of SE-150 was also improved, but above 25 mN/m, it was of no effect. The very high surface pressure results in the instability of the transferred film, so 25 mN/m was chosen for the following experiments. The dipping speed for the transfer of the of PAAS of SE-150 was examined, but there is no tendency up to 30 mm/min.. And, various substrates (Si-wafer, ITO-glass, slide glass and Al-foil) were tested, and on the whole, PAAS of SE-150 was well transferred as a Y-type regardless of the substrates, contrary to other experiments of nearly a Z-type deposition using DMC 16[4]. It was well transferred onto a Si-wafer up to 100 layers with no transition from a Y-type to a Z-type. This improvement might be inherited from the fact that DMC 18, instead of DMC 16, is more effective in adjusting the amphiphilic balance, as well as the characteristics of the given polyamic acid. In addition, the width of the substrate was also tested up to 45 mm, and this widening of substrates also did not affect the transferability. In such a wide substrate of 45 mm, the transferability was not affected by the increase of the dipping speed, either.

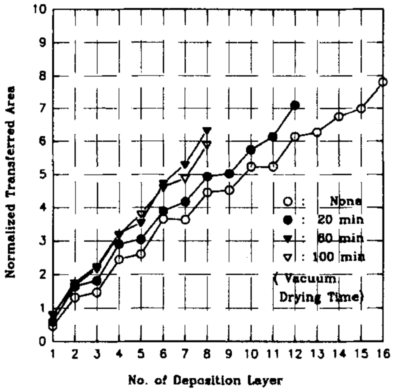

FIGURE 5 Vacuum drying effect on the transferred area of PAAS (PMDA-3,3'-ODA) of DMC 16

Characteristics of LB films

The transferred PAAS film of SE-150 was converted to the PI film through 1 hour heating at 300 °C, confirmed by the appearance at 1720 cm^{-1} due to the imide CO stretching mode and disappearance at 2920 and 2850 cm^{-1} due to CH stretching mode in the IR spectrum.

The total thickness of the LB films were measured using ellipsometry, and good linearity between no. of layers and total thickness confirms the well transferred films as a Y-type, and the thickness of one layer of PASS in average is about 16.7 Å In the case of the PI films, the thickness of 100 layers is about 560 Å in average, and this is consistent with the value from the direct measurement by α-step. So, one layer thickness of the PI LB film is about 5.6 Å.

The rough estimation of tilting angle of the alkylchains, following the method of Kakimoto et al.[5], with the equation $\theta_{cal} = \sin^{-1}(16.7/22.5)$ is about 48 °.

The XRD measurement shows only first-order peak(Figure 6). But, this is not so bad, since no peak was observed for the PAAS LB film using DMC 16 by other report, and only they could obtain the peaks using tertiary amines to give the large volume of alkylamine, so to get more packed structures[6]. The lattice spacing (two layers) calculated from the Bragg's equation well coincides with the result from the ellipsometry measurement (one layer = 16.7 Å).

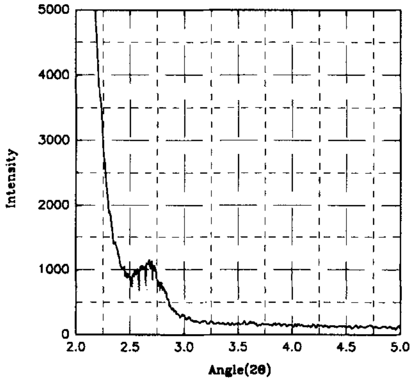

FIGURE 6 The XRD measurement of PAAS LB films (SE-150) of DMC 18

CONCLUSION

The monolayer of PAAS of SE-150 was most stable when the DMC 18 was added as a stoichiometric ratio, and showed hysteresis.

The PAAS of PMDA-3,3'-ODA was transferred with a Z-type characteristic. But, the transfer could be improved by lengthening the alkychain length of alkylamine or applying vacuum drying. At low surface pressure, the PAAS of SE-150 was transferred better as the surface pressure increased, but above 25 mN/m, there was no effect. It was well transferred as a Y-type onto various substrates, and the transfer was not significantly affected by the dipping speed up to 30 mm/min and the width of the substrate up to 45 mm. One layer thickness of the PAAS of SE-150 was about 16.7 Å, and some ordered structure was found.

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