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Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/qmcl19

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Version of record first published: 04 Oct 2006

To cite this article: Young-Mo Koo, Mu-Hyun Kim, Myongsoo Lee & Jong-Duk Kim (1997): Liquid Crystal Alignment Film with Mixture of Polyimide and Side Chain LC by Langmuir-Blodgett Technique, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 304:1, 247-252

To link to this article: http://dx.doi.org/10.1080/10587259708046967

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LIQUID CRYSTAL ALIGNMENT FILM WITH MIXTURE OF POLYIMIDE AND SIDE CHAIN LC BY LANGMUIR-BLODGETT TECHNIQUE

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Abstract The mixed films of poly(amic acid) and a side-chain liquid crystal, 11-[(4-cyano-4'-biphenyl) oxy] undecanyl vinyl ether(CN-11-M) were investigated as a LC alignment film to control the pretilt angle of a nematic LC. The mixed films were fabricated by the Langmuir-Blodgett technique. A stable monolayer of poly (amic acid) alkylamine salt(PAAS) and CN-11-M was formed at the air-water interface. A Y-type film on ITO glass was established at 25 mN/m and room temperature and was confirmed by FTIR spectroscopy. The number of layer was 4, and the ratio of PAAS and CN-11-M was varied. Surface tensions of these films were observed by measuring the contact angle of test liquid. Antiparallel cells were made to measure the pretilt angle of LC by crystal rotation method. Polar force in the mixed film increased with the amount of CN-11-M, but showed a maximum. The pretilt angles of nematic liquid crystal also showed the maximum at a fixed ratio of PAA and CN-11-M.

INTRODUCTION

The uniform alignment can be obtained by several methods, namely, oblique evaporation¹, Langmuir-Blodgett film², unidirectional stretching³, optical alignment⁴, and rubbing⁵. Among the alignment techniques, the rubbing methods with slight modifications are believed to be the most reliable, but there are still many problems in processing. As a non-rubbing process, the optical alignment of the side-chain liquid crystal polymers and the use of Langmuir-Blodgett films of several kinds of poly(amic acid) salts^{6,7} are increasingly interesting.

The Langmuir-Blodgett(LB) method has been of interest as a powerful technique for fabricating ultrathin organic films for many applications to electronic devices⁸.

Among others, the alignment layers of liquid crystals can be fabricated by transferring the proper monolayers. The advantage of LB film is that it does not require rubbing. Recently, liquid crystal alignment layer using poly(amic acid) alkylamine salt(PAAS) has been reported^{6,7}.

In general, pretilt angles obtained by rubbing procedures are not sufficiently high, and LB film does not provide enough pretilt angles. In order to get a higher pretilt angle, There are many efforts such as Mosley⁹, Nehring¹⁰, and Kobayashi¹¹ et al.

In this paper, we report the method for having high pretilt angle of PAAS LB films. The films were mixed with CN-11-M, a liquid crystal of having a polymerizable vinyl group.

EXPERIMENTAL

The monolayers of poly(amic acid) salt (PAAS) were formed by adding alkylamine to poly(amic acid). PAA used is SE-150 (Nissan Co.), and alkylamine is N,N-dimethyl octadecylamine (Tokyo Kasei Kogyo Co.). For mixed film, 11-[(4-cyano-4'-biphenyl) oxy] undecanyl vinyl ether (CN-11-M) were also added to PAAS. This chemical was synthesized as reported elsewhere¹². Figure 1 shows the synthetic procedure of CN-11-M. PAAS and CN-11-M were prepared as a solution of 1 mmol/L, diluted with a DMAc. Number of all layers is 4 at 25 mN/m surface pressure. All experiments were carried out at room temperature with KSV 3000 and constant perimeter type trough.

The prepared films were examined by FT-IR (Bomem FT-IR), ellipsometrer, and contact angle. As testing liquids of a known surface tension, Water/Ethanol mixtures¹³

FIGURE 1 Synthesis of 11-[(4-cyano-4'-biphenyl) oxy] undecanyl vinyl ether

are used to measure the contact angles of LB films at specified temperatures using goniometer-microscope. A polar and dispersion components of surface tensions are determined from contact angles 14,15. Two opposite deposited substrate was anti-parallely assembled. Nematic liquid crystal E7 (Merck Co.) was used. Crystal rotation method was used to measure the pretilt angle of liquid crystal.

RESULTS

π -A isotherm and deposition of CN-11-M and PAAS

Figure 2 shows the π -A isotherms of CN-11-M and PAAS. The isotherms were obtained by moving the barrier at 2 Å² min⁻¹molecule⁻¹ at the air-water interface. In this figure, CN-11-M and PAAS form a reproducible monolayer. The limiting area of CN-11-M was about 17 Å² molecule⁻¹ at room temperature. The collapse pressure was above 40 mN/m. PAAS was well deposited on ITO glass, but pure CN-11-M was not deposited on several substrates such as ITO-polyimide coated, Si wafer, glass, and silanized glass. Probably it is because interaction of CN-11-M molecules is stronger than that of CN-11-M with substrates. However, mixed monolayer of PAAS and CN-11-M was well deposited on ITO glass.

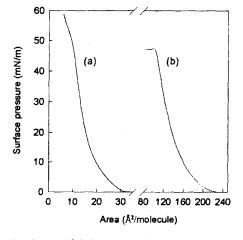


FIGURE 2 π-A isotherm of CN-11-M and PAAS at room temperature (a) CN-11-M, (b) PAAS

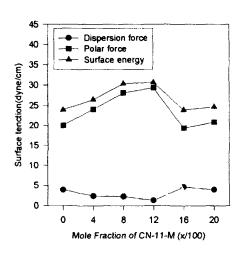


FIGURE 3 The surface tension of mixed LB film with the amount of CN-11-M

Surface tension of mixed LB films

Figure 3 shows the surface tension of deposited films as the mole fraction of CN-11-M to the PAAS. The polar force is higher than the dispersion force in all range. In this figure, polar force increases with the amount of CN-11-M, but shows the maximum at the mole fraction in 8 or 12.

For mixed monolayer in the various mole fraction at 25 mN/m, the transfer ratio was good until mole fraction of CN-11-M in 12, but above this mole fraction transfer ratio decreased abruptly. Above some concentration of CN-11-M, it may be aggregated each other. From these results, above mole fraction of CN-11-M in 12 the transfer of CN-11-M was not good.

Microscope texture

Figure 4 shows the alignment states of nematic cell made by LB films by polarizing microscope. In figure 4(a), liquid crystal was not aligned as good as rubbed cell. However, the alignment state was improved with an addition of CN-11-M molecule in figure 4(b). CN-11-M molecule added to the PAAS alignment layer might induce the homogeneous alignment of nematic liquid crystal, but the film made by using only CN-11-M molecule can not align the liquid crystal.

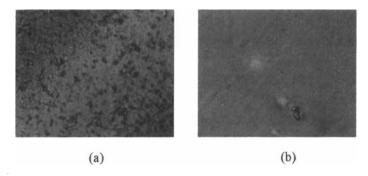


FIGURE 4 The polarizing micrographs(x40) of liquid crystal cell

- (a) PAAS without CN-11-M
- (b) The mole ratio of PAAS and CN-11-M is 100:8 (See Color Plate X).

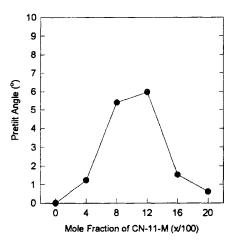


FIGURE 5 The pretilt angles of liquid crystal cell with the amount of CN-11-M

Pretilt angle with mole fraction of CN-11-M

Figure 5 shows the pretilt angles with mole fraction of CN-11-M. Pretilt angles were measured by crystal rotation method in the antiparallely aligned liquid crystal cell. Pretilt angle increases with the amount of CN-11-M, but shows the maximum at the mole fraction in 8 or 12. This behavior of pretilt angle follows exactly the behavior of the

surface tension along the amount of CN-11-M. As results, CN-11-M molecule in PAAS alignment layer increases the pretilt angle of nematic liquid crystal.

CONCLUSION

CN-11-M and PAAS form reproducible monolayer. CN-11-M by itself was not deposited on several substrates, because interaction of CN-11-M molecules may be stronger than that of CN-11-M with substrates. However, mixed monolayer of PAAS and CN-11-M was well transferred on ITO glass. Polar force increases with the amount of CN-11-M, but shows the maximum at the mole fraction in 8 or 12. The behavior of pretilt angle of nematic liquid follows the same trends of surface tension. Also, CN-11-M molecule improved the alignment of state of nematic liquid crystal cell.

Therefore, it is concluded that side-chain molecules added to the polyimide can be used to control the properties of LC cells.

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