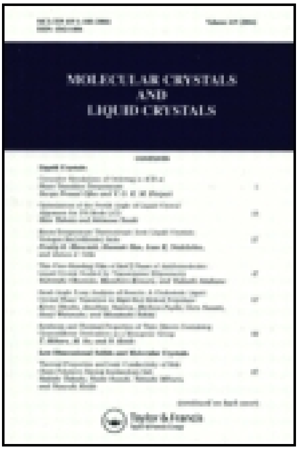

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Surface Modification of Liquid Crystal Alignment Layer by Photochemical Reaction

Fumiaki Yamada [a] , Akiko Nishikai [a] & Yoichi Taira [a]

[a] Tokyo Research Laboratory, IBM Research, 1623-14, Shimotsuruma, Yamato-shi, Kanagawa-ken, 242-8502, Japan

To cite this article: Fumiaki Yamada, Akiko Nishikai & Yoichi Taira (1999): Surface Modification of Liquid Crystal Alignment Layer by Photochemical Reaction, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 329:1, 357-364

To link to this article: http://dx.doi.org/10.1080/10587259908025957

Mol. Cryst. Liq. Cryst., 1999, Vol. 329, pp. 357-364
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Surface Modification of Liquid Crystal Alignment Layer by Photochemical Reaction

FUMIAKI YAMADA, AKIKO NISHIKAI and YOICHI TAIRA

Tokyo Research Laboratory, IBM Research, 1623–14, Shimotsuruma, Yamato-shi, Kanagawa-ken 242–8502, Japan

Photochemical attachment of functional group of Liquid Crystal process in the presence of chemical vapor are discussed.

Keywords: photochemical reaction; photo alignment; chemical contamination

Introduction

Pretilt angle is controlled by the molecular design of polyimide, and could be modified by photo-processes, such as unpolarized ultra violet (UV) light exposure[1][2] for multi-domain TN, or oblique polarized UV exposure[3] during non rubbing photo-alignment processes.

We found a new type of patternable surface chemical property modification scheme by photochemical attachment of functional group[4][5]. Unpolarized UV light (253.7nm) is exposed on to the surface of polyimide while the source of functional group was supplied as gas phase material. This scheme can be applied to change a pretilt angle.

We also found the possibility that this reaction mechanism may cause a chemical contamination during LCD photo process.

Experiments

Polyimide films were exposed to unpolarized UV light (253.7nm) in the presence of N_2, air, water vapor, and benzyl alcohol vapor in a vacuum chamber as shown in figure 1.

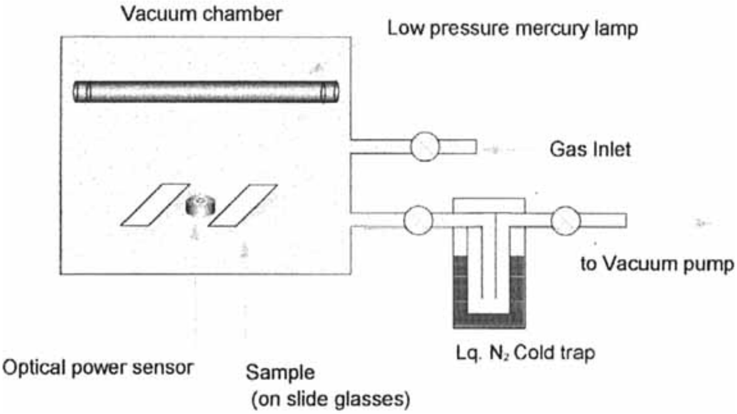

FIGURE 1. Vacuum / Gas Chamber for UV Exposure

The pretilt angle of the liquid crystal cell, the reduction / increase in the mass of the polyimide film, and the absorption spectrum were measured. Polyimide film was also exposed to UV light in the presence of vapor from poly-vinyl-chloride sheet and the reduction / increase in the mass of the

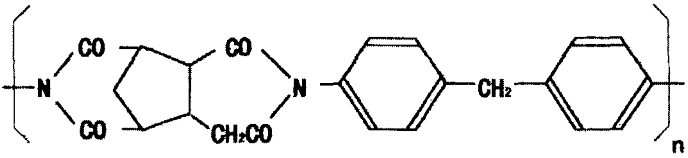

FIGURE 2, Structure of Polyimide Used in This Study
(AL1254 and AL1054 by JSR)

polyimide film was measured. We chose a commercially available soluble polyimide (JSR AL 1254 and AL 1054 as shown in figure 2.) for this study. AL1254 and AL1054 have different concentrations to form different film thickness but consist of essentially the same chemical components.

The polyimide solution is spin-coated on a substrate and prebaked on a hot plate for 10 minutes at 85 C, and then cured for 65 minutes in a 180 C oven. An AL 1054 film with an approximate thickness of 470 nm was used for mass change and UV absorption measurement, and an AL 1254 film with an approximate thickness of 46 nm was used for UV absorption and pretilt angle measurement. A low-pressure mercury lamp was used as an unpolarlized UV light source of mostly 253.7 nm line spectrum. Sample films were exposed to UV in the vacuum chamber. Air was introduced to the chamber through a molecular sieve column, to reduce the influence of moisture. Liquid samples were degassed and introduced to the chamber with their vapor pressure at room temperature. To study the polyimide alignment property of liquid-crystal pretilt angles, ITO-glass substrate was coated with polyimide and exposed to UV light in the chamber. Liquid-crystal cells were then assembled after rubbing, and filled with Merck K-15 liquid crystal for the pretilt angle measurement.

Results and discussion

Figure 3 shows the pretilt angle measurement results. The pretilt angle was increased when the polyimide alignment film surface was exposed to UV light in the presence of benzyl alcohol vapor. On the other hand, the pre-tilt angle was not changed or slightly decreased when the polyimide film was exposed to UV light in the presence of N_2, air, or water vapor.

The weight of the film was increased by UV exposure in the presence of benzyl alcohol vapor, as shown in figure 4. On the other hand, the weight was not increased by UV exposure in the presence of N_2 or air. The weight was not increased in the presence of benzyl alcohol vapor without UV exposure. The

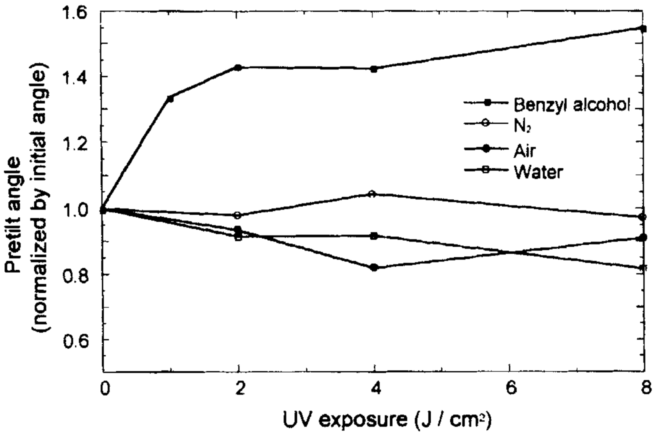

FIGURE 3, Pretilt angle before and after exposure of polyimide (AL 1254) to UV light in the presence of benzyl alcohol, N_2, air, and water

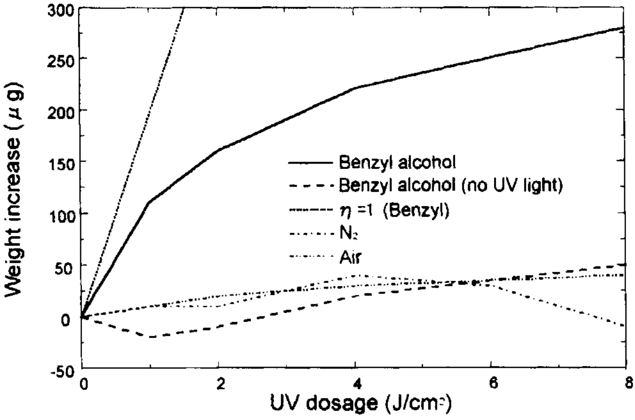

FIGURE 4, Weight increase of UV exposed polyimide (AL 1054) films in the presence of benzyl alcohol, N_2, and air (Broken line : sample was exposed to benzyl alcohol vapor with no UV light for a comparable period of time) line with a note of " $\eta = 1$ " in figure 4 indicates the expected weight increase if the quantum efficiency equals to one when the sample was exposed to UV in the presence of benzyl alcohol vapor.

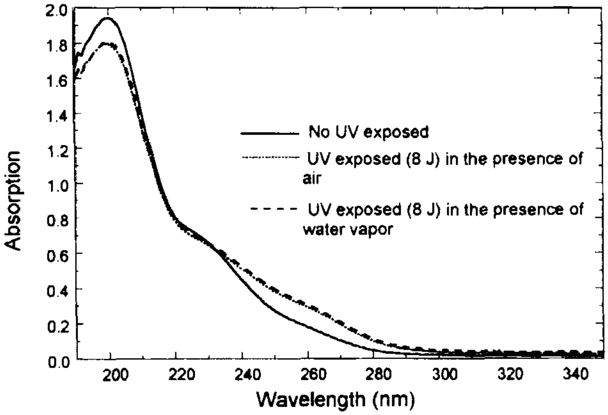

FIGURE 5, Absorption spectra of polyimide (AL 1254) before and after UV exposure in the presence of benzyl alcohol

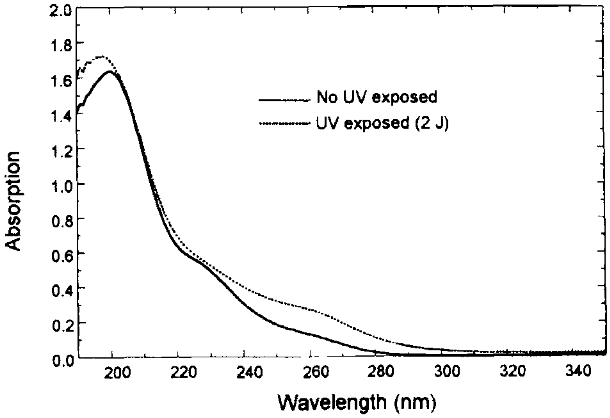

FIGURE 6, Absorption spectra of polyimide (AL 1254) before and after UV exposure in the presence of dry air and water vapor

These results indicate that the weight increase is due to an attachment of phenyl group to the polyimide film by a photochemical reaction between benzyl alcohol and polyimide. The pretilt angle of the assembled LC cell was increased as a result of the attachment of phenyl group, most likely due to a steric effect.

As shown in figure 5, UV absorption at around 200 nm, which most likely corresponds to a π - π * transition of a phenyl group, was increased when the polyimide was exposed to UV in the presence of benzyl alcohol, but was decreased when the polyimide film was exposed to UV light in the presence of air and water vapor as shown in figure 6. These results also indicate that the phenyl ring was attached to the polyimide.

We think that the reaction starts by π - π * electronic excitation of the phenyl group of the polyimide, followed by the scissoring of polyimide chain to form radicals at the surface of the polyimide film. The radical is then react with environmental gas molecules. When the polyimide film is exposed to UV light in the presence of gas phase benzyl alcohol, the phenyl group was attached to the polyimide film surface.

Quantum efficiency of this reaction at the beginning was close to one, as shown in figure 4, which means that one phenyl group attaches per one UV photon exposure. This quantum efficiency was extremely high, considering that the absorption coefficient of the polyimide film at 253.7nm, which was about 1% / 1nm, calculated from the absorption measurement as shown in figure 5. This result indicate the possibility of radical chain reaction. Also, as shown in figure 3 and 4, this reaction was a higher order reaction. This result can be explained that the reaction sites are at the surface of the film which were quickly occupied by the attached phenyl groups.

The weight of the film was increased by UV exposure in the presence of vapor from polyvinyl chloride sheet as shown in figure 7. The weight increases as a function of UV dosage, however the amount of increase in weight was not large as the case of benzyl alcohol vapor, as shown in figure 4.

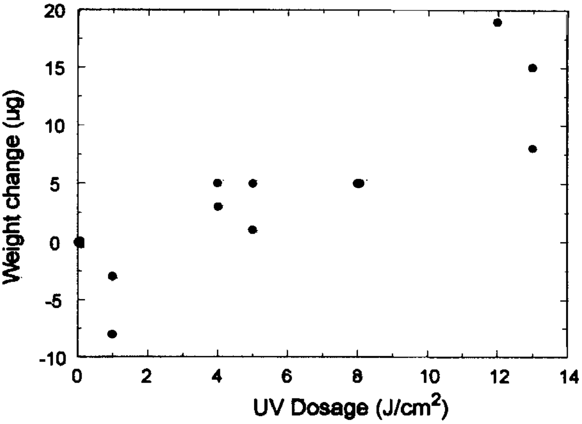

FIGURE 7. Weight increase of UV (253.7nm) exposed polyimide (AL 1254) in the presence of PVC (A-F ; distribution of measured results)

With this new technique, we succeeded in increasing the pretilt angle of the LC cells.

The weight increase of polyimide film by UV exposure in the presence of gas from poly-vinyl-chloride indicate the chemical attachment of gas phase materials during LCD process which include photochemical reaction. Since poly-vinyl-chloride is widely used in laboratories and manufacturing facilities, this reaction may lead chemical contamination.

Conclusion

We found a patternable surface chemical property modification scheme by photochemical attachment of a functional group. The source of the functional group was supplied as a gas phase material. This scheme can be applied to a photo alignment of liquid crystal display to control its pretilt angle.

This experiment also suggest us that we need to take precautions against the possibility of unexpected photochemical surface modification by the presence of contamination source in the air.

Acknowledgment

This work is partly supported by NEDO. The authors would like to express appreciation to NEDO.

References

[1] Y. Saitoh, H. Takano, C.J. Chen, and A. Lien, *SID'96 Digest,* **662** (1996)
[2] F. Yamada, and Y. Taira, *AM-LCD '96 digest,* **253** (1996)
[3] M. Nishikawa, B. Taheri, and J.L. West, *SID'98 Digest,* **131** (1998)
[4] F. Yamada, A. Nishikai, and Y. Taira, *SID'97 Digest,* **715** (1997)
[5] F. Yamada, M.G. Samant, J. Stohr, A. Nishikai, and Y. Taira, *Proceedings Int'l Display Research Conference,* L-13 (1997)