Synthesis and characterization of new liquid crystalline polymer for in-cell retardation film

Lei Wang, Yeong Jin Lim, Hoon Kang, Min Oh Choi, Seung Hee Lee and Myong-Hoon Lee*

Department of Polymer Science and Technology, Chonbuk National University, 664-1 Dukjin, Chonju, Chonbuk 561-756, Korea

Phone: +82-63-270-2337, E-mail: mhlee2@chonbuk.ac.kr

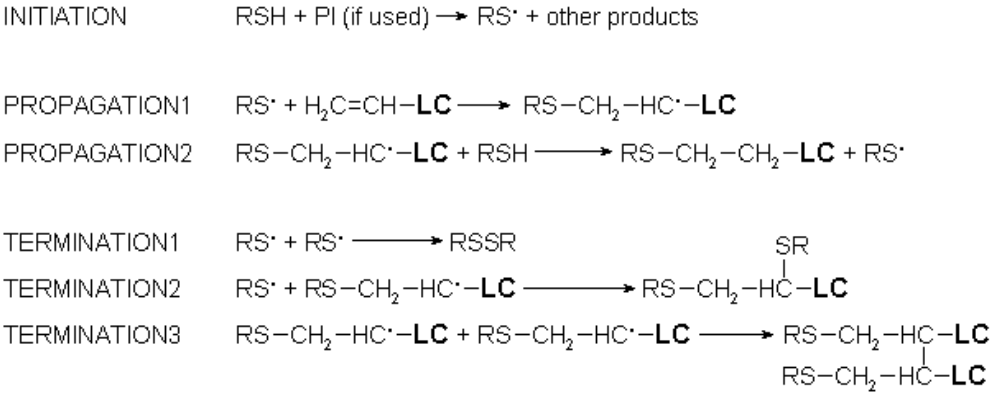
Abstract

A new rod-like liquid crystalline monomer having divinyl terminal groups was synthesized and polymerized by using thiol-ene UV polymerization technique. High quality thin film with good retardation value was prepared on a rubbed alignment layer without the inert gas purging. The retardation value of the resulting film was controlled by experimental conditions such as spin speed, concentration, and spin time. From the retardation value and thickness measurement, Δn was calculated to be 0.169 for the resulting film having thickness of 815.1 nm.

1. Introduction

Retardation film has become a standard component of liquid crystal display (LCD) for high quality imaging related with contrast, coloration, and viewing angle performance. Stretched film was firstly introduced to LCD device as a retardation film about 2 decades ago for improving the coloration and viewing angle characteristics. However, stretched film has several intrinsic drawbacks. It can not be made to roll-to-roll lamination of the stretched film with the polarizer or another stretched film, and the mismatch of optical axes between the liquid crystal (LC) cell and the stretched film prevents optimal compensation. So the next generation of retardation film, LCP (liquid crystal polymer) emerged, as the times require. Nevertheless, thick retardation film unavoidable due to its supporting and adhesive layer is not suitable for the future LCD technology. Recently, Merck and Nisseki have developed an in-cell retardation film by using LCP, in which acrylates or epoxy functional groups are polymerized to form a thin film polymer. However, there still remains a big challenge to explore more appropriate materials for this purpose in the sense of performance and processibility.

In this paper, we report the synthesis of new liquid crystalline monomer (LCM) having divinyl terminal groups and its polymerization method for the preparation of in-cell retardation film based on the famous thiol-ene UV polymerization reaction. This system offers many advantages including: fast curing rates, low oxygen inhibition during the



Scheme 1. Thiol-ene polymerization

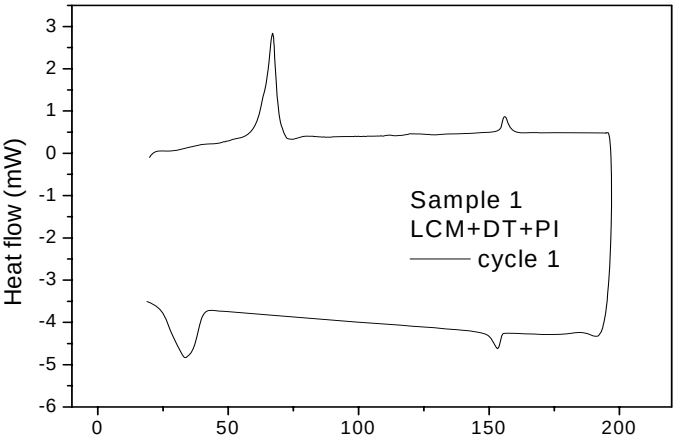


Figure 1. DSC thermogram of polymerization mixture

curing process, low film shrinkage, and flexible film property. Scheme 1 shows the theory of thiol-ene polymerization. In this polymerization, free radical produced by the decomposition of photoinitiator initiate polymerization by abstracting hydrogen radical from sulfide. Then the sulfinyl radical undergoes addition reaction to the olefin group of divinyl monomers. This kind of polymerization has main advantage against the ordinary free-redical polymerization of acrylate type monomers in the sense that the polymerization is less affected by the presence of oxygen so that no nitrogen purging is required during the photo-polymerization, which is useful for high productivity.

We synthesized divinyl LC monomer having two olefinic group at both chain ends. The mesogenic core was employed to impart nematic liquid crystalline properties. In addition to this, various dithiol and polythiol compound were used together to copolymerize the divinyl monomer. The polymerization composition was varied to obtain optimum results for the film coating and preparation process. Additionally, coating conditions were also investigated for optimum results.

2. Experimentals

LCM was synthesized from the esterification reaction of ω-alkenyloxybenzoic acid and methyl-hydroquinone in the presence of *p*-toluene sulfonic acid and organic bases in dry dichloromethane. The LCM was obtained as a white crystal in 90 % yield after the column chromatography and a subsequent recrystallization. In addition to LCM, the mixture of our system is composed by dithiol (DT) and photoinitiator (PI) with xylene as a solvent. Figure 1 shows differential scanning calorimetry (DSC)

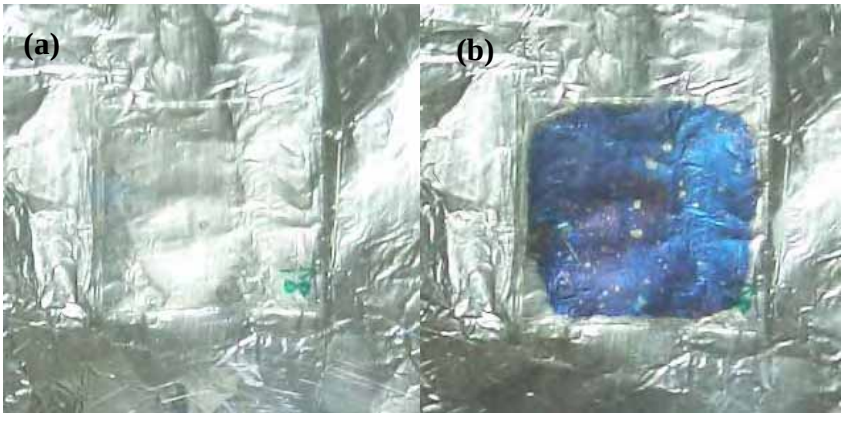


Figure 2. pictures taken for the resulting film with the polarizer on the top (a) in the parallel direction, and (b) 45^{o} to the rubbing direction, respectively.

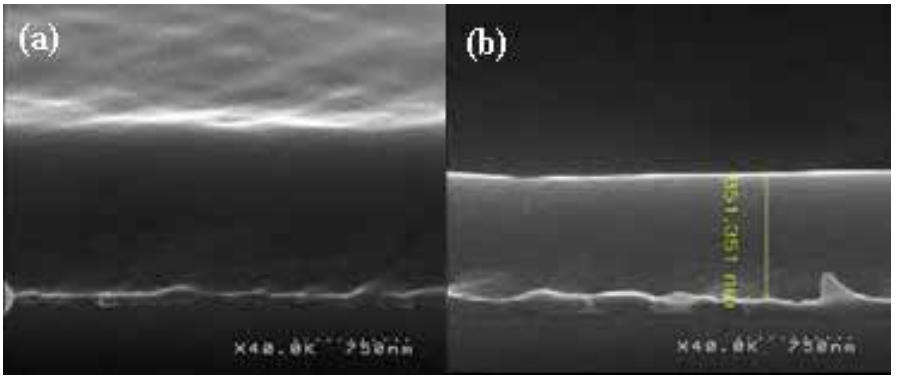


Figure 3. Scanning electron micrographic images of resulting polymer film: (a) top and (b) side view, respectively.

thermogram of polymerization mixture, in which LC phase was observed between T_{CN} = 65 °C, and T_{NI} = 157 °C.

Firstly, rubbed polyimide aligning layer (AL) on a glass substrate was prepared by spin coating the AL solution on a glass substrate, and heating at 80 °C for 5mins, and 220 °C for 1h, respectively, followed by rubbing. The retardation film was made on the substrate by spin coating the formulated solution composed of LCM, DT and PI. UV was exposed from a 1000W high pressure mercury lamp immediately after spin coating for 120s at room temperature. The thin solid polymer film was instantaneously formed after 30 s, and become harder after the irradiation process. Particularly, the irradiation was performed under ambient atmospheric condition, which was not possible in the case of other free radical photo-polymerization systems. This aerobic irradiation condition could make it possible to prepare a large area panel with homogeneous film thickness and property control.

3. Results and Discussion

In Figure 2, were shown the pictures taken for the resulting film with the polarizer on the top (a) in the parallel direction, and (b) 45° to the rubbing direction, respectively. As shown in the figure, coating of the polymerization composition and subsequent photo-irradiation resulted in a homogeneous transparent film, which make sure that the new polymerization technique is worthwhile. However, some of the samples showed inhomogeneous film having many defect on the film. Exploring the best coating composition is still on the progress, and the result of which will be reported in the subsequent report.

Retardation value measured by cross-polarized microscope was averaged to be 138.0 nm, and d (film thickness) measured by scanning electron micrograph (SEM) (Figure 3) to be 815.5 nm. From the equation $R = d\Delta n$, the Δn was calculated to be *0.169*.

4. Conclusion

Compared to other systems employing free-radical photo-polymerization technique, this system utilizes thiol-ene polymerization technique, which allows photo-polymerization under ambient atmospheric condition without using inert gas environment. This processing condition would be more favorable for the large-size panel preparation.

5. Acknowledgements

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6. References

[1] H. T. A. Wilderveek,, M. G. M. Van Der Meer, M. A. G. Jansen, L. Nelissen, H. R. Fischer, J. J. G. S. Van Es, C. W. M. Bastiaansen, J. Lub and D. J. Broer, Liquid Crystal, 30, 93–108(2003).

[2] T. Seki, G. Suzaki, A. Mutou, T. Uesaka, S. Nishimura and H. Mazaki , IDW/AD 1333-1336(2005).

[3] Sang Min Oh, Seung Jai Kim, Myoung-Hoon Lee, Seung Hee Lee, Jeoung-Yeon Hwang, Dae-Shik Seo, Mol. Cryst. Liq. Cryst., 433, 97–104(2005).