LC Aligning Ability of the Liquid Crystal Display using Photopolymer Layers Containing an Acrylate unite Photopolymerized by a Photoinitiator

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Abstract

Photoalignment materials of PGMAcr, poly[3-(acryloyloxy)-2-hydroxypropyl methacrylate] using an acrylate unit photopolymerized by a photo-initiator and PGMA4Ch, poly[3- (4-chalconyloxy)-2-hydroxypropyl methacrylate] using photodimerization by the chalcone group were synthesized. Also, the liquid crystal (LC) alignment capabilities on the photopolymer layers were studied. A good LC alignment with UV exposure on the PGMAcr surface can be obtained. However, LC alignment defects were observed on the PGMA4Ch surface. The LC alignment capability of the PGMAcr surface by the photoinitiator was better than that of the PGMA4Ch surface by the chalcone group which is a photosensitive moiety.

1. Introduction

The physical mechanisms involved in both surface and bulk liquid crystal (LC) alignment are not only of fundamental interest but also find application in electrooptic LC cells. Uniform alignment of the LC layer can be achieved by several methods, such as with rubbed polymer film,[1-4)] Langmuir-Blodgett films,[5)] and oblique evaporation of SiO films.[6)] The most widely used technique for the production of LC cells is the rubbing of polymer-coated glass substrates. This method produces characteristics such as high transparency, uniform alignment, and pretilt angle stability. However, the rubbing method creates several problems, such as the generation of electrostatic charges and the contamination of particles.[7)] Recently, many investigators have proposed photoalignment by methods such as photodimerization [8-12)] and photodissociation methods.[13,14)]

Conventional negative-working photoresists, poly(vinyl cinnamates) (PVCi), have played a prominent and leading role in the science and technology of photopolymers since their invention four decades ago. The photochemistry of cinnamates involves two photoreactions: (2+2) photodimerization and E/Z photoisomerization[15)]. These two photoreactions affect the LC aligning capability, and the LC photoalignment using these two photoreactions will be poor.

In this article, we report on the synthesis of the photoalignment material PGMAcr, poly[3-(acryloyloxy)-2-hydroxypropyl methacrylate], an acrylate unit photopolymerized by a photo-initiator and a PGMA4Ch, poly[3- (4-chalconyloxy) -2-hydroxypropyl methacrylate] using photodimerization by the chalcone group, and nematic liquid crystal (NLC) alignment capabilities with UV exposure on the photopolymer surface were studied.

2. Experimental

Poly(glycidyl mathacrylate) (**1**)

In a 100 mL round-bottom flask were placed glycidyl methacrylate (14.22g,0.1mol) and AIBN(0.15 g) in THF (60 ml), and then the reaction mixture was slowly stirred for 12 h at 60℃. After the reaction, the crude mixtur e was precipitated in ethyl ether. The precipitate was collected and vacuum dried.

Poly[3-(acryloyloxy)-2-hydroxypropyl methacrylate] (**2**)

4.27g of **(1)** was dissolved in tetrahydrofuran (THF), and then 2.16g (0.03mol) of acrylic acid was added to this solution. The reaction was stirred with triphenylphosphine (TPP) as a catalyst for 6h at 60℃. After the reaction, the crude mixture was precipitated

in ethyl ether. The precipitate was collected and vacuum dried. ^{1}H-NMR(500MHz, $CDCl_3$),? ?(ppm): 6.13(s, 1H, -C-C$\underline{H}_2$- of methacrylate), 5.59(s, 1H, -C-C$\underline{H}_2$- of methacrylate), 1.93(s, 3H, CC$\underline{H}_3$), 4.40~4.41 (m, 2H, C$\underline{H}_2$CHCH_2), 4.29~4.40 (m, 2H, CH_2C$\underline{H}$CH_2), 4.29~4.40 (m, 2H, CH_2CHC$\underline{H}_2$), 3.03(s, 1H, O$\underline{H}$), 4.2 (t, 2H, COOCH_2). FT-IR (KBr), ?(cm^{-1}): 3500 (OH stretching), 1713 (C=O of and ester stretching), 1638 (C=CH_2 of acrylate). The chemical structure of (**2**) is represented in Fig. 1.

Poly[3-(4-chalconyloxy)-2-hydroxypropyl methacrylate] **(3)**

(**1**) was dissolved in THF, and then 4-methoxychalcone (7.62g, 0.03mol) was added to this solution. The reaction was stirred with triphenylphosphine (TPP) as a catalyst for 5h at 60℃. After the reaction, the crude mixture was precipitated in ethyl ether. The precipitate was collected and vacuum dried. ^{1}H-NMR(500MHz, DMSO),? ? (ppm): 6.13(s, 1H, C=C$\underline{H}_2$ of methacrylate), 5.59(s, 1H, C=C$\underline{H}_2$ of methacrylate), 1.93(s, 3H, CC$\underline{H}_3$), 4.40~4.41 (m, 2H, C$\underline{H}_2$CHCH_2), 4.29~4.40 (m, 2H, CH_2C$\underline{H}$CH_2), 4.29~4.40 (m, 2H, CH_2CHC$\underline{H}_2$), 3.03(s, 1H, O$\underline{H}$), 4.2 (t, 2H, COOCH_2), 6.3 (m, 1H, Ar-C$\underline{H}$=CH), 7.7 (m, 1H, Ar-CH=C$\underline{H}$), 6.9(m, 2H, Ar-H), 7.5(m, 2H, Ar-H), 7.7 (m, 1H, Ar-CH=C$\underline{H}$). FT-IR (KBr), ? (cm^{-1}): 3500 (OH stretching), 1713 (C=O of and ester stretching), 1599 (C=C of aromatic stretching), 1600 (CH=CH of chalconyl). The chemical structure of (**3**) is represented in Fig. 2.

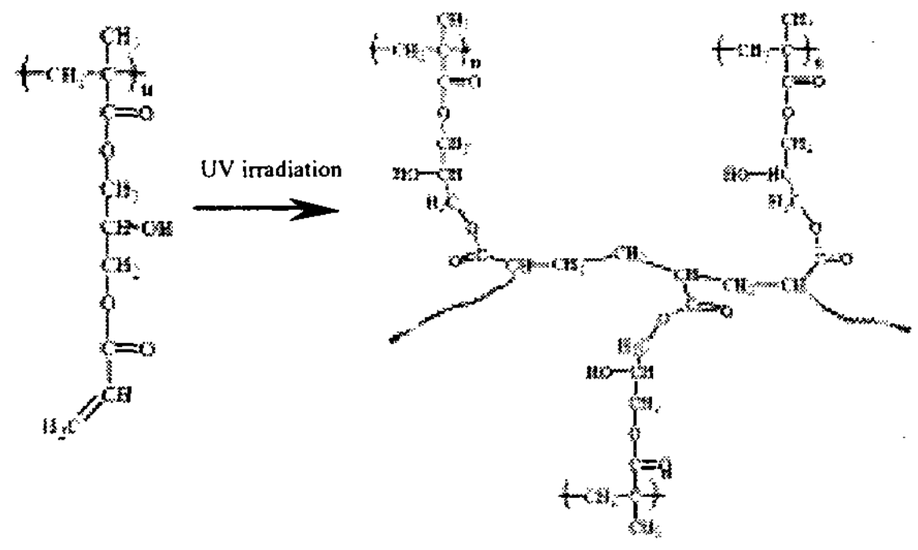


Figure 1 Chemical structure of (2) and photopolymerization reaction of acrylate group by UV irradiation.

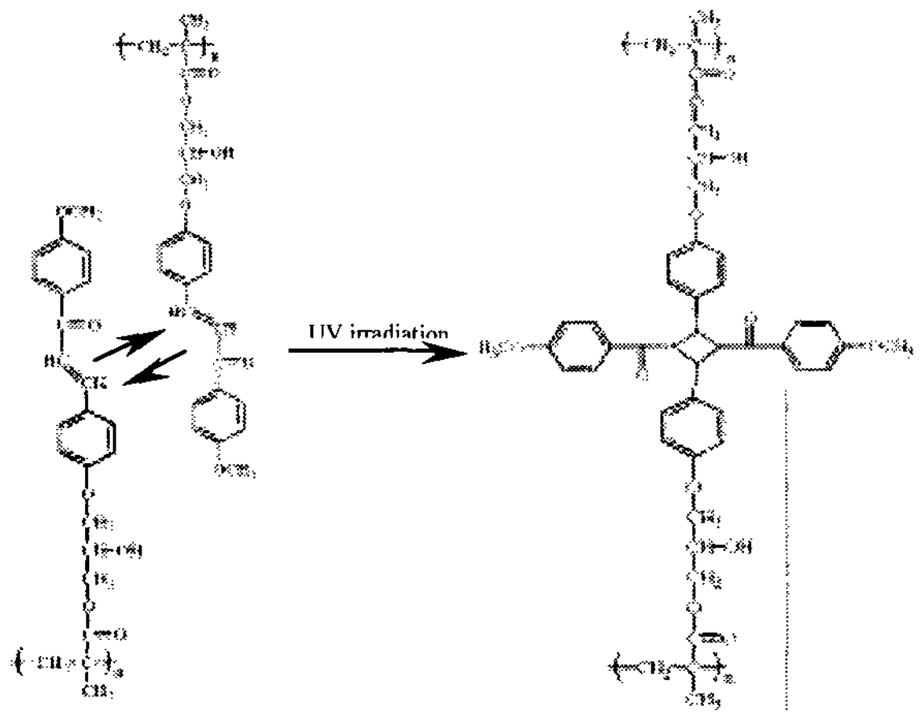


Figure 2 Chemical structure of (3) and [2+2] photodimerization reaction of the 4-chalconyl group by UV irradiation.

The polymers were coated on indium-tin-oxide (ITO) coated glass substrates by spin-coating, and were cured at 100℃ for 30 min. The thickness of the polymer layer was 500Å. The UV exposure system is shown in Fig. 3. The UV source was a 500 W Mercury lamp. UV energy density was 15.5 mW/cm^2. The thickness of the LC layer was 60 ?m. The NLC used was a fluorinated mixture type (Tc=72℃, MJ97359, from Merck Co.). The crystal rotation method was used to measure the pretilt angle (TBA: tilt-bias angle evaluation, from Autronic Co.).

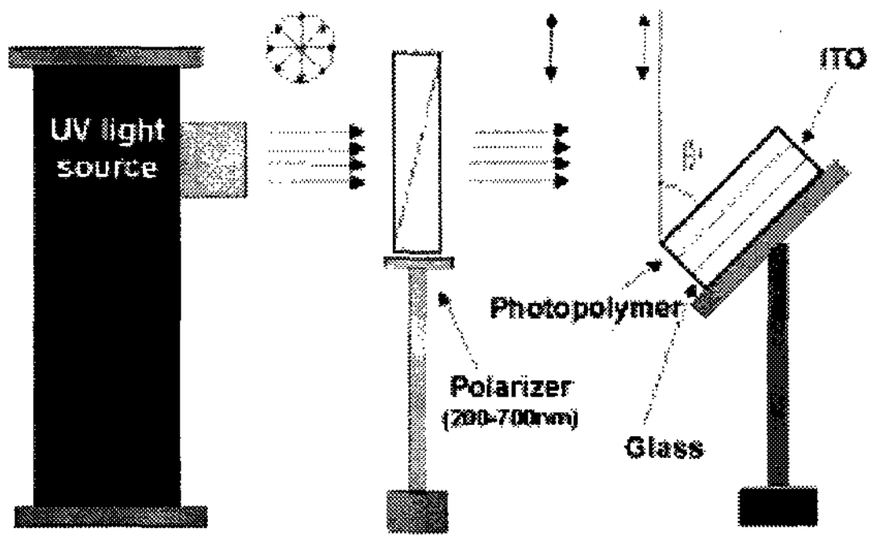


Figure 3 Schematic diagram of the UV exposure system.

3. Results and discussion

Figure 4 shows the spectral absorbance of the UV spectrum for the (**2**) film. This UV spectrum showed the maximum absorption band of (**2**) with the photoinitiator (BK-7, Miwon Chem. Co.) where the acrylate unit by photoinitiator has been absorbed at 340nm. The acrylate unit has no absorption band at conventional UV range. It could be photopolymerized by the photoinitiator.

Figure 5 shows the spectral absorbance of the UV spectrum for the (**3**) film. This UV spectrum confirmed the maximum absorption band of (**3**) where conjugated 4-chalconyl groups had been absorbed at 350nm. This film could be photodimerized due to [2+2] photocycloaddition reaction by UV irradiation without the photoinitiator.

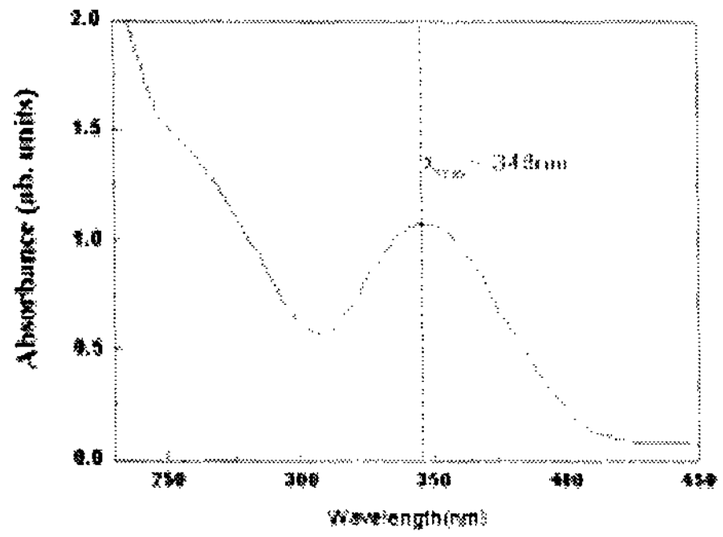


Figure 4 UV absorption spectrum of (2). The maximum absorption band of (2) with photoinitiator is 340nm.

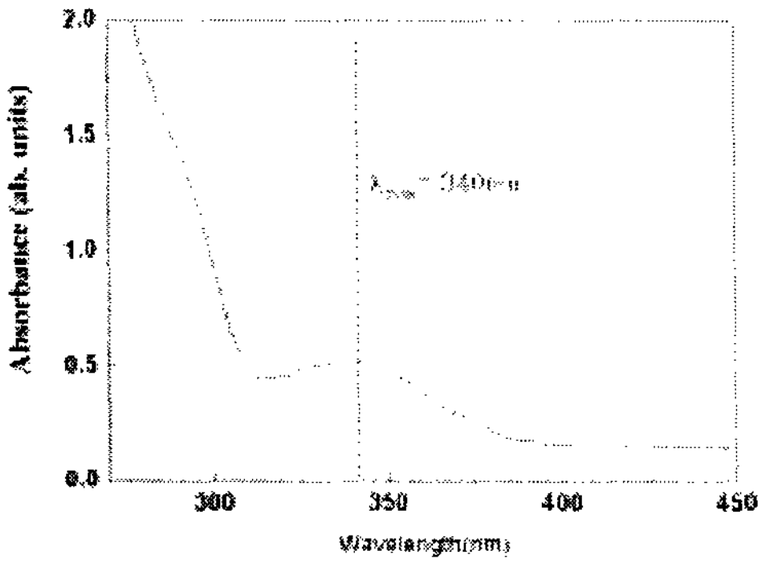
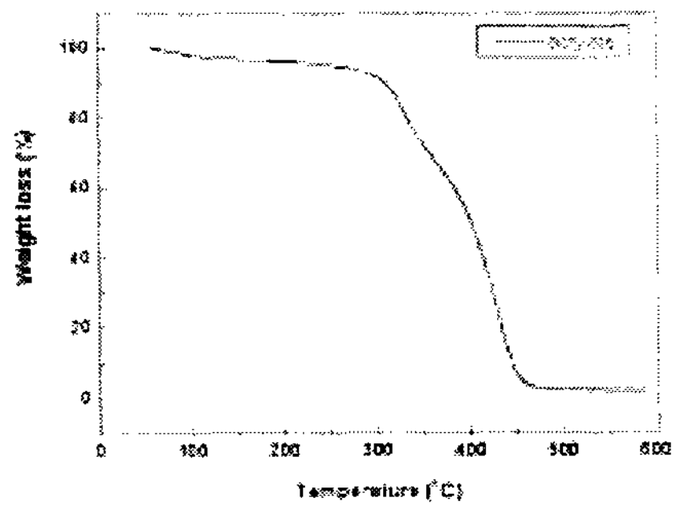
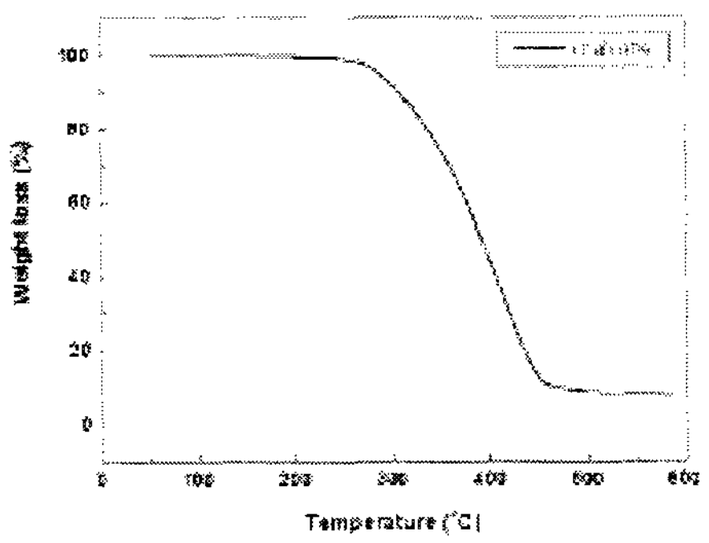


Figure 5 UV absorption spectrum of (3). The maximum absorption band of (3) without photoinitiator is 348nm.

Figure 6 does not exhibit an weight loss below 260°C (**2**) or 300°C (**3**). The TGA thermograms show that these two photoreactive polymers have good thermal stability up to 260 °C and 300 °C, respectively.



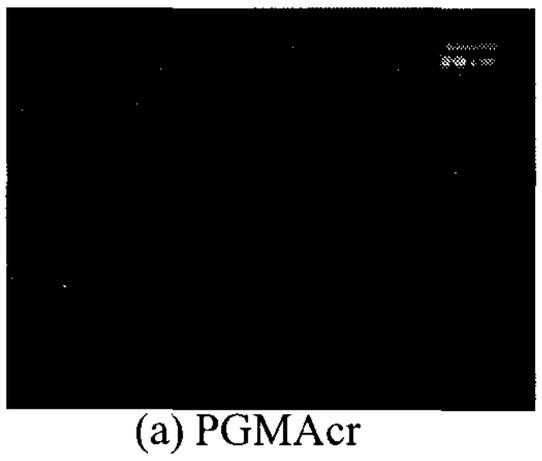
(a) PGMAcr



(b) PGMA4Ch

Figure 6 TGA thermograms of (2) and (3) at the heating rate of 10 ℃/min under a nitrogen atmosphere.

Micrographs of the aligned LC with polarized UV exposure on the PGMAcr surface using an acrylate unit photopolymerized by a photo-initiator and the PGMA4Ch surface using photodimerization by the chalcone group (in crossed Nicols) are shown in Fig.7. It is shown that good LC alignment was observed with UV exposure on the PGMAcr surface as shown in Fig 7(a). However, many discliations were observed via the linearly polarized UV exposure on the PGMA4Ch surface as shown in Fig. 7(b). The LC alignment capability of the PGMAcr surface by the photoinitiator was better than that of the PGMA4Ch surface by the chalcone group that is a photosensitive moiety. Also, the LC pretilt angle below 1° was obtained at the all-incident angle on the PGMAcr surface.



(a) PGMAcr

(b) PGMA4Ch

Figure 7 Micrographs of aligned LC with polarized UV exposure on the photopolymer surface for 3min (in crossed Nicols).

4. Conclusion

In conclusion, the new photoalignment material consisting of a PGMAcr using an acrylate unit photopolymerized by a photo-initiator and a PGMA4Ch using photodimerization by the chalcone group was synthesized. Also, the NLC alignment capabilities on two photopolymer surfaces were studied. Good LC alignment with UV exposure on the PGMAcr surface can be obtained. However, LC alignment defects were observed on the PGMA4Ch surface. The LC alignment capability of the PGMAcr surface by the photoinitiator was better than that of the PGMA4Ch surface by the chalcone group that is a photosensitive moiety.

5. Acknowledgement

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6. References

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