

Effect of Oligomeric Photoinitiator on the Preparation and Electro-optical Properties of Polymer Dispersed Liquid Composite Films

Lee Soon Park, Hae Sang Yoon, Young June Hur* Sang Woo Kim*,

Sung Ho Lee**, Jae Wook Seok***, Young Hwan Kwon****

Department of Polymer Science, Kyungpook National University

1370 Sankyuk-Dong, Buk-gu, Daegu, 702-701, South Korea

*Advanced Display Manufacturing Research Center

**Gumi Institute of Electronics Technology, Gumi, Gyeongsangbuk-do

730-030, Korea

***Department of Materials Science & Engineering, University of Tennessee

****Department of Chemical Engineering, Daegu University, Gyeongbuk

Abstract

Effects of such factors as polymerization temperature and a newly synthesized oligomeric photoinitiator (PEDI380) on the electro-optic characteristics of polymer/LC composite films prepared by the UV-curing method were investigated. The polymer-dispersed liquid crystal cells were made with oligomeric photoinitiator PEDI380 by UV-curing method exhibited both low driving voltage (V_{90}) and high contrast ratio under optimum formulation condition.

1. Objectives and Background

PDLC films, having great potential for electro-optic devices such as large-area display, open-curtain, light valve, etc., are heterogeneous systems composed of dispersed or continuous LC phases in various polymer matrix.¹⁻² Since Ferguson and Doane et al. introduced the practical use of PDLC films, remarkable interest has been focused on both applied and basic researches³⁻⁴ for the development of PDLC devices in order to control electro-optical properties in PDLC films. PDLC films can be prepared by various methods such as thermally induced phase separation (TIPS), solvent-induced phase separation (SIPS), polymerization-induced phase separation (PIPS), and encapsulation. Among these methods, PIPS with the aid of UV-light is one of the most common methods for preparing PDLC films, in which polymerization is induced by a photoinitiator in a mixture of low MW LC, UV-polymerizable oligomers and multifunctional monomers. From an initially homogeneous single

phase, the formation of a heterogeneous composite film composed of LC-rich and polymer-rich phases is induced by increased immiscibility between the LC and matrix-forming material as polymerization proceeds. Since the performance of the PDLC cell is proportional to the volume fraction of LC phases, the LC concentration should be taken to the maximum allowed by the specific matrix. To do this, it is required to optimize processing variables such as the kind of LCs, monomers/functional oligomers, UV-light intensity, polymerization temperature, and photoinitiator concentration. Photoinitiator concentration, for example, needs to be optimized to get a uniformly phase-separated PDLC film. Excess amount of a photoinitiator used in the polymerizing mixture may remain as impurities either in the matrix or in LC droplets due to inefficient initiation, causing long-term instability of the resulting PDLC film.

In the present work, we investigated structural effect of photoinitiators on the electro-optical properties of the resulting PDLC cells.

2. Experimental Results

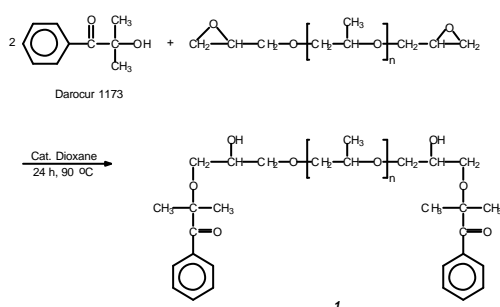
2-1 Materials

BL-002, eutectic LC mixture (BDH Co., $\Delta n = 0.246$, $T_{NI} = 72$ °C, $\Delta e = +15.6$) and 7CB, single LC (Merck Co., $\Delta n = 0.178$, $T_{KN} = 30$ °C, $T_{NI} = 42$ °C, $\Delta e = +11.5$) were used as received. 2-Hydroxy-2-methyl-1-phenylpropan-1-one (Darocur 1173, Merck Co.), and poly(propyleneglycol) diglycidylether (PPGDGE, Aldrich Chem. Co.) (Mw=380 g/mol) were used to

synthesize a new type of α,ω -telechelic oligomeric photoinitiator (**1**). Poly(ethyleneglycol) dimethacrylate (PEGDM) (Mw=400 g/mol) and 1,1,1-trimethylolpropanetriacrylate (TMPTA) from Aldrich Chem. Co. were used as di-functional oligomer and tri-functional monomers, respectively. Methacryloyl chloride, triethylamine, 4-cyano-4'-hydroxybiphenyl, and 10-bromo-1-decanol were purchased from Aldrich Chem. Co. and used as received. Tetrahydrofuran (Aldrich Chem. Co.) was distilled over sodium prior to use. Other solvents and chemicals were reagent grades and used without further purification.

2-2 Synthesis of Oligomeric Photoinitiator(**1**)

Oligomeric photoinitiator (**1**) was synthesized as shown in Scheme 1. 0.5g of Darocur 1173 was added to 10g of dioxane solution in which 0.586g of PPGDGE was dissolved under a nitrogen atmosphere in a dark room. The reaction of photoinitiator Darocur 1173 with the epoxy groups at both ends of PPGDGE was performed with 100 ppm of acid catalyst (H_2SO_4) diluted in dioxane for 24 hrs at 90 °C. After the reaction the resulting solution was neutralized with 0.1N NaOH solution and dioxane was removed by using a rotary evaporator. Salt formed by adding ethyl ether to the resulting product was removed by washing several times with distilled water. The remaining moisture was removed by stirring with anhydrous magnesium sulfate, followed by filtration. α,ω -Telechelic oligomeric photoinitiator (**1**) was purified by using a column chromatography filled with silica gel and a mixture of ethyl acetate/*n*-hexane = 1/5 (v/v) as an eluent.



Scheme 1. α,ω -Telechelic oligomeric photoinitiator

2-3 Synthesis of Polymeric Photoinitiator with Mesogen Moieties

2-3-1 Vinyl Monomer with a Photoinitiating Group(**2**)

The mixture of 2.5 g of methacryloyl chloride, 3.0 g of Darocur1173 and 2.8 g of triethylamine (TEA) in dried 15 mL of THF was reacted in a dark room at 0 °C for 24 h, as seen in Scheme 2. The reaction mixture was filtered in order to remove the precipitated salt, then concentrated by evaporating THF using a rotary evaporator. The final product, **2**, was purified by using a column filled with silica gel and a mixture of ethyl acetate/*n*-hexane = 1/6 (v/v) as an eluent. 1H -NMR ($CDCl_3$) δ : 7.35-8.03 (m, 5H, Ar H), 5.55-6.20 (d, 2H, =CH₂), 1.82 (s, 3H, -CH₃), 1.80 (s, 6H, -CH₃). FT-IR (KBr) cm^{-1} : 1690(C=C), 1000-1200(C-O-C), Hydroxyl peak (3600 cm^{-1}) from Darocur1173 disappeared.

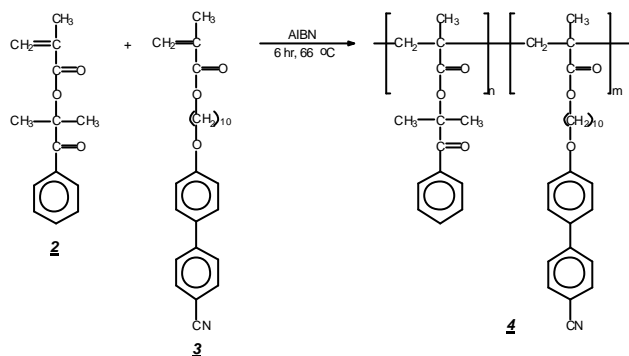
2-3-2 Vinyl Monomer with a Mesogenic Group(**3**)

4-[α -(2-Methylpropenoxy)decanoxy]-4'-cyanobiphenyl (**3**) was obtained as shown in Scheme 3. In the first step, 7.0 g of 4-cyano-4'-hydroxybiphenyl was dissolved in 150 mL of ethanol with slow heating, then stirred for 30 min. after adding 7.0 g of K_2CO_3 . The solution of 7.0 g of 10-bromo-1-decanol in 25 mL of DMF was slowly added to the previously prepared solution, followed by reflux for 24 h. After removing KBr, byproduct, through hot filtration the filtrate was poured into distilled water. The precipitate was recovered by filtration and dried at 40 °C for 24 h. Then, 4-(hydroxydecanoxy)-4'-cyanobiphenyl intermediate was recrystallized in benzene. (Yield 46%)

A solution of 7.0 g of 4-(hydroxydecanoxy)-4'-cyanobiphenyl and 4.0 g of methacryloyl chloride in 100 mL of THF was prepared with stirring for 30 min. under N_2 atmosphere and then reacted for 24 h after adding a solution of 4.0 g of TEA in 100 mL of THF at 0 °C. The resulting product (**3**) was recovered and purified same way as in the preparation of vinyl monomer (**2**). (Yield 45%) 1H -NMR ($CDCl_3$) δ : 6.9-7.7(m, 8H, Ar H), 5.5-6.1(d, 2H, =CH₂), 4.0-4.2(d, 4H, -O-CH₂-), 2.0(s, 3H, =C-CH₃), 1.2-1.9(m, 16H, -(CH₂)₈-). FT-IR (KBr) cm^{-1} : 2200(-CN), 1700(C=C), Hydroxyl peak (3600 cm^{-1}) from 4-(hydroxydecanoxy)-4'-cyanobiphenyl disappeared.

2-3-3 Polymeric Photoinitiator(**4**)

As seen in Scheme 2, polymeric photoinitiator (**4**) was prepared by polymerizing **2** and **3** monomers in THF solvent using 2,2'-azobisisobutyronitrile (AIBN) (0.5 mol%) in a dark room under N_2 atmosphere for 6 h at 60 °C. The feed ratios of **3** / **2** were varied as 100/0, 90/10, and 80/20 mol%. After polymerization, the polymeric photoinitiator (**4**) was purified by repeated dissolution/precipitation method and dried for 48 h at 40 °C.



Scheme 2. Polymeric Photoinitiator

2-4 Electro-optical Properties of PDLC films

To investigate the performance of photoinitiators on the electro-optic properties of PDLC cells three different types of photoinitiators were used; low MW photoinitiator (Darocur 1173), ω,ω' -telechelic oligomeric photoinitiator (1), and polymeric photoinitiator (4) with mesogenic side groups. The formulations for the fabrication of PDLC cells are shown in Table 1. The concentration of photoinitiators was based on the same amount of net photoinitiating groups as determined by UV-Vis spectroscopy. When the polymeric photoinitiator (4) was employed, MMA was added to reduce the viscosity of initial mixture.

Composition	LC (wt%)	Photoinitiator (wt%)	PEBDDM (wt%)	MMA ^a (wt%)	TMPTA ^a (wt%)	MM (wt%)
A	80.0 ^b	3.2	15.8	---	1.0	---
B	80.0 ^b	7.0 ^c	12.0	---	1.0	---
C	80.0 ^b	2.6	6.0	8.0	---	3.4
D	80.0 ^b	6.0 ^c	6.0	8.0	---	---

Table 2. Formulations with different types of photoinitiators employed for the fabrication of PDLCs

3. Impact

The optimum fabrication temperature of PDLC cells with the oligomeric photoinitiator (1) or polymeric photoinitiator (2) was found to be 50 °C, slightly above T_{cloud} of the initial LC/matrix-forming material mixture. Studies on electro-optic properties revealed that the PDLC cell fabricated with the oligomeric photoinitiator (1) exhibited higher transmittance value

under optimum fabrication conditions due to increased immiscibility of the oligomeric photoinitiator (1) with LC phase. In the case of polymeric photoinitiator (4), it was observed that the polymeric photoinitiator possessing structurally similar mesogenic moieties to LC molecules further improved the electro-optical properties of the PDLC cell, resulting in low driving voltage and high contrast ratio. Consequently, these results indicated that the electro-optical performance of PDLC cells could be improved by designing the structure and molecular weight of photoinitiators used in the formulation of LC/matrix forming materials.

Important results of this work are as following. Firstly, new oligomeric photoinitiator was synthesized. Since the molecular weight of the oligomeric photoinitiator was similar to that of UV oligomers, the oligomeric photoinitiator was effectively phase-separated from low MW LCs in the matrix-forming domains, resulting in improved electro-optical performance of PDLCs due to less contamination of LC phases. Second, we synthesized a polymeric photoinitiator with mesogenic groups in the main chain in order to increase chemical affinity to LC molecules at the LC/matrix interface, and to reduce the concentration of unreacted fragments of photoinitiators inside LC phases. This could reduce the response time of the LC phases and hence, the performance of the PDLC cells.

4. Acknowledgements

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5. References

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