

Effect of Liquid Crystal Structures on Polymerization-induced Phase Separation Behavior by Simultaneous Resistivity and Turbidity Measurement

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Keywords : PDLC, photopolymerization, phase separation

Abstract

Photopolymerization and phase separation behavior during the PDLC formation process were investigated by simultaneous resistivity and turbidity measurement. Using this experimental method, we investigated the effect of liquid crystal structure on photopolymerization and phase separation behavior.

1. Introduction

Polymer dispersed liquid crystal (PDLC) is used in switchable glass and imaging technology due to its intrinsic electro-optical characteristics¹⁻³. PDLC is normally made by photopolymerization induced phase separation (PIPS) in a homogeneous mixture of prepolymers and liquid crystals (LC). PIPS process involves curing of prepolymers and phase separation of liquid crystals to form nematic microdomains.

A number of researches have been reported to correlate PDLC morphology with electro-optical performance like off-scattering, on-transmittance and switching voltage⁴⁻⁵. Because the morphology of PDLC is strongly influenced by both the photopolymerization and phase separation process, it is important to understand the mechanism of these processes during the formation of PDLC. For this purpose, some experimental methods were introduced to examine the polymerization and the LC phase separation simultaneously on the formation of PDLC utilizing real-time FTIR spectroscopy⁶ and photo-DSC combined with a turbidity accessory⁷.

The polymerization and phase separation are largely influenced by the physical and chemical nature of liquid crystals and prepolymers⁷⁻⁹, such as the solubility parameters and diffusion coefficient. Many researches have studied E7 as nematic liquid crystal mixture and NOA65 as prepolymer. E7 is a eutectic liquid crystal mixture which consists of several cyanobiphenyl and cyanoterphenyl compounds.

Despite the significant use of E7, the phase separation behavior of individual components has rarely been studied. Investigation of phase separation behavior of the individual components during the polymerization process would provide fundamental information to understand the PDLC process and formulate LC mixtures.

In this study, we will present an experimental setup to monitor the photopolymerization and phase separation process of PDLC simultaneously by resistivity and transmittance measurement. Using this method, we will investigate the effect of chemical structure of liquid crystal component on photopolymerization and phase separation behavior.

2. Experimental

Materials. Formulated UV curable adhesive, NOA65 (Norland products Inc.) was used as prepolymer. To investigate the effect of chemical structure of LC compounds, we selected four LC compounds having different ring structure and length of alkyl group; 4-n-pentyl-4'-cyanobiphenyl (5CB), 4-n-heptyl-4'-cyanobiphenyl (7CB), 4-trans-pentyl cyclohexyl cyanobenzene (5PCH) and 4-trans-heptyl cyclohexyl cyanobenzene (7PCH). PDLC formulations were 1:1 mixture of NOA65 and each LC compound by weight.

Measurements. The experimental setup is illustrated in Fig. 1. Resistivity meter (Megaresta H0709, Shishido Electrostatic Ltd.) was used to measure the resistivity of PDLC cell. Halogen lamp (Avalight-HAL, Avantes Corp.) and CCD detector (Avaspec 2048, Avantes Corp.) coupled with fiber optical cable was used to measure the transmittance of PDLC cell. Photopolymerization was initiated by a black light lamp (B-14N, Spectronics Corp.) using 365nm light with 1.6mW/cm² intensity. All measurements were performed at room temperature.

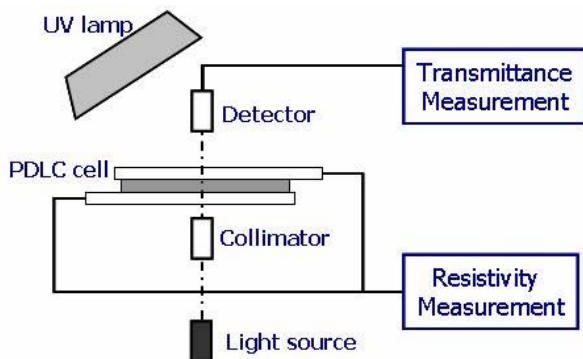


Fig. 1 Experimental setup for simultaneous measurement of transmittance and resistivity of PDLC during photopolymerization.

3. Results and discussion

The monitoring of photopolymerization has been usually carried out using differential calorimetry (DSC), FTIR spectroscopy, dielectric and rheological analysis.¹⁰⁻¹² Electrical conductivity measurement can also be used to follow the photo-polymerization process. Electrical conductivity of the material consists of an ionic and a dipolar component. The dipolar component arises from rotational motion of molar dipoles and the ionic component arises from the diffusion of ionic impurities, which might be introduced during synthesis. As the polymerization progresses, the electrical effects due to these conducting species will be reduced. Prior work has shown that the conductivity analysis can be well used for in-situ monitoring of photo-polymerization process.¹¹⁻¹² The relation between conductivity and resin viscosity can be expressed by:

$$\text{viscosity} = \text{resistivity} = 1/\text{conductivity} \quad (1)$$

Fig. 2 shows the photo-DSC thermograms of the mixtures of NOA65 and LC compounds. Significant difference in photopolymerization behavior between CBs and PCHs can be seen. The PCHs show faster photopolymerization and earlier termination than CBs. For LC compounds having same ring structure, it can be seen that the longer alkyl group causes slightly earlier and faster photopolymerization. The parameters from the photo-DSC thermograms were listed in Table 1. The enthalpy of PCHs, which is related to the conversion of NOA65, is higher than those of CBs. The reason why the CBs have slower photopolymerization and lower conversion compared with PCHs can be thought as followings;

1) According to the UV spectra of CBs and PCHs

(which were not shown in this paper), CBs has absorption in 320~370nm while PCHs has no absorption. The photopolymerization was initiated by UVA black light. The lamp emits UV light in 310~400nm and having a peak at 365nm. Due to the shielding or absorption of UV light by CBs, the photopolymerization rate of NOA65 can be reduced.

2) The photopolymerization of NOA65 propagates by addition of thiyl radicals to ene monomers. In the homogeneous mixture of LC and NOA65, the addition reaction is restricted by LC molecules. In the point of photopolymerization kinetics, the photopolymerization rate might be higher if the LC molecules are separated into droplets earlier. In comparing the molecular structure, PCH molecules are more flexible and have higher mobility than CB. Due to the difference of molecular mobility, the PCH might tend to be separated easier than CB, which might cause the earlier photopolymerization of NOA65. This expectation can also explain the cause of the second exothermic peaks in DSC thermograms of 7PCH, 5PCH and 7CB. The time at second exothermic peak well coincides with the time at incipient of turbidity in Fig. 4. Therefore, the second exothermic peak is originated from the accelerated photopolymerization due to the LC phase separation. In the case of 5CB, it cannot be separated from the matrix enough to form droplets from the turbidity data. Consequently 5CB might show no second exothermic peak in DSC thermogram.

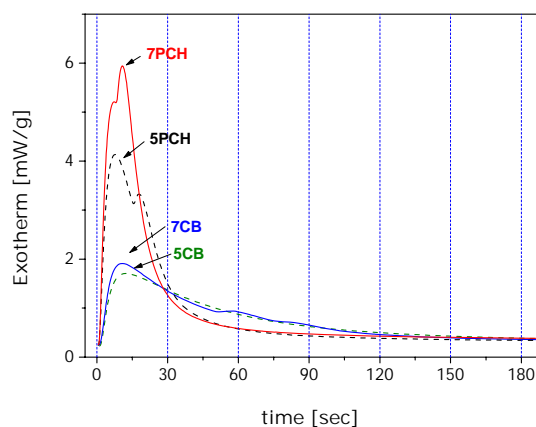


Fig. 2 Photo-DSC thermograms of the mixture of NOA65-liquid crystal compounds.

TABLE 1. Parameters for NOA65 and LC compounds from DSC thermograms.

	$t_{\max 1}$	$t_{\max 2}$	$w_{1/2}$	ΔH
5CB	12.3	-	58.4	180.3
7CB	10.7	57.9	45.4	179.9
5PCH	7.8	17.7	22.9	198.8
7PCH	7.3	10.7	16.4	222.3

$t_{\max 1}$ (s) : time at first peak maximum

$t_{\max 2}$ (s) : time at second peak maximum

$w_{1/2}$ (s) : full width at half maximum

Fig. 3 shows the resistivity of PDLC cells as a function of irradiation time. As polymerization reaction of NOA65 progresses, the resistivity increases in accordance to the viscosity increase. Similar to the photo-DSC thermograms, the resistivity of PCHs increases much faster than that of CBs. And the resistivity having longer alkyl group increases faster and reaches higher level. The resistivity results well coincide with photo-DSC results. Therefore, the resistivity analysis can be used to monitor the photopolymerization process of PDLC.

However, we can find out the difference between the enthalpy in DSC thermograms and final resistivity values; while the enthalpy is $7PCH > 5PCH > 7CB \approx 5CB$, the final resistivity is $7PCH > 5PCH > 7CB > 5CB$. To explain the difference, we have to consider the meaning of these two values. The enthalpy measured by DSC thermogram arises from the heat released by reaction of NOA65 and is directly associated with the conversion of NOA65 regardless of phase separation of LC molecules. But the resistivity arises from the bulk viscosity of PDLC which is associated with the plasticization effect of LC molecules as well as the conversion of NOA65. The LC molecules dissolved in polymer matrix act as a plasticizer and reduce the viscosity of PDLC. According to this approach, we can explain the difference as followings;

- 1) Despite the conversion of NOA65 reaches to same level for NOA65-5CB and NOA65-7CB system, higher extent of 5CB molecules is remained in the matrix and plasticizes the matrix much more than 7CB. This can be confirmed by the turbidity results in Fig. 4.
- 2) While the conversion of NOA65 is higher about 10% for NOA65-7PCH than NOA65-5PCH system. The difference of final resistivity is very small. In contrary to CB, 5PCH and 7PCH can be significantly separated and form droplets. This can be crudely estimated from the turbidity data. Therefore, the 10% difference in the final conversion cannot affect the final resistivity value

significantly.

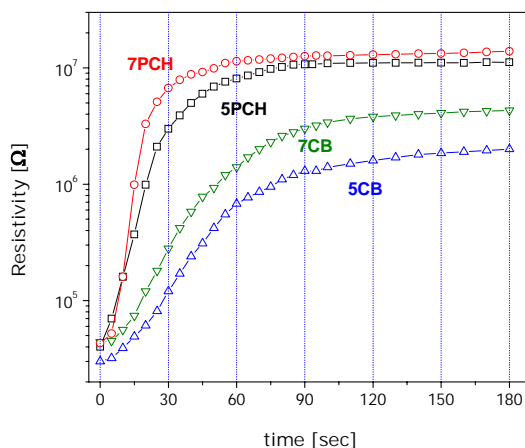


Fig. 3 Resistivity of PDLC cells as a function of time during photo-polymerization.

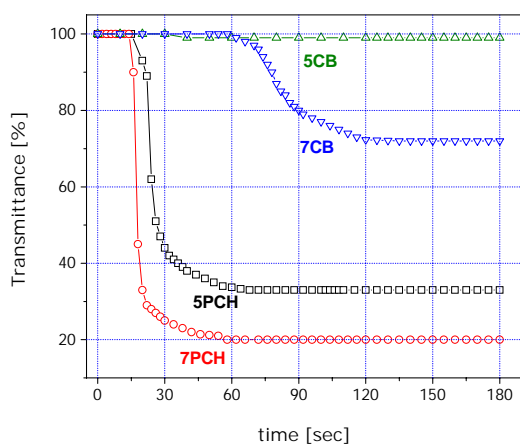


Fig. 4. Transmittance of PDLC cells as a function of time during photo-polymerization.

Fig. 4 shows the transmittance as a function of irradiation time. 5CB showed no turbidity change. This indicates that 5CB molecules cannot be separated from the matrix enough to form droplets to scatter the light, despite of significant conversion of NOA65. The turbidity of 7CB decreases from 60s and the final turbidity is still low, high transmittance. This indicates that an extent of 7CB molecules is separated from matrix and form droplets. But the amount or size of droplets is very small to scatter the light efficiently. In contrary, the turbidity of PCHs changes earlier and reaches much higher level than CBs. This behavior clearly shows that the PCH molecules are easily separated during the photopolymerization process

compared with CB molecules. On the other hands, the turbidity of 7PCH increases earlier and reaches higher level compared with 5PCH.

The resistivity and enthalpy values at incipient of turbidity are listed in Table 2. The time at incipient turbidity is 15s and 18s for 7PCH and 5PCH, respectively. At these times, the enthalpy of 7PCH and 5PCH is 67.0J/g and 56.0J/g, respectively. It is interesting that although 7PCH requires higher conversion of NOA65 than 5PCH, 7PCH reaches the required conversion faster than 5PCH. On the other hand, 7CB requires much higher conversion to form droplets compared with PCHs.

TABLE 2. Resistivity (R_{turb}) and enthalpy (ΔH_{turb}) at incipient turbidity.

	t_{turb}	$R_{\text{turb}}(\Omega)$	$\Delta H_{\text{turb}}(\text{J/g})$
5CB	-	-	
7CB	66	1.7×10^6	82.0
5PCH	18	7.4×10^5	56.8
7PCH	15	9.9×10^5	67.0

According to the photo-DSC and resistivity results, the polymerization reactions terminate is about 60s for PCHs and 120s for 5CBs. In transmittance results, the transmittance values don't changes any more from these times. From the results, we can also see the followings;

- 1) The photopolymerization of NOA65 is largely restricted by CB molecules and the gelation is delayed due to both restricted photopolymerization and the plasticization of CB molecules dissolved in matrix.
- 2) At gel point, phase separation of LC molecules and droplet growth is terminated because the mobility of LC molecules is largely reduced.

4. Summary

The photopolymerization and phase separation behavior during the process of PDLC formation were examined by simultaneous resistivity and turbidity measurement. The photopolymerization behavior by resistivity measurement was compared with photo-DSC measurement. While the photo-DSC exhibits only the reaction behavior of polymer components, the resistivity provides the information on the degree of polymerization and liquid crystal phase separation.

The effect of structure of liquid crystals on the photopolymerization and phase separation behavior was investigated. CB and PCH showed significantly difference in phase separation behavior. PCH can be

phase separated much easily compared to CB. Due to their phase separation characteristics, they showed very different photopolymerization behavior. PCH results in higher photopolymerization rate and conversion than CB.

5. References

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