

# Preparation and properties of photocurable, high refractive, 2-naphthol epoxy-modified urethane acrylate

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**Abstract** The back light unit (BLU) is a core component of liquid crystal displays (LCDs) that are used in notebook computers, mobile phones, navigation devices, flat screen TVs, and public information display (PID) devices, among many others. To enhance the optical efficiency of LCDs, optical films with a high refractive index have been used in the BLU. In particular, high refractive chemicals have been the subject of recent investigations to enhance the optical efficiency of BLUs. In this study, we efficiently synthesized photocurable, high refractive 2-naphthol epoxy-modified urethane acrylate (2-NEUA) from 2-naphthol via a three-step reaction. The refractive index of 2-NEUA was higher than that of 2-naphthol epoxy acrylate (2-NEA), presumably because it contains more integrated aromatic rings and therefore has a higher electron density than 2-NEA. Furthermore, we critically evaluated the effects of 2-NEUA on the mechanical properties of UV curable films in this article.

**Keywords** High refractive · 2-Naphthol · Urethane acrylate · Photocurable

## Introduction

Recent technological trends in thin film transistor-liquid crystal displays (TFT-LCDs) include thinning, lightening, decreasing power consumption, and decreasing costs. In particular, low power-consuming products are in high demand worldwide because of increased energy-saving awareness. The electrical power consumption of

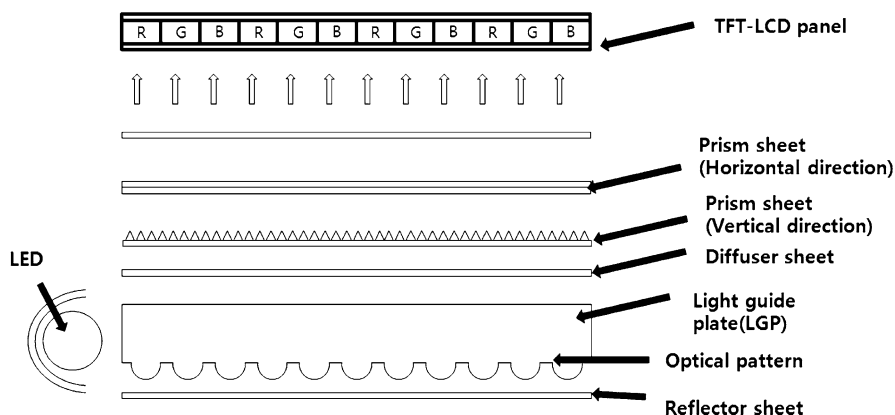
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**Fig. 1** Schematic structure of a liquid crystal display-back light unit (LCD-BLU)

a TFT-LCD is determined primarily by the back light unit (BLU). To ensure brightness uniformity and high luminance, the BLU is composed of several kinds of optical materials, namely a light source, reflective sheet, light guide plate (LGP), diffuser sheet, prism sheet, and a mold frame as shown schematically in Fig. 1 [1–11]. Therefore, high refractive materials play an important role in determining LCD efficiency. Sulfur and bromine-containing polymers have been developed for advanced integrated optical applications [12–14]. However, due to increasing environmental issues, halogenated materials are forced to replace with halogen-free high refractive materials [15]. To improve the optical efficiency of LCDs, biphenyl acrylates (*o*-phenylphenoxyethyl acrylate and 2-hydroxy-3-(*o*-phenylphenoxy)propyl acrylate) are currently used, though there is great interest in further enhancing the refractive index and mechanical properties of the refractive materials used in the BLU of LCDs.

In this article, we report the synthesis of 2-NEUA from 2-NEA and diisocyanate to obtain photocurable 2-naphthol with a high refractive index. After mixing the photocurable 2-naphthol with a photoinitiator, we investigated the curing properties, such as hardness and adhesion, of the photocurable 2-naphthol modified by urethane acrylate [16–19].

## Experimental

### Materials

The following reagents were used without further purification in the 2-naphthol glycidyl ether synthesis: 2-naphthol (Aldrich) and epichlorohydrin (ECH, Aldrich). The 2-NEA was prepared by using 2-naphthol glycidyl ether (2-NGE, synthesized in our laboratory), acrylic acid (AA, LG), monomethyl ether hydroquinone (MEHQ, Eastman) as an inhibitor, and benzyltriethylammonium chloride (BTEAC, Double Bond). The 2-NEUA was synthesized using 2-NEA, toluene 2,4-diisocyanate (TDI,

Sankyo), and dibutyltin dilaurate (DBTL, Songwon) as a catalyst.  $\alpha$ -Hydroxy- $\alpha$ -methylpropiophenone (Darocure 1173, CIBA) was used as a curing agent and *o*-phenylphenoxyethyl acrylate (OPPEA, Miwon) was used to measure certain properties of 2-NEUA and the intermediate 2-NEA.

### Synthesis of 2-NEUA

A 500-mL round-bottomed, four-necked separable glass reactor with a mechanical stirrer, thermometer, and nitrogen inlet was used to prepare the acrylate polymer. Dry nitrogen gas was continuously purged through the reactor to remove oxygen and moisture. The 2-NEUA was synthesized by three-step reactions as follows.

### Preparation of 2-NGE

2-Naphthol (3.70 g, 25 mmol) and KOH (1.50 g, 25 mmol) were dissolved in methanol. Then, the methanol was removed by rotary evaporation. The resulting solid was mixed with toluene (100 mL) and ECH (10.0 mL, 125 mmol) was added. The resulting suspension was stirred at reflux temperature for 1 h. After completion of the reaction, the mixture was concentrated in vacuo. After purification by flash silica gel column chromatography ( $R_f$ : 0.20, hexane:ethyl acetate = 16:1, v/v), 4.62 g (92%) of 2-NGE was obtained.

$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz);  $\delta$  7.75 (m, 3 H, Hs at ArH), 7.44 (m, 1 H at ArH), 7.35 (m, 1 H, ArH), 7.17 (m, 2 H, Hs at ArH), 4.35 (dd,  $J = 11.1, 3.0$  Hz, 1 H, H at C-j), 4.07 (dd,  $J = 11.3, 6.0$  Hz, 1 H, H at C-j), 3.44 (m, 1 H, H at C-i), 2.95 (dd,  $J = 4.8, 4.7$  Hz, 1 H, Hs at C-h), 2.82 (dd,  $J = 5.0, 2.6$  Hz, 1 H, H at C-h).

### Preparation of 2-NEA

2-NGE (7.35 g, 36 mmol), AA (2.65 g, 36 mmol), MEHQ (0.01 g, 0.08 mmol), and BTEAC (0.1 g, 0.37 mmol) were added all at once. The mixture was stirred at 60 °C and the reaction temperature was increased gradually to 100 °C. The reaction mixture was agitated vigorously at 100 °C for 5 h. When the acid value was below 3, the reaction was terminated. The crude product was purified by flash silica gel column chromatography ( $R_f$ : 0.20, hexane:ethyl acetate = 3:1, v/v), and 9.89 g (99%) of 2-NEA was obtained.

$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz);  $\delta$  7.76 (m, 3H, Hs at ArH), 7.46 (m, 1H, H at ArH), 7.37 (m, 1H, H at ArH), 7.19 (d,  $J = 8.5$  Hz, 1H, H at ArH), 7.17 (s, 1H, H at ArH), 6.49 (dd,  $J = 20.0, 1.5$  Hz, 1H, H at C-m), 6.20 (dd,  $J = 17.0, 10.5$  Hz, 1H, H at C-l), 5.91 (dd,  $J = 10.5, 1.5$  Hz, 1H, H at C-m), 4.45 (m, 2H, Hs at C-h), 4.37 (q,  $J = 5.5$  Hz, 1H, H at C-i), 4.19 (m, 2H, Hs at C-j), 2.67 (d,  $J = 5.0$  Hz, 1H, H at OH).

### Preparation of 2-NEUA

2-NEA (7.57 g, 27 mmol) and MEHQ (0.01 g, 0.08 mmol) were placed into a 500-mL round-bottomed reactor and then stirred vigorously. Calculated TDI (2.43 g, 27 mmol) was added by drop-wise addition using a dropping funnel.

The hydroxyl group (OH) on the side chains of 2-NEA was reacted with the -NCO group of TDI. DBTL (0.002 g, 0.0003 mmol) was added to the reaction mixture and the reaction was incubated at 75 °C to complete the reaction. It was clear from monitoring the IR spectrum according to reaction time when the reaction terminated. The crude product was purified by flash silica gel column chromatography ( $R_f$ : 0.23, hexane:ethyl acetate = 2:1, v/v), and 9.31 g (93%) of 2-NEUA was obtained.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz);  $\delta$  7.75 (m, 7H, Hs at ArH), 7.45 (t,  $J = 7.6$  Hz, 2H, Hs at ArH), 7.36 (t,  $J = 7.5$  Hz, 2H, Hs at ArH), 7.19 (m, 5H, Hs at ArH), 7.10 (d,  $J = 8.2$  Hz, 1H, H at ArH), 6.78 (s, 1H, H at -NH), 6.53 (s, 1H, H at -NH), 6.46 (dd,  $J = 17.4, 1.4$  and  $17.4, 1.9$  Hz, 2H, two set of Hs at C-l), 6.17 (dd,  $J = 17.3, 10.5$  and  $17.4, 10.5$  Hz, 2H, two set of Hs at C-k), 5.88 (dd,  $J = 10.5, 1.3$  Hz, 1H, H at C-l), 5.87 (dd,  $J = 10.5, 1.3$  Hz, 1H, H at C-l), 5.50 (m, 2H, Hs at C-i), 4.59 (m, 4H, Hs at C-h), 4.35 (m, 4H, Hs at C-h), 2.20 (s, 3H, Hs at C-q).

### Formulation and measurements

Fourier-transformed infrared (FT-IR) spectra were recorded with an Alpha FT-IR spectrometer. The nuclear magnetic resonance (NMR) spectra were obtained using Bruker 400 MHz and Varian 500 MHz superconducting FT-NMR spectrometers using  $\text{CDCl}_3$  as a solvent. The refractive index was measured by an ABBE refractometer (ATAGO Co. Ltd) at 25 °C.

To measure the physical properties of 2-NEUA effectively, 2-NEUA was mixed with OPPEA and Darocure1173 in the ratio of 47.5:47.5:5, respectively. The viscosity and index of refraction of 2-NEUA was 120,000 cps and 1.593 at 25 °C, respectively. For the film hardness test, 2-NEUA was cast to a depth of about 90  $\mu\text{m}$  on glass plates and then the 2-NEUA samples were evaluated using a MITSUBISHI pencil.

A patterned 2-NEUA film was obtained by placing 2-NEUA, additives, and polyethylene terephthalate (PET) on a prism-shaped film under a press. The samples were prepared by UV curing with 400 mJ of light quantity followed by removal of the prism film. We also performed an adhesion test.

The thermal properties of the 2-NEA and 2-NEUA were measured by differential scanning calorimetry (DSC, TA Instrument DSC 2010) at a heating rate of 20 °C/min in a nitrogen atmosphere. A second scan was performed after rapid cooling of the 2-NEA and 2-NEUA after the first scan. Thermogravimetric analysis (TGA, NETZSCH) was conducted under a nitrogen atmosphere at a heating rate of 10 °C/min.

## Results and discussion

### Characterization of 2-NEUA

The overall scheme of 2-NEUA synthesis from 2-naphthol is described in Scheme 1. The synthesized 2-NGE, 2-NEA, and 2-NEUA were characterized and

confirmed by  $^1\text{H}$  NMR (Figs. 2, 3, 4). FT-IR measurements were used to monitor the synthesis of 2-NEUA (Fig. 5). The  $-\text{N}=\text{C}=\text{O}$  peak ( $2273\text{ cm}^{-1}$ ) decreased as the reaction proceeded and eventually disappeared from the spectrum of the final product.

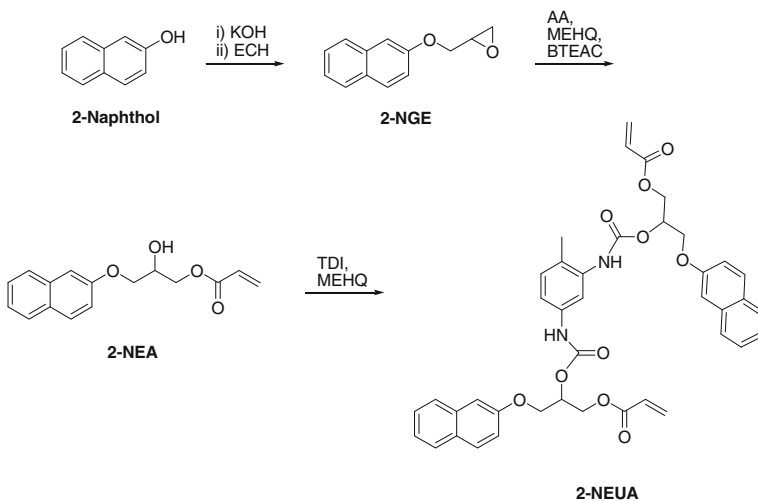
### Thermal properties of 2-NEUA and 2-NEA

Figure 6 shows the second run DSC curves of the UV-cured 2-NEUA and 2-NEA samples. The thermograms for 2-NEUA and 2-NEA exhibited a single transition at  $26.47$  and  $-2.68\text{ }^\circ\text{C}$ , respectively. 2-NEUA and 2-NEA showed a single transition corresponding to the glass transition temperature ( $T_g$ ) at each onset point with a heat capacity change ( $\Delta C_p$ ) of  $0.059$  and  $1.210\text{ J g}^{-1}\text{ }^\circ\text{C}^{-1}$ , respectively. Therefore, the amorphous domain in 2-NEUA was significantly decreased relative to that in 2-NEA.

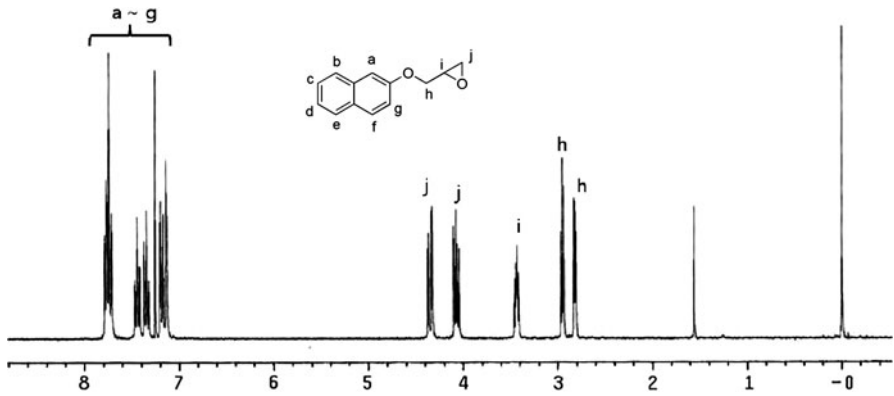
The TGA results for 2-NEUA and 2-NEA prepared by photocuring are shown in Fig. 7. The 2-NEUA sample exhibited a higher residual weight percent than 2-NEA in the high temperature area. This suggests that 2-NEUA has more of a network structure than 2-NEA.

### Measurement of refractive index and density

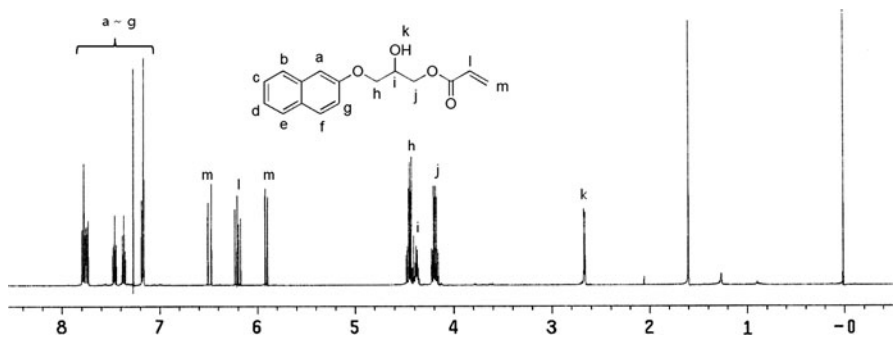
Table 1 shows the refractive indices of 2-naphthol, 2-NGE, 2-NEA, and 2-NEUA. The refractive index of 2-NEA was lower than that of 2-naphthol, because the refractive index of a compound decreases as the molecular weight and density of the compound increase, and 2-NEA has more aliphatic chains than 2-naphthol. The refractive index of 2-NEUA ( $1.611$ ) was slightly higher than that of 2-NEA ( $1.588$ ).



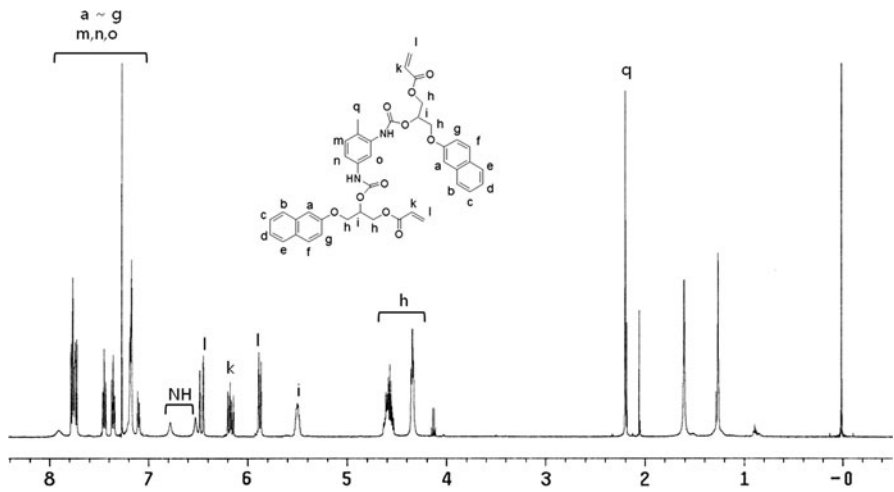
**Scheme 1** The synthesis of 2-NEUA from 2-naphthol



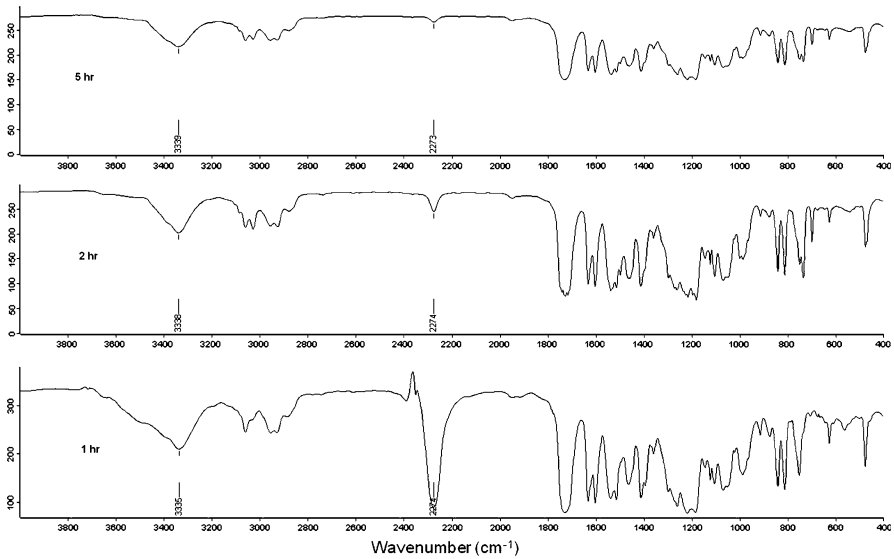
**Fig. 2**  $^1\text{H}$  NMR spectrum of 2-NGE



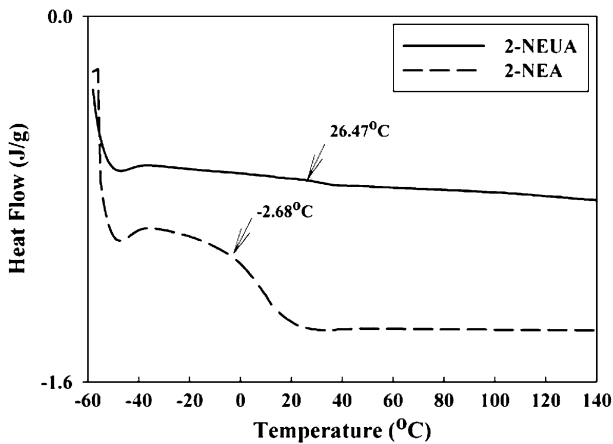
**Fig. 3**  $^1\text{H}$  NMR spectrum of 2-NEA



**Fig. 4**  $^1\text{H}$  NMR spectrum of 2-NEUA



**Fig. 5** FT-IR spectrum of 2-NEUA according to reaction time

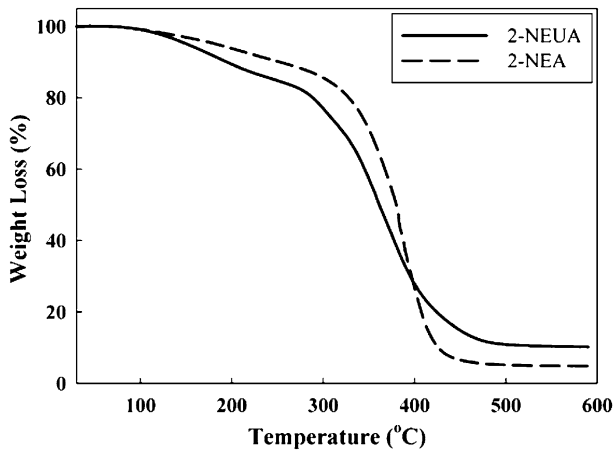


**Fig. 6** DSC curves of 2-NEUA and 2-NEA

We attribute this to the more integrated aromatic rings of 2-NEUA, which would increase the electron density of the compound, resulting in a higher refractive index.

#### Hardness and adhesion tests

To measure the hardness and adhesion properties of the photocured films of 2-NEUA and 2-NEA, we performed pencil hardness and crosshatch adhesion tests, respectively. The pencil hardness of 2-NEA was *F* and that of 2-NEUA was *H*. The higher amount of cross-linking in 2-NEUA relative to 2-NEA may explain the



**Fig. 7** TGA curves of 2-NEUA and 2-NEA

**Table 1** Material properties of 2-naphthol, 2-NGE, 2-NEA, and 2-NEUA

Material	Refractive index (25 °C)	Density (g/mL, 20 °C)	Molecular weight (g/mol)
2-Naphthol	1.659	1.22	144
2-NGE	1.613	1.20	200
2-NEA	1.588	1.17	272
2-NEUA	1.611	1.24	718

increased pencil hardness of 2-NEUA. 2-NEUA and 2-NEA both showed good adhesion to a PET prism sheet.

## Conclusions

In this study, photocurable, high refractive, 2-naphthol epoxy-modified urethane acrylate (2-NEUA) was efficiently synthesized from 2-naphthol via a three-step reaction. The refractive index of 2-NEA was lower than that of 2-naphthol because of the increased molecular weight of 2-NEA compared to 2-naphthol and its higher density. 2-NEUA had a slightly higher refractive index than 2-NEA, presumably because it contains more integrated aromatic rings and therefore has a higher electron density than 2-NEA.

The thermal properties of 2-NEUA and 2-NEA were measured by DSC and TGA. The DSC measurements of 2-NEUA and 2-NEA indicated that the amorphous domain in 2-NEUA was significantly decreased compared to that in 2-NEA. The TGA results revealed that 2-NEUA had a higher residual weight percent than 2-NEA in the high temperature area, indicating that 2-NEUA has more of a network structure than 2-NEA. The pencil hardness of 2-NEA was *F* and that of 2-NEUA was *H*, likely due to the higher cross-linking of 2-NEUA than 2-NEA. Both



2-NEUA and 2-NEA adhered well to prism film sheets. The excellent material properties of 2-NEUA indicate that it is a potentially valuable monomer that can be used in the liquid display industry.

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