

# Waveguide용 Functional Acrylate Monomer와 Polymer film의 제조 및 특성

권지윤, 도정윤\*

(재)한국섬유기계연구소, \*부산대학교 첨단정보 및 디스플레이소재학과

## Preparation and Properties of Functional Acrylates and Polymers Producing High Refractive Index

Ji Yun Kwon and Jung Yun Do\*

*Korea Textile Machinery Research Institute, Gyeongbuk, Korea*

*\*Department of Advanced Information and Display Material, Pusan National University, Busan, Korea*

### 1. Introduction

Organic optical polymers have been utilized for various optical applications which are required to be colorless and transparent, such as lenses, prism, non-linear optics, photochromic materials, optoelectronics, optical wave guides, optical coatings, and fiber optics.<sup>1</sup> For the practical fabrication of waveguide devices, it is essential for the optical materials to have excellent properties in terms of low optical loss, low birefringence, and high thermal stability. High optical transmission is intensively required for the waveguide materials at the near-IR wavelengths from around 850 to 1550 nm. For the optical thin film, acrylate polymers made from several acrylate monomers have been utilized to improve physical properties such as adhesion, surface compatibility, wettability, hardness, and cross-linking density. Acrylate polymers with similar monomer compositions have been employed to construct a multilayered waveguide film because they tend to be physically compatible with each other. The refractive indices of each layer were conveniently controlled by a monomer content inducing a high or low RI. Fluorinated monomers have been reported to decrease the RI. Besides, several hetero atoms including sulfur, bromine, phosphorus, iodine, germanium, and titanium were introduced to promote higher refractive indices.<sup>2</sup>

This research is aimed at developing a new, high RI acrylic monomer. We designed UV-curable difunctional methacrylate derivatives with an electron-withdrawing group and an electron-donating group in their structures. For the convenient optical measurement of the acrylic polymers, thin optical film was prepared with a comonomer mixture of various compositions. We investigated the various acrylic monomer structures and polymer composition on the refractivity and thermal stability of the polymers. The polymerization of each monomer mixture was accomplished with UV illumination using a photo initiator. The refractive indices of the polymer films were determined at wavelenghtes of 850 nm, 1330 nm, and 1550 nm by using the prism coupling method.

## 2. Experimental

### 2.1. Synthesis of Dimer-Amino (Monomer 2)

Triethylamine (60 mmol, 6.10 g) was mixed with N-phenyldiethanol amine (20 mmol, 3.60 g) in dichloromethane (60 ml). A catalytic amount of 4-dimethyl amino pyridine (1 mmol, 0.12 g) was then added to the solution. Methacrylic anhydride (50 mmol, 7.4ml) was combined with the resultant reaction mixture for 2 h at room temperature and then poured into water and extracted with diethyl ether. The resulting organic extracts were washed with brine and dried over magnesium sulfate. The solvents were removed by a rotary evaporator and the crude product was purified via silica-gel column chromatography using ethyl acetate and n-hexane as co-elutants (1/2 = v/v) to provide 6.0 g of the product.

### 2.2. Synthesis of Dimer-CN (Monomer 9)

6.3 g of 4-[Bis (2-hydroxyethyl) amino] benzaldehyde 3 and 9.0 g of triethylamine were mixed in 90 ml of dichloromethane at room temperature for 10 min. Then 9.3 g of acetic anhydride was added. To this solution were added catalytic amounts of 4-dimethyl aminopyridine (1.5 mmol, 0.18 g) at 0°C and the temperature was gradually raised to 25°C. After 2 h at 25°C, the reaction mixture was diluted with dichloromethane and washed with water. The combined organic layer was dried over MgSO<sub>4</sub> and concentrated to give product 4. The solution of hydroxylamine hydrochloride (90 mmol, 6.30 g) in pyridine (90 ml) was added to crude 4 and stirred for 5 h at 25°C. After drying the solution over anhydrous MgSO<sub>4</sub>, it was concentrated to yield oxime 5. The oxime 5 was dissolved in 90 ml of dichloromethane. Triethyl amine (120 mmol, 12.13 g) was then added. Methanesulphonyl chloride (39 mmol, 4.5 g) was added to this solution at 0°C. Then the temperature was gradually raised to 25°C. After 2 h, nitrile compound 7 was obtained without isolating 6. The mixture was diluted with dichloromethane and washed with water and brine, and subsequently dried over MgSO<sub>4</sub>. The 7 was deprotected with 3.60 g of NaOH in a solution of methanol at room temperature. It was concentrated by a rotary evaporator and the crude product was purified by silica-gel column chromatography using ethyl acetate and n-hexane as co-elutants (1/4 = v/v) to provide 5.80 g of 4-[bis (2-hydroxyethyl) amino] benzonitrile 8. Dimer-CN monomer 9 was prepared by acrylation of 8 through a similar synthetic procedure as the Dimer-Amino monomer 2.

### 2.3. Preparation of Copolymer Films Containing the Functional Acrylates

Tris (2-methylacrylic acid) ester of 2-hydroxymethyl-2-methylpropane-1,3-diol (Trimer MS (*m/z*): calcd for C<sub>17</sub>H<sub>24</sub>O<sub>6</sub> 324.16, found 325.90) was employed as a comonomer to improve the film property of the resulting polymer. It was then mixed with the photo initiator (0.5 wt%), bis-(2,4,6-trimethylbenzoyl)-phenylphosphine oxide (IRG819). Various monomers mixtures (10/90, 30/70, 50/50wt%/wt% of functional monomer/Trimer) were diluted with 50 wt% of cyclohexanone. The solution was spin-cast onto a silicon wafer and exposed to ultraviolet light (365 nm, 2500 mJ/cm<sup>2</sup>) for 3 min under a nitrogen atmosphere. The thickness of the copolymer films ranged from 0.1 to 0.2 μm as measured with a Tencor Instruments Alpha-Step 200 profilometer.

### 3. Results and Discussion

#### 3.1. Identification of the Difunctional Methacrylate and the Polymer Structures.

The **Trimer/Dimer-Ar** and **Trimer/Dimer-CN** in Figure 2 and 3 were prepared through acrylations of 1,1,1-tris (hydroxymethyl) ethane and 1,2-dihydroxymethylbenzene, respectively. IR spectral analysis evidently presented characteristic bands of the cyano group at  $2216\text{ cm}^{-1}$  and  $543\text{ cm}^{-1}$ . The monomers were copolymerized with **Trimer** by UV illumination in a nitrogen atmosphere and then baked at  $100^\circ\text{C}$  for 2 h for the thin film analysis. Additional thermal treatment was utilized to induce thermal hardening of the remaining methacrylate groups and remove any volatile solvent. The IR spectra of the monomers in Figure 2 and 3 indicate the absorption bands at  $1625 - 1635\text{ cm}^{-1}$  specifying the existence of methacrylic groups. The sharp band at  $1700 - 1750\text{ cm}^{-1}$  is caused by the stretching vibrations of the C=O group. The characteristic bands at  $1150 - 1350\text{ cm}^{-1}$  correspond to the stretching vibrations of the C-O of ester. The complicated absorption bands at  $802 - 815\text{ cm}^{-1}$ , including the C=C twist mode of the acrylic group in each monomer, were simplified after polymerization. The disappearance of the acrylic C=C stretching bands at  $1625 - 1635\text{ cm}^{-1}$  of the monomers were also observed under UV illumination. The peak at  $1625 - 1600\text{ cm}^{-1}$  is assigned to the characteristic stretches of aromatic C=C bond for Dimers.

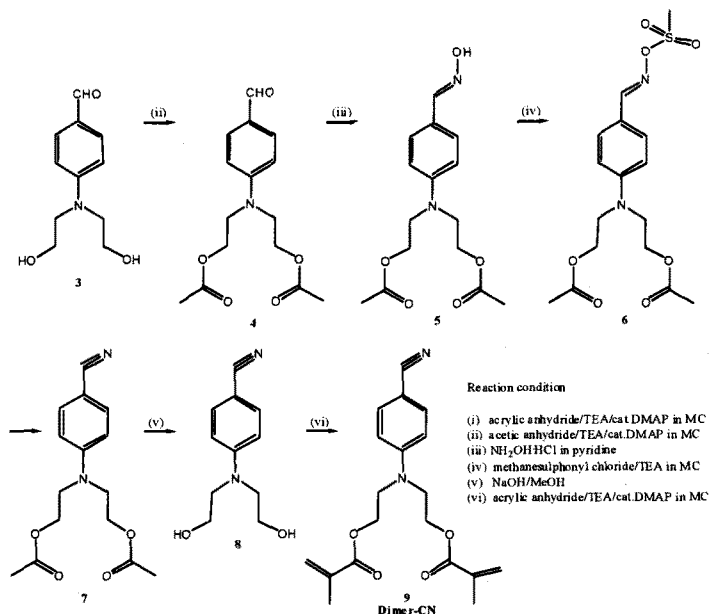
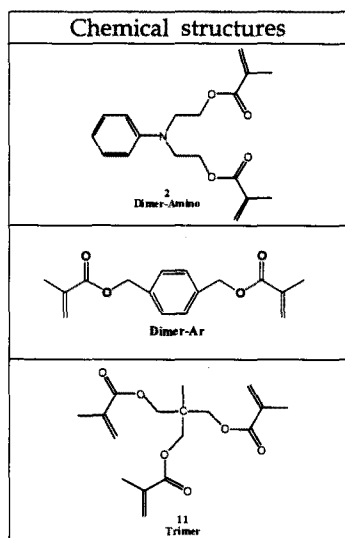
#### 3.2. Optical Property.

The refractive index of the polymer film was measured with a prism coupling method using TE-guided light ( $n_{\text{TE}}$ ) and TM-guided light ( $n_{\text{TM}}$ ). The homopolymer of **Trimer** was measured with the indices of 1.488, 1.490, and 1.499 at 1550 nm, 1330 nm, and 850 nm, respectively. Both  $n_{\text{TM}}$  and  $n_{\text{TE}}$  of copolymer films containing 50 wt% of Dimers were observed at a higher range than those of **Trimer** homopolymer. **Dimer-Ar** is understood to have a higher index than aliphatic **Trimer** because it contains an aromatic ring. The amino-attached monomer evidently contributed to the index increment by producing a higher index than **Dimer-Ar**. The copolymer of 50/50 using **Dimer-CN** exhibited the highest refractive index among the prepared monomers. Figure 4 shows linear fits of refractive index of copolymers toward the weight contents of the difunctional acrylate combined. The copolymers for higher contents were not measured due to a phase separation which occurred during film casting. Two homopolymers from **Dimer-Amino** and **Dimer-CN** formed brittle and rough thin films inadequate for optical measurement. However, their refractive indices were determined with an extrapolating method as viewed in Figure 4. The indices relating with **Dimer-Amino** and **Dimer-Ar** were calculated with 1.538 and 1.564, respectively, at 850 nm. The homopolymer of **Dimer-CN** revealed on index of 1.595 at 850 nm. The increasing trend of the index was clearly observed with homopolymers at all measured wavelengths.

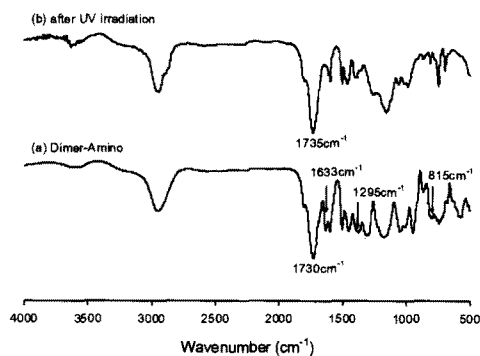
### 4. References

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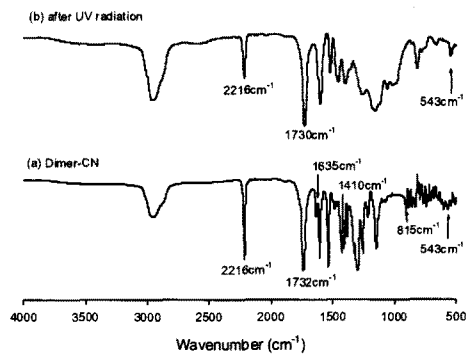
**Table 1.** Chemical structure of acrylate monomers



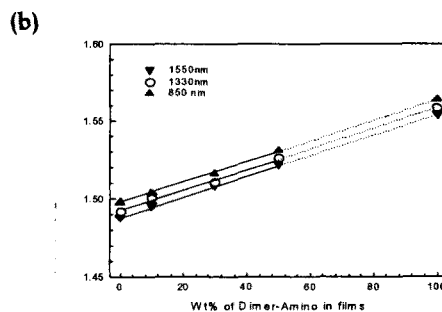
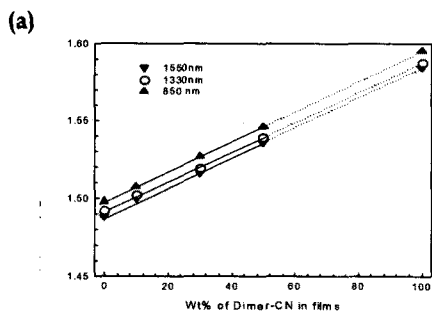
**Figure 1.** Synthesis of Dimer-CN (Monomer 9)



**Figure 2.** FTIR spectra of (a) Dimer-Amino and (b) Dimer-Amino/Trimer (50/50 wt/wt%) copolymer film.



**Figure 3.** FTIR spectra of (a) Dimer-CN and (b) Dimer-CN/Trimer (50/50 wt/wt%) copolymer film.



**Figure 4.** Refractive index ( $n_{TE}$ ) of polymers according to monomer content for (a) Dimer-Amino/Trimer copolymer film and (b) Dimer-CN/Trimer copolymer film.