

Polarizing Group Attached Acrylates and Polymers Viewing High Refractive Index

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Abstract: We designed and successfully synthesized UV curable, functional acrylate monomers having a polarizing group, i.e., an electron-withdrawing and/or electron-donating group for the optical materials of high refractive index. Optical polymer films made from the functional methacrylate monomers were achieved with photo crosslinking under UV illumination. A monomer having amino and cyano groups (Dimer-CN) exhibited the highest refractive index ($n_{TE} = 1.595$ at 850 nm) among the studied methacrylate derivatives, due to the large polarizability of the dipolar monomer structures with electron-donating and withdrawing groups. By controlling the compositions of the functional acrylate monomer of copolymers, the refractive indices of the polymers were readily adjusted within a wide range of 1.498-1.595. The copolymers showed a high glass transition temperature (T_g) and good thermal stability, which are desirable for optical applications. T_g and $T_{10\%}$ (10%-weight loss occurred) of the copolymers ranged from 120-140 °C and from 329-387 °C, respectively.

Keywords: high refractive index, dipolar methacrylates, UV curing, thermal stability.

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.¹⁻⁷ 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. This is especially important for the optical communication.⁸ A refractive index (RI) is an important material property for manipulating light and has been elaborately controlled in the optical waveguides.⁹ A waveguide structure consisting of core and cladding layers needs at least two materials with different RIs along with sufficient thermal stability.^{10,11} The optical thin films contribute to reducing the volume of space in optical assemblies, which can advantageously make an optical apparatus lightweight and small-sized.¹² High RI materials can be rendered as a thinner film than low RI materials to give the same focal distance of the optical lens.⁹ For the optical thin film, acry-

late polymers made from several acrylate monomers have been utilized to improve physical properties such as adhesion, surface compatibility, wettability, hardness, and crosslinking density.¹³ 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.¹⁴ Besides, several hetero atoms including sulfur, bromine, phosphorus, iodine, germanium, and titanium were introduced to promote higher refractive indices.¹⁵

The RI resulted from the materials interaction with the traveling light and was expected to be affected by the constituent organic groups. π -Conjugated or aromatic groups exhibited high RI compared to saturated aliphatic groups.¹⁶ This property was also found in nonlinear optical materials with π -conjugated dipolar chromophores.¹⁷ The RI of acrylic polymers is thought to be changed by introducing polar aromatic groups into the monomer structures. The high polarizability of nitrogen-containing substituents such as amino and cyano groups on aromatic rings may disturb aromatic π electrons and induce favorable field interactions which would in turn delay the propagating speed of light.¹⁸ The refractive indices of the polymer can be controlled by

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changing parameters such as components used, composition ratios, and UV curing time. Yinghua *et al.* prepared highly halogenated poly(arylene ether ketone)s and poly(arylene ether sulfone)s with different bromine contents. The refractive index of these polymers were readily adjusted within a wide range from 1.51-1.57 (at 1550 nm) by changing the ratio of the bromine-containing bisphenol in the feed.⁸ Matsuda *et al.* reported sulfur containing aliphatic methacrylate or alicyclic methacrylate polymer with various compositions. Poly-S-methyl thiomethacrylate (MTMA) exhibited a high refractive index of 1.582 (at 850 nm) by the effect of sulfur atom. The refractive index of copolymer films of MTMA-styrene was controllable within 1.560-1.569.¹²

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 resulting polymers were characterized via a FT-IR, differential scanning calorimeter (DSC), and thermal gravimetric analysis (TGA). The refractive indices of the polymer films were determined at wavelengths of 850, 1330, and 1550 nm by using the prism coupling method.¹⁹

Experimental

Materials and Characterization. All reagents were purchased from Sigma-Aldrich Chemical Co. and the reagent-grade solvents were dried when necessary and purified by a vacuum distillation. ¹H-NMR and ¹³C-NMR spectroscopy experiments (Bruker AM-300 spectrometer) were used to characterize the molecular structure of the intermediate compounds and functional methacrylate monomers. The mass spectra were recorded on a Agilent 1200LC/1100 MSD SL mass spectrometer. A MAGNA-IR 750 spectrometer (Nicolet Instrument Co., USA) recorded the FT-IR spectra. The refractive indices of the polymer films were measured at the wavelengths of 1550, 1310, and 852 nm using a prism coupling technique with an uncertainty of ± 0.0004 . DSC and TGA were performed on a Mettler Toledo DSC 822^c and on a TAG/SDTA 851^c, respectively, using a heating rate of 10 °C/min under a nitrogen atmosphere.

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, 7.4 mL) 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. Yield: 95.2%. ¹H-NMR (CDCl₃, ppm): δ =7.08 (d, 2H), 6.60 (m, 1H), 6.59 (d, 2H), 6.15 (s, 2H), 5.58 (s, 2H), 4.38 (t, 4H, CH₂-O), 3.63 (t, 4H, CH₂-N), 1.93 (s, 6H, CH₃). ¹³C-NMR (CDCl₃, ppm): δ =167.2, 147.0, 136.1, 129.7, 125.2, 117.5, 111.8, 62.1, 49.6, 18.0. MS (*m/z*): calcd for C₁₈H₂₃NO₄ 317.16, found 318.90.

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 MgSO₄ 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. The mixture was diluted with ethyl acetate and washed with water. After drying the solution over anhydrous MgSO₄, 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. Methanesulfonyl 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 MgSO₄. The **7** was deprotected with 3.60 g of NaOH in a solution of methanol at room temperature. After being stirred for 1 h, the reaction mixture was diluted with water and extracted with ethyl acetate. The solution was dried over anhydrous MgSO₄. 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] benzoni-trile **8**. Yield: 87%. ¹H-NMR (CDCl₃, ppm): δ =7.33 (d, 2H), 6.77 (m, 2H), 3.76 (m, 4H, CH₂-O), 3.54 (m, 4H, CH₂-N), 2.0 (s, 2H, OH).

Dimer-CN monomer 9 was prepared by acrylation of **8** through a similar synthetic procedure as the **Dimer-Amino** monomer **2**. The resulting crude product was precipitated in methanol (100 mL), filtered and dried under a vacuum. Yield: 90.0%. ¹H-NMR (CDCl₃, ppm): δ =7.33 (d, 2H), 6.77 (d, 2H), 6.15 (s, 2H), 5.58 (s, 2H), 4.38 (t, 4H, CH₂-O), 3.63 (t, 4H, CH₂-N), 1.93 (s, 6H, CH₃). ¹³C-NMR (CDCl₃, ppm): δ =167.2, 150.3, 136.1, 125.8, 120.1, 115.8, 98.7, 61.5, 49.6,

18.0. MS (m/z): calcd for $C_{16}H_{22}N_2O_4$ 342.16, found 343.90.

Synthesis of Dimer-Ar (Monomer 10). The **Dimer-Ar** monomer was prepared by acrylation of 1,4-benzenedimethanol through a similar synthetic procedure to the **Dimer-Amino** monomer **2**. The reaction mixture was poured into water and extracted with diethyl ether. The resulting organic extract was washed with brine and dried over magnesium sulfate. The solvent was removed by a rotary evaporator and the crude product was purified by silica-gel column chromatography using ethyl acetate and *n*-hexane as co-eluants (1/4=v/v) to provide **Dimer-Ar 10**. Yield: 98.0%. $^1\text{H-NMR}$ (CDCl_3 , ppm): δ =7.38 (s, 4H), 6.18 (s, 2H), 5.58 (s, 2H), 5.20 (s, 4H), 1.93 (s, 6H, CH_3). MS (m/z): calcd for $C_{16}H_{18}O_4$ 274.31, found 275.80.

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 $C_{17}H_{24}O_6$ 324.16, found 325.90) was employed as a comonomer to improve the film property of the resulting polymer. The monomer solution was prepared by dissolving the functional monomers together with the **Trimer** in cyclohexanone. Prior to the polymer conversion, the monomer solution was filtered through a 0.2 μm -polymer filter to remove undissolved particles. 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, 50/50 wt%/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, 2,500 mJ/cm^2) for 3 min under a nitrogen atmosphere. This was followed by a post baking at 100 $^\circ\text{C}$ for 2 h under a vacuum. The thickness of the copolymer films ranged from 0.1 to 0.2 μm as measured with a Tencor Instruments Alpha-Step 200 profilometer.

Results and Discussion

The refractive index is a key feature in the application of optical polymers and significantly depends on their constitutional formula. We attempted to enhance the refractive index of an acrylic polymer by introducing polarizing groups into a monomer structure. Electron donating substituents on an aromatic ring such as amino group can predispose π -electrons to approach an electric field.¹⁸ This electron polarization also occurs when an electron withdrawing group is attached to a π -conjugated structure. Therefore, a dipolar structure with both donating and withdrawing groups should retard the propagation of light through electric field interaction. For a simple experiment, a dipolar monomer was derived with an acrylate functionality to be photo-polymerized. Thermosetting polymers are often advantageous for thin film applications requiring high thermal stability or durability, multi-layer processing, and mechanical hardness and toughness. Cross linkable photo-

polymers need at least two linkable acrylic groups in a monomer structure for the similar thermosetting properties. However, photo-polymerized homopolymers exhibited weak adhesion so that its film was easily removed from a silicon surface by thermal treatment in this research. Thus, the copolymer was schemed to study increasing refractive index increment of the dipolar diacrylate monomer. A copolymerized linear polymer was previously reported with a carbazole-containing acrylate to induce a high refractive index.²⁰ Triacrylate of 1,1,1-tris(hydroxymethyl)ethane (**Trimer**) was introduced as a comonomer inducing strong adhesion and high cross-linking efficiency. The aliphatic triacrylate polymerized to present a homopolymer of which the refractive index was the standard for evaluating the index increment by constituent polar monomers of a copolymer.

Identification of the Difunctional Methacrylate and the Polymer Structures. In order to synthesize difunctional methacrylate monomers, molecules containing two hydroxyl groups were formed and acrylation was carried out with a methacrylic anhydride and triethylamine base as a scavenger for any evolved acrylic acid. Amino attached diacrylate (**Dimer-Amine**) was prepared through acrylation of *N*-phenyldiethanolamine. The synthesis of the dipolar acrylate monomer (**Dimer-CN**) was achieved via several conventional synthetic procedures. Compound **3** from the substitution reaction of 4-fluorobenzaldehyde and diethanolamine was acetyl-protected to convert aldehyde to a cyano group. The conversion was accomplished through an oxime formation and the elimination of an oxime sulfonate intermediate. This provided high yields. The detailed synthetic schemes and reaction conditions are described in Figure 1. The prepared difunctional acrylates, which were liquid at ambient temperature, were compatible with the liquid **Trimer** and mixed with contents of various weights. The **Trimer** and **Dimer-Ar** in Figure 1 were prepared through acrylations of 1,1,1-tris (hydroxymethyl) ethane and 1,2-dihydroxymethylbenzene, respectively. All of the monomers were structurally confirmed by $^1\text{H-NMR}$. $^{13}\text{C-NMR}$ spectra of **Dimer-Amino** and **Dimer-CN** revealed resonances corresponding to all carbons of the given structure. The electron-withdrawing cyano group induced a peak shift of a benzene carbon to a higher field. The peaks at 117.5 and 120.1 ppm are attributed to the amino-attached carbon of the **Dimer-Amino** and **Dimer-CN**, respectively. The cyano-attached carbon of **Dimer-CN** was observed at 98.7 ppm. IR spectral analysis evidently presented characteristic bands of the cyano group at 2216 and 543 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 Figures 2 and 3 indicate the absorption bands at 1625-1635 cm^{-1} specifying

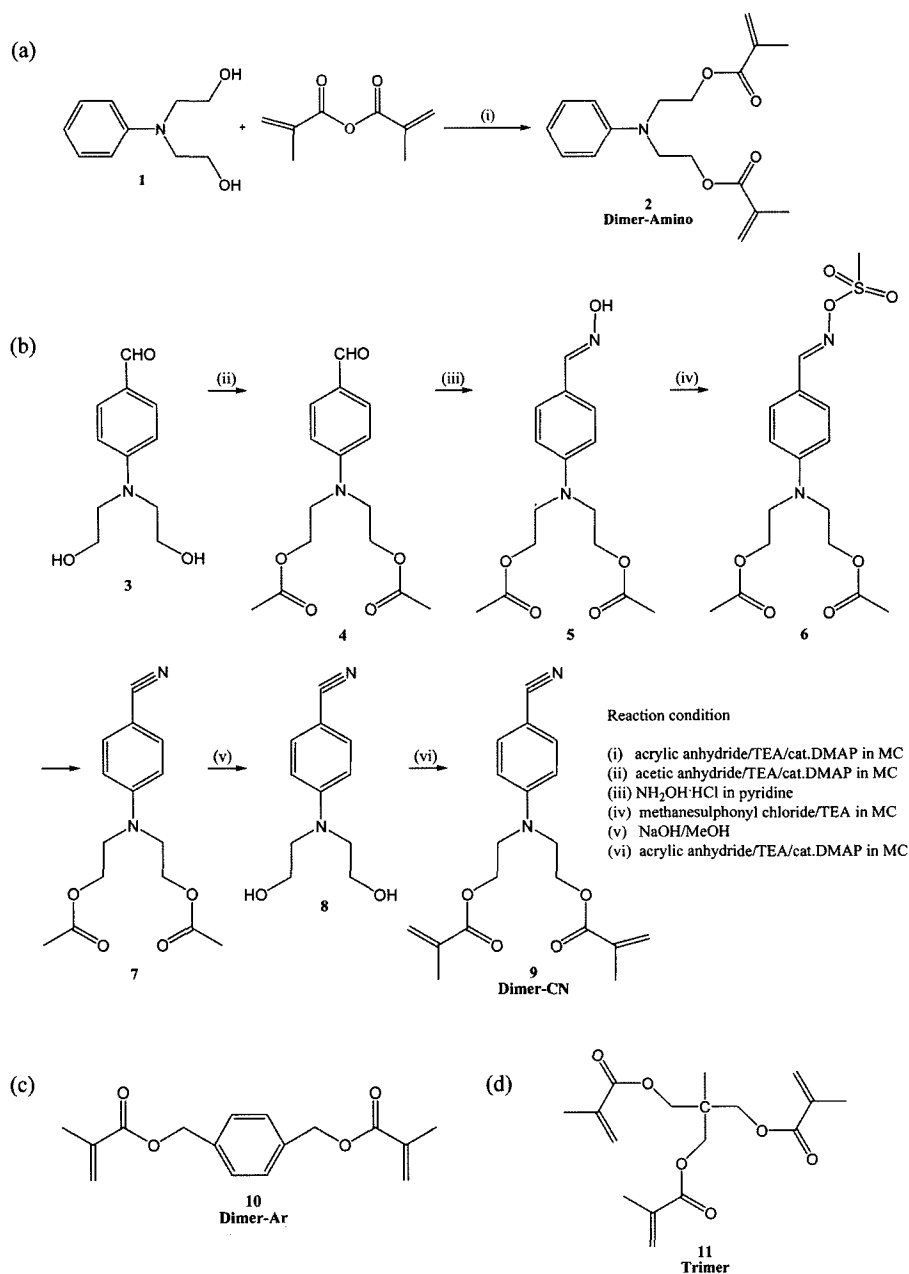


Figure 1. Synthesis and structure of (a) Dimer-Amino, (b) Dimer-CN, (c) Dimer-Ar, and (d) Trimer.

the existence of methacrylic groups. The sharp band at $1700\text{--}1750\text{ cm}^{-1}$ is caused by the stretching vibrations of the $\text{C}=\text{O}$ group. The characteristic bands at $1150\text{--}1350\text{ cm}^{-1}$ correspond to the stretching vibrations of the $\text{C}-\text{O}$ of ester. The complicated absorption bands at $802\text{--}815\text{ cm}^{-1}$, including the $\text{C}=\text{C}$ twist mode of the acrylic group in each monomer, were simplified after polymerization. The disappearance of the acrylic $\text{C}=\text{C}$ stretching bands at $1625\text{--}1635\text{ cm}^{-1}$ of the monomers were also observed under UV illumination. The peak at $1625\text{--}1600\text{ cm}^{-1}$ is assigned to the characteristic stretches of aromatic $\text{C}=\text{C}$ bond for Dimers. For the effi-

cient polymerization of the monomers, the UV polymerization was carried out using a photo initiator. Furthermore, the illuminating period (3–20 min) was prolonged to attain more coupling of the acrylate groups. However, any structural changes occurring in the few acrylates were undetectable with IR spectral analysis which showed nearly the same absorption results. Because polymer yellowing occurs after extended exposure to light, all polymerizations were completed within a 3 min illumination period.

Optical Property. Organic optical materials such as dipolar molecules, highly conjugated molecules, and metal con-

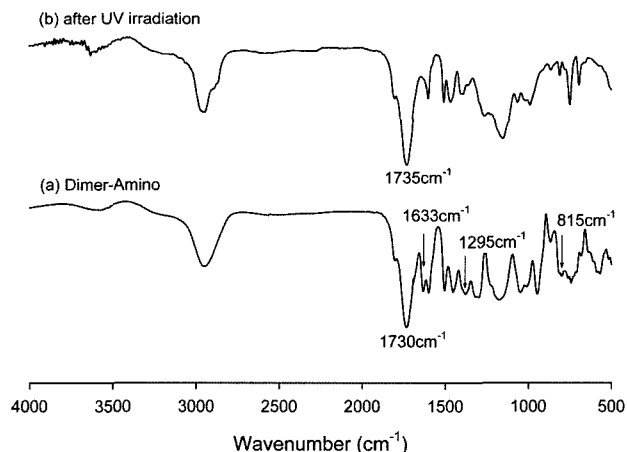


Figure 2. FT-IR spectra of (a) Dimer-Amino and (b) Dimer-Amino/Trimer (50/50 wt/wt%) copolymer films after UV illumination.

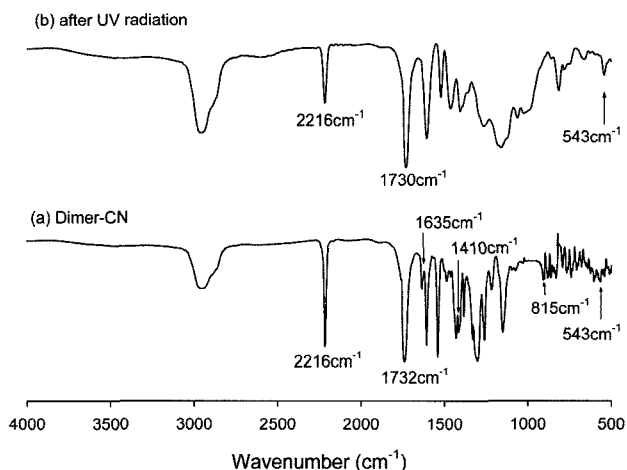


Figure 3. FT-IR spectra of (a) Dimer-CN and (b) Dimer-CN/Trimer (50/50 wt/wt%) copolymer films after UV illumination.

taining molecules sometimes exhibit a distinctive color due to the inevitable electronic energy levels or their instability.^{16,17} The prepared acrylic polymers with polar groups in

this research were transparent when exposed to wavelengths longer than 500 nm. The UV absorption spectra of **Dimer-CN** presented λ_{max} of 300 nm and $\lambda_{cut-off}$ of 500 nm in chloroform solvent. The copolymer of **Dimer-CN** broadened to some extent in cut-off wavelength as compared to the monomer. Nevertheless, a film transparency of more than 90% was measured at longer wavelengths than 500 nm.

The refractive index of the polymer film was measured with a prism coupling method using TE-guided light (n_{TE}) and TM-guided light (n_{TM}).²¹ The refractive index of an organic polymer is determined, to a large extent, by the combined polar groups such as fluorine, bromine, and oxygen. Monomers having cyano and amino polarizing groups attached are expected to increase the index of the corresponding polymer. Table I summarizes the refractive indices of homo and copolymer films. The indices for homo polymers of **Dimer-Ar**, **Dimer-Amino**, and **Dimer-CN** were estimated through a linear plotting of comonomers with varying contents. Generally, the refractive index of a copolymer is determined with numeric averaging of the refractive index of each homopolymer, especially when two acrylic monomers are combined. The comonomer contribution for the refractive index is known to be almost linearly proportional to the compositional weight ratio.²² The homopolymer of **Trimer** was measured with the indices of 1.488, 1.490, and 1.499 at 1550, 1330, and 850 nm, respectively. Both n_{TM} and n_{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. Generally, the refractive indices of the copolymer can be controlled by changing parameters such as components used, composition ratios, and UV curing time. As expected, the dipolar structure was more effective in attaining a higher refractive index than a simple polar structure or a structure with an aromatic group attachment. Figure 4 shows linear fits of refractive index of copolymers toward

Table I. Refractive Index (n) of Homo and Copolymer Films^a

Specimens (wt/wt%)	n_{TE} [n_{TM}] ($\lambda=1550$ nm)	n_{TE} [n_{TM}] ($\lambda=1330$ nm)	n_{TE} [n_{TM}] ($\lambda=850$ nm)
Trimer	1.488	1.492	1.498
Dimer-Ar/Trimer (50/50)	1.510 [1.496]	1.513 [1.498]	1.518 [1.508]
Dimer-Amino/Trimer (50/50)	1.522 [1.516]	1.526 [1.518]	1.531 [1.525]
Dimer-CN/Trimer (50/50)	1.536 [1.516]	1.539 [1.517]	1.546 [1.523]
Dimer-Ar ^b	1.534	1.536	1.538
Dimer-Amino ^b	1.554	1.558	1.564
Dimer-CN ^b	1.585	1.588	1.595

^aThe measurement of n was performed with TE and TM mode-guided lights. ^bPredicted refractive index from the copolymer films measurement.

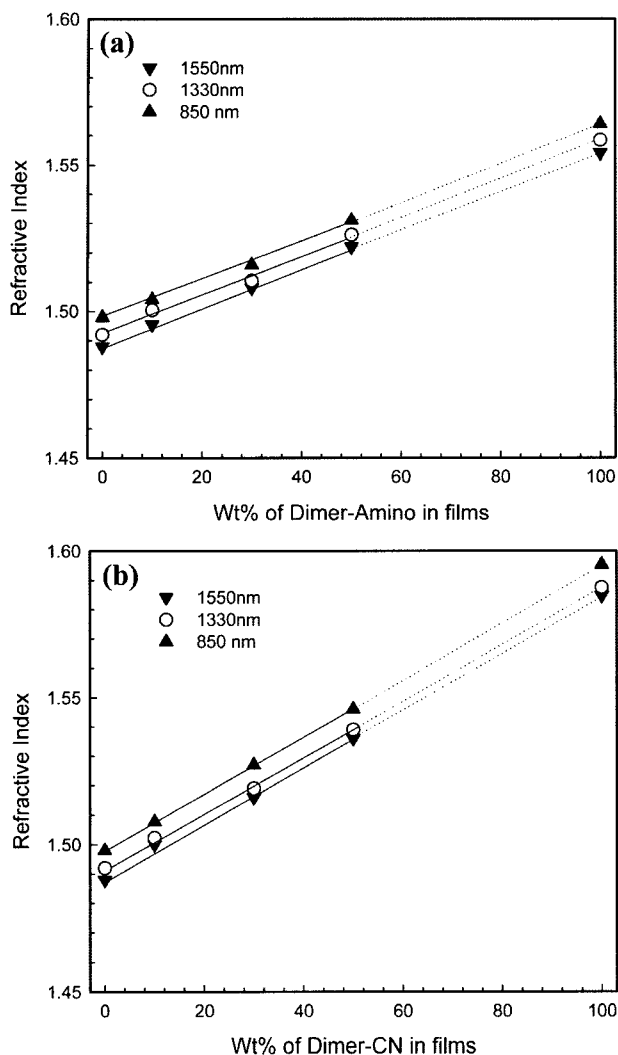


Figure 4. Refractive index (n_{TE}) of polymers according to monomer content for (a) Dimer-Amino/Trimer copolymer film and (b) Dimer-CN/Trimer copolymer film. The solid curves represent the best linear fits to the data and the dashed curves represent the expected behavior of Dimer-Amino and Dimer-CN homopolymers.

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. Figure 5 shows the refractive index dispersion of

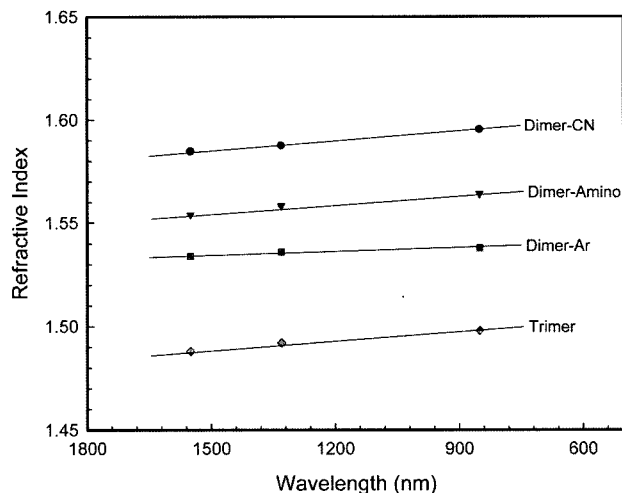


Figure 5. Refractive index (n_{TE}) dispersion of homopolymers vs. wavelengths.

the homopolymers toward wavelengths and the plots clarify these results. The refractive index was easily controlled by blending monomers. Because poly(methyl methacrylate) is well-known as a cladding material with a refractive index of 1.490 (at 1300 nm),²³ the copolymers developed in this research are promising for use as the core material of a waveguide.

Thermal Property. The softening temperature of a polymer is an essential for optical applications because it is closely associated with the processing and operating conditions of related devices. Thermal stability has been issued for the thermosetting polymer and enhanced with high crosslinking density. Unreacted monomers may cause thermal and chemical instability and change physical properties such as, glass transition temperature (T_g), thermal degradation temperature (T_d), hardness.²⁴ Photopolymerization of acrylic monomers is achieved with UV illumination and accelerated with radical initiators. The monomer solution containing 0.5% IRG819 was cast on a silicon substrate in this research, and hardened with UV light and thermal exposure. The resultant polymer was removed for DSC and TGA analysis. Table II contains several polymer T_g s determined from a DSC thermogram. The copolymers exhibited a higher T_g than the **Trimer** homopolymers. The transition was viewed at around 104 °C. The broad endothermic behaviors around 112–141 °C shown in Figure 6 correspond to the T_g of the copolymers. It is known that the T_g of thermosetting polymers increases with the conversion of reactive functions.²⁵ The high content of triacrylate was expected to increase the T_g of the copolymers because it is often introduced as a crosslinking agent. However, the T_g of the copolymer gradually decreased with an increasing content of the triacrylate. Increasing the content of the diacrylates from 30 to 50% led to a rise of the T_g from 125 to 127 °C for **Dimer-**

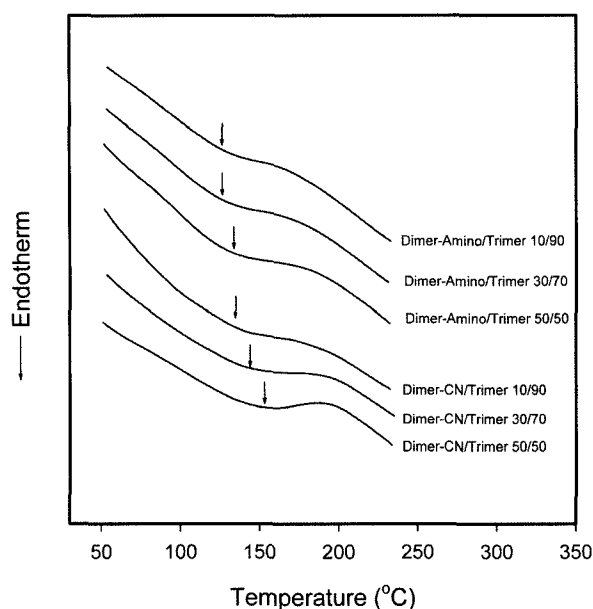


Figure 6. DSC thermograms of Dimer-Amino/Trimer and Dimer-CN/Trimer polymer films.

Amino and 129 to 141 °C for **Dimer-CN**. It was thus concluded that the increased T_g of the copolymer was due to the restricted polymer chain mobility, which was caused by the rigid aromatic ring of the diacrylates.

The thermal decomposition behavior of the homo and copolymers were investigated by TGA by heating them at a rate of 10 °C/min under a nitrogen atmosphere. This is illustrated in Figure 7. As the copolymers showed a slight weight loss at lower temperatures, diacrylate structures are somewhat unstable relative to the **Trimer** structure. The loss of amino and cyano groups was the main reason for the weight loss of the copolymers and apparently compared with **Dimer-Ar** in Figure 7. The copolymers showed a similar degradation trend above 200 °C. The abrupt decomposition of the alkyl chain and aromatic groups occurred over 350 °C. For the **Trimer** film, no appreciable weight loss was observed at temperatures below 400 °C. The final residual weights of the **Trimer** homopolymer, **Dimer-Amino** copolymer, and **Dimer-CN** copolymer were 8.1, 7.0, and 4.3 wt%. The **Dimer-CN** copolymer (50/50 wt/wt%) exhibited a higher 10%- and 50%-weight loss temperature ($T_{10\%}$ and

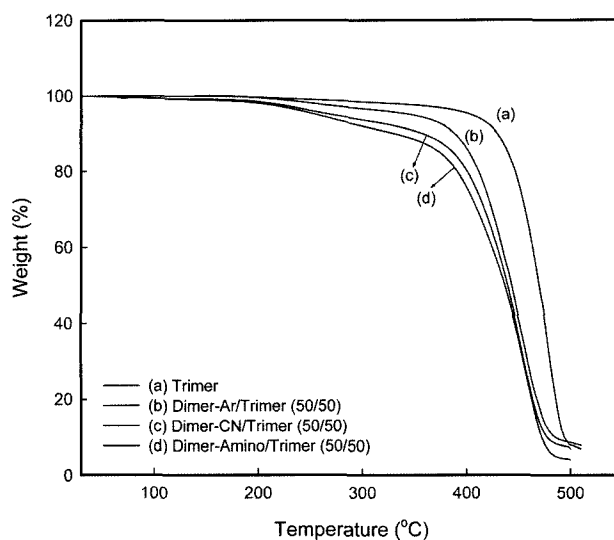


Figure 7. TG thermograms of Dimer/Trimer (50/50 wt/wt%) copolymers and Trimer films.

$T_{50\%}$) than the **Dimer-Amino** copolymer. The relative thermal stabilities of the copolymers can be assessed by their integral procedural decomposition temperature (IPDT), as proposed by Doyle.²⁶ The calculated IPDT values are given in Table II. The IPDT of the **Trimer** homopolymer was higher than both of the copolymer films. IPDT results of two copolymers indicate that the thermal stability of the **Dimer-CN** copolymer is better than that of the **Dimer-Amino** copolymer.

Conclusions

We provided novel photocurable diacrylate monomers yielding a high refractive index of relating optical polymer. Attaching amino and cyano phenyls mainly contributed to increasing the refractive index. As expected, the resulting copolymer film shows a refractive index that increases with the amount of Dimers. From the comparison of polymers containing **Dimer-CN** and **Dimer-Amino**, a dipolar structure was shown to be more effective in increasing the refractive index than a polar structure. The refractive indices of **Dimer-CN** homopolymer were 1.585, 1.588, and 1.595 at 1550, 1330, and 850 nm, respectively. The indices

Table II. Glass Transition Temperature and Thermal Stability of Homo and Copolymer Films

Specimens (wt/wt%)	T_g (°C)	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	Residue at 550 (wt%)	A^*	K^*	IPDT ^a (°C)
Homopolymer (Trimer)	104	428.5	468.0	8.1	0.917	1.196	502.4
Dimer-Ar/Trimer (50/50) copolymer	113	386.4	442.5	8.8	0.861	1.113	480.4
Dimer-Amino/Trimer (50/50) copolymer	127	329.0	435.6	4.3	0.826	1.054	439.2
Dimer-CN/Trimer (50/50) copolymer	141	348.8	439.3	7.0	0.843	1.082	468.2

^aIPDT (°C) = $A^*K^*(T_f - T_i) + T_i$ (A^* : ratio of area under the curve and the total area of the thermogram, K^* : coefficient of A^* , T_i and T_f : initial and final temperatures).

of the copolymers were correlated with the monomer content and linearly increased with the increasing content of constitutive diacrylates. Since the homopolymers of the polar and dipolar diacrylates form brittle thin films and exert weak adhesion on a silicon surface, the use of an aliphatic comonomer is more desirable for thin film applications. In addition to increasing the refractive index, these diacrylates raised the glass transition temperature of the copolymers. Dipolar diacrylate copolymers exhibited better thermal stability, a higher degradation temperature and a higher IPDT value than the polar diacrylate copolymer.

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