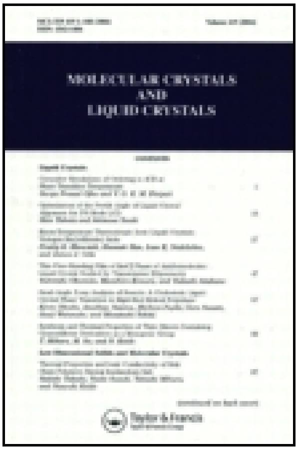

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Synthesis of Photocurable Fluorenylidene Diacrylate for Optical Application

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We reported on synthesis and characterization of fluorenylidene diacrylate, which has high refractive index and low optical loss for optical application. Polymer film was easily prepared by spin-coating a solution of monomer with photoinitiator (Irgacure 369) and cured under 365 nm UV light illumination. This film has a good chemical/mechanical resistance as well as a high thermal stability. The refractive index of this film at 830 nm was obtained as 1.5948 and 1.5947 for TE and TM polarization, respectively. Also, this film shows extremely low birefringence of 0.0001 and very low propagation loss of 0.08 dB/cm at 830 nm for TE polarization. It was demonstrated that these newly synthesized fluorenylidene diacrylate was promising candidate for optical waveguide materials.

Keywords: high refractive index; low birefringence; low propagation loss; optical waveguide; photocurable

INTRODUCTION

In recent years, polymer optical waveguides have attracted much attention for use in optical interconnects in devices and for optical communications in the excess network and home network areas [1–3], because polymeric optical waveguides have been ease of manufacture at low temperature and low cost of processing [4].

For polymer waveguide materials to be used for optical waveguides, the following properties should be considered. Low propagation losses

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at the optical communication wavelengths, high thermal stability to provide compatibility with high-performance electronic device fabrication, controllability of refractive index for the easy control, smaller birefringence and adhesion to a substrate [5].

Hydrocarbon polymers have high optical loss in the near-infrared region resulting mostly from the second harmonic vibrational absorption of C-H bond, and can be decreased by substituting hydrogen with heavy atoms such as deuterium, fluorine, and chlorine atoms [6]. Recently, the low loss polymeric devices were fabricated using fluorinate acrylate and fluorinated polyimides. Perfluorinated polymer materials are good candidate materials for the optical waveguide devices due to their excellent thermal stability, mechanical properties, low moisture absorption, and low inherent optical absorption at the near-infrared region [7,8]. Unfortunately, these materials did not show high refractive index. Tunneling light occurs when the electromagnetic waves undergo total internal reflection and thus cannot exit the waveguide until it reaches the end [9].

In the previous paper, we described the feasibility of newly synthesized photocurable phosphine oxide type diacrylate monomer for holographic data storage system and this monomer showed very high diffraction efficiency of 93.5% and low shrinkage ($<0.5\%$) [10]. So, we have a lot of experiences to tune the refractive index and thermal stability of photocurable acrylic monomers and we intend to develop photocurable monomer system having high refractive index, thermal stability, and low loss. It is important to be able to control refractive index of a polymer, which is a key technique for the fabrication of optical components using the polymers [11]. The UV-induced polymerization is attractive because of its simplicity and low cost [12]. In the studies described below, we have developed diacrylic monomer containing fluorenyl group and studied on the photophysical chemistry of this monomer for application to optical waveguide materials.

EXPERIMENTAL

Materials

4-4′-(9-fluorenylidene)diphenol, 2-(2-Chloroethoxyethanol), acryloyl chloride, triethylamine, methylene chloride, and other reagents were purchased from Aldrich Chemicals and used without further purification. Photoinitiators were kindly donated from CIBA-Geigy Corp.

Synthesis of the Optical Waveguide Materials

Synthesis of Compound 1

The reactants 4-4′-(9-fluorenylidene)diphenol (2.00 g, 5.71 mmol), potassium carbonate (1.89 g, 13.6 mmol), potassium iodide (0.47 g, 2.83 mmol) were placed under in a flame-dried two neck flask containing a magnetic stirrer and a condenser was added 30 ml of DMF and chloroethoxyethanol (1.70 g, 13.6 mmol) was slowly added and the reaction mixture was heated to 90°C. The reaction was allowed to proceed for about 9 hr after which it was stopped and cooled to room temperature. After filtration, extraction was carried out with use of ethyl acetate. The combined organic layers were washed with water (3 × 100 ml) and then dried over anhydrous magnesium sulfate. Filtration followed by solvent removed. The crude compound **1** was also purified by column chromatography using the ethyl acetate to produce transparent oil with 85% yield.

^{1}H NMR ($CDCl_3$, ppm) δ 7.73 (2H, d), 7.37–7.23 (6H, m), 7.11–7.08 (4H, d), 6.75–6.72 (4H, d), 4.04–4.01 (4H, t), 3.80–3.77 (4H, t), 3.76–3.70 (4H, t), 3.69–3.60 (4H, t), 2.43 (2H, s).

Synthesis of Compound 2

To a 100 ml round-bottom flask, compound **1** (3.00 g, 5.30 mmol) and 50 ml of dichloromethane were added acryloy lchloride (1.93, 21.2 mmol). The stirred mixture was cooled to 0°C by ice water and triethylamine (1.62 g, 15.9 mmol) was slowly added. The reaction mixture was warmed to room temperature and then stirred for 3 hr. The organic layers were washed with water (3 × 100 ml) and extraction was carried out with use of chloroform, and then dried over magnesium sulfate. Filtration followed by solvent removed. Further purification was carried out by short column chromatography using the mixture of ethyl acetate and hexane (1:1) to produce compound **2** as transparent oil with 92% yield.

^{1}H NMR ($CDCl_3$, ppm) δ 7.75–7.73 (2H, d), 7.37–7.31 (4H, t), 7.28–7.25 (2H, d), 7.11–7.10 (4H, d), 6.77–6.74 (4H, d), 6.38–6.37 (2H, d), 6.17–6.07 (2H, t), 5.78–5.77 (2H, d), 4.33–4.30 (4H, t), 4.07–4.04 (4H, t), 3.83–3.76 (8H, m); ^{13}C NMR ($CDCl_3$, ppm) δ 166.55, 157.87, 152.18, 140.34, 138.78, 131.54, 129.57, 128.65, 128.14, 127.81, 126.45, 120.56, 114.64, 70.06, 69.64, 67.75, 64.59, 64.09.

Instruments

^{1}H-NMR and ^{13}C-NMR spectra were obtained from a BRUKER ARX-300 spectrometer at 300 MHz and 75 MHz, respectively. Differential

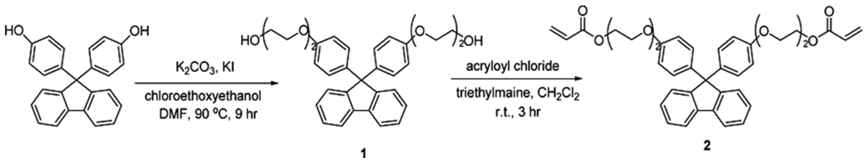
Scanning Calorimetry (DSC) and thermal gravimetric analysis (TGA) were performed on TA instruments DSC-2910 and TGA-2950, respectively. The temperature was raised from 30 to 500°C at heating rate of 10°C/min in nitrogen atmosphere with a gas flow rate of 100 ml/min. The rate of polymerization and conversion were determined by Differential Scanning Calorimetry (DSC-7, Perkin Elmer) equipped with 532 nm monochromatic light source (35 mW) and optical compartments. Refractive index and propagation loss of the polymer films were measured with a prism coupler (SAIRON Co., SPA-4000). Thickness of the films was measured by using a surface profiler (Tencor Ins., Alpha-Step 500).

RESULTS AND DISCUSSION

As fluorenylidene diphenol is well-known as a very high refractive index and high thermal stability, this material has been used as a good intermediate for various optical applications. As this reason, we incorporated fluorenylidene diphenol moiety to our photocurable monomer system. Compound **1** was synthesized via nucleophilic substitution of 4-4′-(9-fluorenylidene)diphenol with 2-chloroethoxyethanol. The fluorenylidene diacrylate compound (**2**) was easily prepared by the reaction of **1** with acryloyl chloride in methylene chloride with 92% yield. Synthesis of the monomer is shown in Scheme 1. The compound was identified by spectroscopic methods, such as ^{1}H and ^{13}C NMR spectroscopy. Compound **2** showed high refractive index of 1.595 with a probe beam of 830 nm, which is beneficial to achieve large refractive index modulation and ultimately to high diffraction efficiency.

The rate of photopolymerization of photopolymer film was studied by using photo-DSC. Figure 1 shows the rate of polymerization (a) and double bond conversion (b) vs. time in polymerization system. The rate of polymerization (Rp) was monitored by measuring the heat flow ($\mathrm{d}H/\mathrm{d}t$) evolved in highly exothermic reaction according to the Eq. (1)

$$Rp = (\mathrm{d}H/\mathrm{d}t)/\Delta H_0 \tag{1}$$



SCHEME 1 Synthesis of compound **2**.

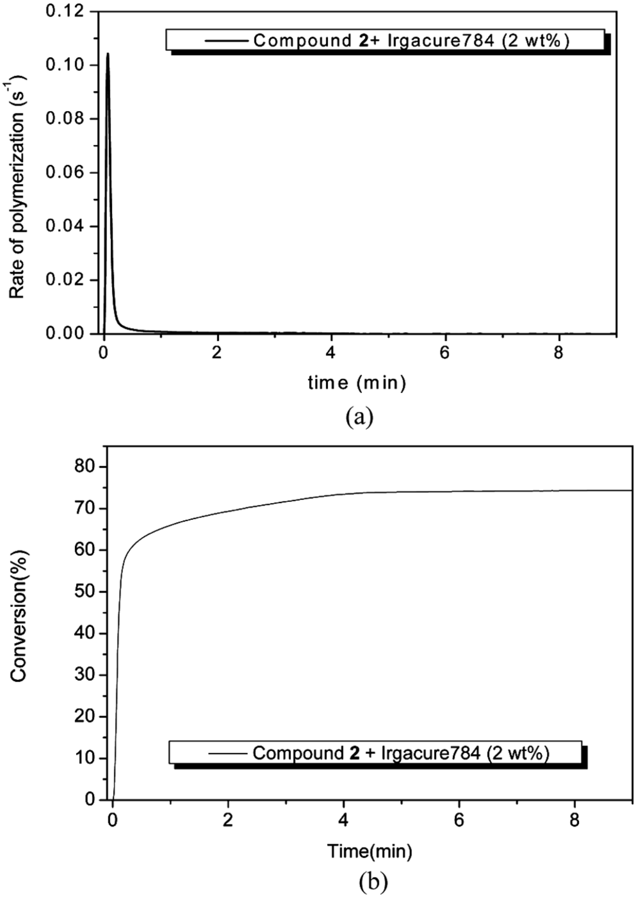


FIGURE 1 (a) Rate of photopolymerization (b) conversion of compound **2**.

$$C = \Delta H_{\mathrm{t}}/\Delta H_{\mathrm{T}} \tag{2}$$

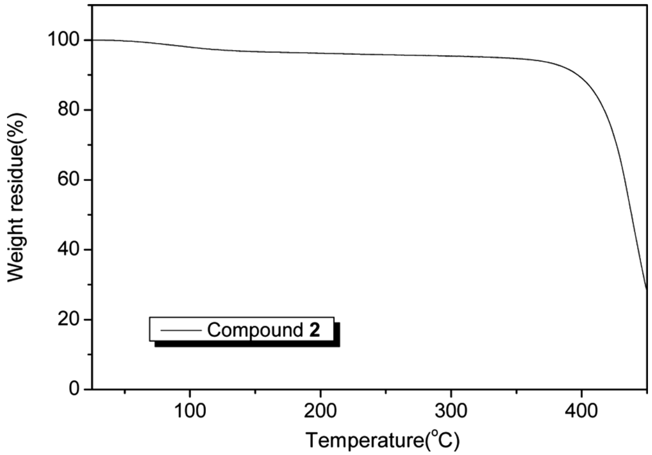
where ΔH_0 is the theoretical heat evolved for complete conversion, ΔH_{t} is the total heat of reaction evolved by time t, and ΔH_{T} was calculated as 86.17 kJ/mol [13]. The conversion of double bond could be calculated by the Eq. (2).

Figure 1(a) shows the plot of the polymerization rate that irradiation time during the photocuring. The photoreaction of the photocurable solution was fast, and the conversion of monomer to polymer reached about 75% within 10 sec.

Thermal stability is also an important issue for the optical polymer. As shown the thermal gravimetric analysis curve in Figure 2, the fluorenylidene monomer exhibited high thermal stability over 400℃.

Photocurable fluorenylidene solution was prepared by mixing propylene glycol *mono*-methyl ether acetate (50 wt%), initiator (Irgaqure 369), and compound **2**. The solutions were filtered through a syringe with a 0.2 μm PTFE membrane, after spin coated on the silicon wafer having 200 nm SiO_2 cladding layer with a spin speed of 500 rpm for 10 s and 1000 rpm for 20 s. Spin-coated film was then irradiated with 365 nm UV light (80 mW/cm^2) for 5 min, after drying at 120℃ for 1 hr.

The refractive index and propagation loss were measured by prism coupler as shown in Figure 3. Prism coupling is a very accurate and reliable technique to measure the thickness, refractive indices, and propagation loss of films. Laser light is coupled into the waveguide layer through the air gap between the prism and the film. The coupling phenomenon is observed at certain angles. When the diffracted beam from the prism is viewed, at those coupling angles, a decrease in the light intensity is observed as a vertical dark line. After measuring the coupling angles for all the available nodes, the thickness and the indices of the waveguide layer may be obtained. To determine the propagation loss, the prism coupling method also was used according to the waveguide length. This method uses a prism to couple the light into the waveguide and detectors, to measure the reflective mode position and transmitted intensity [14]. The optical loss of the



FIGUER 2 Thermogram of photocurable monomer.

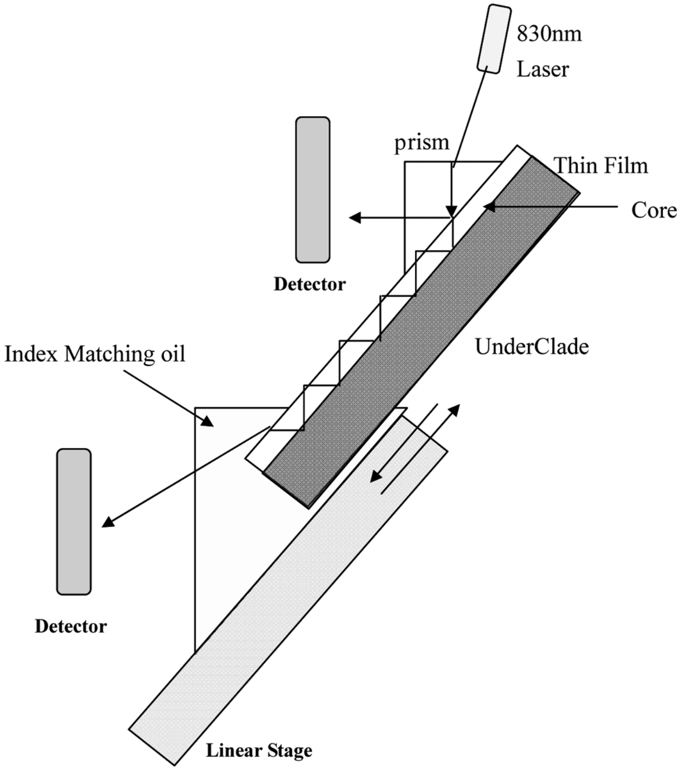
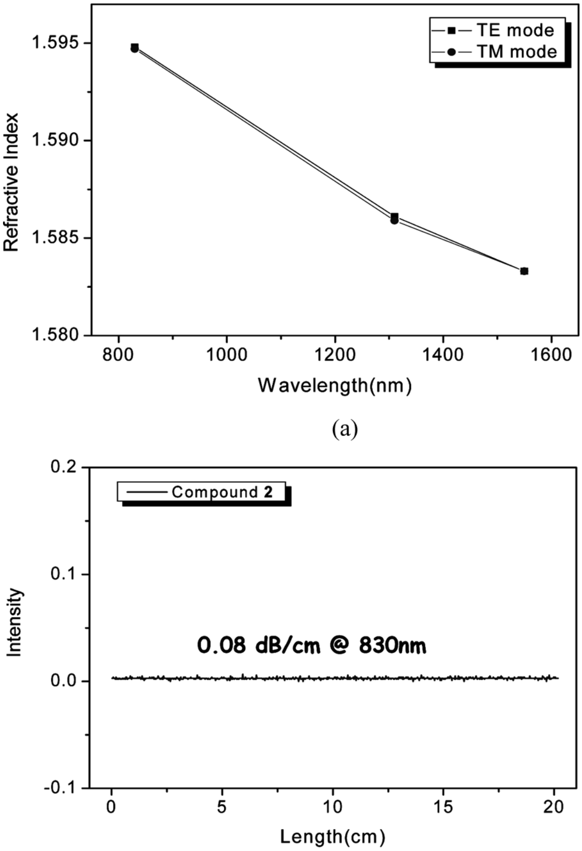


FIGURE 3 Prism couple setup.

photo-cured film was determined by immersing the film into the slightly higher refractive index matching oil than that of the film.

Figure 4(a) shows TE mode refractive indices of polymer films are 1.5948, 1.5861, and 1.5833 at 830 nm, 1310 nm, and 1550 nm wavelength, respectively. For TM polarization condition, refractive indices can be found as 1.5947, 1.5859, and 1.5833 at 830 nm, 1310 nm, and 1550 nm wavelength, respectively. From this result, we can confirm photocured film of compound **2** has extremely low birefringence ($\Delta n = n_{\mathrm{TE}} - n_{\mathrm{TM}}$) around 0.0001. Also, we can determine the propagation loss of this film is 0.08 dB/cm at 830 nm by calculation of the slope from the transmitted power of the slab waveguide vs. waveguide length curve in Figure 4(b).

In conclusion, photocurable fluorenylidene diacrylate monomer (**2**) was synthesized as high yield and thick film using this monomer was fabricated by applying a simple photocuring process. The



(a)

(b)

FIGURE 4 (a) Refractive indices and (b) propagation loss of photocured film at 830 nm.

refractive indices of this film were obtained under 830 nm laser light as 1.5948 and 1.5947 for TE and TM polarization, respectively. Also, this film shows extremely low birefringence of 0.0001 and very low propagation loss of 0.08 dB/cm for TE polarization. It was demonstrated that these newly synthesized fluorenylidene acrylate compound was promising candidate for optical waveguide materials.

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