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Fluorinated Polymers Derived from Tetrafunctional Cyclic Siloxanes Possessing Low Optical Loss and High Thermo-Optic Property

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We have prepared UV-curable fluorinated polymeric materials based on tetrafunctional cyclic siloxanes substituted with perfluoropolyether structure in order to have low optical loss, low birefringence, high thermo-optic coefficient, and good thermal stability. Perfluoropolyether structure with hydroxyl as one end and allyl as the other was prepared by reaction between fluorinated diols and allyl bromide. Then it was reacted with cyclic siloxane with platinum catalyst in a fairly high yield. The terminal hydroxyl was converted to acryl by reaction with acryloyl chloride. Transparent and stable films were obtained from the fluorinated monomers by UV irradiation. The photo-cured film was found to be thermally durable up to 300°C, where 2% weight loss occurred. The polymer films showed $-1.59 \times 10^{-4}/K$ *of thermo-optic coefficient, 0.0002 of birefringence, and 0.121 dB/cm of optical loss, which were measured by prism coupler at 1550 nm of laser source.*

Keywords Birefringence; fluorinated polymers; optical loss; tetrafunctional siloxanes; thermo-optic coefficient

1. Introduction

Silica-on-silicon has been a leading technology in the optical communication network because of its low optical loss and high thermal stability [1]. However, silica requires complicated and expensive fabrication processes. Moreover, its small thermo-optic coefficient of $10^{-5}/K$ makes it difficult to achieve some types of optical devices such as optical switches and a thermally tunable wavelength filter. These limitations of silica have drawn the researchers' interest toward polymeric materials, because they exhibit 10 times higher thermo-optic coefficient and are able to easily tune the properties by structural modification [2–5].

However, the polymers have critical weaknesses in optical loss, thermal stability and chemical resistance. Hydrocarbon based polymeric materials contain C-H bonds which absorb strongly in the 1550 nm wavelength range that is commonly used in the telecommunication system, causing the devices made from such materials to have

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Address correspondence to Dong Wook Kim, Advanced Materials Division, Korea Research Institute of Chemical Technology 100 Jang-dong, Yusong-ku, Daejeon 305-600, Korea. E-mail: dongwook@krict.re.kr high optical loss. Fortunately, the optical loss could be greatly reduced by replacing the C–H bonds with C–F, which shifts the vibrational overtone absorption to longer wavelength. Such fluorination is also helpful for enhancing durability of the materials due to the peculiar characteristics given by the fluorine presence, such as hydrophobicity, chemical stability, weathering resistance, and water impermeability [6–8].

Thermal stability is also required for optical polymeric materials to withstand the harsh condition involved with the fabrication process. Aromatic polymers such as polyimides and poly(arylene ethers) have been attempted to address the stability issue, but the aromatic ordering associated with the aromatic-rich polymers have inevitably resulted in high birefringence and high polarization dependence loss [9]. Instead of aromatic structures, introduction of crosslinked network by thermal or photo method is another useful strategy to achieve the materials' stability as well as a low birefringence. For this purpose many classes of materials such as perfluorocyclobutyl polymers, styrene or acetylene-ended polymers, and fluorinated polyacrylates have been studied. Among them, the multifunctional fluorinated acrylates are highly interesting due to their several advantages including 1) low optical loss, 2) solvent-free process, 3) a precise control of refractive index by copolymerizing with the appropriate monomers, and 4) high production yield and patternability via photo-crosslinking process [9].

In this work, a novel multifunctional fluorinated acrylate was synthesized by attaching acrylate-terminated perfluoroether onto cyclic tetrasiloxane. Siloxane materials have been attempted in numerous works for optical devices due to high optical transparence at telecom wavelength, thermal and chemical stability, and flexibility. Cyclic tetrasiloxane was chosen in this work to utilize those unique properties as well as to make multifunctional fluorinated acrylates. High quality films were easily obtained by UV curing method and then their optical and thermal properties were studied.

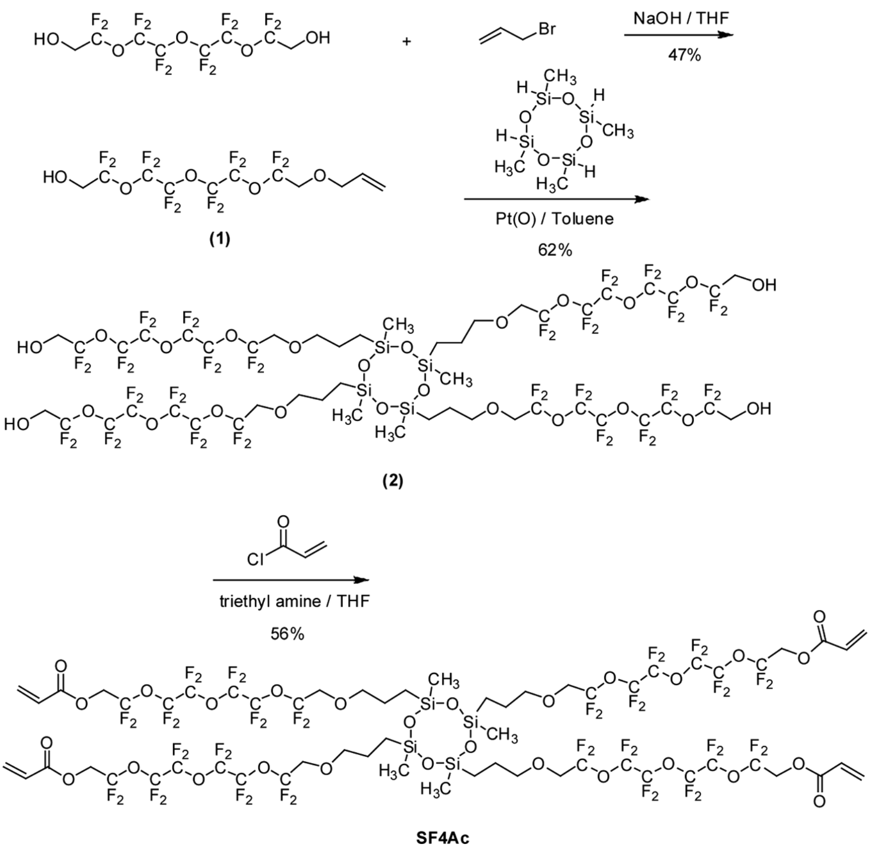
2. Experimental

Materials

Fluorinated tetraethylene glycol was purchased from Exfluor Research Co. and used as received. 2,4,6,8-Tetramethyl cyclotetrasiloxane was obtained from Aldrich Chem. Co. and acryloyl chloride was purchased from TCI. Irgacure369 was obtained from Ciba Co. and was used as a photo-initiator. Multifunctional perfluoroether acrylate (SF4Ac) was synthesized as shown in Scheme 1 and the detailed procedures are as follows.

Synthesis of Compound (1)

NaOH (24.38 mmol) was added into the solution of fluorinated tetraethylene glycol (10 g, 24.38 mmol) in anhydrous THF under an atmosphere of dry argon at room temperature. The mixture was stirred for 15 min and then allyl bromide (24.38 mmol) was added slowly. After the mixture was stirred for 15 h at room temperature, solid particles were filtered out and the solvent was removed in vacuo. The remaining organic layer was washed with water several times. After drying it over $MgSO_4$ and evaporating the solvent, the crude product was purified by column chromatography



Scheme 1. Synthesis of the fluorinated monomer, SF4Ac.

(ethyl acetate/hexane = 1/5) to produce a colorless liquid in 47% yield: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.94–5.81 (m, 1H), 5.35–5.26 (m, 2H), 4.16 (d, $J = 5.7$ Hz, 2H), 3.94–3.89 (t, 2H), 3.85–3.79 (t, 2H), 2.88 (–OH, 1H).

Synthesis of Compound (2)

Into a 250 ml 3-neck flask was placed a toluene solution of 2,4,6,8-tetramethyl cyclotetrasiloxane (3.12 mmol) and a 0.1 wt% Pt(0) catalyst (Pt(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex). To the vigorously stirred mixture, a 20 ml toluene solution of compound (1) (6.17 g, 13.7 mmol) was added dropwise under a dry argon atmosphere. The reaction mixture was heated to reflux overnight. The reaction solution was cooled to room temperature and activated carbon was added and stirred for 12 h. The activated carbon was filtered off and the solvent was evaporated. The crude product was purified by a column chromatography (ethyl acetate/hexane = 1/3) to produce a colorless liquid in 62% yield: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.87–3.80 (t, 8H), 3.75–3.68 (t, 8H), 3.51–3.46 (t, 8H), 2.59 (–OH, 4H), 1.59–1.49 (m, 8H), 0.48–0.42 (m, 8H), 0.00 (s, 12H).

Synthesis of SF4Ac

Compound (2) (1.86 mmol) and triethylamine (8.38 mmol) were dissolved in dry THF under an atmosphere of dry argon. Acryloyl chloride (8.38 mmol) was slowly added into the solution at 0°C and then the reaction mixture was heated to reflux for 15 h. After the reaction was completed, the resulting mixture was filtered and the solvent was evaporated. The organic residue was washed with water several times. After drying over $MgSO_4$, the organic layer was purified by column chromatography (ethyl acetate/hexane = 1/3) to produce a colorless liquid in 56% yield: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.47–6.41 (d, J = 17.1 Hz, 4H), 6.14–6.04 (q, 8H), 5.92–5.87 (d, J = 10.5 Hz, 4H), 4.49–4.43 (t, 8H), 3.74–3.68 (t, 8H), 3.50–3.45 (t, 8H), 1.58–1.49 (q, 8H), 0.47–0.43 (t, 8H), 0.00 (s, 12H): ^{13}C NMR (300 MHz, $CDCl_3$) δ, 164.16, 132.80, 126.65, 124.91, 123.65, 122.68, 121.44, 120.45, 119.23, 116.96–116.37, 114.99–113.80, 112.38–111.87, 75.24, 69.87–69.39, 61.75–61.21, 23.11, 12.74, −1.165: DEPT 135 ($CDCl_3$) δ (+) 164.16, 126.65, −1.165, δ (−) 132.80, 75.24, 69.87–69.39, 61.75–61.21, 23.11, 12.74. LC-MS (*m/e*): 2275 $(M + NH_4)^+$.

Measurement of Optical Properties

Photocurable solution was prepared by mixing propylene glycol *mono*-methyl ether acetate (0.3 ml), initiator (0.006 g, Irgacure 369, 2 wt%), and SF4Ac (0.3 g). The solution was filtered through a syringe with a 0.2 μm PTFE membrane and was spin coated on the silicon wafer having 300 nm SiO_2 cladding layer with a spin speed of 400 rpm for 10 s and 600 rpm for 50 s. Spin-coated film was dried on the hot plate at 90°C for 5 min then irradiated with 365 nm UV light (80 mW/cm^2), after drying at 160°C for 30 min. The refractive index of the polymer films was measured by a prism coupler (SPA-4000, Sairon Technology Inc.) with a 1550 nm diode laser as a monitoring beam with an experimental error of ±0.00005. The optical losses of the polymer films were measured on slab waveguide samples using high-index liquid (RI = 1.55) immersion technique. The temperature dependence of the refractive indexes of the polymer films were measured by the prism coupler equipped with a temperature-control apparatus to measure the change of refractive index at the elevated temperature. The variation in the refractive index of the films was obtained in the temperature range of 25–100°C with the interval of 25°C.

3. Results and Discussion

The synthesis of the fluorinated monomer (SF4Ac) was started with the preparation of cyclic siloxane substituted with perfluoro-polyalkylethers as shown in Scheme 1. Perfluoro-polyalkylether structures are capable of making readily processible acrylates with extremely low C–H content. The perfluoro-polyalkylether structure precursors are commercially available, and their chemistry has been well developed [10]. Even at very high molecular weight, multifunctional acrylate monomers derived from these alcohols remain as liquids. From a molecular design point of view, the flexibility of the perfluoroether linkage is a key to its performance achieving a very low optical loss at 1550 nm wavelength range that is commonly used in telecommunications applications. Perfluoropolyether structure with hydroxyl as one end and allyl as the other was prepared by reaction between fluorinated diols and allyl bromide. Then it was reacted with cyclic siloxane with platinum catalyst in a fairly high

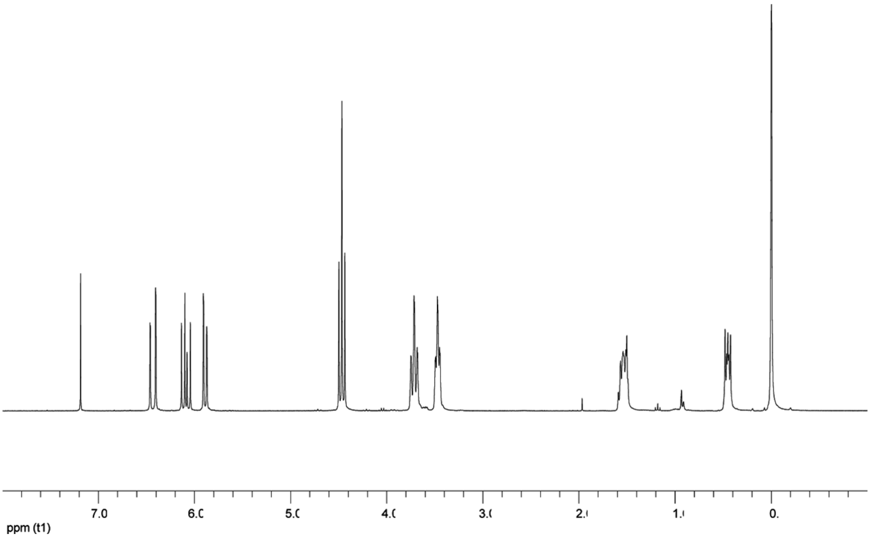


Figure 1. ^{1}H NMR spectrum of the fluorinated monomer, SF4Ac.

yield. The terminal hydroxyl was converted to acrylate by reaction with acryloyl chloride and purified by column chromatography to yield a colorless liquid.

The chemical structure and purity of SF4Ac were verified by ^{1}H NMR spectroscopy as shown in Figure 1. The characteristic peaks due to the acrylate are shown at 6.44, 6.10, 5.90 ppm. Methyl protons directly attached to the cyclic siloxane were verified by the singlet peak at 0.00 ppm. The NMR spectrum indicates that all the relevant peaks clearly existed and the product has been successfully synthesized.

Photocurable solution was prepared by dissolving SF4Ac and an initiator in a solvent. Spin-coated film from the solution was dried and then irradiated with UV light. Figure 2 shows the FT-IR spectrum of UV cured films. The stretching

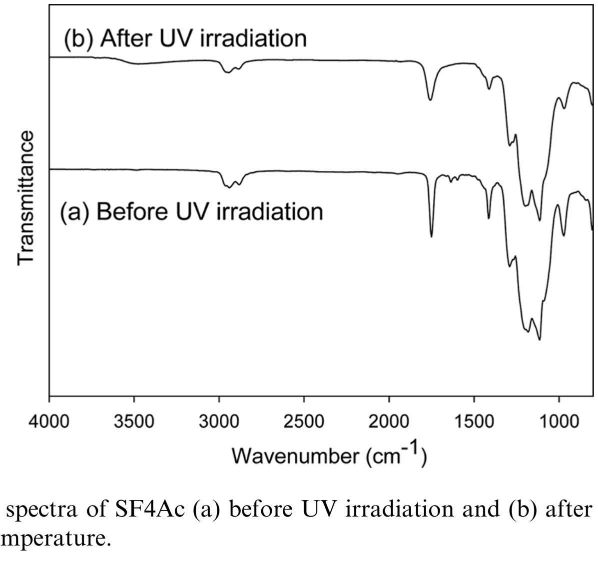


Figure 2. FT-IR spectra of SF4Ac (a) before UV irradiation and (b) after UV irradiation of 5 min at room temperature.

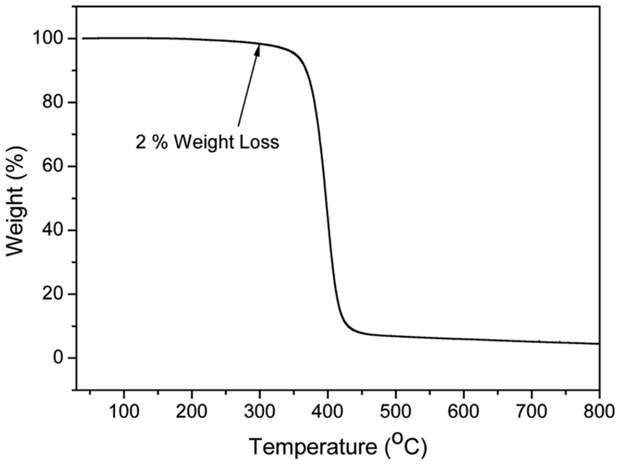


Figure 3. Thermal degradation behavior of the crosslinked film of SF4Ac. The arrow indicates the point of 2% decomposition.

vibration band due to the acrylate double bond at around 1635 cm^{-1} disappears completely after the photo-irradiation. Other peaks such as the one due to the carbonyl in the acrylate at 1700 cm^{-1} was intact after the curing process. A transparent film was easily obtained by the photo-curing process in 5 min.

Thermal decomposition stability was evaluated by TGA as shown in Figure 3. The photo-cured film was found to be thermally durable up to 300°C, where 2% weight loss occurred.

The refractive index and propagation loss were measured by prism coupler. 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. Table 1 shows that refractive index of polymer film is 1.3804 and 1.3806 at 1550 nm by TE and TM polarization mode, respectively. From this result, we confirmed that the photocured films had extremely low birefringence ($\Delta n = n_{TE} - n_{TM}$) of 0.0002. When compared with the aromatic optical materials such as polyimides and poly(arylene ethers), the fluorinated polymers from SF4Ac showed much lower birefringence [9]. Such very low birefringence was very important for optical communication application requiring a very low polarization dependent loss. The propagation loss of the polymer films was measured as low as 0.121 dB/cm by the immersion method using the prism coupler at 1550 nm.

Thermo-optic coefficient was also evaluated by measuring the temperature dependence of the refractive index of the polymer film. Figure 4 shows that the

Table 1. Optical properties of the crosslinked film of SF4Ac

Refractive index				
TE	TM	Birefringence	Optical loss (dB/cm)	Thermo-optic coefficient
1.3804	1.3806	0.0002	0.121	-1.59×10^{-4}

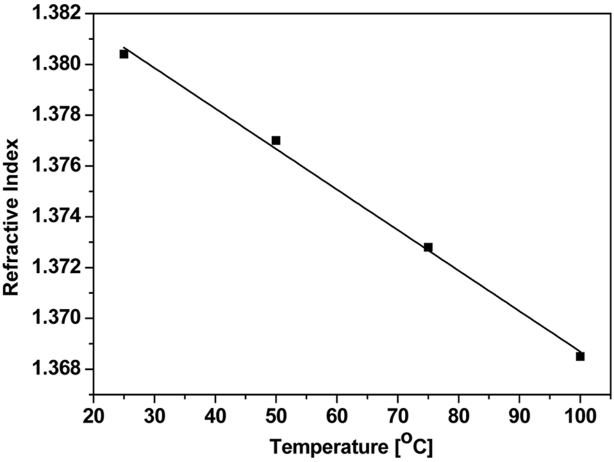


Figure 4. Refractive index change of the crosslinked film of SF4Ac as a function of heating temperature at 1550 nm of TE mode light. The average line was drawn for clarity.

refractive index of the film decreased linearly as the film was heated in the temperature range of 25–100°C, indicating a volumetric expansion of the film and a consequent lowering of its density. From the Figure 4, the thermo-optic coefficient of the film was estimated -1.59×10^{-4}, which was more than 10 times larger than silica. Such high thermo-optic coefficient combined with the high thermal stability may make the polymer films promising for the active optical switches and wavelength filter devices with low power consumption and low failure rate of the device.

4. Conclusions

In this work, we prepared UV-curable fluorinated polymeric materials based on multifunctional siloxane group containing perfluoropolyether structure. ^{1}H NMR spectroscopy verified the successful synthesis of the product. Transparent and stable films were obtained from the acryl product by UV irradiation. The curable films was thermally stable up to 300°C, which was verified by TGA analysis. The polymer films showed -1.59×10^{-4}/K of thermo-optic coefficient, 0.0002 of birefringence, and 0.12 dB/cm of optical loss. We believe the fluorinated polymers are promising for the optical communication applications such as the active optical switches and wavelength filter devices.

Acknowledgments

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