

# Effect of organic modifiers on the thermo-optic characteristics of inorganic–organic hybrid material films

Eun-Seok Kang, Jang-Ung Park, and Byeong-Soo Bae

Laboratory of Optical Materials and Coating (LOMC), Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Korea

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The thermo-optic coefficient ( $dn/dT$ ) of inorganic–organic hybrid material films prepared by the sol-gel process of organoalkylsilanes is measured using a prism coupler equipped with a hot stage. The effect of the organic modifier on the variation of  $dn/dT$  in inorganic–organic hybrid material films has been investigated. The value of  $dn/dT$  becomes more negative with increasing molecular weight of the organic modifier or with an increase in the proportion of modifier in the sample. On the other hand,  $dn/dT$  increases with an increase in the degree of organic photopolymerization. From these results, it can be seen that the value of  $dn/dT$  in these films can be varied between  $-0.83 \times 10^{-4}/^{\circ}\text{C}$  to  $-2.43 \times 10^{-4}/^{\circ}\text{C}$  by changing the organic modifier concentration and type.

## I. INTRODUCTION

The thermo-optic effect is defined as the temperature dependence of the refractive index ( $dn/dT$ ) of a material.<sup>1</sup> The thermo-optic characteristics of the dielectric optical materials, such as silica and polymer, are an important consideration in their application for optical waveguide devices. Silica has a positive  $dn/dT$  of approximately  $10^{-5}/^{\circ}\text{C}$  and polymer has a negative  $dn/dT$  of the order  $-10^{-4}/^{\circ}\text{C}$ .<sup>2,3</sup> Such disparity in the values of  $dn/dT$  is due to the fact that the thermo-optic effect exhibited by a material is determined by the combined influence of the temperature dependence of two factors: density and electronic polarizability. Density typically decreases with increasing temperature, causing a decrease in the number of polarizable species per unit volume and resulting in a decrease in the refractive index. Polarizability of the individual species in the material increases with increasing temperature and, therefore, the refractive index increases.<sup>4</sup> In general, the value of  $dn/dT$  for inorganic materials such as silica is determined by the competition between these two factors.<sup>5</sup> However, in the case of polymers,  $dn/dT$  is principally determined by the density change term because the density changes experienced by a polymer with changing temperature are considerably greater than the corresponding polarization changes. Consequently, most optical polymers have a negative value of  $dn/dT$ .<sup>3</sup>

In the design of optical communication networks, the thermo-optic properties of the waveguide material are of considerable importance. A waveguide material with a high  $dn/dT$  allows easy modulation of factors such as the optical path, the phase, and the intensity through the

controlled application of thermal energy. Polymers with high negative values of  $dn/dT$  are thus preferred for use in thermo-optic waveguide devices.<sup>6,7</sup> On the other hand, polymers exhibiting low negative values of  $dn/dT$  are preferred when fabricating athermal silica waveguide devices. For example, channel wavelength in dense wavelength division multiplexing devices is very sensitive to ambient temperature because of the temperature dependence of the optical path length of the silica core. Athermal waveguide devices, where the optical path is unaffected by ambient temperature variations, can be fabricated using a hybrid waveguide structure consisting of a polymer overcladding layer (with specific and negative values of  $dn/dT$ ) exhibiting specific properties that compensate for any temperature-induced refractive index changes of the silica core.<sup>8</sup> As can be seen from this brief discussion, the ability to control the negative values of  $dn/dT$  for polymers over a wide range is attractive when attempting to design and produce an effective thermo-optic waveguide device.

Recently, a sol-gel-derived inorganic–organic hybrid material (HYBRIMER) composed of silica and an organic material is receiving attention as a promising candidate for a waveguide material that might be used to replace silica and polymer. Fabrication of thermo-optic waveguide devices exhibiting high values of  $dn/dT$  using this HYBRIMER material has been demonstrated.<sup>9</sup> In a previous study,<sup>10</sup> we reported on a novel and straightforward technique for measuring  $dn/dT$  for HYBRIMER films using a prism coupler equipped with a hot stage. It was found that the  $dn/dT$  values of the films were negative and as high as the order  $-10^{-4}$ ,

comparable to those of a polymer. In addition, the value of  $dn/dT$  was mainly sensitive to variations in the thermal expansion coefficient.

In this study, a range of organic modifiers in the HYBRIMER films was changed to determine what effect these variations might have on the value of  $dn/dT$ . From this, the manipulation of organic component is proposed as a method for controlling  $dn/dT$  in the HYBRIMER films.

## II. EXPERIMENTAL

### A. Preparation of HYBRIMER films

To observe the effect of organic modifier variation on the value of  $dn/dT$  of the HYBRIMER, a range of precursors was used to manufacture the various HYBRIMER solutions. The solutions were prepared by combining alkyltrimethoxysilane [ $\text{RSi}(\text{OCH}_3)_3$ ] and tetramethylorthosilicate [TMOS;  $\text{Si}(\text{OCH}_3)_4$ ]. Methyltrimethoxysilane [MTMS;  $\text{CH}_3\text{Si}(\text{OCH}_3)_3$ ], ethyltrimethoxysilane [ETMS;  $\text{C}_2\text{H}_5\text{Si}(\text{OCH}_3)_3$ ], phenyltrimethoxysilane [PhTMS;  $\text{C}_6\text{H}_5\text{Si}(\text{OCH}_3)_3$ ], and 3-methacryloyloxypropyltrimethoxysilane [MPTMS;  $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}_2(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ ] were used as the alkyltrimethoxysilane precursors, allowing controlled variation of the organic species present in the HYBRIMER.

As a first step, alkyltrimethoxysilane was prehydrolyzed at room temperature for 3 h with 0.75 equivalent water in the presence of 0.1 N HCl as catalyst to compensate for the difference in reaction rate between alkyltrimethoxysilane and TMOS. TMOS was then added to the prehydrolyzed solution, and the mixture was stirred for another 30 min. The mixed solution was reacted with additional water to enhance the hydrolysis, and condensation was then allowed to occur for 12 h at room temperature. The total amount of water was equal to 1.5 times the equivalent amount of alkoxides in solution. The prepared solution was spin-coated onto silicon substrate at 3000 rpm for 30 s and the resultant films were heat treated at 180 °C for 12 h.

Specifically to observe the effect of organic photopolymerization on the thermo-optic properties of the HYBRIMER, 1-hydroxycyclohexyl phenyl ketone (igacure 184;  $\text{C}_{13}\text{H}_{16}\text{O}_2$ )—serving as a photoinitiator—was added to the MPTMS/TMOS solution (the MPTMS contains polymerizable C=C bonds). The concentration of igacure 184 was 1 mol% of the total polymerizable C=C bonds. After film formation, the degree of polymerization in the HYBRIMER was controlled by varying the time of exposure of the sample to ultraviolet (UV) radiation generated by a UV lamp (1 kW Xe/Hg, 220–240-nm wavelength). The UV-illuminated films were then heat treated at 180 °C for 12 h.

### B. Characterization

Refractive index measurements were made of the films using the prism coupling method. A He–Ne laser of 632.8-nm transverse electric (TE) mode was used as the light source. The prism coupler, equipped with an auto-controlled hot stage, was used to measure the temperature dependence of the refractive index ( $dn/dT$ ) of the HYBRIMER film. The flexible heater, thin enough not to affect the optical coupling between the prism and the film, was used to elevate sample temperature. A film-type thermocouple was attached to the surface of the sample, and the refractive index was measured over the temperature range 30–100 °C. Refractive index variation due to film thickness change with temperature can be neglected because it is possible to calculate independently thickness and refractive index using the prism coupler. More details on the measurement technique can be found in a previous publication.<sup>10</sup>

Structural evolution of the films on Si wafer was examined by Fourier transform infrared spectroscopy (FTIRS) using a Bruker EQUINOX55 spectrometer (Bruker EQUINOX55, Billerica, MA). All measurements were performed in the 4000–400  $\text{cm}^{-1}$  range at a resolution of 4  $\text{cm}^{-1}$ .

## III. RESULTS

### A. Effect of organic modifier concentration

To investigate the effect of organic modifier concentration on the HYBRIMER's value of  $dn/dT$ , the PhTMS/TMOS ratio in the solution was varied from PhTMS/TMOS = 0.5 to PhTMS/TMOS = 3. Figure 1(a) shows the FTIRS absorbance spectra of the HYBRIMER films for various ratios of PhTMS to TMOS. The bands at 1130  $\text{cm}^{-1}$ , 740  $\text{cm}^{-1}$ , and 700  $\text{cm}^{-1}$  represent Si–( $\text{C}_6\text{H}_5$ ) vibration modes.<sup>11</sup> In particular, the Si–( $\text{C}_6\text{H}_5$ ) band at 1130  $\text{cm}^{-1}$  increases considerably with increasing PhTMS/TMOS ratio. On the other hand, the Si–O–Si bands at 1063  $\text{cm}^{-1}$  remain virtually unchanged regardless of the PhTMS/TMOS ratio.<sup>12</sup> These results suggest that the organic modifier in the films increases with increasing PhTMS/TMOS ratio due to the phenyl group in the PhTMS. Figure 1(b) shows the refractive index change (at 30 °C) of the HYBRIMER films as a function of the PhTMS/TMOS ratio. The values gradually increase from 1.4936 (PhTMS/TMOS = 0.5) to 1.5415 (PhTMS/TMOS = 3). This trend is due to the higher refractive index of the phenyl-containing PhTMS precursor in comparison to that of the TMOS precursor, confirming that the organic modifier concentration in the HYBRIMER films is a function of the PhTMS/TMOS ratio of the initial solution.

Figure 2(a) shows the variation of the refractive index with temperature as a function of the PhTMS/TMOS ratio. For all the compositions, the refractive index

changed linearly with temperature, with the slope of the curve corresponding to  $dn/dT$  for the HYBRIMER films. As the PhTMS/TMOS ratio increased, its slope became more negative. The variation of  $dn/dT$  as a function of composition is shown in Fig. 2(b). The value of  $dn/dT$  for the PhTMS/TMOS films is negative and of the order  $-10^{-4}$ . The values become more negative from  $-1.35 \times 10^{-4}/^{\circ}\text{C}$  (PhTMS/TMOS = 0.5) to  $-2.43 \times 10^{-4}/^{\circ}\text{C}$  (PhTMS/TMOS = 3), indicating that  $dn/dT$  for the HYBRIMER decreases with an increase in the organic modifier concentration.

## B. Effect of organic modifier species

To observe the dependence of  $dn/dT$  on the organic modifier species in the HYBRIMER, alkyltrimethoxysilane precursors having the methyl, ethyl, and phenyl groups were alternately used in sample production. The FTIRS absorbance spectra confirmed the presence of the organic modifier species in the HYBRIMER. Figure 3 shows the variation of refractive index with temperature

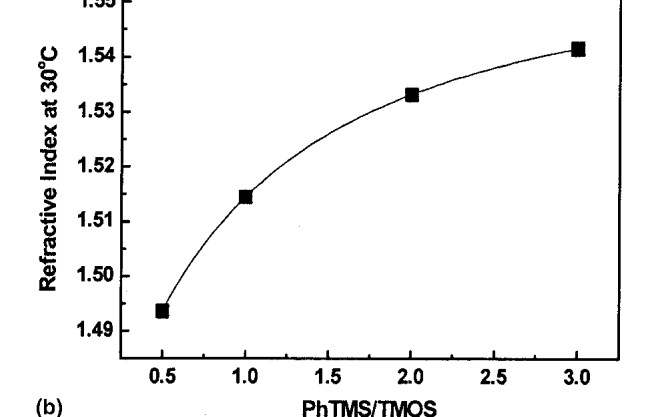
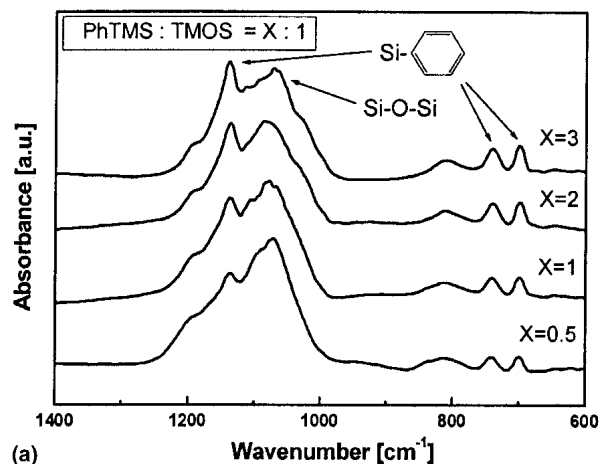
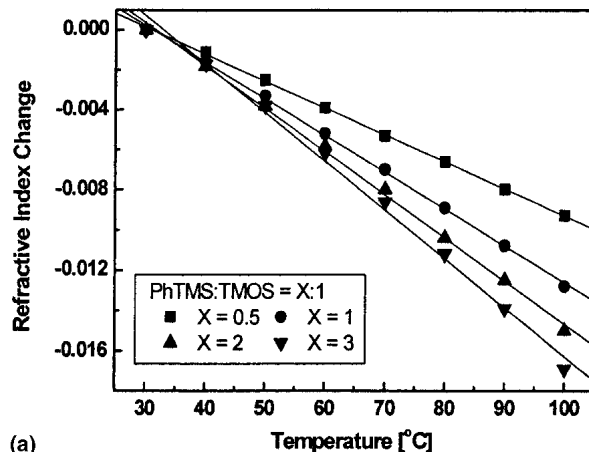
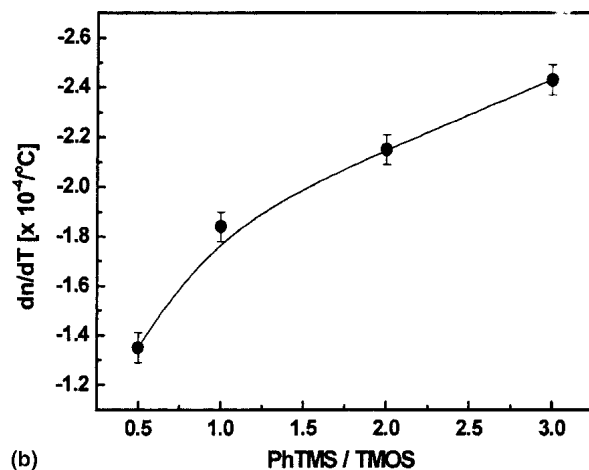


FIG. 1. (a) The FTIRS absorbance spectra and (b) the change of refractive index at 30 °C for the PhTMS/TMOS HYBRIMER films as a function of the solution composition.

as a function of the species of alkyltrimethoxysilane precursor. The refractive index decreased linearly with temperature regardless of the organic species present in the HYBRIMER film. The  $dn/dT$  values varied from  $-0.83 \times$



(a)



(b)

FIG. 2. The temperature dependence of (a) the refractive index change and (b)  $dn/dT$  of the PhTMS/TMOS HYBRIMER films as a function of solution composition.

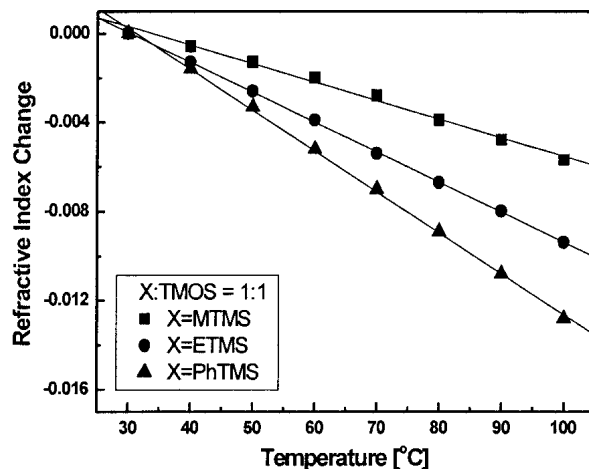


FIG. 3. Temperature dependence of the refractive index change of the HYBRIMER films as a function of precursor.

$10^{-4}/^{\circ}\text{C}$  (MPTMS/TMOS = 1) to  $-1.84 \times 10^{-4}/^{\circ}\text{C}$  (PhTMS/TMOS = 1), with  $dn/dT$  decreasing with an increase in the molecular weight of the organic modifier species used (methyl < ethyl < phenyl) despite the HYBRIMER films being made with the same alkyltrimethoxysilane/TMOS ratio in the precursor solution. Thus, the value of  $dn/dT$  for these HYBRIMER materials can be controlled by varying the organic modifier species.

### C. Effect of organic polymerization

To observe the effect on  $dn/dT$  of degrees of organic polymerization in the HYBRIMER films, 1 mol% igacure 184 over total polymerizable C=C bonds was added to the solution (MPTMS/TMOS = 2). UV dose was used to control the degree of organic polymerization in the HYBRIMER. Figure 4(a) shows the FTIRS absorbance spectra of the HYBRIMER films as a function of UV dose. The bands at  $1720\text{ cm}^{-1}$  and  $1638\text{ cm}^{-1}$  represent the carbonyl group C=O stretching mode and the

vinyl group C=C stretching mode, respectively. As the UV dose increases, the C=C stretching mode disappears, indicating that photopolymerization proceeded further with longer exposure times. In addition, as polymerization proceeds, the C=O band shifts to higher wavenumbers because the carboxyl group no longer conjugates with the carbon double bond.<sup>12</sup> Figure 4(b) shows the change of refractive index at  $30^{\circ}\text{C}$  in the HYBRIMER films as a function of the UV dose. The refractive index increases dramatically in the early stage of exposure, but continued exposure has a steadily weakening effect. The change in refractive index with UV exposure is due to the increase in density caused by the polymerization process. According to the Lorentz–Lorenz relation, the variation in refractive index is related to the change in the density term if the polarizability term remains constant. In the early stage of UV illumination, the C=C bonds are rapidly consumed as organic polymerization proceeds. However, the consumption rate of the C=C bonds decreases because the propagation step requires diffusion of the monomeric species, which becomes progressively more difficult as the reaction occurs. In other words, initial exposure to UV produces a rapid polymerization, but as exposure continues the polymerization process slows. This is reflected in the behavior of the refractive index with UV exposure.<sup>13</sup> As can be seen from the absorbance spectra and the refractive index behavior, UV dose can be used to control the degree of polymerization.

Figure 5 shows the variation of  $dn/dT$  in the HYBRIMER films as a function of UV dose. The value of  $dn/dT$  gradually increases from  $-1.75 \times 10^{-4}/^{\circ}\text{C}$  ( $0\text{ J/cm}^2$ ) to  $-1.18 \times 10^{-4}/^{\circ}\text{C}$  ( $162\text{ J/cm}^2$ ) as the degree of polymerization increases. Therefore, UV dose can be used to control simultaneously both the refractive index and the  $dn/dT$  value of the HYBRIMER.

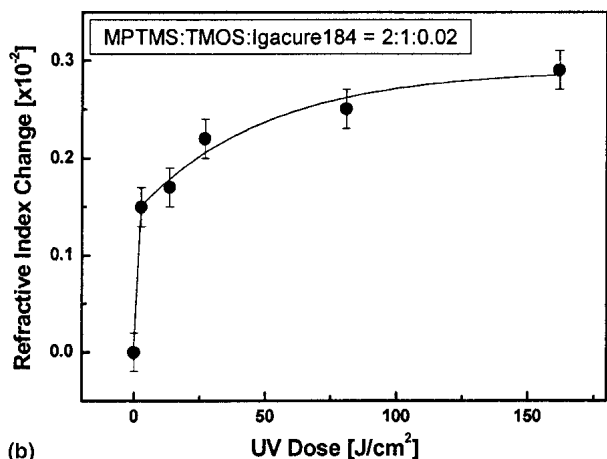
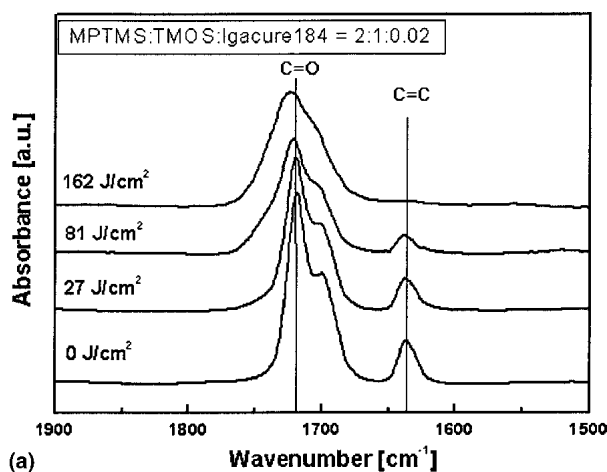


FIG. 4. (a) The FTIRS absorbance spectra and (b) the refractive index change of the MPTMS/TMOS HYBRIMER films as a function of UV dose.

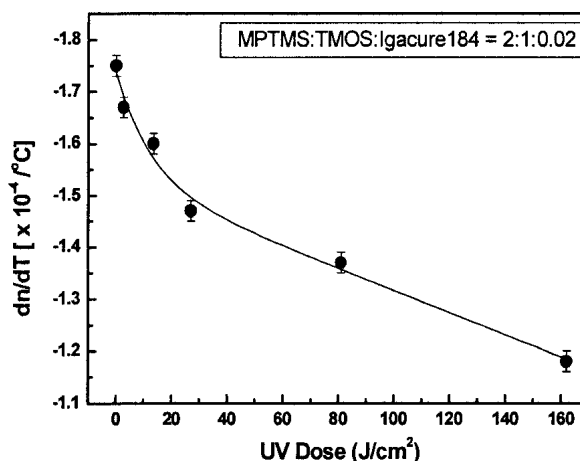


FIG. 5. Variation of the  $dn/dT$  in the MPTMS/TMOS HYBRIMER films as a function of UV dose.

#### IV. DISCUSSION

The most widely quoted theory of the thermo-optic effect is that of Prod'homme,<sup>14</sup> according to whom  $dn/dT$  can be described by:

$$\frac{dn}{dT} = f(n)(\Phi - \beta) \quad , \quad (1)$$

where  $f(n) = (n^2 - 1)(n^2 + 2)/6n$ ,  $\Phi$  is the temperature coefficient of the electronic polarizability, and  $\beta$  is the thermal expansion coefficient. This theory accounts for both positive and negative values of  $dn/dT$  in the materials under study here. When the  $\Phi$  term is dominant, the refractive index becomes positive and increases with temperature. On the other hand,  $dn/dT$  becomes negative and decreases with increasing temperature when the  $\beta$  term dominates. Generally, the  $dn/dT$  value of inorganic materials is a result of competition between  $\Phi$  and  $\beta$ . For example,  $\Phi$  for silica is higher than  $\beta$ , resulting in silica's positive  $dn/dT$ . However, the value of  $dn/dT$  displayed by organic polymers depends almost exclusively upon the thermal expansion coefficient term because the  $\beta$  values of organic polymers are always much higher than their  $\Phi$  values. Actually,  $dn/dT$  for most organic polymers are negative and of the order  $-10^{-4}/^\circ\text{C}$  because their  $\beta$  values are of the order  $10^{-4}/^\circ\text{C}$ . Thus, in the case of organic polymers, Eq. (1) can be rewritten as:<sup>3</sup>

$$\frac{dn}{dT} = -f(n)\beta \quad . \quad (2)$$

In previous work,<sup>10</sup> the origin of the thermo-optic effect in HYBRIMERS was investigated and was found to be mainly determined by the thermal expansion term in the same way as for organic polymers. It is already known that the thermal expansion of a polymer is sensitive to the concentration and species of the organic components as well as to the degree of polymerization.<sup>15</sup> Therefore, organic modifiers were used to control  $dn/dT$  because the organic variation in the HYBRIMER directly affects the coefficient of thermal expansion.

The organic-modifier-induced variation of  $dn/dT$  in the HYBRIMER can be explained in reference to changes such a modifier makes to the thermal expansion coefficient. As shown in Fig. 2(b),  $dn/dT$  becomes more negative with growing organic modifier concentration. It is known that the  $\beta$  of silica is about  $0.49 \times 10^{-5}/^\circ\text{C}$  and that that of organic polymers is of the order  $10^{-4}/^\circ\text{C}$ .<sup>3,5</sup> Thus, it may be deduced that the thermal expansion coefficient of the HYBRIMER increases as the organic concentration is increased, thereby decreasing  $dn/dT$ .

As shown in Fig. 3,  $dn/dT$  for the HYBRIMER films is dependent on the species of the organic modifier. Generally, the HYBRIMER film with the larger molecular organic modifier exhibits a lower value of  $dn/dT$  because

the thermal expansion coefficient increases with the molecular size of the modifier. Thus, the phenyl-modified HYBRIMER has the lowest  $dn/dT$  value while the methyl-modified HYBRIMER has the highest. Another issue must also be considered when discussing factors that affect the thermal expansion coefficient, and thereby  $dn/dT$ , of the HYBRIMER: changing the species of organic modifier produces changes in the sol-gel reaction, resulting in subsequent changes in the HYBRIMER structure. For example, the phenyl-modified HYBRIMER can have more unreacted alkoxy groups because the phenyl sterically hinders the sol-gel reaction. These unreacted alkoxy groups remain in the HYBRIMER and increase its thermal expansion coefficient, contributing to the lower value of  $dn/dT$  in the phenyl-modified sample. In either case, the decrease of  $dn/dT$  in the HYBRIMER depends on the organic modifier used and is due to organic-modifier-associated changes of the thermal expansion coefficient term in Eq. (2).

As seen in Fig. 5, photopolymerization of the methacrylate group increases the  $dn/dT$  values of the HYBRIMER. It is known that the value of  $dn/dT$  is generally higher for polymer networks of higher molecular weight, as the polymerization of the organics reduces the thermal expansion coefficient considerably.<sup>15</sup> Thus, it is expected that the thermal expansion coefficient of the HYBRIMER may decrease as the degree of organic polymerization increases, due at least in part to the growth of the organic network. This decrease in  $\beta$  with growing organic polymerization results in a growth of  $dn/dT$  of the HYBRIMER, as suggested by Eq. (2).

As a result, the variation of  $dn/dT$  in the HYBRIMER as a function of the organic modifier can be explained by the thermal-expansion-induced changes of  $dn/dT$ . The value of  $dn/dT$  can therefore be easily controlled by changing the organic modifier in the HYBRIMER.

#### V. CONCLUSIONS

The values of  $dn/dT$  of the HYBRIMER films prepared by sol-gel process of organoalkylsilanes were measured using a prism coupler equipped with an auto-controlled hot stage. Organic modifier concentration in the HYBRIMER was controlled by changing the precursor ratio in the solution, with  $dn/dT$  decreasing as the organic modifier concentration was increased. Organic modifier species in the HYBRIMER were varied by using different alkyltrimethoxysilane precursors, with the HYBRIMER films containing larger-molecular-weight organic modifiers exhibiting lower values of  $dn/dT$ . UV dose was used to control the degree of organic polymerization in the HYBRIMER. The value of  $dn/dT$  gradually increased with growing UV exposure. The value of  $dn/dT$  of the HYBRIMER was principally sensitive to variations in the thermal expansion term of the material. Thus,

the  $dn/dT$  value of the HYBRIMER can easily be controlled between  $-0.83 \times 10^{-4}/^{\circ}\text{C}$  to  $-2.43 \times 10^{-4}/^{\circ}\text{C}$  by changing the organic modifier concentration and species. This ability to fine-tune the thermo-optic effect makes these materials highly flexible when used in the design and fabrication of thermo-optic waveguide devices.

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## REFERENCES

1. H. Nishihara, M. Haruna, and T. Suhara, *Optical Integrated Circuits* (McGraw-Hill, New York, 1989), p. 124.
2. D.N. Nikogosyan, *Properties of Optical and Laser-Related Materials* (John Wiley & Sons, New York, 1997), p. 169.
3. P. Michel, J. Duglas, J.M. Cariou, and L. Martin, *J. Macromol. Sci., Phys.* **25**(4), 379 (1986).
4. J.M. Jewell, *J. Non-Cryst. Solids* **146**, 145 (1992).
5. T. Izumitani and H. Toratani, *J. Non-Cryst. Solids* **40**, 611 (1980).
6. S.V. Kartalopoulos, *Introduction to DWDM Technology* (SPIE Optical Engineering Press, Washington, DC, 2000), p. 141.
7. Y. Hida, H. Onose, and S. Imamura, *IEEE Photo. Tech.* **7**, 782 (1993).
8. Y. Kokubun, N. Funato, and M. Takizawa, *IEEE Photo. Tech. Lett.* **5**(11), 1297 (1993).
9. O.S. Roesch, W. Bernhard, R. Muller-Fiedler, P. Dannberg, A. Brauer, R. Buestrich, and M. Popall, *SPIE Proc.* **3799**, 214 (1999).
10. E.S. Kang, T.H. Lee, and B.S. Bae, *Appl. Phys. Lett.* **81**(8), 1438 (2002).
11. D.R. Anderson, *Analysis of Silicones* (Wiley-Interscience, New York, 1974), Chapter 10.
12. K. Saravanamuttu, X.M. Du, S.I. Najafi, and M.P. Andrews, *Can. J. Chem.* **76**, 1717 (1998).
13. O.H. Park, J.I. Jung, and B.S. Bae, *J. Mater. Res.* **16**, 2143 (2001).
14. L. Prod'homme, *Phys. Chem. Glasses.* **4**, 119 (1960).
15. J. Zhai, L. Qiu, J. Zhou, Y. Zhao, Y. Shen, Q. Ling, and M. Yang, *Adv. Mater. Opt. Electron.* **10**, 3 (2000).