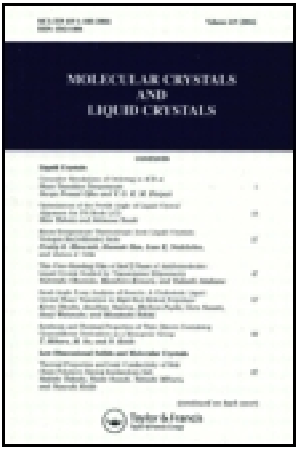


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Organic-Inorganic Hybrid Materials for Nonlinear Optics Applications

Kwang-Sup Lee [a], Tae-Dong Kim [a], Yu Hong Min [b], Choon Sup Yoon [b], Marek Samoc [c] & Anna Samoc [c]

[a] Department of Polymer Science & Engineering, Hannam University, Taejon, 306-791, Korea

[b] Department of Physics, KAIST, Taejon, 305-701, Korea

[c] Laser Physics Centre, Australian National University, Canberra, 0200, Australia

To cite this article: Kwang-Sup Lee, Tae-Dong Kim, Yu Hong Min, Choon Sup Yoon, Marek Samoc & Anna Samoc (2000): Organic-Inorganic Hybrid Materials for Nonlinear Optics Applications, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 353:1, 525-537

To link to this article: http://dx.doi.org/10.1080/10587250008025686

Mol. Cryst. and Liq. Cryst., 2000, Vol. 353, pp. 525-537
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Organic-Inorganic Hybrid Materials for Nonlinear Optics Applications

KWANG-SUP LEE[a], TAE-DONG KIM[a], YU HONG MIN[b], CHOON SUP YOON[b], MAREK SAMOC[c] and ANNA SAMOC[c]

[a]*Department of Polymer Science & Engineering, Hannam University, Taejon 306–791, Korea,* [b]*Department of Physics, KAIST, Taejon 305–701, Korea and* [c]*Laser Physics Centre, Australian National University, Canberra 0200, Australia*

Three types of organic-inorganic hybrid materials were prepared by the sol-gel processable monomers derived from 3-isocyanatopropyltriethoxysilane with three different hydroxy-functionalized nonlinear optical chromophores. The measured values of NLO coefficient strongly depended on conditions such as poling temperature, poling time and heating rate. The hybrid films heated at 200°C exhibited d_{33} = 50–58 pm/V in Maker-fringe measurement. It was found that the thermal stabilities of the films were greatly enhanced as poling time increased and a poling temperature became higher. Also, we observed good waveguiding properties of the films at 810 nm and 1064 nm. The optical propagation losses of the films for TE mode were about 2 dB/cm at 810 nm and 0.5 dB/cm at 1064 nm.

Keywords: organic-inorganic hybrid films; second-order nonlinearity; poling condition; thermal relaxation; optical loss

INTRODUCTION

Sol-gel processes have been intensively studied as the potentially superior route for the preparation of ceramics, glasses and composites due to advantages and uniqueness of these processes compared to conventional melt and sintering techniques[1-3]. Using sol-gel techniques, it is possible to make optical layers for photonics applications using organic-inorganic hybrid materials[4-8].

Most nonlinear optical (NLO) chromophores have generally not been found to be good photonic media due to large absorption and high optical losses. Inorganic glasses, however, are excellent photonic media because of their high optical quality and extremely low optical losses. Therefore, combining inorganic glass and organic photo-functional molecules is probably one of the best ways of making optical materials with large optical nonlinearity and low losses[9-11]. In addition, the use of highly cross-linked silica matrix can remarkably reduced the thermal relaxation of the molecular dipoles[12-15].

Taking advantages of these, we have recently developed three different azosulfone dye/silica glass hybrid materials. They are characterized as vertical (V) parallel (P) and vertical-parallel (VP), depending on the bonding direction between chromophores and silica matrixes. Their poling conditions and the stability of poling-induced dipole of three hybrids are compared. In addition, we had interest on the application of these hybrid films to optical waveguiding devices. Optical loss may be caused by either intrinsic absorption of NLO chromophores at the operating wavelength, or by the light scattering from physical scattering centers generated during processing. For the optical waveguiding device, the optical losses measured with CCD camera technique depended both on the absorption and scattering contributions[16-18].

EXPERIMENTAL

Reagents

N,N-Dimethylformamide (DMF) (Junsei) was dried over $MgSO_4$, distilled under reduced pressure, and dried further on 4 Å molecular sieves. 3-Isocyanatopropyltriethoxysilane (Aldrich) and *N*-(2-hydroxyethyl)-*N*-methylaniline (TCI) were distilled and kept in nitrogen atmosphere before use. *N,N*-Bis(hydroxyethyl)aminobenzene (Aldrich) was purified by recrystallization in ethanol/water. 4-Aminophenyl 6-hydroxyhexyl sulfone and 4-aminophenyl butyl sulfone were synthesized according to the published literature[19]. All other starting materials, reagents, and solvents were of analytical-grade quality and were purchased commercially and used as received.

Monomers Synthesis

4-[N,N-Bis(hydroxyethyl)amino-4'-butylsulfonyl]azobenzene(**AZOOH-2V**): To a solution of 10.6 g (0.05 mol) of 4-aminophenyl butyl sulfone in 100 mL of 50% aqueous ethanol, was added 12.5 mL (0.15 mol) of conc. HCl. The solution was mechanically stirred for 30 min and cooled to 0°C in an ice bath. 3.5 g (0.05 mol) of sodium nitrite in 10 mL of water was then added dropwise to this solution and stirred for another 30 min to yield a clear orange solution. The reaction temperature was maintained below 5°C throughout the reaction to prevent the decomposition of the intermediate diazonium salt. On adding 9.3 g (0.05 mol) of *N,N*-bis(hydroxyethyl)aminobenzene with heavy stirring, the color of the solution changed to dark red. After stirring the solution for 6 hrs with slowly rising to ambient temperature, it was poured into 15 mL of 20% aqueous sodium hydroxide solution to neutralize. The solution was stirred for 4 hrs at room temperature and then poured into an excess amount of water (1 L). The precipitated product was separated by filtration and washed with water several times. After drying the solid in a vacuum oven, product was recrystallized from isopropanol/hexane mixture. Yield: 10.2 g (48.7%), M.P. 101°C

^{1}H NMR ($CDCl_3$): δ = 8.0, 7.9, 7.8, 6.8 (8H, *d*, Ar-C*H*), 4.8 (2H, *s*, O*H*), 3.6 (4H, *t*, $N(CH_2CH_2OH)$), 1.5, 1.3 (6H, *m*, $SO_2(CH_2)_3CH_3$), 0.8 (3H, *d*, CH_2CH_3)

FT-IR (KBr pellet) : 3600-3100 (OH), 3300-3200 (Ar-CH), 1600 (C=C), 1375-1300 (C-N), 1000-1200 (SO_2)

4-[(N-(2-Hydroxyethyl)-N-methylamino)-4'-(6-hydroxyhexyl)sulfonyl]azobenzene (**AZOOH-2P**): AZOOH-2P was prepared by a similar method as for the preparation of AZOOH-2V using *N*-(2-hydroxyethyl)-*N*-methylaminobenzene and 4-aminophenyl 6-hydroxyhexyl sulfone instead of *N,N*-bis(hydroxyethyl)-aminobenzene and 4-aminophenyl butyl sulfone, respectively. Yield: 11.9 g (58.7%), M.P. 141°C.

^{1}H NMR ($CDCl_3$): δ = 8.1, 7.9, 7.8, 6.8 (8H, *d*, Ar-C*H*), 4.8, 4.3 (2H, *s*, O*H*), 3.8 (4H, *t*, $N(CH_2CH_2OH)$), 3.1 (3H, *s*, NCH_3), 1.6, 1.2 (12H, *m*, $SO_2(CH_2)_6$-OH)

FT-IR (KBr pellet): 3600-3100 (OH), 3300-3200 (Ar-CH), 1600 (C=C), 1375-1300 (C-N), 1000-1200 (SO_2)

4-[N,N-Bis(hydroxyethyl)amino-4'-(6-hydroxyhexyl)sulfonyl]azobenzene (**AZOOH-VP**): AZOOH-VP was prepared by a similar method as for the preparation of AZOOH-2V using 4-aminophenyl 6-hydroxyhexyl sulfone instead of 4-aminophenyl butyl sulfone. Yield: 9.8 g (43.6%), M.P. 83°C.

^{1}H NMR ($CDCl_3$): δ = 8.0, 7.9, 7.8, 6.9 (8H, *d*, Ar-C*H*), 4.8, 4.3 (3H, *s*, O*H*), 3.6 (4H, *t*, $N(CH_2CH_2OH)$), 1.6, 1.2 (12H, *m*, $SO_2(CH_2)_6OH$)

FT-IR (KBr pellet): 3600-3100 (OH), 3300-3200 (Ar-CH), 1600 (C=C), 1375-1300 (C-N), 1000-1200 (SO_2)

Sol-Gel Process and Film Preparation for Organic-Inorganic Hybrids

The basic sol-gel process involved sequential hydrolysis and polycondensation of silicon alkoxide. In a typical reaction, the alkoxysilane were synthesized by the coupling reaction between NLO chromophore and 3-isocyanatopropyltriethoxysilane at 60°C for 2 days in *N,N*-dimethylformamide (DMF) solvent. After two days, the resulted solutions were dropped slightly excess amount of acidic water (1N HCl) and then were stirred for 5 days in room temperature, for a homogeneous solutions. The viscosity of reaction solutions increased after the hydrolysis and polycondensation reaction. The solutions were filtered through a 0.45 μm Teflon membrane to remove insoluble particles, and then spun at various angular speed for 5 min, depending on the desired film thickness on Fisher glass plate and ITO coated glass substrate. The films (i.e., SIAZO-2V, SIAZO-2P, and SIAZO-VP) were dried in a vacuum oven at 45°C to remove residual solvent.

Measurements

The ^{1}H NMR spectral data were obtained from the Varian NMR (300 MHz) spectrometer. The FT-IR spectra were recorded on a Perkin-Elmer paragon 1000PC spectrometer and UV/vis absorption spectra were measured using a Perkin-Elmer Lambda14 spectrophotometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on TA Instruments 2910DSC analyzer for the study of thermal behavior and thermal stability of organic-inorganic hybrid materials. The refractive index and the thickness of these materials were determined by a prism coupler (Metricon PC-2000). The SHG experiments were performed with the *p*-polarized beam at the fundamental frequency of a mode locked Q-switched Nd;YAG laser operating at 500 Hz with forty 135 ps sub-pulses in each pulse train. Y-cut quartz of 4.65 mm thickness was used as the reference (d_{11} = 0.5 pm/V) for d_{33} coefficient calculation of samples. The optical propagation losses were measured with a 810 nm laser diode and 1064 Nd;YAG laser by the CCD camera technique.

RESULTS AND DISCUSSION

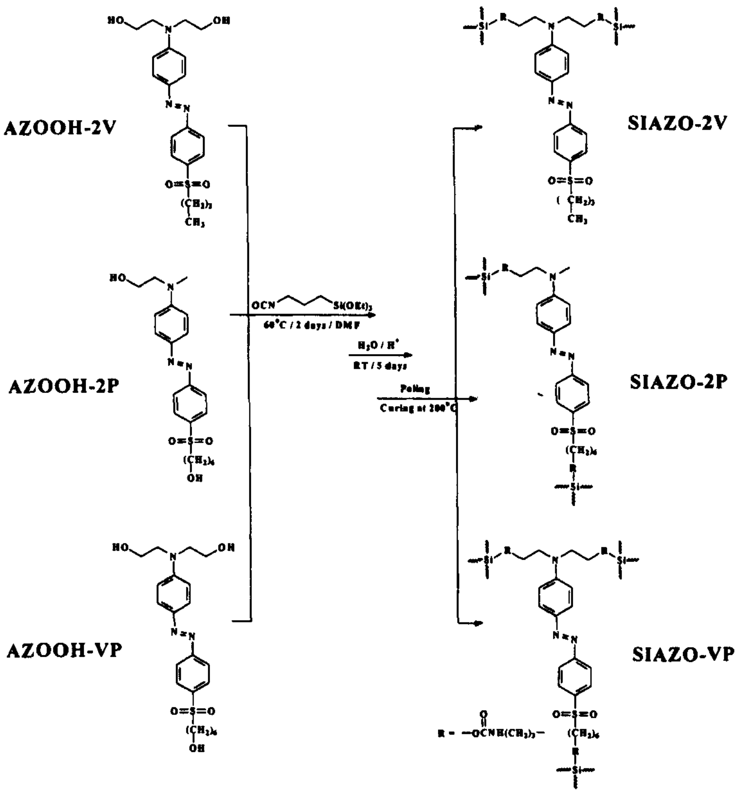
Synthesis and Characterization

In our experiments, we used 4-aminophenyl butyl sulfone, which was prepared by the methods published in the literature[19], and *N,N*-bis(hydroxyethyl)aminobenzene to synthesize the chromophore monomer 4-[*N,N*-bis(hydroxyethyl)-amino-4'-butylsulfonyl]azobenzene (AZOOH-2V) by the diazonium coupling reaction. The chromophore monomer AZOOH-2V obtained was purified using recrystallization method. Also, AZOOH-2P and AZOOH-VP were prepared by the similar method using 4-aminophenyl 6-hydroxyhexyl sulfone and *N*-(2-hydroxyethyl)-*N*-methylaminobenzene. The sol-gel processes of these compounds are outlined in Scheme 1. The structures of AZOOH-2V, AZOOH-2P and AZOOH-VP were confirmed by FT-IR spectrum, ^{1}H NMR spectrum and UV/vis absorption spectroscopy. SIAZO-2V, SIAZO-2P and SIAZO-VP were synthesized by coupling AZOOH-2V, AZOOH-2P and AZOOH-VP with 3-isocyanatopropyltriethoxysilane under hydrochloric acid catalyst system, respectively.

Figure 1 shows the FT-IR spectra of AZOOH-2V, pre-SIAZO-2V (hybrid precursor solution), and an organic-inorganic hybrid material (SIAZO-2V). The characteristic difference between the monomer (AZOOH-2V) and the hybrid precursor solution (pre-SIAZO-2V) were shown as the large differences in the intensity of strong peaks at 1710 cm^{-1}, which is attributed to the vibration of the carbonyl group of urethane linkage. After curing at 200°C for 1 hr, the peaks of the hydroxyl group at 3400 cm^{-1} almost disappeared, and the new absorption peak of Si-O-Si at 1070 cm^{-1} became stronger. This suggests that the condensation reaction occurred between the hydrolyzed Si-OH and Si-OEt.

Thermal Properties

The thermal properties of the organic-inorganic hybrid materials were examined by the differential scanning calorimetry (DSC) and thermogravimetric



SCHEME 1 SIAZO-2V, SIAZO-2P and SIAZO-VP synthesis by sol-gel processes.

analysis (TGA). We did not observe clearly the glass transition temperatures of SIAZO-2V, SIAZO-2P and SIAZO-VP. The TGA data under the nitrogen atmosphere exhibited initial decomposition temperatures due to the thermal breaking of azo-group at 223, 235 and 252°C for SIAZO-2V, SIAZO-2P and SIAZO-VP, respectively (Figure 2). All materials showed residual weights of more than 40% at 800°C in nitrogen atmosphere due to the presence of aromatic ring contents and Si compounds in the hybrid structures.

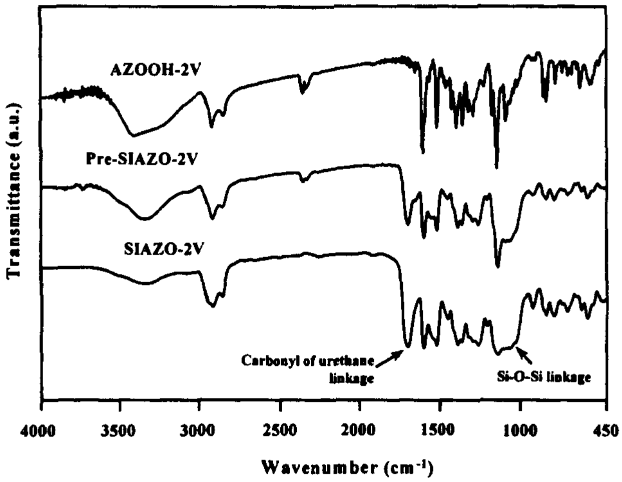


FIGURE 1 The FT-IR spectra of monomer (AZOOH-2V), Pre-SIAZO-2V before curing and SIAZO-2V after curing at 200°C for 1 h with KBr pellets.

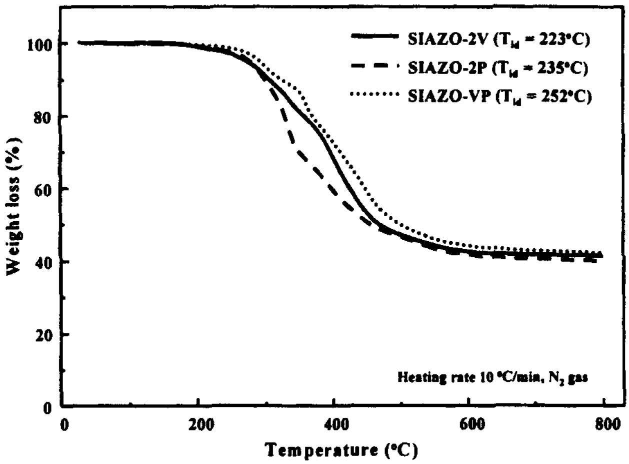


FIGURE 2 TGA thermograms of SIAZO-2V, SIAZO-2P and SIAZO-VP with a heating rate of 10°C/min.

Linear and Nonlinear Optical Properties

The UV/vis spectra, shown in Figure 3, were taken using AZOOH-2V solution in DMF and SIAZO-2V thin film coated on an ITO glass slide. A blue shift of absorption peak after poling and crosslinking is seen, which is also observed in other organic-inorganic crosslinked NLO hybrid systems. AZOOH-2V gives an absorption maximum at 436 nm and its absorption edge at 545 nm. Also, the absorption maximum and absorption edge for SIAZO-2V thin film coated on an ITO glass slide were 421 nm and 553 nm, respectively.

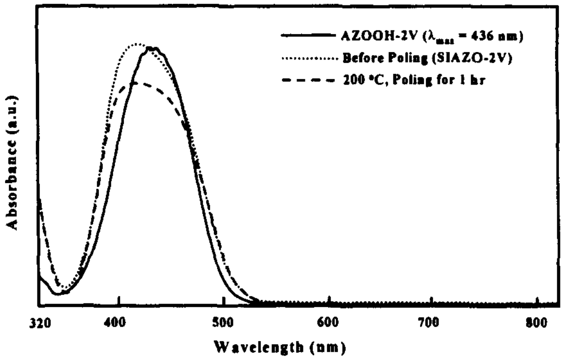


FIGURE 3 UV/vis spectra of AZOOH-2V solution in DMF and SIAZO-2V thin film before poling and after poling.

It is noted that an absorbance change occurred after the film was poled and crosslinked. The absorbance decrease after poling is a result of the alignment of chromophore dipoles. The order parameters ($\phi = 1\text{-}A_1/A_0$, A_0 and A_1 are the absorbances of the film before and after corona poling, respectively) were used to characterize the poling efficiency. Under 5 kV poling voltage applied to the corona needle at 200°C for 1 hr, the order parameter values for SIAZO-2V, SIAZO-2P and SIAZO-VP were estimated to be 0.31, 0.25 and 0.24, respectively. The development of axial order was probed as a function of poling time and poling temperature by following changes in the optical absorption spectra. As shown in Figure 4, the order parameter increases rapidly at first and then saturated at a maximum value $(\phi)_{max}$ that lies in the range of 0.30-0.33 at 160°C. This value is larger than those obtained at 120°C.

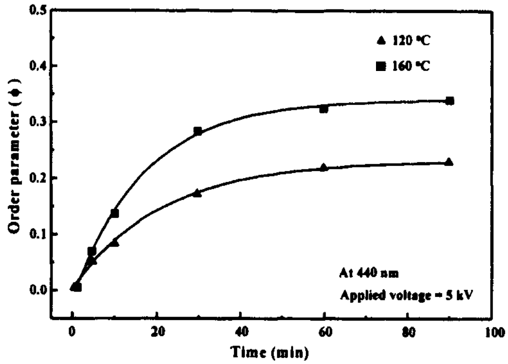


FIGURE 4 Change of order parameter of hybrid system SIAZO-2V on time.

The second-order NLO properties of the poled films were characterized by the second harmonic generation (SHG) at 1064 nm fundamental wavelength with Y-cut quartz crystal (d_{11} = 0.5 pm/V) as the reference. We obtained d_{33} values of 58, 50 and 53 pm/V for SIAZO-2V, SIAZO-2P and SIAZO-VP, respectively, by using a standard Maker fringe technique[20]. Figure 5 shows the relationship between the SHG intensity and the incident angle of an exciting

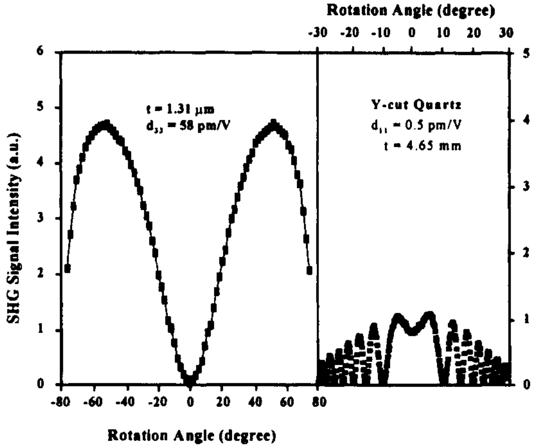


FIGURE 5 Comparison of angular SHG dependence between poled SIAZO- 2V film and Y-cut quartz as reference (t : thickness).

beam of SIAZO-2V. The input beam was *s*-polarized and the output second-harmonic intensity, after having passed through a band pass filter and a *p*-polarizer, was detected by a photomultiplier tube. From the calculation, we obtained d_{31} value of 19.3 pm/V for SIAZO-2V. Since the relationship $d_{33} \fallingdotseq 3d_{31}$ in polymer systems[21], the d_{33} value should be about 58 pm/V. The SHG coefficient (d_{33}) of SIAZO-2V calculated from the angular dependence of the SHG intensity was about 58-60 pm/V when the sample was poled for 1-5 hrs at 160°C or for 1 hr at 200°C. However d_{33} of the SIAZO-2V poled for 5 hrs at 200°C was reduced to 15.4 pm/V due to thermal breaking of azo-chromophores. For the thermal stability investigation, temperature dependent SHG experiments were carried out *in-situ* by monitoring the SHG signal while heating at a rate of 2°C/min. Figure 6 shows the dynamic stability for hybrid

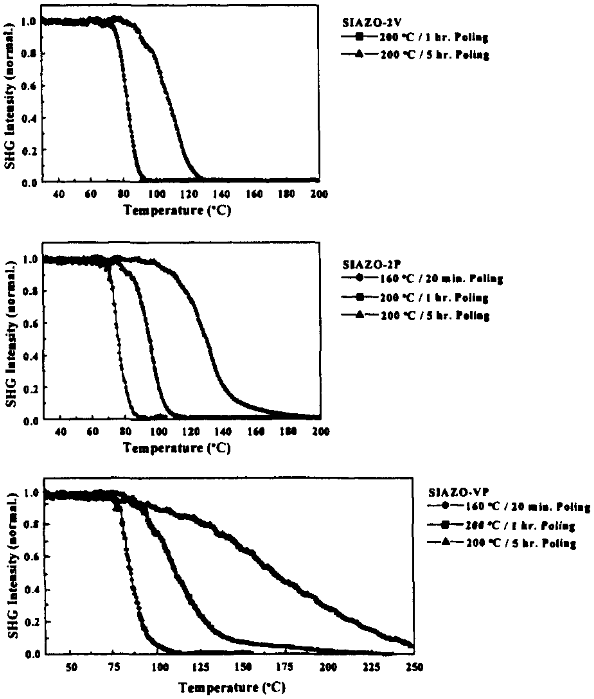


FIGURE 6 Dynamic stability for hybrid films that were poled for 20 min at 160°C and 1 hr and 5 hrs at 200°C.

films that were poled for 20 min at 160°C and for 1 hr and 5 hrs at 200°C. It was found that the thermal stabilities of the films were greatly enhanced as poling time increased and poling temperature became higher. The decay of thermal stability in SIAZO-VP was minimized owing to the lattice hardening of organic-inorganic hybrid materials with three bonding sites. It also shows that the SHG signal of SIAZO-VP poled for 5 hrs at 200°C remained stable up to about 100°C, beyond which the SHG signal starts to decay slowly. It completely disappeared as the temperature went above 250°C. These results may be attributed to the thermal relaxation of oriented dipoles that is related to the free volume in the silica bond.

The major problem with using the NLO properties of organic-inorganic hybrid material in a device is in obtaining good quality and highly transparent films suitable for waveguiding applications. Optical waveguide devices may involve propagation of light through distances of many centimeters. Figure 7 shows the principal setup for coupling light into a thin-film waveguide using a prism coupler. The film on a substrate is pressed against a high-refractive-index prism and the whole assembly is rotated to find angular positions at high coupling into waveguide modes. For low-loss samples, it is also possible to observe the propagation of guided light by detecting the light scattered from the sample with a suitably positioned CCD camera and the loss factor can be determined. Figure 8 shows a series of CCD camera images of waveguiding propagation of the 810 nm and 1064 nm laser beam in the films of SIAZO-2V.

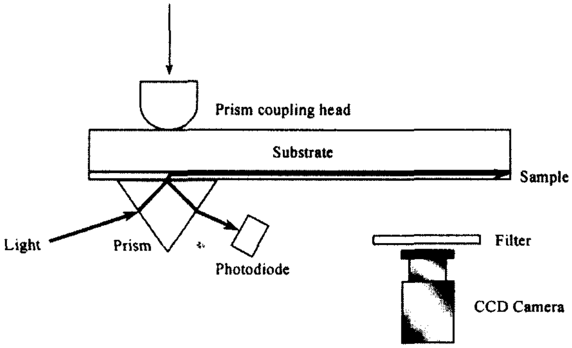


FIGURE 7 A measurement of waveguiding propagation by prism coupling.

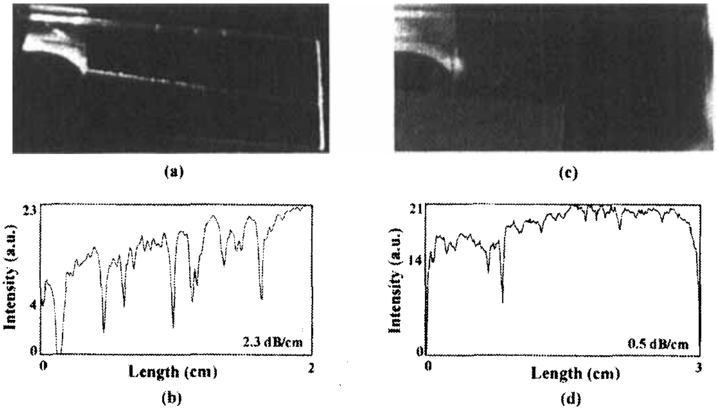


FIGURE 8 The side-view image of the waveguiding propagation (a : 810 nm, c : 1064 nm) captured with a CCD camera and plot profile (b : 810 nm, d : 1064 nm) for reduction of the intensity of scattered light in SIAZO-2V films.

The streak of light propagating was visible because of the scattered light out of the waveguide. If there is a reduction in the intensity of the propagating beam, then a reduction in the intensity of the scattered light is also observed. We determine waveguiding losses with the measurements of the decay of intensity of scattered light measured along the distance of the propagation. We used in our determination the logarithmic form of the Lambert-Beer Law : $\log_{10}I = \log_{10}I_0-(\varepsilon'/10)L$, where I_0 is the incident intensity, I is the transmitted intensity through the distance L, and ε' is the loss factor. This method provided us with information on the total intrinsic losses arising both from absorption and scattering. The optical propagation losses of the SIAZO-2V for TE mode were about 2 dB/cm at 810 nm and 0.5 dB/cm at 1064 nm. Similar values were also determined for SIAZO-2P and SIAZO-VP.

In conclusion, three types of second-order NLO organic-inorganic hybrid materials were successfully prepared by the sol-gel process using 3-isocyanatopropyltriethoxysilane with corresponding functionalized NLO chromophores. We could not observe clearly the glass transition temperature of resulting hybrid materials up to 220°C. From the TGA thermogram, the initial decomposition temperatures of SIAZO-2V, SIAZO-2P, and SIAZO-VP were

223, 235 and 252°C, respectively. Three resulting materials exhibited high second-order activities as given by their d_{33} values between 50-58 pm/V. The poled and thermally cured polymeric films demonstrated the improved temporal stability of their NLO properties with increasing number of cross-linking sites. We also observed good waveguiding properties of the films at 810 nm and 1064 nm. The optical propagation losses of the films for TE mode were about 2 dB/cm at 810 nm and 0.5 dB/cm at 1064 nm.

Acknowledgments
This research was supported by the Basic Science Institute Program, Ministry of Education of Korea (Project No. BSRI 97-3436).

References

[1] C. J. Brinker and G. W. Scherer, *Sol-Gel Science,* Academic Press, Boston (1990).
[2] K. Tadanaga, K. Azuta and T. Ninami, *J. Ceram. Soc. J.,* **105:** 555 (1997).
[3] J. M. Yang, H. S. Chen, Y. G. Hsu and W. Wang, *Angew. Makromol. Chem.,* **251:** 49 (1997).
[4] J. D. Mackenzie, *Sol-Gel Optics III, SPIE Proc.,* 2288, San Diego (1994).
[5] J.-P. Boilot, F. Chaput, J. Biteau, J.-P. Galaup, D. Riehl and Y. Levy, *Ann. Phys. Fr.,* **20:** 727 (1995).
[6] I. R. Whittall, A. M. Mcdonagh, M. G. Humphrey and M. Samoc, *Adv. Organomet. Chem.,* **42:** 291 (1998).
[7] H. K. Kim, S.-J. Kang, S.-K. Choi, Y.-H. Min and C.-S. Yoon, *Chem. Mater.,* **11:** 779 (1999).
[8] P.-H. Sung and T.-F. Hsu, *Polymer,*39: 1453 (1998).
[9] C. J. Wung, K.-S. Lee, P. N. Prasad, J.-C. Kim, J.-I. Jin and H.-K. Shim, *Polymer,* **33:** 4145 (1992).
[10] G.-H. Hsiue, R.-H. Lee and R.-J Jeng, *Chem. Mater.,* **9:** 883 (1997).
[11] H. W. Oviatt, K. J. Shea, S. Kalluri, Y. Shi and L. R. Dalton, *Chem. Mater.,* **7:** 493 (1995).
[12] Z. Yang, C. Xu, B. Wu, L. R. Dalton, W. H. Steier and Y. Shi, *Chem. Mater.,* **6:** 1899 (1994).
[13] P.-H Sung, T.-F. Hsu, Y.-H. Ding and A. Y. Wu, *Chem. Mater.,* **10:** 1642 (1998).
[14] H. Jiang and A. K. Kakkar, *Adv. Mater.,* **10:** 1093 (1998).
[15] Y. H. Min, K.-S. Lee, C. S. Yoon and L. M. Do, *J. Mater. Chem.,* **8:**1225 (1998).
[16] A. Skumanich and J. C. Scott, *Mol. Cryst. Liq. Cryst.,* **183:** 365 (1990).
[17] C. H. Seager, M. Sinclair, D. Mcbranch, A. J. Heeger and G. L. Baker, *Synth. Mat.,* **49:** 91 (1992).
[18] A. Samoc, M. Samoc, M. Woodruff and B. L. Davies, *Photonic Polymer Systems,* Marcel Dekker, Inc., 373, New York (1998).
[19] W. Kohler, D. R. Robello and C. S. Willand, *Macromolecules,* **24:** 4589 (1991).
[20] W. N. Herman and L. M. Hayden, *J. Opt. Soc. Am. B.,* **12:**416 (1995).
[21] P. N. prasad and D. J. Williams, *Introduction to Nonlinear Optical Effect in Molecules and Polymers,* Wiley, p.66, New York (1991).