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# Control of Thermo-Optic Effect in Siloxane-Containing Polyimide/Silica Hybrid

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Refractive index is one of the most important properties of optical materials. We have been investigating methods for controlling the temperature dependence of refractive index, *i.e.* thermo-optic (TO) effect of polymers[1-3] because the TO effect is readily applicable to the dynamic control of lightwave circuits. A large temperature gradient of refractive index (TO coefficient, *dn*/*dT*) that provides small power consumption and high-speed response is favorable for such active applications. On the other hand, too large |*dn*/*dT*| makes the properties of optical components instable to the atmosphere. Recently, we have investigated polyimides (PIs) containing siloxane (–O–Si–O–) linkages in the main chains (Fig. 1a). Those PIs exhibit distinct glass transition below 100°C, and the values of *dn*/*dT* significantly change at $T_g$ (TO coefficients are ~150 ppm/K below $T_g$ and ~350 ppm/K above $T_g$). This behavior would be favorable to achieve both stability around the room temperature and small power consumption/high-speed response. However, these PIs show low resistance to polar organic solvents. For improving the solvent stability and to control the transition temperatures of *dn*/*dT*, we employed the technique of silica hybridizations using *in situ* sol-gel reactions.

PI/silica hybrids were prepared by dissolving tetramethoxysilane (TEOS) into precursor solution of PI (poly(amic acid): PAA). TEOS was added to the PAA solution and reacted with $H_2O$ (TEOS : $H_2O$ = 1 : 4) under acidic condition ($H_2O$ : HCl = 1 : 0.005). Clear solutions thus obtained were spin-coated onto Si-substrates, dried at 70°C for 1 h, and then cured at 220°C for 1 h to complete the sol-gel reaction of TEOS and the imidization of PAA. The hybrid PI films are transparent and insoluble to polar organic solvents. The 5 wt% weight loss temperatures are higher than 300°C for all hybrid films. As shown in Fig. 1b, the $T_g$ for hybrids can be well controlled by the amount of silica. The transition temperatures of *dn*/*dT* are also controlled due to the change in $T_g$ by silica contents. On the other hand, the values of *dn*/*dT* are still large for PI/silica hybrids. Moreover, the large |*dn*/*dT*| values are retained after the thermal treatment at 300°C for 1 h. In conclusion, these PI/silica hybrids exhibit favorable properties as active optical materials such as the controllability in temperature responses, the resistance to organic solvents, and the high thermal stabilities.

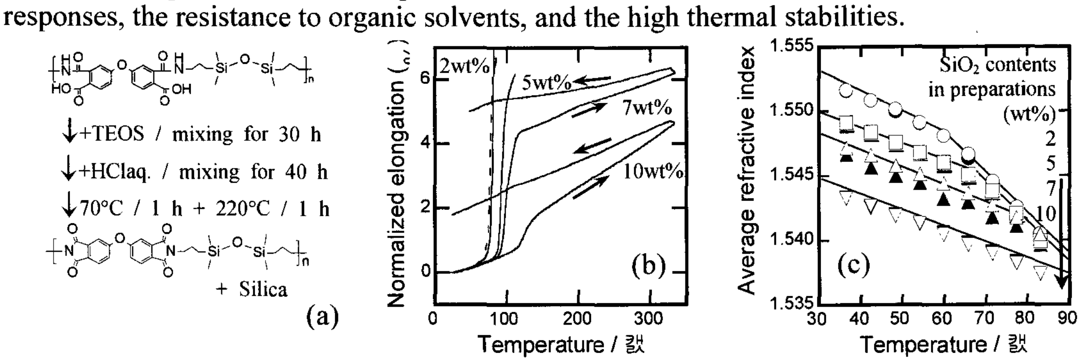


**Figure 1.** (a) Preparation scheme, (b) thermal expansion, and (c) temperature dependence of refractive indices for the PI/silica hybrid films on Si-substrates. Open and closed symbols in Fig. 1(c) represent the refractive indices before and after the annealing at 300°C for 1 h.

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2. Terui, Y.; Ando, S. *Proc. SPIE* **5724**, 336 (2005).
3. Terui, Y.; Ando. S. *J. Photopolym. Sci. Technol.* **18**, 337 (2005).