Polyphenylsilsesquioxane Partially-substituted with Germanium: Refractive Index Controllability and Thermal Stability

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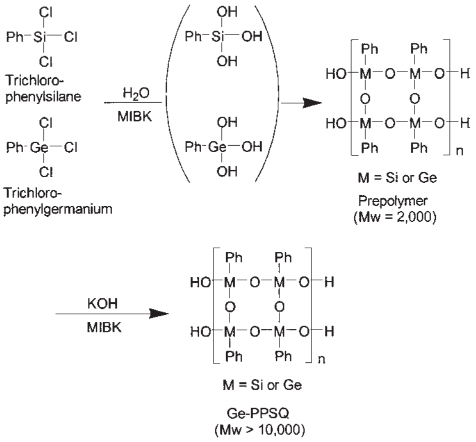
The refractive index of a novel silicon-germanium ladder copolymer synthesized by partially substituting silicon in the main chain of polyphenylsilsesquioxane by germanium could be controlled between 1.558 and 1.573 by changing the content of germanium up to 10 mol%, without losing thermal stability over 500 °C.

Optical polymers are attractive for economical and practical optoelectronic devices and optical communication systems. In particular, polymer optical waveguides have been investigated for use as flexible and low cost optical interconnections and optoelectronic integrated circuits.[1] For many applications, polymers offer significant advantages over waveguide materials such as SiO_2, $LiNbO_3$ and GaAs. Polymers can be deposited on almost any substrate at relatively low temperatures and can be spin-coated directly onto Si wafer or hybrid circuits. Organic polymers such as poly(methyl methacrylate), polystyrene, and polycarbonate have excellent transparency in the visible wavelength, and they are used as materials for a variety of optical components.[2] However, these polymers do not have sufficient thermal stability for the application of optoelectronic integrated circuits because the current manufacturing processes for ICs include curing processes at temperatures of up to 400 °C.[1]

Polyphenylsilsesquioxane (PPSQ) is an inorganic polymer with a ladder type structure of siloxane bonds as main chain and phenyl groups as side chain.[3] PPSQ has received considerable interest in the microelectronic industry due to high thermal resistance over 500 °C, high chemical and mechanical stability, and low dielectric constant.[4] As PPSQ has also high optical transparency, PPSQ has been suggested as promising materials for wafer-scale optical waveguide interconnects. Furthermore, precise control of the refractive index in the range below 1.0% of its value is essential for fabricating single-mode optical waveguides with core/cladding systems and for optical interconnections between different materials.[2] In the case of the inorganic optical materials, the refractive index is controlled by doping heavy elements such as germanium and phosphorus, or light elements such as boron and fluorine. On the other hand, that of optical polymers can be controlled by introducing different substituents or atoms to the polymer structure, or controlling the polymer blend and the copolymerization.[2]

We had developed silicone ladder polymers having high transparency and high thermal stability,[4] and therefore, have attempted precise control of their refractive index aiming at application to materials for optical waveguides in this work. We report here the refractive index controllability and the thermal stability of a novel random copolymer synthesized by partially substituting silicon atoms of PPSQ by germanium atoms (Ge-PPSQ; Scheme 1) through the condensation reaction of the hydrolysate of organotrichlorosilane and organotrichlorogermanium in the presence of KOH as a base.[3]



Scheme 1. Synthesis of Ge-PPSQ.

Methyl isobutyl ketone (634 mL), trichlorophenylsilane (0.9 mol) and trichlorophenylgermanium (0.1 mol) were introduced into a 2 L three neck flask equipped with a reflux condenser. Pure water (270 mL) was added dropwise over 2 h under stirring at 0 °C. The mixture containing the hydrolysate product was washed with pure water to be neutralized to give prepolymer with average molecular weight of 2.0×10^3. The methanol solution (7.6 ml) of KOH (0.38 g) was added into the prepolymer solution under reflux for 20 h, resulting in polymerization by dehydration condensation. The reaction mixture was purified by pouring into an aqueous solution (3 L; $MeOH/H_2O = 50/50$) to give white precipitate, that was dried in vacuo. The resulting Ge-PPSQ with 10 mol% Ge atoms was obtained at the yield of 48%. The average molecular weight measured by gel permeation chromatograph (JASCO TRI ROTER-IV) was 5.2×10^4 with low dispersion as well as PPSQ. The Ge-PPSQ films could be formed by spin-coating the anisole solution of Ge-PPSQ on the substrates. Ge-PPSQ was identified by FT-IR (Perkin-Elmer 240C), ^{29}Si, ^{1}H, ^{13}C-NMR (JEOL EX-270, 270 MHz, $CDCl_3$, TMS as an internal standard at room temp.) and X-ray photoelectron spectroscopy (Shimadzu XPS1000).[5]

The IR absorption bands at 1130 and 1038 cm^{-1} attributed to Si-O asymmetrical stretching vibrations of Ge-PPSQ were observed. These bands indicated the presence of the *cis*-syndiotactic double-chain structure[6] of Ge-PPSQ. We also observed the IR absorption peaks at 1430, 1260, and 880 cm^{-1} attributed to Si-C, Ge-C, and Ge-O stretching vibrations, respectively. Furthermore, we observed the new IR absorption shoulder at 1080 and 980 cm^{-1}, and a peak at 560 cm^{-1}. The shoulders were respectively shifted to lower wavenumber by 50 and 58 cm^{-1} than the absorption bands attributed to Si-O asymmetrical stretching vibrations. The latter

Table 1. Refractive indices and thermal resistance of Ge-PPSQ and PPSQ

Polymer	Ge Content/mol%[a]	Mw[b]	I_{Ge}/I_C[c]	Refractive index	Thermal decomposition temperature/°C[d]
Ge-PPSQ	10	5.2×10^4	0.0132	1.573	503
Ge-PPSQ	5	5.4×10^4	0.0068	1.566	513
PPSQ	0	6.0×10^4	0	1.558	530

[a] The content trichlorophenylgermanium at the synthesis of Ge-PPSQ. [b] Average molecular weight.
[c] The values of I_{Ge} and I_C are the intensities at 1223 and 286 eV of XPS spectra, respectively. [d] N_2 atmosphere.

peak was shifted to lower wavenumber by 35 cm^{-1} than the absorption attributed to Si-O-Si deformation vibration (595 cm^{-1}), suggesting its attribution to Si-O-Ge deformation vibration. The shifts of vibration modes should be due to the presence of neighboring Ge in the chain structure, supporting the formation of Si-O-Ge moiety in Ge-PPSQ.

The presence of Ge atoms in Ge-PPSQ was ensured by the observation of the signal of Ge in the X-ray photoelectron spectrum. The signals attributed to Ge atoms were observed at the binding energies of 122 (Ge $3p_{3/2}$), 342 (Ge LMN), and 1223 eV (Ge $2p_{3/2}$), clarifying that Ge atoms were contained in the structure of Ge-PPSQ. Furthermore, the intensity ratio, I_{Ge}/I_C where I_{Ge} and I_C were respectively the intensities of 1223 (Ge $2p_{3/2}$) and 286 eV(C 1s), was proportional to that of the quantity of Ge atoms in Ge-PPSQ (see Table 1).

The ^{13}C-NMR spectrum of PPSQ showed the signals at 134.0, 131.4, 129.9, and 127.4 ppm assigned to the C atoms of the 2, 1, 4, and 3 positions of the phenyl group in PPSQ, respectively (Figure 1(a)).[7] The same signals at 134.0 and 127.4 ppm assigned to the C atoms of 2 and 3 positions were also observed in the ^{13}C-NMR spectrum of Ge-PPSQ (Figure 1(b)). And the signals assigned to the C atoms of ipso and meta positions of phenyl groups in Ge-PPSQ were shifted slightly to the higher magnetic field than those assigned to the C atoms of the 1 and 4 positions of PPSQ, indicating the superimposed signals of 1 and 1′, and 4 and 4′. In addition to the above-mentioned signals, new signals were observed at 132.9 and 128.3 ppm only for Ge-PPSQ. The assignment of these new peaks of the 2′ and 3′ carbons was supported by estimating the magnetic shielding tensors of $PhSi(OH)_3$ and $PhGe(OH)_3$ by the 3–21G basis set and the Hartree Fock method in the Gaussian 98 program. The signals attributed to the C atoms of the 2′ and 3′ positions of $PhGe(OH)_3$ were expected to be shifted to the higher magnetic field and the lower magnetic field compared with those of the 2 and 3 positions of $PhSi(OH)_3$, respectively.

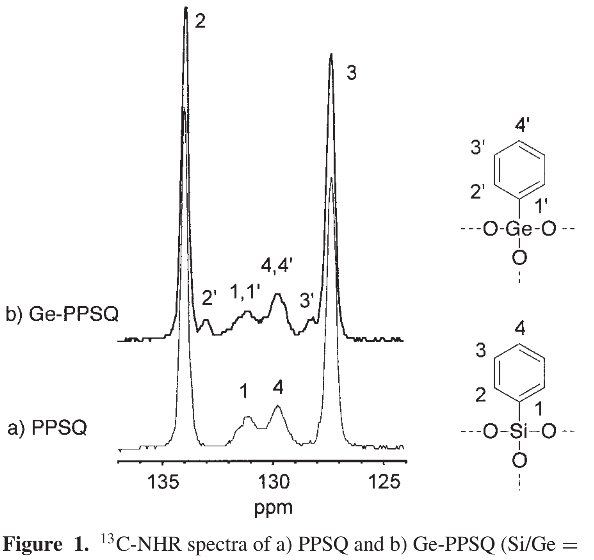


Figure 1. ^{13}C-NHR spectra of a) PPSQ and b) Ge-PPSQ (Si/Ge = 90/10).

The characteristics of refractive index and thermal stability were measured with polymer films after curing at 350 °C, at which Ge-PPSQ and PPSQ changed to insoluble polymers through condensation of terminal silanol groups. As the refractive index is expressed by the molecular refraction and the molecular volume,[8] the introduction of Ge atoms to the main chain of PPSQ is expected to change it. The in-plane refractive indices (n_{TE}) of PPSQ and Ge-PPSQ films with 10 μm thickness were measured with a Metricon PC-2010 prism coupler using light from a 0.63 μm helium-neon laser diode. The refractive index increased linearly with increasing the Ge content in the copolymer, as shown in Table 1. The n_{TE} values of Ge-PPSQ films with 10 mol% Ge content after curing at 350 °C was 1.573, which was higher by 0.96% than that of PPSQ (1.558). The difference of the refractive index between Ge-PPSQ (Ge: 10 mol%) and PPSQ should be large enough for the application to single-mode optical waveguides with core/cladding systems.[9] This shows that the refractive indices of PPSQ can be controlled by changing the Ge content in the main chain. From thermogravimetric analyses, the thermal decomposition of Ge-PPSQ (Ge: 10 mol%) under N_2 atmosphere initiated at 503 °C, indicating that Ge-PPSQ kept the high thermal stability equivalent to PPSQ (530 °C).[3] Ge-PPSQ film also had no peaks at around the telecommunication wavelengths of 1.30 and 1.55 μm as well as PPSQ film in the near-infrared spectrum.[10]

We have developed a novel polyphenylsilsesquioxane polymer partially containing Ge atoms in the main chain with high heat resistance and high transparency at 1.30 and 1.55 μm, used for telecommunication. The refractive index can be also controlled by changing the Ge content. Ge-PPSQ can be applied to polymer waveguides of integrated optical devises as a substituent material of conventional ones.

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5 Spectral data: for Ge-PPSQ: IR (KBr): 3435 (st, Si-OH), 1430 (st, Si-C), 1260 (st, Ge-C), 1130, 1038 (st, Si-O), 880 (st, Ge-O), 595 (δ, Si-O-Si), 560 (δ, Si-O-Ge) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 7.25 (br, Ph), 1.42 (s, OH) ppm. ^{29}Si-NMR($CDCl_3$) δ: −78.0 (s, $RSiO_3$) ppm.
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