A Novel Heat-Resist Silicone Polymeric Material with Refractive Index Controllability

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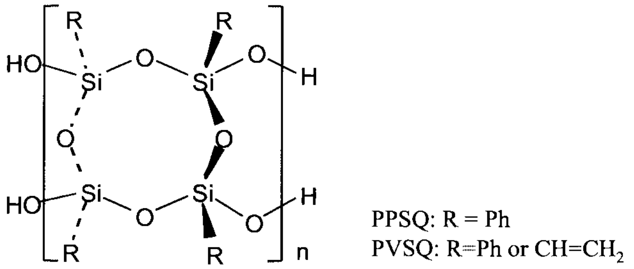
(Received August 2, 2001; CL-010737)

A novel heat-resist optical waveguide silicone copolymer was successfully developed, with refractive index controllability between 1.558 and 1.523 by partially changing the substituent in the side chain, and high transparency in the visible and near-infrared region, 0.6–1.7 µm.

Polymer waveguides have been investigated for use as flexible and low cost optical interconnects and optoelectronic integrated circuits. For many applications, polymers offer significant advantages over waveguide materials such as SiO_2, $LiNbO_3$ and GaAs.[1,2] Polymers can be deposited on almost any substrate at relatively low temperatures and can be spin-coated directly onto Si wafer or hybrid circuits. They can also be fabricated easily and at low cost. The current manufacturing process for ICs includes short–term processes at temperatures of up to 400 °C. Therefore, waveguide polymeric materials should have high thermal stability and a high polymer decomposition temperature as well as high transparency at the wavelengths of optical communication, 0.6–1.7 µm. Precise control of the refractive index also is essential for fabricating single-mode optical waveguides with core/cladding systems and for optical interconnections between different materials. The refractive index of optical polymers can be controlled by introducing different substituents and atoms to the polymer structure or controlling the polymer blend and the copolymerization. Matsuura et al. fabricated singlemode waveguides with high thermal stability by using fluorinated polyimides.[3–5] The refractive index was controlled by changing fluoroalkyl groups contents or polymer blend. M. Usui et al. applied a deuterated polysiloxane to singlemode channel waveguides.[6] The C–H vibration absorptions in the infra-red region were reduced by substituting hydrogen with deuterium therein. L. A. Honark et al. reported the refractive index controllability of polysilynes, amorphous alkyl silicon network polymers, by using photo-oxidation of Si–Si bonds with UV irradiation (λ = 310 nm).[7] It is, however, still necessary to develop the much cheaper optical waveguide materials with high heat stability and good mechanical stability.

Silicone ladder polymer (PPSQ) is an inorganic polymer with a ladder type structure consisting of siloxane bonds as a main chain and phenyl groups as a side chain (Scheme 1).[8–11] PPSQ has received considerable interest in the microelectronic industry due to high thermal resistance over 400 °C, good chemical and mechanical stability, and low dielectric constant.[11] As PPSQ has also high optical transparency in spite of a non-deuterated or non-fluorinated structure[11] and the synthetic cost is lower than deuterated or fluorinated polymers, PPSQ has been suggested as a promising material for wafer-scale optical waveguide interconnects. Controllability of the refractive index is a requisite for optical waveguide materials. However, no report can be found in which the refractive index of the silicone ladder polymer is controlled. We have developed a novel silicone ladder copolymer (PVSQ; Scheme 1) with a controllable refractive index by partially substituted vinyl groups for phenyl groups in the side chain of PPSQ.



Scheme 1.

PVSQ copolymers were prepared in the two steps, i. e., hydrolysis and condensation of organotrichlorosilane.[9–11] At first, the starting materials, a mixture of trichlorophenylsilane and trichloro(vinyl)silane having the almost same reactivity to hydrolysis, in the desired molar ratio, was hydrolyzed in methyl isobutyl ketone (MIBK) under stirring at 0 °C. After removal of the acid layer of the hydrolysate product, the MIBK solution was sufficiently washed with pure water to be neutralized, and then the prepolymer was obtained. The prepolymer solution was heated in KOH aqueous under reflux, resulting in polymerization by dehydration condensation reaction. The reaction mixture was purified by pouring into a methanol aqueous solution to give white precipitate. The polymer was dried sufficiently in vacuo. We synthesized polymers of the average molecular weight of 4×10^4–5×10^4 with various vinyl groups content from 0 mol% to 50 mol% in the side chain.[12]

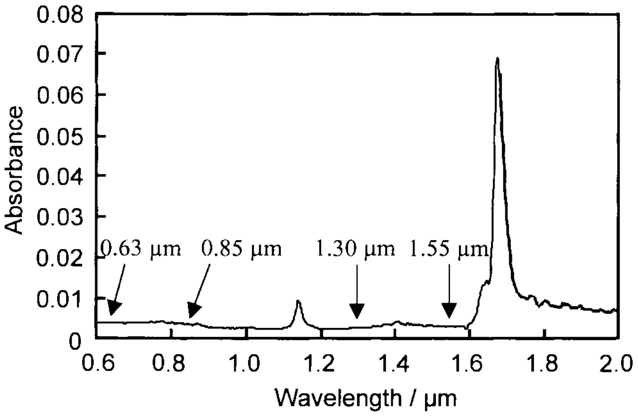


Figure 1. The visible–near-infrared spectrum of PVSQ film with the 10 mol% vinyl group content in the side chain.

The visible–near-infrared absorption spectra were measured with a Nihon Bunkou V-570-DS. The visible–near-infrared absorption spectra of the PVSQ film with 10 mol% vinyl groups showed the same shape as that of the PPSQ film (Fig. 1), indicating that the partial introduction of vinyl groups to the side chain of PPSQ hardly gave influence on the transparency at the optical communication wavelengths. For the PVSQ film cured at 350 °C for 1 h, three peaks were observed in the near-infrared region: the third harmonics of stretching vibration of the C–H bond ($3\nu_{CH}$, 1.15 µm), the combination of the second harmonics of the stretching vibration and the deformation vibration of the C–H bond ($2\nu_{CH}+\delta_{CH}$, 1.41 µm), and the second harmonics of stretching vibration of the C–H bond ($2\nu_{CH}$, 1.68 µm). We emphasize that there were no peaks at the wavelengths of 0.63, 0.85, 1.30, and 1.55 µm used for data communication and telecommunication (indicated by the arrows in Fig. 1). PVSQ showed a high transparency over the entire optical communication wavelengths due to the specific inorganic-like polymer with a ladder type structure consisting of siloxane bonds such as a waveguides material of SiO_2.

As the refractive index is a function of the molecular refraction and the molecular volume,[13] the introduction of vinyl groups to the side chain of PPSQ is expected to induce the change of the refractive index. The in-plane refractive indices (n_{TE}) were measured with a Metricon PC-2010 prism coupler using light from a 0.63 µm helium–neon laser. The n_{TE} values of PVSQ films cured at 200 °C with various vinyl group content of 0–50 mol% are shown in Figure 2. The refractive indices decreased with increasing the vinyl group content, and can be precisely controlled between 1.558 and 1.523.

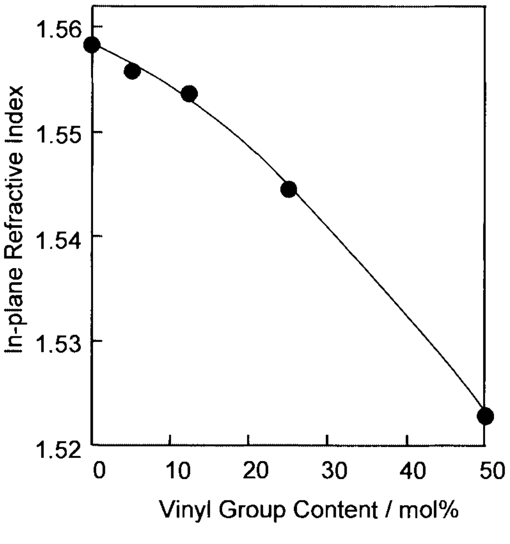


Figure 2. The correlation between the vinyl group content in the side chain of PVSQ and the in-plane refractive index (n_{TE}).

The thermogravimetric analyses (TGA) were performed by a Du Pont Model 951 thermogravimetric analyzer. All the polymers with less than 50 mol% vinyl group content showed the thermal decomposition temperatures, defined as 10% weight loss in air, above 415 °C, which is enough thermal stability for polymer waveguide application.

We have developed a novel heat-resist optical waveguide silicone ladder copolymer with high transparency in the visible and near-infrared region, 0.6–1.7 µm, which is the region used for data communication and telecommunication. And the refractive index can be controlled by introducing the different substituents to the side chain of PPSQ and changing the content. This indicates the potential of these polymer waveguides for applications to integrated optical devises.

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12 Determination of molecular weight was obtained with a JASCO Model of TRI ROTER-IV gel permeation chromatography (GPC). Fourier transform infrared (FT-IR) spectra were measured on a JASCO Model FT/IR-230 spectrometer. ^1H and ^{29}Si NMR data were obtained with a Bullker Model MSL-300(230 MHz) instrument in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. FT-IR : 3435 (Si–OH), 1430 (Si–Ph), 1405 (Si–C=C), 1130, 1038 (Si–O–Si) cm^{-1}. ^1H NMR (chloroform-*d* / TMS) : δ = 7.25 (br, Si–Ph), 5.80 (br , Si–C= C), 1.50 (s, Si–OH) ppm. ^{29}Si NMR (chloroform-*d* / TMS) : δ = –78.0 (s, $RSiO_3$) ppm.
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