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Preparation and Characterization of Methylsilsesquioxane Thin Film Containing Tris(ethylenediamine)cobalt(III) Chloride as a Photobase Generator

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Porous methylsilsesquioxane thin films were prepared using the sol−gel process, with tris(ethylenediamine)cobalt(III) chloride ($Co(en)_3Cl_3$) as a photobase generator and polypropylene glycol (PPG) as a template. The generation of amines was confirmed for more than 2 min of ultraviolet (UV) irradiation. The prepared film with the UV irradiation and subsequent heat treatment showed a low refractive index of $n = 1.35$. Subsequent field-emission scanning electron microscopy (FE-SEM) observations confirmed that shrinkage of the film with the heat treatment was suppressed in the film with UV irradiation. The photogenerated amines from $Co(en)_3Cl_3$ worked as a catalyst for the condensation reaction in the gel films during the initial stage of heat treatment. A porous structure was obtained using the thermal decomposition of PPG without collapse of the gel network.

1. Introduction

Photoacid and photobase generators, which generate acid and base materials through photoirradiation, are used in a chemically amplified photochemistry process. They have attracted much attention in the electronics, optical, and coatings industries.[1−3] An advantage of the chemically amplified photochemistry process using such photosensitive compounds over the standard processes is their high sensitivity to light. Commonly used photoinitiators are organic compounds that produce radicals and/or acids upon irradiation. Organic photoacid generators as a chemically amplified cure resist are indispensable for the practical manufacture of large-scale integration (LSI).[3] Base-catalyzed cross-linking reactions have also been investigated and developed extensively, especially in the field of adhesive agents and coatings. Consequently, photobase generators have been sought for use as a novel photolabile catalyst. However, only a few examples, such as carbamates, O-acyloximes, ammonium salts,[1] and cobalt(III) amine complexes,[4] have been reported as photobase generators.

The sol−gel process has been widely used for the preparation of inorganic or inorganic−organic hybrid materials. Especially, organically modified siloxane materials have attracted much attention for use in optical, electrical, and mechanical applications.[5] For example, methylsilsesquioxane thin films have been studied for use as a dielectric layer with a low dielectric constant.[6] We have also been studying silsesquioxane materials using trifunctional alkoxysilanes.[7−9]

In sol−gel reactions, compounds that exhibit an acid or base character are commonly used as catalysts for hydrolysis and condensation reactions, because the rate of hydrolysis and condensation are strongly dependent on pH. Control of the precursor gel shrinkage is very important in the preparation of thin films or bulk materials using sol−gel processing. Tamaki et al. have reported that photolithographic patterning can be achieved through the combination of siloxane oligomers and a photoacid generator.[10] They showed that both negative and positive patterns were fabricated through control of the sol−gel reaction with a balance between the photoacid generator and the amine content added as a catalyst.

In this study, methylsilsesquioxane thin films containing an inorganic photobase generator were prepared using the sol−gel method with methyltriethoxysilane (MTES). The effects of ultraviolet (UV) irradiation on the structure and optical properties of the films were investigated. In this study, a cobalt(III) amine complex was used as a photobase generator.[4] Cobalt complexes coordinated by nitrogenous base molecules release bases such as ammonia and

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alkyl amine when subjected to UV irradiation. Among the cobalt(III) complexes, we specifically addressed tris(ethylenediamine)cobalt(III) chloride ([Co(en)$_3$]Cl$_3$), because this complex is easily synthesized, soluble in water and ethanol, stable at elevated temperature, and strongly absorbent of light in the UV region, because of the presence of N-to-Co charge transfer.

2. Experimental Section

Methylsilsesquioxane thin films that contained tris(ethylenediamine)cobalt(III) chloride was prepared from methyltriethoxysilane (MTES), ethanol (EtOH), 0.4 wt % phosphoric acid (H_3PO_4) aqueous solution, polypropylene glycol (PPG, M_w = 1000), and tris(ethylenediamine)cobalt(III) chloride ([Co(en)$_3$]Cl$_3$). A mixture of MTES, EtOH, and H_3PO_4 as a catalyst, and PPG as a template for porous structure, was stirred at room temperature for 1 h. Subsequently, [Co(en)$_3$]Cl$_3$ was dissolved in the obtained solution. Molar ratios of starting materials (MTES:EtOH:H_2O (containing 0.4 wt % H_3PO_4):PPG (M_w = 1000):[Co(en)$_3$]Cl$_3$) equal to 1:6:12:3.51 × 10^{-3}: x (where $x = 0-2.48 \times 10^{-4}$, 0.33 wt %) were used to prepare the sol.

The coating was conducted on quartz substrates (n = 1.45), using a dipping−withdrawal technique (withdrawal speed = 3 mm/s). The films were coated onto one side of the substrates. One side was covered with cellophane tape during coating, and the tape was removed before heat treatment. The obtained gel films were irradiated with a deep UV-type ultrahigh-pressure mercury lamp (3 mW/cm^2 at 254 nm; from Ushio, Inc.). After UV irradiation, the films were heat-treated at 400 °C for 30 min.

The cross section of the film was observed using field-emission scanning electron microscopy (FE-SEM) (Model S-4500; Hitachi, Ltd.). Optical transmission spectra were measured using an ultraviolet−visible light (UV−vis) light spectrophotometer (Model V-570; Jasco Corp.). The refractive index of the film was calculated from the transmittance using Fresnel's equation.[11] To monitor the sol−gel reaction in the film, a Fourier transform infrared (FT-IR) spectrophotometer (Model Spectrum GX; Perkin−Elmer, Inc.) was used. The sample films were coated onto one side of the silicon substrates, which were irradiated with N_2-O_2 plasma beforehand, to improve their adhesion to the films.

3. Results and Discussion

Figure 1 shows the ultraviolet−visible (UV−vis) absorption spectra of the coating sol that consists of 0.33 wt % tris(ethylenediamine)cobalt chloride ([Co(en)$_3$]Cl$_3$) with UV irradiation for 0, 2, 5, 10, and 20 min. The UV−vis spectra were measured using a quartz cell with a light path length of 1 mm. An intense band at 210 nm, arising from N-to-Co charge transfer transition of the cobalt complex, is observed. The intensity decreased as the irradiation time increased, indicating the liberation of ethylenediamine with a photoredox process. The color of the coating sol that contained Methyl Orange as a pH indicator was changed from red to yellow with UV irradiation. This change also supports the liberation of ethylenediamine with UV irradiation.

Figure 2 shows the transmission spectra of quartz substrates coated with heat-treated methylsilsesquioxane films with 0.33 wt % of [Co(en)$_3$]Cl$_3$, which were UV-irradiated for 0, 0.5, 2, 5, and 10 min before heat treatment. The films were formed only on one side of the substrates. The spectrum for 0 min of irradiation corresponds to the substrate with a methylsilsesquioxane film, where no bases were generated from [Co(en)$_3$]Cl$_3$ in the gel film before heat treatment. The transmittance of the films with UV irradiation for more than 2 min and subsequent heat treatment at 400 °C is increased, indicating that the film became porous because of the generation of amines upon photolysis of [Co(en)$_3$]Cl$_3$. The spectra for 2, 5, 10 min are almost identical, confirming that more than 2 min of irradiation on gel film brought a sufficient photoredox reaction and

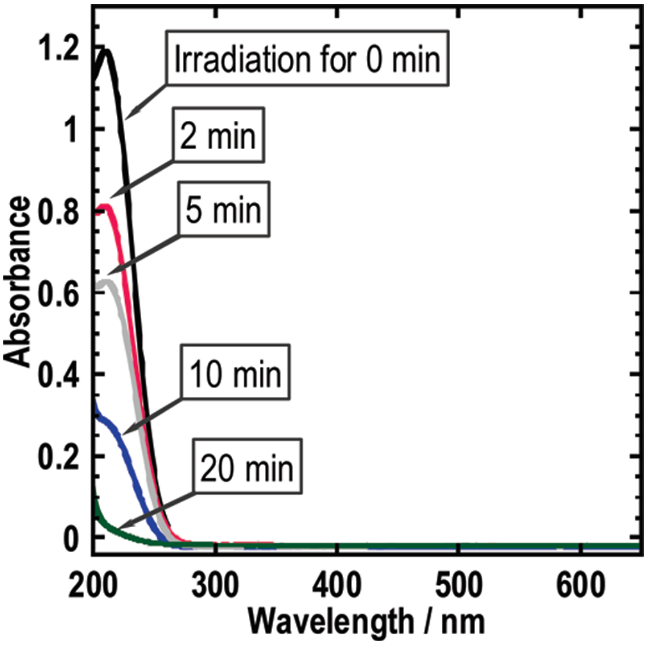

Figure 1. Absorption spectra of the coating sol that contained [Co(en)$_3$]Cl$_3$, subjected to UV irradiation for 0, 2, 5, 10, and 20 min.

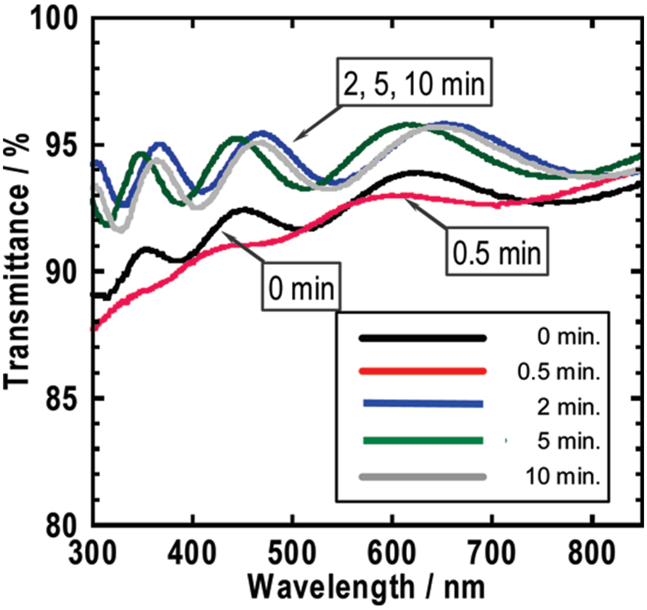

Figure 2. Transmission spectra of the coatings that contained [Co(en)$_3$]Cl$_3$, subjected to UV irradiation for 0, 0.5, 2, 5, and 10 min.

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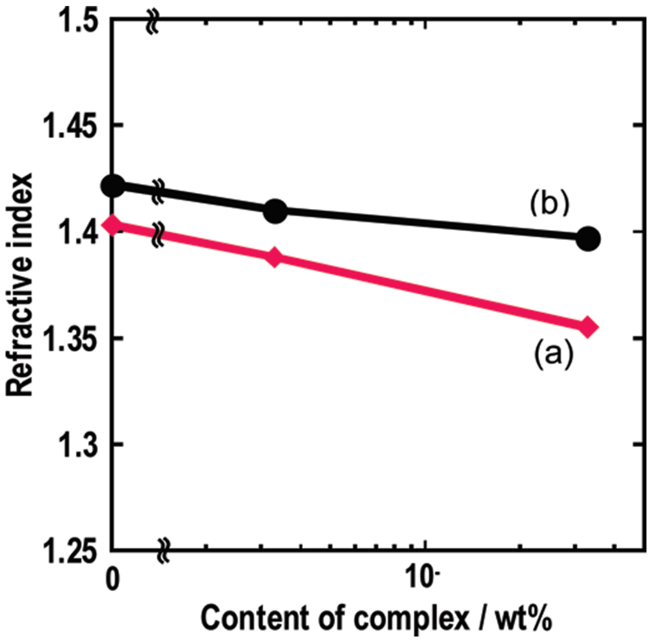

Figure 3. Relationship between the refractive index of the heat-treated films and the content of the $[Co(en)_3]Cl_3$ in the coating solutions: with UV irradiation (curve a) and without UV irradiation (curve b).

the generation of bases in the film. The spectra for 2, 5, and 10 min also indicate that optical thickness of the heat-treated films was not changed by the UV irradiation.

Figure 3 presents the relationship between the content of the $[Co(en)_3]Cl_3$ in the coating solution and the refractive index of the heat-treated films with UV irradiation (curve a) and without UV irradiation (curve b). UV light was irradiated for 10 min. The refractive index of the films with a $[Co(en)_3]Cl_3$ content of 0 wt % corresponds to that of cobalt-complex-free films. In the methylsilsesquioxane film without $[Co(en)_3]Cl_3$, the refractive index of the film that had been only heat-treated at 400 °C was 1.42, whereas that of the film with UV irradiation and subsequent heat treatment at 400 °C was 1.40. The difference in the refractive index (Δn) is 0.02. This slight decrease in the refractive index in the film without $[Co(en)_3]Cl_3$ must be the result of infrared (IR) light irradiation from the mercury lamp with no IR-cutting filter. In the methylsilsesquioxane film with 0.33 wt % $[Co(en)_3]Cl_3$, the refractive index of the irradiated film that contained $[Co(en)_3]Cl_3$ was 1.35, whereas that of nonirradiated film was 1.40, meaning that Δn was 0.05. The change in the refractive index of the heat-treated film that contained the complex is greater than that without the complex, indicating that $[Co(en)_3]Cl_3$ in the methylsilsesquioxane gel film assisted a decrease in the refractive index through UV irradiation.

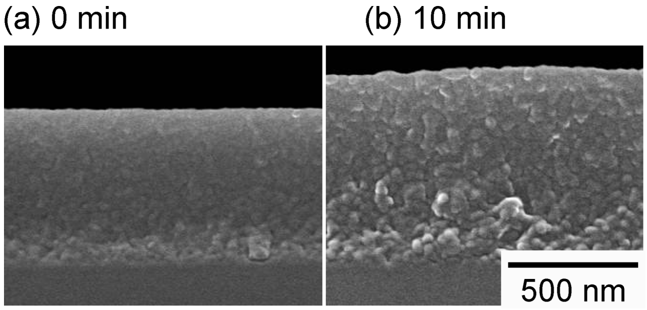

Figure 4. FE-SEM images of the cross section of the methylsilsesquioxane films containing $[Co(en)_3]Cl_3$ irradiated for (a) 0 min and (b) 10 min.

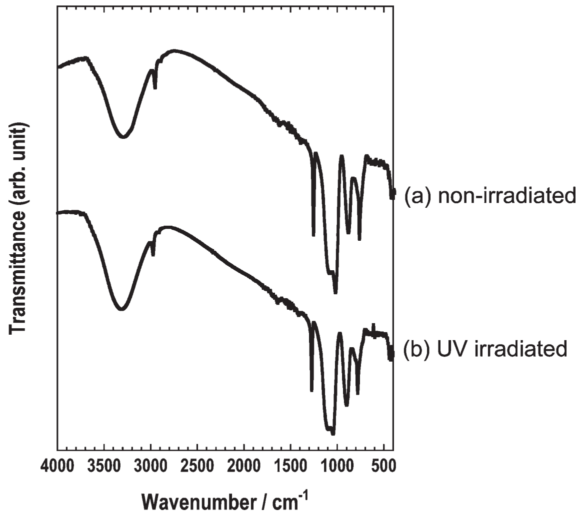

Figure 5. FT-IR spectra of methylsilsesquioxane gel film containing $[Co(en)_3]Cl_3$ without UV irradiation (spectrum a) and with UV irradiation (spectrum b).

Figure 4 presents FE-SEM images of the cross section of the methylsilsesquioxane film that contained 0.33 wt % $[Co(en)_3]Cl_3$, subjected to UV irradiation for 0 min (Figure 4a) and 10 min (Figure 4b). The thickness of the heat-treated methylsilsesquioxane film without UV irradiation is 610 nm, whereas that of the film with UV irradiation is 720 nm. Furthermore, images show that the irradiated film is more porous than the nonirradiated film. These results suggest that shrinkage in the direction of the film thickness during heat treatment was suppressed. The photoreaction of the cobalt complex must play an important role in the formation of the porous film.

Two types of $[Co(en)_3]Cl_3$-containing films were prepared: one was UV-irradiated and the other was not irradiated but dried in darkness. The FT-IR spectra of these films were collected, and their spectral difference was calculated. In a calculated difference spectrum, peaks and valleys are usually observed. A peak corresponds to the increase in the amount of a bond, while a valley corresponds to a decrease in the amount of a bond.

Figure 5 shows the FT-IR spectra of the gel films that contained $[Co(en)_3]Cl_3$ without UV irradiation and with UV irradiation. Figure 6 portrays the differential spectrum, where the spectrum of a nonirradiated gel film (Figure 5a) was subtracted from that with UV irradiation (Figure 5b). Four valleys (at 1270, 1123, 1027, and 780 cm^{-1}) and one peak (at 884 cm^{-1}) are visible. The band at 1270 cm^{-1} is assigned to the Si−C bond in MTES, the bands at 1123 and 1027 cm^{-1} are assigned to vibration of the O−Si−O chains. The band at 780 cm^{-1} is assigned to the O−Si−O bending mode. The band at 884 cm^{-1} is assigned to the Si−OH stretching mode. Consequently, the differential spectrum shows that more Si−OH groups remain in the UV-irradiated gel films. Because of the formation of bases with UV irradiation in the gel film that contained

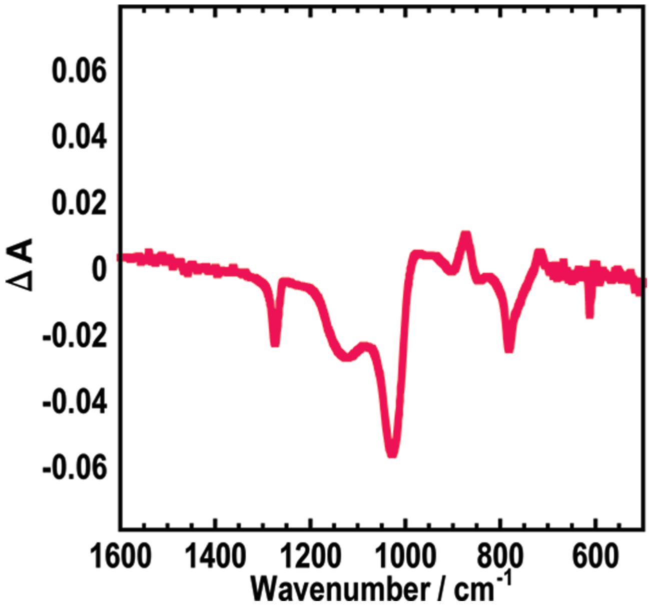

Figure 6. Differential spectrum calculated using the spectrum of the irradiated gel film and nonirradiated gel film: the spectrum of nonirradiated gel film (Figure 5a) was subtracted from that with UV irradiation (Figure 5b).

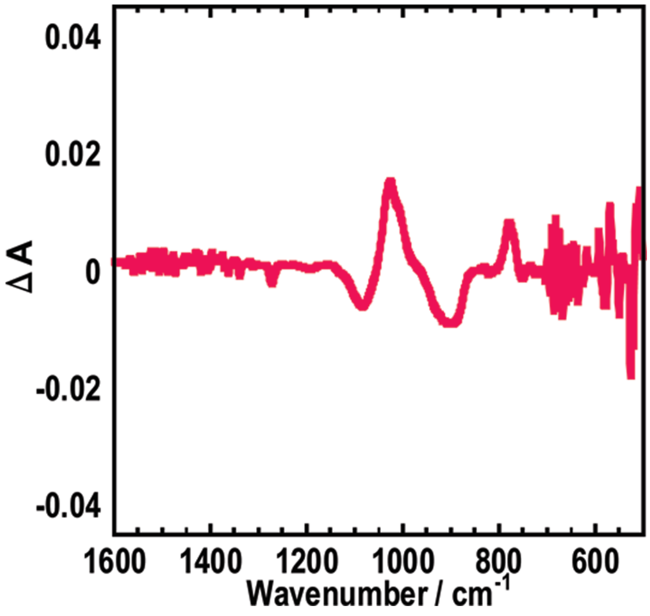

Figure 7. Differential spectrum calculated using the spectrum of the irradiated gel film and nonirradiated gel film heat-treated at 20 °C for 3 min: the spectrum of nonirradiated gel film was subtracted from that with UV irradiation.

$[Co(en)_3]Cl_3$, the base might suppress the formation of Si−O−Si during drying at room temperature.

To elucidate reaction processes in the irradiated film during heat treatment, the gel film was heat-treated at 120 °C for 3 min. Heat treatment at 120 °C for 3 min can be assumed to be the initial stage of the heat treatment at 400 °C for 30 min. Figure 7 shows the "irradiated" minus "nonirradiated" FT-IR difference spectrum of the gel film that contained $[Co(en)_3]Cl_3$ after heat treatment at 120 °C for 3 min. The spectrum exhibits two valleys (at 1083 and 884 cm^{-1}) and two peaks (at 1027 and 780 cm^{-1}). The band at 1083 cm^{-1} corresponds to vibration of the O−Si−O chain. The band at 884 cm^{-1} is assigned to the Si−OH stretching mode. Consequently, Si−OH bonds were decreased, whereas O−Si−O networks were formed with the heat treatment. This result suggests that the heat treatment after the UV irradiation on the gel film that contains $[Co(en)_3]Cl_3$ forms the cross-linked network at the initial stage. Amines from $[Co(en)_3]Cl_3$ must work as a catalyst for the condensation reaction in the low-temperature heat treatment.

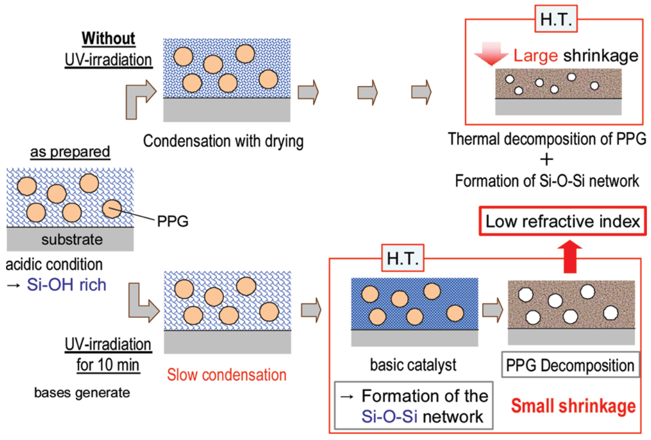

Figure 8. Schematic showing the preparation of the porous methylsilsesquioxane film with UV irradiation, using $[Co(en)_3]Cl_3$ as a photobase generator.

Figure 8 presents a schematic sketch for the preparation of porous methylsilsesquioxane film with UV irradiation, using $[Co(en)_3]Cl_3$ as a photobase generator. In the as-dried film, many Si−OH groups exist under acidic conditions, because phosphoric acid is added as a catalyst. Although the condensation reaction to generate Si−O−Si bonds proceeds during the drying process, most Si−OH groups remain. Subsequent heat treatment at 400 °C must result in both the thermal decomposition of polypropylene glycol and the formation of Si−O−Si bonds simultaneously, leading to the collapse of the gel network. This must cause a reduction in both the pore size and the pore volume. Consequently, the film thickness should be decreased significantly and a certain level of porous film with a refractive index of 1.40 was formed. In contrast, in the gel film with UV irradiation, the condensation reaction of Si−OH groups does not proceed during UV irradiation at room temperature, because the generation of amines upon photolysis of the $[Co(en)_3]Cl_3$ suppresses Si−O−Si formation at room temperature. However, the heat treatment after UV irradiation on the gel film triggers two processes: condensation of Si−OH to form rigid Si−O−Si networks and subsequent decomposition of polypropylene glycol. In the first step, Si−OH groups undergo condensation under the amine catalyst in the gel film that contains polypropylene glycol, and a matrix with rigid networks should be formed. In the second step, polypropylene glycol is decomposed without collapse of the rigid surrounding matrix. Consequently, the thickness reduction was suppressed, leading to a more porous film, with a refractive index of 1.35.

This process can control the condensation reaction in the gel films with UV irradiation. Therefore, this process is applicable to the micropatterning of thin films. The micropatterning of gel films containing $[Co(en)_3]Cl_3$ as a photobase generator is now under study. The results will be described in future reports.

4. Conclusion

Methylsilsesquioxane thin films that contained $[Co(en)_3]Cl_3$ as a photobase generator were prepared using the sol−gel method. The prepared film with the UV irradiation and subsequent heat treatment at 400 °C showed a low refractive index ($n = 1.35$). The field-emission scanning electron microscopy (FE-SEM) observation confirmed that the shrinkage of the film with heat treatment was suppressed in the film with UV irradiation. From these results and Fourier transform infrared (FT-IR) measurements, we elucidated the reaction process through UV irradiation and subsequent heat treatment. In the irradiated film, there were more Si−OH groups and less of an O−Si−O network than that observed with the nonirradiated film. The subsequent heat treatment at 400 °C is divisible into two stages. The initial stage of the heat treatment is the promotion of the cross-linking of Si−OH groups around the remaining polypropylene glycol, under the basic condition. The second stage is removal of the polypropylene glycol without collapse of the gel network. Consequently, the film shrinkage was suppressed during heat treatment with the photobase generator. The porous film, with a refractive index of $n = 1.35$, was obtained using the present procedure.

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