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Letter

Relationship between polysilsesquioxane molecular structure and low dielectric properties for high-frequency applications

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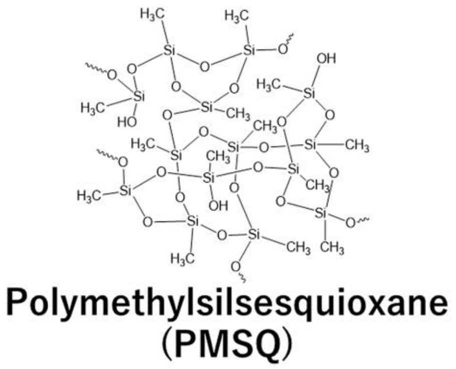
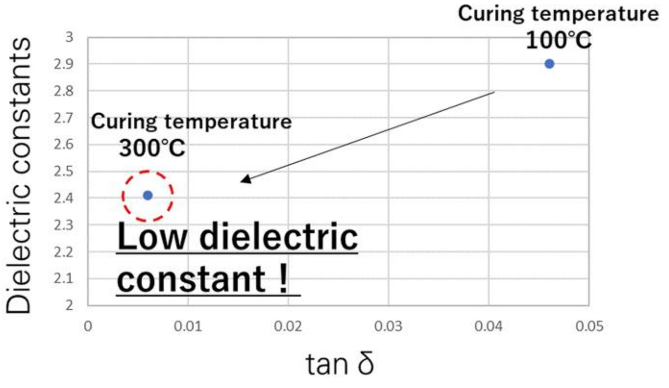
Abstract

In this study, polysilsesquioxane was synthesized under various polymerization conditions using trimethoxymethylsilane, which contains a methyl group as an organic substituent, as the starting material. The high-frequency dielectric properties of the synthesized material were evaluated, revealing that the polymer with reduced silanol groups exhibited low-dielectric properties ($\varepsilon_r = 2.41$, $\tan \delta = 0.006$ at 18.4 GHz). These results highlight the potential of polysilsesquioxanes as promising candidates for heat-resistant, low-dielectric materials in high-frequency applications.

Keywords: high-frequency dielectric properties, low-dielectric material, polysilsesquioxane.

Graphical Abstract





Due to the increasing use of high-frequency communications in recent years, high-speed transmission and low transmission loss have become critical challenges. Addressing these issues requires reducing signal transmission delay and dielectric loss. Since both are related to the dielectric constant and dielectric loss tangent of polymer insulating materials, the demand for low-permittivity, low-dielectric-loss substrate materials is growing.[1] Low dielectric loss tangent is particularly important for reducing transmission loss. Polymers such as PTFE, LCP, and polyimide have been considered as low dielectric constant materials, but they face challenges related to their coefficient of linear thermal expansion and processability.[2] Polysilsesquioxanes (PSQs), silicon-based polymers, have attracted significant interest in both academic and industrial fields as organic–inorganic hybrid materials due to their unique properties.[3–9] These materials feature a siloxane skeletal structure, granting them excellent electrical properties, flame retardancy, and chemical resistance. As high-frequency communications transmit and receive large amounts of data at high speeds, materials may become hot, making high heat

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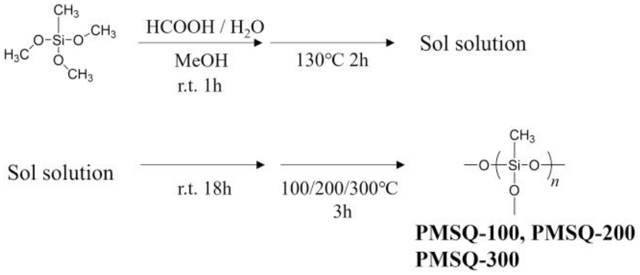
resistance a critical requirement. Regarding the dielectric properties of materials composed of siloxane bonds, polydimethylsiloxane ($\varepsilon_r = 2.6$, $\tan\delta = 0.01$) and quartz ($\varepsilon_r = 3.8$, $\tan\delta = 0.0038$) are known to exhibit low dielectric constants or low loss tangents.[10] Regarding the low-dielectric properties of PSQs, it has been reported that silsesquioxanes with bulky alkyl groups exhibit low dielectric constants of 3 or blower at 1 MHz.[11] Furthermore, several nanocomposite materials derived from polyhedral oligomeric silsesquioxane (POSS) and polyimide (PI) have also been reported to exhibit low dielectric constants.[12,13] However, the dielectric properties of these materials at high frequencies (above 1 GHz) have not been thoroughly investigated. The dielectric constant of a material is determined by 4 distinct polarization mechanisms: electronic polarization, ionic polarization, dipolar polarization, and interfacial polarization. Since these polarization mechanisms respond to different frequency ranges, the dielectric properties exhibit frequency dependence.[14] Therefore, for the development of materials for high-frequency applications, it is essential to evaluate the dielectric properties in the specific frequency band of interest. This study synthesized PSQs using different polymerization conditions and examined their dielectric properties above 1 GHz. The aim was to determine how the dielectric properties of PSQs were influenced by the various end groups and crosslinking structures present in the polysilsesquioxane backbone.

First, polymethylsilsesquioxanes (PMSQs) were synthesized from trimethoxymethylsilane by sol-gel reaction (Scheme 1). The progress of the hydrolysis was confirmed by FT-IR measurement (Fig. 1). Specifically, the loss of the methoxy group (2840 cm^{-1}) resulting from the hydrolysis reaction was observed in the IR spectrum. Once the synthesized sol solution was dried at room temperature, PMSQ-100, PMSQ-200, and PMSQ-300 were produced by heat curing at 100 °C, 200 °C, and 300 °C, respectively.

The dielectric constant and dielectric loss tangent of PSQs were measured at 18.4 GHz using the open coaxial resonator Type C. Table 1 summarizes the dielectric properties of PMSQ-100, PMSQ-200, and PMSQ-300, while Figs. 2 and 3 show the plots of dielectric constant and dielectric loss tangent, respectively. Our results demonstrate that the dielectric properties of PMSQ decrease with increasing curing temperature. Specifically, PMSQ-300 exhibits a significantly lower dielectric constant and dielectric loss tangent compared to FR-4 glass epoxy ($\varepsilon_r = 4.3$ and $\tan\delta = 0.02$),[15] a material widely used as a printed wiring board. Furthermore, it demonstrates a comparable loss tangent and a lower dielectric constant than polyimide ($\varepsilon_r = 3.1$ to 3.6 and $\tan\delta = 10^{-3}$ order),[16] which is extensively utilized as a heat-resistant insulating material in flexible and multilayer printed circuit boards.

The results of solid-state ^{29}Si-NMR measurements for each sample showed the absence of T^1 signals (T^1: 1 siloxane bond formed), while T^2 (T^2: 2 siloxane bonds formed) and T^3 (T^3: 3 siloxane bonds formed) signals were observed. Each spectrum was fitted using a Gaussian function, and the integrated values of the T^2 and T^3 signals were calculated (Supplementary Fig. S1, Supplementary Table S1). Subsequently, longitudinal relaxation curves measured by saturation recovery NMR for T^2 and T^3 were plotted, and the magnetization recovery rate after 90 s was calculated (Supplementary Fig. S2). Given that the T^3 structure exhibits approximately 6% faster recovery, it is presumed that the integrated value overestimates T^3 by approximately 6%. Finally, we illustrate the adjusted ratio of T structures of PMSQ in Fig. 4, based on the magnetization recovery rates of T^2 and T^3. With the increase in curing temperature, the transformation of T^2 structure to T^3 structure has been confirmed. The T^2 ratio for PMSQ-100 was 42.6%, while the T^3 ratio was 57.4%. In the case of PMSQ-200, the T^2 ratio stood at 24.2%, accompanied by the T^3 ratio of 75.8%. PMSQ-300 displayed the T^2 ratio of 18.1%, and the T^3 ratio of 81.9%. The conversion from T^2 structure to T^3 structure signifies a decrease in silanol groups and an increase in crosslinking. Similarly, in FT-IR measurements, the peak attributed to silanol groups around 3,300 cm^{-1} was confirmed to disappear with the increase in T^3 structure (Supplementary Fig. S3).



Scheme 1. Synthesis pathways for PMSQ-100, PMSQ-200, and PMSQ-300.

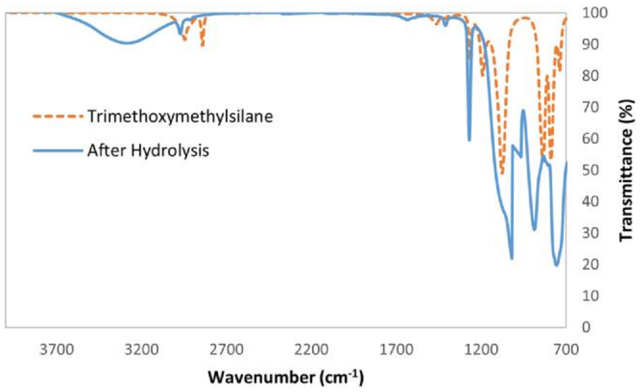


Fig. 1. FT-IR spectra of trimethoxymethylsilane before hydrolysis and after hydrolysis.

Table 1. Dielectric constants and dielectric loss tangents of PMSQ-100, PMSQ-200, and PMSQ-300.

	ε_r	$\tan\delta$
PMSQ-100	2.90	0.046
PMSQ-200	2.39	0.019
PMSQ-300	2.41	0.006

Figure 5 displays the TGA thermograms of PMSQ, which show 2 distinct weight loss patterns. The weight loss occurring below 400 °C is believed to be caused by the dehydration and condensation of silanol groups. Conversely, the mass loss observed within the temperature range of 400 °C to 600 °C is attributed to the decomposition of methyl groups. Indeed, considering the complete combustion of PMSQ-300 with the empirical formula $CH_3SiO_{1.5}$ in air, resulting in the formation of SiO_2, the theoretical mass reduction of approximately 10% is consistent with this observation. The weight losses at 350 °C were −6.5%, −3.6%, and −0.3% for PMSQ-100, PMSQ-200, and PMSQ-300, respectively. These results suggest that the

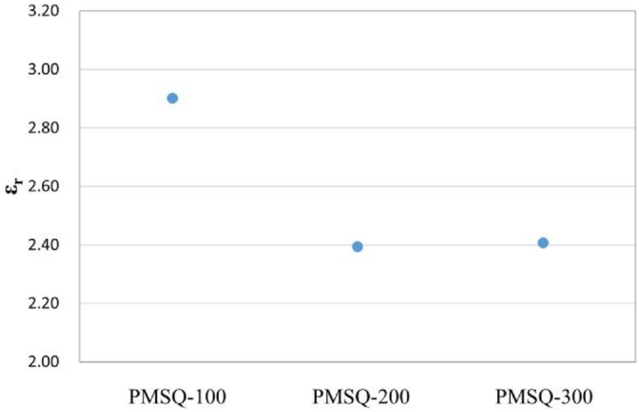


Fig. 2. Dielectric constant (ε_r) plots of PMSQ-100, PMSQ-200, and PMSQ-300.

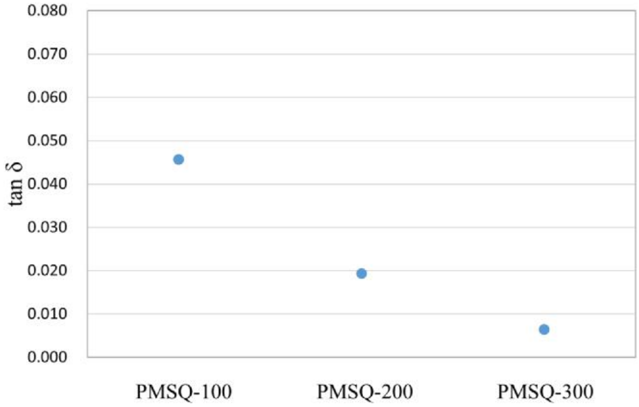


Fig. 3. Dielectric loss tangent (tan δ) plots of PMSQ-100, PMSQ-200, and PMSQ-300.

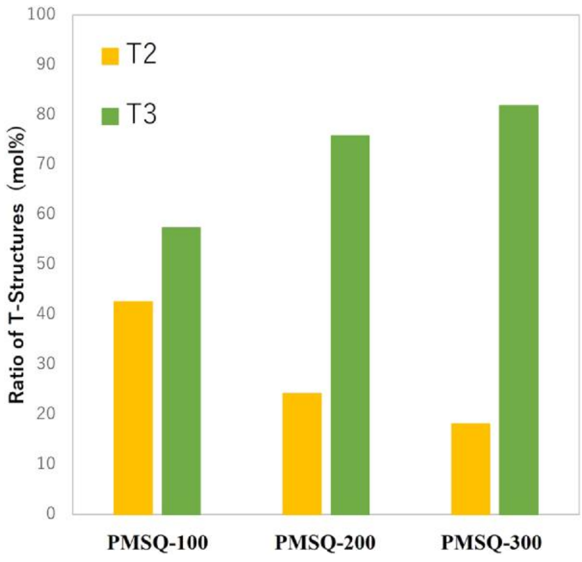


Fig. 4. Ratio of T structures of PMSQ calculated from ^{29}Si-NMR.

amount of residual silanol groups decreased as the curing temperature increased.

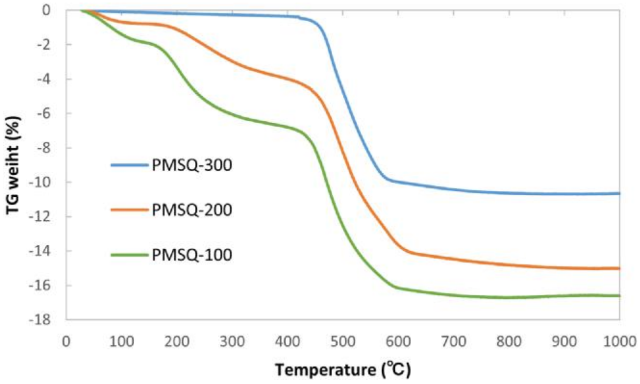
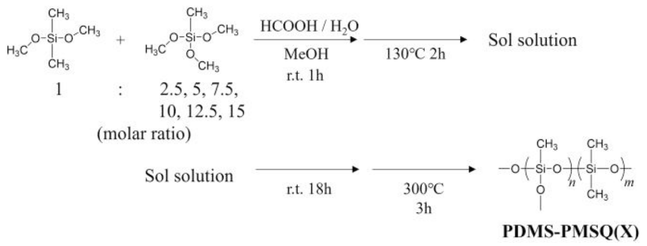


Fig. 5. TGA thermograms of PMSQ-100, PMSQ-200, and PMSQ-300 (under air, 10 °C/min).

Table 2. Dielectric constants and dielectric loss tangents of PMSQ-100, PMSQ-200, and PMSQ-300.

	T_{d5} (°C)	Water contact angle (°)	Specific gravity
PMSQ-100	242	85.5 ± 7.2	0.83
PMSQ-200	454	98.3 ± 4.8	0.62
PMSQ-300	503	127.9 ± 4.0	0.64



Scheme 2. Synthesis pathways for PDMS-PMSQ(X).

Table 3. Dielectric constants and dielectric loss tangents of PDMS-PMSQ(X).

	ε_r	tan δ
PDMS-PMSQ(2.5)	2.70	0.018
PDMS-PMSQ(5)	2.61	0.014
PDMS-PMSQ(7.5)	2.36	0.013
PDMS-PMSQ(10)	2.32	0.007
PDMS-PMSQ(12.5)	2.35	0.012
PDMS-PMSQ(15)	2.37	0.010

The high dielectric constant and dielectric loss tangent of PMSQ-100 were consistent with the presence of residual silanol groups in the polymer, as silanol groups have a high polarization rate. Table 2 shows the 5% weight loss temperature (T_{d5}), water contact angle, and specific gravity, with the specific gravity measured using a pycnometer. PMSQ-300 exhibited a high T_{d5}, indicating excellent heat resistance, as expected from silicone-based polymers. Additionally, PMSQ-300 exhibited a high water contact angle, indicating high hydrophobicity and low hygroscopicity.

By copolymerizing dialkoxysilane and trialkoxysilane, the density and hardness of the resulting polymer can be controlled. The polymer's density exhibits a strong correlation with its dielectric constant, while its hardness and conformational structure influence the molecular dipole moment, consequently affecting dielectric loss.[17] To investigate the relationship between polymer structure and dielectric behavior, PDMS-PMSQ(X) copolymers, where X represents the molar ratio of trimethoxymethylsilane to dimethoxydimethylsilane (X = 2.5, 5, 7.5, 10, 12.5, 15), were synthesized by copolymerization under the same

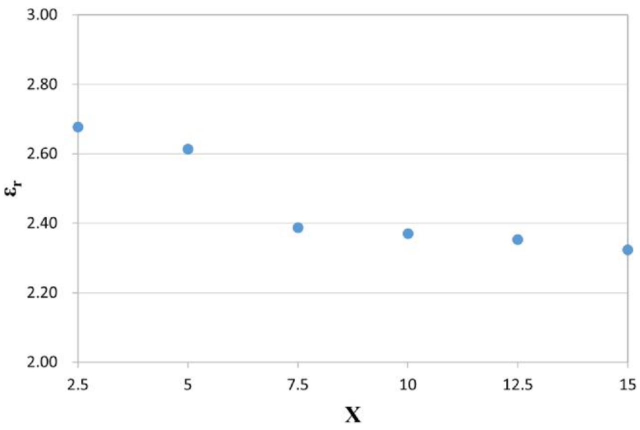


Fig. 6. Dielectric constant (ε_r) plots of PDMS-PMSQ(X).

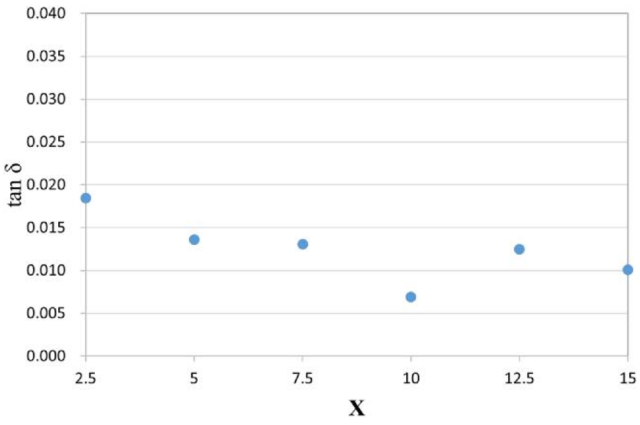


Fig. 7. Dielectric loss tangent (tan δ) plots of PDMS-PMSQ(X).

conditions as PMSQ and then thermally cured at 300 °C (Scheme 2). FT-IR measurements conducted to confirm polymerization revealed the absence of the peak attributed to silanol groups around 3,300 cm^{-1} in all the synthesized copolymers. This observation suggests that the synthesized copolymers achieved a degree of polymerization similar to that of PMSQ-300 (Supplementary Fig. S4).

The dielectric properties of PDMS-PMSQ(X) are summarized in Table 3 and Figs. 6 and 7. It was confirmed that the dielectric constant decreases as the molar ratio of T-structure increase. No significant difference in the dielectric loss tangent was observed due to the effect of the ratio of the D and T structures.

Table 4 shows the results of specific gravity measurements for PDMS-PMSQ(2.5), PDMS-PMSQ(7.5), and PDMS-PMSQ(15). It is observed that as the ratio of X increases, the specific gravity decreases. This is thought to be caused by the generation of 3-dimensional voids due to an increase in the ratio of the T structure. The decrease in dielectric constants is attributed to the reduced density.

In summary, we synthesized polysilsesquioxane from methyltrimethoxysilane and investigated its dielectric properties under different curing conditions at high frequencies. As a result, we found that the higher the curing temperature, the lower the residual amount of terminal silanol groups, as well as the dielectric constant and dielectric loss tangent. PMSQ-300 demonstrated low dielectric properties and excellent heat resistance, with a T_{d5} value of 503 °C. Furthermore, we confirmed that the dielectric constant of the copolymer (PDMS-PMSQ(X)), which combines the T structure and the D structure, decreased as the content of the T structure increased. Additionally, a decrease in specific gravity was observed, suggesting the generation of voids due to the 3-dimensional structure brought about by the T structure. This density reduction likely contributed to the decrease in the dielectric constant.

Table 4. Specific gravities of PDMS-PMSQ(2.5), PDMS-PMSQ(7.5), and PDMS-PMSQ(15).

	Specific gravity
PDMS-PMSQ(2.5)	0.73
PDMS-PMSQ(7.5)	0.69
PDMS-PMSQ(15)	0.61

Supplementary data

Supplementary material is available at *Chemistry Letters* online.

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Conflict of interest statement. None declared.

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