Synthesis and Properties of Polyimides Incorporating Double-Decker Silsesquioxane for Low-Dielectric Properties

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With the rapid expansion of the Internet and continuous advancements in electronic device performance, the demand for materials with low dielectric constants (D_k) and dissipation factors (D_f) has significantly increased (1). Next-generation wireless communication systems, such as beyond 5G and 6G, are expected to operate at higher frequencies exceeding 20 GHz. These high-frequency systems require materials with superior dielectric properties to support fast data transmission, low latency, and the ability to connect numerous devices simultaneously. Polyimides (PIs) have long been used as interlayer dielectric materials due to their excellent thermal, mechanical, and chemical properties. However, conventional PIs typically exhibit relatively high D_k and D_f values, limiting their suitability for use in high-frequency communication environments. To overcome these challenges, new materials that simultaneously achieve lower D_k and D_f values are needed, and various structural modifications have been considered (2). As a potential alternative, poly(ester imide)s (PEIs), which incorporate ester linkages into their molecular backbone, have drawn attention for their low D_f values resulting from their linear and planar structures (3). To address this issue, we designed PEIs incorporating double-decker silsesquioxane (DDSQ, Fig. 1) units into the polymer backbone. DDSQ possesses a rigid and bulky cage-like structure, which can increase the free volume and reduce chain stacking. This molecular design aims to achieve a balance between low D_k and D_f values while maintaining high thermal stability. This study reports the synthesis of DDSQ-containing PEIs and their evaluation in terms of dielectric performance for potential application in high-frequency devices.

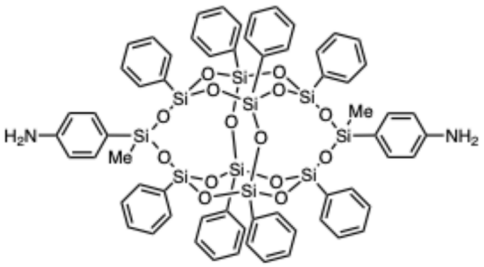

Fig. 1. Structure of double-decker silsesquioxane (DDSQ) diamine

The PEIs were synthesized via a two-step polycondensation method using 1,4-phenylene bis(1,3-dioxo-1,3-dihydroisobenzofuran-5-carboxylate) (TAHQ), a tetracarboxylic dianhydride containing ester linkages, and various diamines including a DDSQ-based diamine. The monomers were dissolved in 1-methyl-2-pyrrolidone at a concentration of 20 wt% and stirred at room temperature for 24 hours to obtain poly(amic acid) (PAA) solutions. The resulting PAAs were purified by reprecipitation in methanol. To prepare PEI films, PAA solutions were cast onto glass substrates. The films were then dried at 80 °C for 1 hour in air, followed by thermal imidization in a vacuum oven at 100 ˚C, 200 ˚C, and 300 ˚C for 1 hour each. The imidization process was confirmed using Fourier transform infrared spectroscopy (FT-IR) by monitoring the disappearance of amide-related bands and the emergence of imide characteristic peaks. The dielectric properties of the resulting self-supporting PEI films were evaluated at 10 GHz and 20 GHz. Refractive indices (n_{TE}) at 1310 nm were also measured. Compared with a reference PEI composed of TAHQ and a planar diamine (ABHQ, 1,4-phenylene bis(4-aminobenzoate)), which showed D_k of 3.08, D_f of 0.0022, and n_{TE} of 1.691, the TAHQ/DDSQ-PEI exhibited D_k of 2.81, D_f of 0.0028, and n_{TE} of 1.564. This improvement in D_k is attributed to the bulky DDSQ structure increasing the molar volume and disrupting chain stacking. DDSQ-based PEIs have the potential to serve as promising candidates for next-generation low dielectric materials in high-frequency wireless communication applications.

References
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Acknowledgement
3,13-bis(4-aminophenyl)-DDSQ was provided by JNC Corporation.