3.Optical and High-Frequency (20GHz) Dielectric Properties of Sulfur- and/or Ether-Containing Polyimides

Daiki KUBOTA, Yoshiyuki TSURUSAKI, Ririka SAWADA, Haonan LIU, Shinji ANDO*

Department of Chemical Science and Engineering, Institute of Science Tokyo, Japan
*ando.s.aa@m.titech.ac.jp

Abstract: Polymer-based dielectrics combining high dielectric constants (D_k) and low dissipation factors (D_f) are demanded for film capacitors and microstrip antennas at GHz frequencies. Polyimides (PIs) are promising candidates for such applications owing to their excellent thermal, mechanical, and chemical stability. In particular, sulfur-containing PIs (S-PIs), incorporating sulfur atoms in their backbones, are expected to exhibit high D_k due to the sulfur's high atomic polarizability [1,2]. Recently, we reported that the D_k and D_f of PIs are strongly affected by relative humidity (RH) and water molecules adsorbed in PI films [3]. In this study, we synthesized a series of S-PIs and ether-containing PIs (**Fig.1**) and investigated their dielectric properties at 20 GHz, including their RH dependence and water-sorption behaviors.

As the weight fraction of sulfur (*S*%) increases, the refractive indices and D_k of PIs increase, which originates from the increased electronic polarization with higher S%. As reported previously, the D_k, D_f, and water uptake of all PIs increase linearly with an increase in RH (10–60 RH%), and their slopes (h_{Dk} and h_{Df}) represent RH sensitivity. Comparing PIs with similar chemical structures (thioether- or ether-containing PIs), h_{Df} linearly increases against the weight fraction of imide groups (*Imide*%), and 3S-3S shows the lowest h_{Df} in all PIs. In particular, TA-SD and DS-SD, containing thianthrene or sulfonyl moieties in the main chain, exhibited higher hygroscopicity due to the expanded free volume, due to their bent structures, which lead to high h_{Dk} and h_{Df}. Detailed analysis of water sorption behavior [4] demonstrated that TA-SD absorbs a larger amount of self-associated water, forming indirect hydrogen bonds with PI chains, and this makes TA-SD more sensitive to RH, despite DS-SD showing comparable water uptake to TA-SD. In conclusion, introducing multiple thioether bonds into PI backbones is an effective way to reduce Imide% and suppress h_{Df} of PIs. Additionally, the D_k and D_f of S-PIs in the GHz range are also significantly affected by not only hygroscopicity but also water sorption behavior.

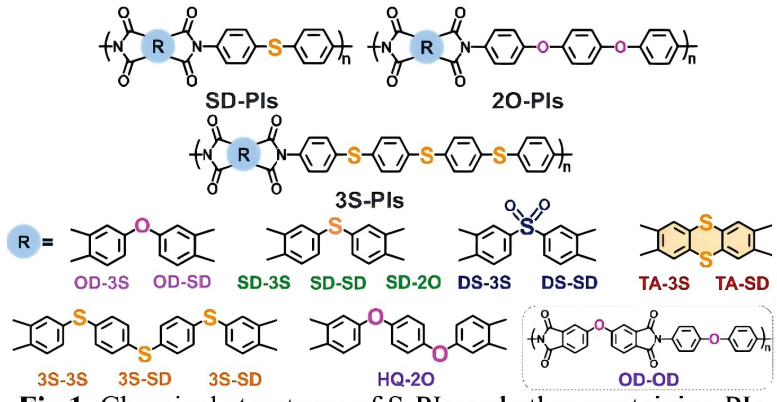

Fig.1 Chemical structures of S-PIs and ether-containing PIs.

Key words: Polyimide, Sulfur, Dielectric constant, Dissipation factor, High refractive index, Humidity dependence, Water sorption

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