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Correlation Analysis of the Structure and Dielectric Properties of Polyimides in the Millimeter Wave Band (30~300 GHz)

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INTRODUCTION:

Insulating materials with low dielectric constant (D_k) and low dissipation factor (D_f)—which refer to a material's ability to store and dissipate electrical energy, respectively—are essential for modern electronics, especially in 5G and upcoming 6G communication technologies. Polyimides (PIs) are particularly promising due to their excellent thermal stability, mechanical strength, and adaptability to harsh environments. In recent years, significant research has focused on the molecular design of low-dielectric PIs [1]. However, testing these materials' dielectric properties has been limited to frequencies below 100 GHz due to the current testing methods, falling short of the 300 GHz band required for 6G applications.

Until now, this limitation has been a serious barrier to fully understanding and optimizing materials for higher frequencies. The recent development of the Fabry–Pérot resonator [2,3] overcomes this problem by enabling dielectric dispersion tests from 25 to 330 GHz, covering the entire millimeter wave band (30~300 GHz). In this study, we measured the dielectric dispersion of 11 types of PIs (Fig. 1) for developing design strategies for novel low-dielectric PIs suitable for 6G technology.

RESULTS AND DISCUSSION:

The D_k of PIs gradually decreases with increasing frequency without exhibiting significant peaks. The millimeter-wave band lies at the transition between the electrical and optical domains. In contrast to the rotational relaxation of molecular chains in the MHz domain or the relaxation of intermolecular vibrations in the THz domain, the local motion of polymers in the GHz domain leads to a statistical decrease in D_k, influenced by various types of relaxation mechanisms. As a result, the decreasing curves of individual PIs tend to run parallel, regardless of the differences in their structures.

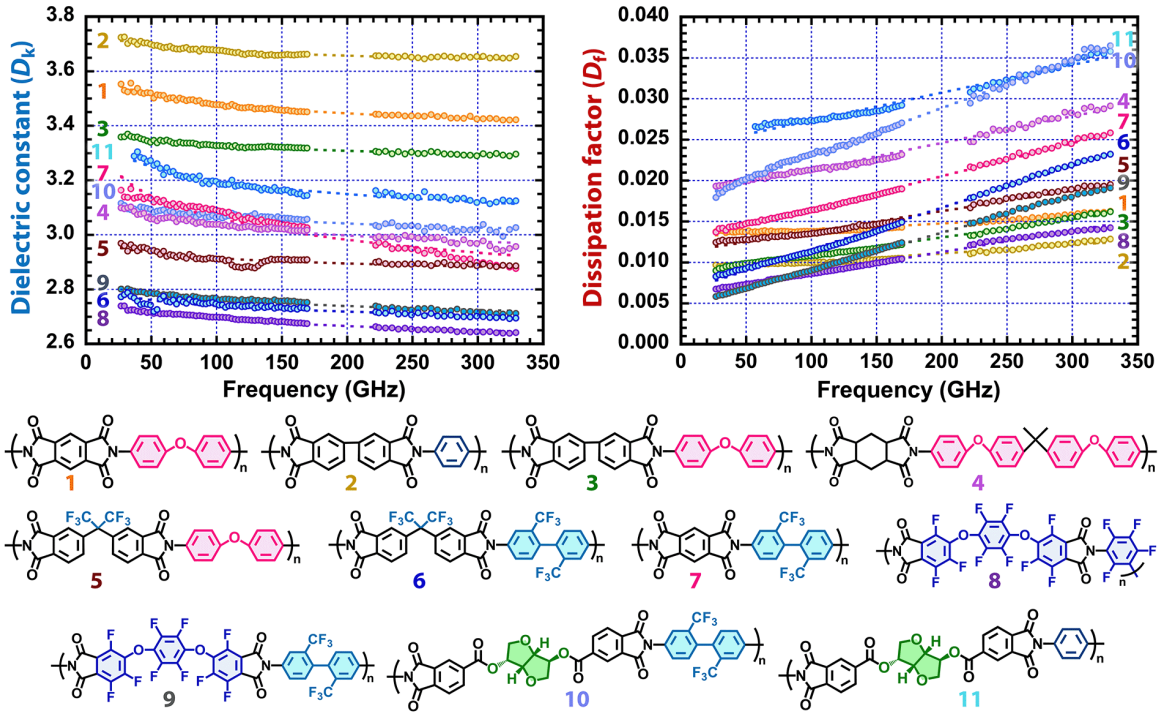

Fig. 1. (left) D_k and (right) D_f of PIs between 25 and 330 GHz.

The D_k of PIs at 10 GHz has been systematically characterized [4]. The magnitude of D_k is primarily influenced by two factors: 1) the weight fraction of polar groups (*polar%*, *e.g.*, imide and ester groups) in the repeating structure, which affects dipole polarization (P_d), and 2) the refractive index of the material in the near-infrared region, which affects electronic polarization (P_e). As shown in Fig. 2 (left), we found that the correlation coefficient (R^2) between each PI and the squared refractive index is as high as 0.93 at 330 GHz. This value decreases to 0.87 at 30 GHz and 0.80 at 10 GHz, which demonstrates that the D_k of PIs is less affected by P_d and more influenced by P_e at higher frequencies. It is worth mentioning that PI #7 differs from the other PIs by a more significant decrease in D_k. This suggests that the severely restricted molecular motion of the rigid-rod chains considerably reduces the dielectric response of P_d. Highly fluorinated PIs #6, #8, and #9 have the lowest D_ks even at 330 GHz due to the low water content and the low atomic polarizability of fluorine atoms.

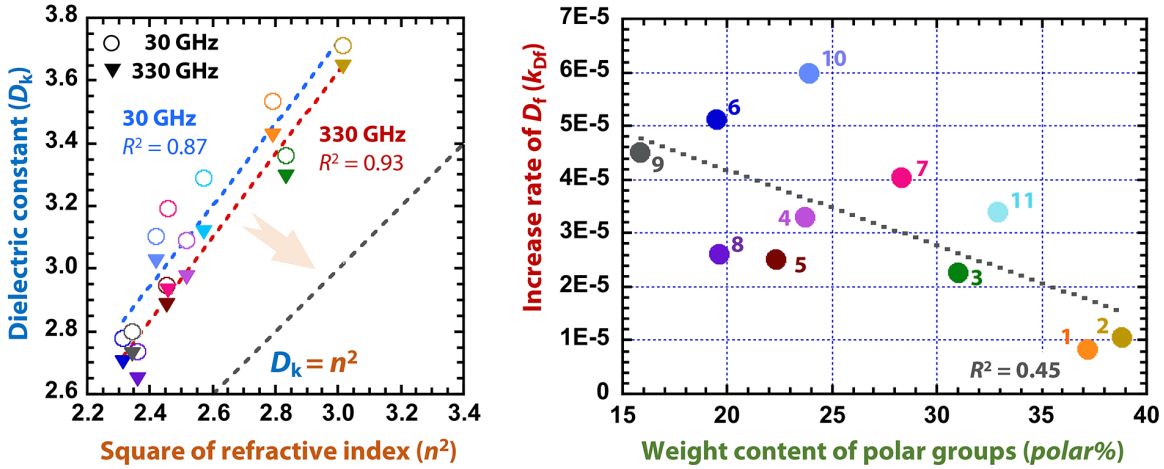

Fig. 2. Relationship between (left) D_k and n^2 and (right) k_{Df} and *polar%* in PIs.

In Fig. 1 (right), D_f rises linearly for all PIs but at different rates, which is indicated by the slope (k_{Df}). Understanding the value of k_{Df} is crucial because PIs with excellent D_f at 10 GHz might not perform well at 330 GHz. At 10 GHz, D_f shows a roughly positive correlation with *polar%* [4]. However, as frequency increases and P_d contribution decreases, this correlation nearly disappears. Interestingly, there is a rough **negative** correlation between *polar%* and k_{Df}. Intriguingly, PIs #1 and #2, which do not perform well at 30 GHz, exhibit relatively low D_f at 330 GHz due to their low k_{Df}. Conversely, PIs #6 and #9, which have the lowest D_f at 30 GHz, lose their advantage at 330 GHz due to the high k_{Df}, which is attributable to the common structure of 2,2'-bis(trifluoromethyl)benzidine (TFDB). Notably, PI #8 [5] maintains low D_k and D_f values across the entire frequency range, making it a strong candidate for use in 6G communications.

In future studies, the relative permittivity of each PI above 330 GHz is expected to be resolved by THz spectroscopy. This will further elucidate the essential factors governing the origin of D_f values at higher frequencies. It is also expected to understand whether the effect of ambient humidity, *i.e.*, the moisture content of materials, on the dielectric properties at 10 GHz still exists at higher frequencies. Moreover, the molecular design of novel highly fluorinated polyimides is underway because a judicious incorporation of fluorine atoms effectively reduces both D_k and D_f.

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