Molecular Design of Free Volume Based on Secondary Relaxation: A Facile Strategy for Intrinsic Low-*k* Dielectric Polymers

Yi Zhang*(张艺), Chao Qian, Runxin Bei, Siwei Liu, Zhenguo Chi, Jiarui Xu

PCFM Lab, GD HPPC Lab, Guangdong Engineering Technology Research Centre for High-performance Organic and Polymer Photoelectric Functional Films, State Key Laboratory of Optoelectronic Materials and Technologies, School of Chemistry and Chemical Engineering, Sun Yat-sen University（中山大学）, Guangzhou 510275, China, E-mail:ceszy@mail.sysu.edu.cn

The development of microelectronics and communication technology has revolutionized the way we live. With the development of the wireless communication industry, the high speed and high frequency transmission, especially the upcoming fifth generation mobile communication technology (5G technology), has been a hot research subject.[1] The signal transmission speed (V) and the signal propagation loss rate (α) are two key indexes in high speed and high frequency transmission technology. The V and α value are both closely related to the dielectric constant (k) of the substrate materials,[2] The V value of the high frequency circuit board is inversely proportional to the k value of the substrate materials, and the α value of the high frequency circuit board is proportional to the k value and dielectric loss of the substrate materials. Hence, an urgent demand for low-k and low loss dielectric materials has arisen in the wireless communications industry.

There are mainly two ways to design low-k dielectric property of polymers. One is to introduce nanosized air voids (with a k value of approximately 1) into bulk polymers; the dielectric constant of these porous polymers can be lowered to a certain level, but the overall properties of the materials will be greatly damaged which limit their real applications.[3] The other is to design the dielectric properties of materials at molecular level, for example, to introduce some chemical bonds with lower molar polarizability (such as -C-F bond),[4] or some rigid and shape-persistent components (such as triptycene moiety) into polymer molecular structure[5].Recently in our group, we have developed a highly-efficient design strategy to fabricate high-performance intrinsic low-k polyimides, using some propeller-like structures such as triphenylamine, triphenylmethane, triphenylethylene and triphenyl units et al. to form series of novel functional diamine monomers with rigid non-planar large conjugated structures. By regulating the chemical structures and aggregation structures of the polymers at the molecular level, low dielectric and even ultra low dielectric constant polyimide films with excellent comprehensive properties can be achieved.[6-12] However, the complicated molecular structure and high manufacturing cost make them difficult to realize commercial production and industrial applications. Therefore, a facile and effective molecular design strategy to low dielectric constant polymers is still a great challenge.

Different from the previously reported methods, here we propose a brand-new molecular design strategy to obtain high-performance intrinsic low-k polymers by fully considering the secondary relaxation of the polymer chains, especially the β relaxation which represents the torsion of groups in the polymer backbone or the rotation of the pendant groups. The principal of this design strategy is using the secondary relaxation behavior of the pendant group, especially the rotation of the meta-terphenyl unit in the pendant group to obtain more free volume in the bulk. Using this strategy, for example, we have successfully obtained a novel polyimide (TmBPHF) (**Figure 1**), which exhibits excellent low-k property (k = 2.09, dielectric loss = 0.0012, 10 kHz). Other two polyimides (TPAHF and TpBPHF) have also been synthesized to discuss the relationship between the chemical structures of pendant group and the dielectric properties. This design strategy is beneficial for lowering the k value and simultaneously maintaining the overall

properties of polyimides. The TmBPHF film shows ultralow moisture rate (~ 0.17%), which is able to maintain the low-*k* property stability in different humid environments. Meanwhile, the TmBPHF film also shows excellent thermal stability and excellent mechanical properties, with a glass transition temperature (T_g) of 302 °C, 5 wt% decomposition temperature ($T_{d5\%}$) of 549 °C, and a residual of 70% at 800 °C under N_2. The tensile strength and tensile modulus of the polyimide film are 85.8 MPa and 2.02 GPa, respectively. In addition, the TmBPHF film is soluble in common solvents, which allows simple solution processing and efficient, low-cost, and continuous roll-to-roll processes. So far as we know, this maybe the first report on molecular design using secondary relaxation behaviors of polymer chains to regulate the free volume in the bulk. It is also our belief that this strategy can be extended to other novel high-performance polymer systems.

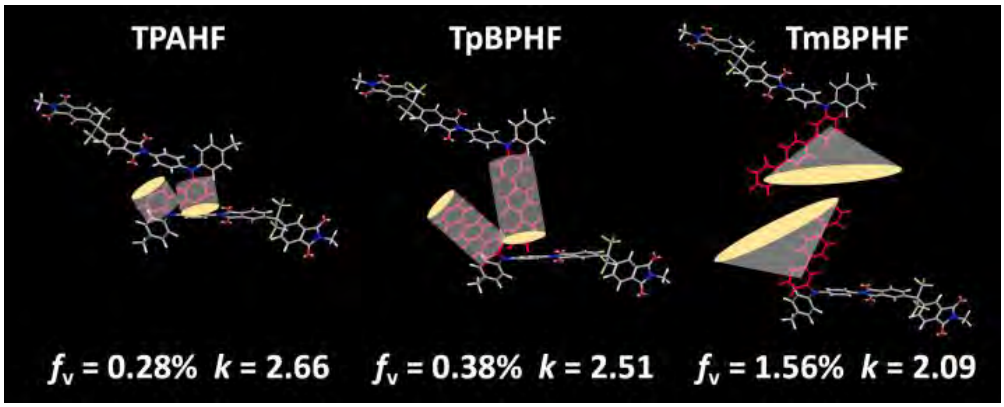

Figure 1 Molecular design for intrinsic low-*k* polyimides based on secondary relaxation behaviors of polymer.

The financial support by the National 973 Program of China (No. 2014CB643605), the National Natural Science Foundation of China (No. 51873239 and 51373204), the Science and Technology Project of Guangdong Province (Nos. 2015B090915003 and 2015B090913003), the Leading Scientific, Technical and Innovation Talents of Guangdong Special Support Program (No. 2016TX03C295), the China Postdoctoral Science Foundation (No. 2017M612801) and the Fundamental Research Funds for the Central Universities (No. 161gzd08) are gratefully acknowledged.

References

[1] H. Jeff *Nature News* **2016**, 536, 139-142.

[2] V. N. Egorov, V. L. Masalov, Y. A. Nefyodov, A. F. Shevchun, M. R. Trunin, V. E. Zhitomirsky, M. McLean, *IEEE Transactions on Microwave Theory and Technique,s* **2005**, 53, 627-635.

[3] B. Lee, Y. H. Park, Y. T. Hwang, W. Oh, J. Yoon, M. Ree, *Nat. Mater.,* **2005**, 4, 147-151.

[4] C. Yuan, K. K. Jin, K. Li, S. Diao, J. W. Tong, Q. Fang, *Adv. Mater.,* **2013**, 25, 4875-4878.

[5] T. M. Swager, T. M. Long, *J. Am. Chem. Soc.,* **2003**, 125, 14113-14119.

[6] Y. W. Liu, Y. Zhang, Q. Lan, S. W. Liu, Z. X. Qin, L. H. Chen, C. Y. Zhao, Z. G. Chi, J. R. Xu, J. Economy, *Chem.Mater.*, **2012**, 24, 1212-1222.

(more references goto p72)