Fluorinated poly(aryl ether nitrile)s containing pendant cyclohexyl groups toward low $k$ materials

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Abstract. To obtain low $k$ materials with good comprehensive performances, fluorinated poly(aryl ether nitrile)s containing pendant cyclohexyl groups (FCPEN) have been designed and synthesized via nucleophilic aromatic substitution polymerization. The polymer exhibits excellent dielectric properties with a dielectric constant of 2.96 and a dielectric loss of $3.95 \times 10^{-3}$ at 1 MHz. Besides, FCPEN displays satisfactory thermostability with a 5% weight loss temperature ($T_{5\%}$) of 489 °C and a glass transition temperature ($T_g$) of 191 °C. The resultant film shows good mechanical performance and optical transmittance. The outstanding comprehensive properties indicate that FCPEN is a promising low $k$ material for the fabrication of microelectronic devices used in 5G communication.

1. Introduction

With the rapid development of the fifth generation (5G) communication technology, low dielectric constant ($k$) polymers have received much attention because of their irreplaceable role as major component in various electrical/electronic devices such as high-frequency printed circuit boards (PCBs) and integrated circuit (ICs)[1]. Currently, two main routes are widely taken to decrease the $k$ values of the dielectric polymers: 1) Decreasing the polarizability of the molecules. Strongly electronegative atoms, notably fluorine, are introduced into the polymeric chain to lower the polarizability of the polymer backbones. Polytetrafluoroethylene is a suitable candidate as low $k$ material, but its poor adhesion to substrates and inferior processability greatly hinder its applications[2]. 2) Introducing pore structure. Developing porous polymers is an effective strategy to obtain low $k$ materials out of the minimum $k$ value of air. Although some porous polymers have achieved much lower $k$ values, the complicated operation progress of pore-forming technologies limits the application of the porous materials. In addition, the size and distribution of the pore cannot be accurately controlled, and the degraded heat resistance and mechanical capacity seem inevitable in such systems[3]. Enlarging intrinsic free volume is an effective way to introduce air component and subsequently dilute the concentration of polar groups and scale down the interactions between the polymer chains. Studies have focused on introducing pendant groups into the polymeric chain, achieving intrinsic porous structure between polymer chains[4].

Ideal low $k$ materials are required to possess satisfactory comprehensive properties[5]. Traditional general polymers including polyethylene, polypropylene, and epoxy resins have low dielectric constant
and dielectric loss, but hardly meet the requirement of high-temperature service. Poly(aryl ether nitrile) is a representative super engineering polymer that has good thermal and mechanical performance, but its $k$ value is not sufficiently low, especially as a high speed communication system material. In this work, we have designed and synthesized fluorinated poly(aryl ether nitrile)s containing pendant cyclohexyl groups (FCPENs). On the one hand, both trifluoromethyl group and aliphatic ring can weaken the polarizability of polymer. On the other hand, homocyclic cyclohexyl moieties act as large rigid pendant groups, which can improve the intrinsic free volume of the polymer. The synergy of trifluoromethyl and cyclohexyl moieties is expected to enhance the comprehensive performances of poly(aryl ether nitrile)s for low $k$ materials.

2. Experimental section

2.1. Materials
4,4’-(Hexafluoroisopropylidene)diphenol (98%), 4,4’-cyclohexylidenebisphenol (98%), and 2,6-difluorobenzonitrile (99%) were purchased from Shanghai D&B Biological Science and Technology Co., Ltd. N-methyl pyrrolidone (NMP, AR), potassium carbonate anhydrous (K$_2$CO$_3$, AR), and toluene (AR) were obtained from Chengdu Chron Chemicals Co., Ltd.

2.2. Preparation of FCPENs and their films
FCPEN copolymers were synthesized via nucleophilic substitution polymerization of 4,4’-(Hexafluoroisopropylidene)diphenol, 4,4’-cyclohexylidenebisphenol, and 2,6-difluorobenzonitrile using K$_2$CO$_3$ as catalyst in NMP-toluene mixed solvent, according to reported works[6-7]. The reaction solution was precipitated into deionized water, washed with boiling water, and dried overnight. For comparison, similar polymerization was performed by replacing the diphenol monomers with bisphenol A. The obtained products were designated as FCPEN and PEN respectively whose chemical structures are shown in Figure. 1. FCPEN and PEN films were prepared through a solution casting method based on their NMP solutions [8].

2.3. Characterization
Fourier transform infrared (FTIR) measurements were performed on an FTIR spectrophotometer (Nicolet IS10, Thermo Fisher Scientific). Thermogravimetric analysis (TGA) (TGA-Q50, TA) and differential scanning calorimetry (DSC) (DSC-Q100, TA) were used for thermostability analysis. Dielectric properties of the PEN and FCPEN films were monitored on a precision LCR meter (TH2826, Tonghui). Mechanical properties were recorded using an electronic universal testing machine (CMT6104, SANS). The light transmittance of the films was measured on a microspectral analyser equipped with a portable spectrometer (NOVA, Ideaoptics).

3. Results and discussion
The FTIR spectra of the FCPEN and PEN polymers are shown in Figure. 2. The strong absorption peaks at around 2231 cm$^{-1}$ correspond to stretching signals of nitrile groups. Compared with the spectrum of PEN, new absorption peaks at around 2937 cm$^{-1}$ and 2861 cm$^{-1}$ indicated the existence of cyclohexyl rings, and the absorption peak at around 1137 cm$^{-1}$ is ascribed to the stretching of the C–F bonds, indicating the successful introduction of trifluoromethyl and cyclohexyl groups.

The thermal properties of FCPEN and PEN were investigated utilizing TGA and DSC (Figure. 3). As shown in Figure. 3a, FCPEN exhibits the glass transition temperature ($T_g$) of 191 °C, which is much higher than that of PEN (173 °C). The increasing $T_g$ is possibly credited to the existence of rigid cyclohexyl rings in the polymer chain. Figure. 3b shows the TGA and DTG curves of FCPEN and PEN polymers. The decomposition temperatures at 5% weight loss ($T_{d5%}$) of FCPEN and PEN are respectively 489 °C and 496 °C. The decomposition temperatures at 10% weight loss ($T_{d10%}$) of FCPEN and PEN are respectively 501 °C and 506 °C. Both polymers have a maximum decomposition rate temperature ($T_{max}$) of 523 °C. The identical or similar $T_{d5%}$, $T_{d10%}$, and $T_{max}$ can be ascribed to the
complementary decomposition temperatures of trifluoromethyl and cyclohexyl groups. These data indicate that FCPEN can fulfill the requirements of high-temperature processing and service in the field of low $k$ materials.

![Figure 1. Synthesis Routes of PEN and FCPEN.](image1)

![Figure 2. FT-IR spectra of PEN and FCPEN.](image2)

The dielectric properties of the FCPEN and PEN films were measured via the capacitance method. Figure 4 shows the relationships of dielectric constant and dielectric loss with respect to frequency. As the frequency rises, the dielectric constant of both films exhibits a slight decrease. This is because the dipoles of the polymers cannot keep pace with the frequency increase, resulting in incomplete polarization at a sufficiently high frequency. The dielectric constant of the FCPEN and PEN films is 2.96 and 3.37 at 1 MHz, respectively. It is known that dielectric loss is a critical parameter that influences the running state of microelectronic devices. The dielectric loss of the FCPEN and PEN films is $3.95 \times 10^{-3}$ and $5.58 \times 10^{-3}$ at 1 MHz, respectively. The dielectric constant and dielectric loss of FCPEN are much lower than those of PEN. Two aspects contribute to the decrease of dielectric constant and dielectric loss: the additional free volume present and the decreasing polarizability.
Figure 3. (a) DSC and (b) TGA-DTG curves of PEN and FCPEN.

Figure 4. (a) Dielectric constant and (b) dielectric loss of PEN and FCPEN films as a function of frequency.

Figure 5. Mechanical properties of PEN and FCPEN films.

Moreover, the FCPEN film exhibits satisfactory mechanical performance, depicted in Figure 5. The tensile strength, tensile modulus, and elongation at break of FCPEN film are respectively 86 MPa, 2.2 GPa, and 7.7%, which are similar to those of PEN film. Meanwhile, we further characterized the optical
transmittance of FCPEN and PEN films (Figure. 6). Both of the test films have a thickness of 70 µm. The average transmittance of FCPEN and PEN films over the visible light spectrum is 63.2% and 80.6%, respectively. It indicates that the resultant FCPEN film has a much better optical transmittance that is attributed to its characteristic molecular structure.

4. Conclusion
In this work, we have successfully synthesized a fluorinated poly(aryl ether nitrile)s containing pendant cyclohexyl groups (FCPEN), which exhibits a dielectric constant of 2.96 and a dielectric loss of $3.95 \times 10^{-3}$ at a frequency of 1 MHz. In particular, FCPEN displays satisfactory thermostability, mechanical properties, and optical transmittance. Such good comprehensive performances demonstrate that FCPEN is a suitable candidate as a low $k$ material for applications in the high-frequency communication field.

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References
[1] Luo, Y., Jin, K., He, C., Wang, J., Sun, J., He, F., Zhou, J., Wang, Y., Fang, Q. (2016) An intrinsically microporous network polymer with good dielectric properties at high frequency. Macromolecules, 49: 7314-7321.
[2] Zhang, Y., Liu, Z., Zhang, X., Guo, S. (2021) Sandwich-Layered Dielectric Film with Intrinsically Excellent Adhesion, Low Dielectric Constant, and Ultralow Dielectric Loss for a High-Frequency Flexible Printed Circuit. Ind. Eng. Chem. Res., 60: 11749-11759.
[3] Lu, H., Li, D., Zhang, Y., Wu, Z., Wang, H., Liu, S., Yan, G., Yan, G., Yang, J., Zhang, G. (2021) Design of low dielectric constant and high transparent polarylate containing spiral ring. Polymer, 228: 123948.
[4] Qian, C., Fan, Z.G., Zheng, W.W., Bei, R.X., Zhu, T.W., Liu, S.W., Chi, Z.G., Aldred M.P., Chen, X.D., Zhang, Y., Xu, J.R. (2020) A facile strategy for non-fluorinated intrinsic low-k and low-loss dielectric polymers: Valid exploitation of secondary relaxation behaviors. Chinese J. Polym. Sci., 38: 213-219.
[5] Hou, J., Sun, J., Fang, Q. (2022) A fluorinated low dielectric polymer at high frequency derived from allylenphenol and benzocyclobutene by a facile route. Eur. Polym. J., 163: 110943.
[6] Duan, F., Liu, C., Liu, X., Wang, L., Zhang, S., Liu, X. (2021) TiO$_2$ immobilized on polyarylene ether nitrile/Fe$^{3+}$ complex for efficient adsorption and photocatalytic degradation towards methylene blue. J. Alloys Compd., 875: 159951.
[7] Xie, J., Jia, K., Liu, C., Ji, Y., Dai, J., Marks, R., Liu, X. (2021) Aromatic block copolymer ligand sensitized lanthanide nanostructures as ratiometric fluorescence probe for determination of residual K2CO3 in super engineering thermoplastics. Sens. Actuators B Chem., 334: 129611.

[8] Liu, C., Liu, S., Lin, J., Wang, L., Huang, Y., Liu, X. (2019). Component adjustment of poly (arylene ether nitrile) with sulfonic and carboxylic groups for dielectric films. Polymers, 11: 1135.