

Synthesis and Characterization of Thermosetting Bisbenzocyclobutene-Terminated Fluorine-Containing Aromatic Imide Resins

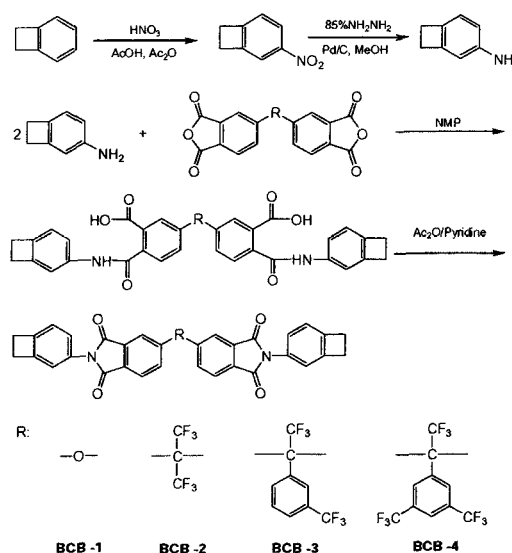
Xiaobiao Zuo, Shiyong Yang, Haixia Yang, Lin Fan*

Laboratory of Advanced Polymer Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 10080, China; Tel: 86-10-6256-4819; Fax: 86-10-6256-9562; E-mail: Fanlin@iccas.ac.cn

Benzocyclobutene (BCB) based polymers are well recognized as high performance materials due to their combined advantages such as good processability, high thermal stability and good dielectric properties, which make them widely applied in advanced microelectronics and aerospace industries. Many researches confirmed that the properties of the benzocyclobutene-terminated polymers are strongly affected by the structural features of the function groups which link the benzocyclobutene moieties.

In this study, a series of bisbenzocyclobutene-terminated fluorine-containing aromatic imide monomers were prepared by condensation between two molar of 4-aminobenzocyclobutene and one molar of dianhydrides, *i.e.*, 4,4'-oxydiphthalic anhydride (ODPA), 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), 4,4'-[2,2,2-trifluoro-1-(3'-trifluoromethylphenyl)ethylidene]diphthalic anhydride (HFDA) and 4,4'-[2,2,2-trifluoro-1-[3',5'-bis(trifluoromethyl)phenyl]ethylidene]diphthalic anhydride (9FDA), respectively (Scheme 1). The ¹H-NMR, FT-IR, MS measurements and elemental analysis confirmed that all the monomers have the expected chemical structures.

The BCB monomers were cured with the thermally cycles of 300 °C/6 h for BCB-1 and 245 °C/2 h, 260 °C/4 h for the other BCB monomers. The effect of the structure, especially the fluorinated groups, on the thermal stability and dielectric properties of their thermally cured resins was investigated. The thermal properties of cured BCB resins evaluated by thermal gravimetric analysis (TGA) and dynamic mechanical analysis (DMA) suggested that these polymers have good thermal stability with the initial decomposition temperatures in nitrogen higher than 400 °C and the glass transition temperatures over 340 °C. Moreover, we found that the BCB resins with the trifluoromethyl groups gave the decomposition temperatures much higher than BCB-1, despite the latter gave the relatively high glass transition temperature. The water absorption and the dielectric properties of the BCB resins were also estimated. It is revealed that BCB-1 showed the water absorption of 0.67% after immersed in water at room temperature for 24 h and gave the dielectric constant of 3.2 at 1MHz as well as the dissipation factor of 3.83×10^{-3} . As comparing with BCB-1, the fluorine-containing BCB resins gave the relatively low water absorptions because of the incorporation of hydrophobic fluorinated substitutes. Moreover, they also exhibited better dielectric properties with the dielectric constants of 2.7-3.0 at 1MHz and the dissipation factors of $1.95-3.83 \times 10^{-3}$. The improved dielectric properties of the fluorine-containing BCB resins could be attributed to the low polarizability of the C-F bond and the increase in free volume. These results suggested that the trifluoromethyl groups in the polymer structure play an important role in the thermal properties and dielectric performance of BCB resins.



Scheme 1. Synthesis of BCB monomers