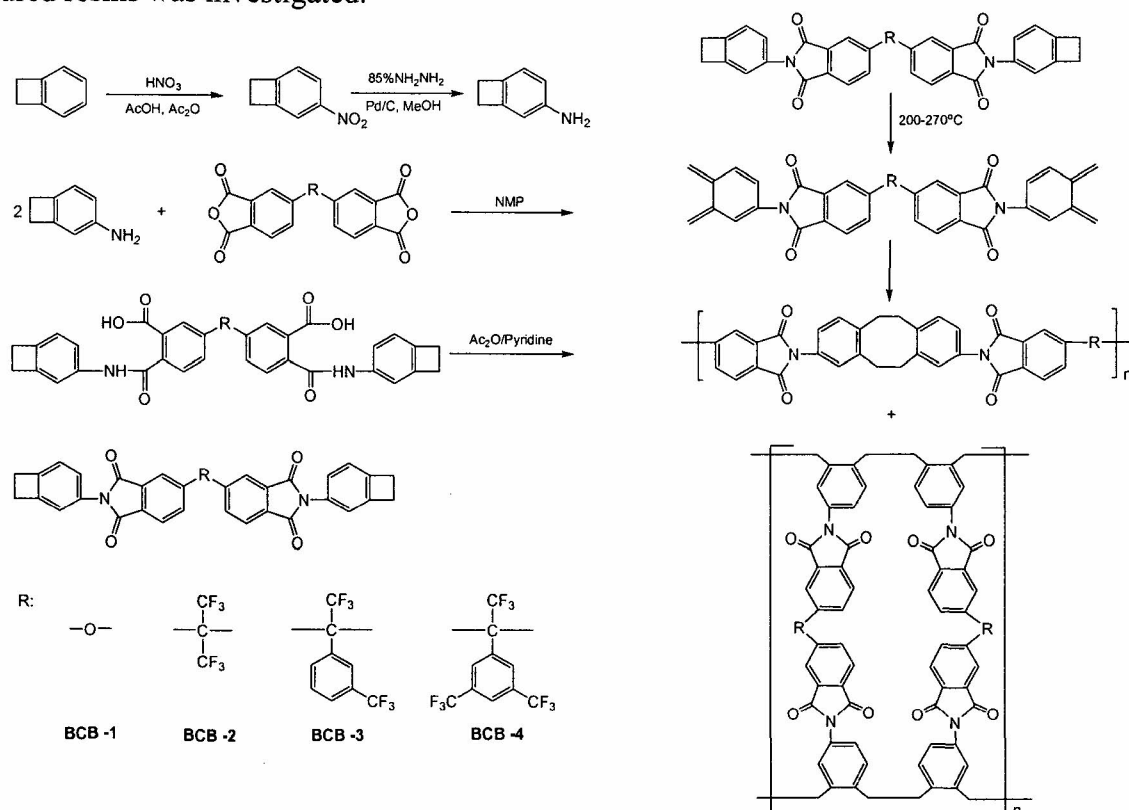


Synthesis and Characterization of Thermosetting Bisbenzocyclobutene-Terminated Fluorine-containing Aromatic Imide Resins

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 [1]. The polymerization of benzocyclobutene monomers is based on the propensity of the four-membered ring to undergo electrocyclic ring opening at elevated temperatures to provide reactive *o*-quinodimethane intermediate, which will then react rapidly with one another to give linear or cyclic polymeric structures [2-3]. For a bisbenzocyclobutene-terminated monomer, it will finally lead to a highly crosslinked polymer. In recent years, many researches have been done on the benzocyclobutene-terminated monomers [4-5]. They found that the properties of the final polymer 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 and characterized. The effect of the structure, especially the fluorinated groups, on the thermal stability and dielectric properties of their thermally cured resins was investigated.



Scheme 1. Synthesis of BCB monomers and their resins

The bisbenzocyclobutene-terminated 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). These monomers were characterized by $^1\text{H-NMR}$, FT-IR, MS measurements and elemental analysis.

Figure 1 shows the FT-IR spectra of these monomers, in which the characteristics absorptions due to CH_2 stretching vibration of benzocyclobutenyl was observed at 2930 cm^{-1} , meanwhile, the asymmetric and symmetric $\text{C}=\text{O}$ stretching vibrations of imide groups in the polymer backbone were also detected at 1780 and 1720 cm^{-1} . In the $^1\text{H-NMR}$ spectra of these monomers, all the protons in the structure were assigned as expected. The elemental analysis results of these monomers were in good agreement with the calculated ones. The characterization by $^1\text{H-NMR}$, FT-IR MS and elemental analysis confirmed that all the monomers have the expected chemical structures.

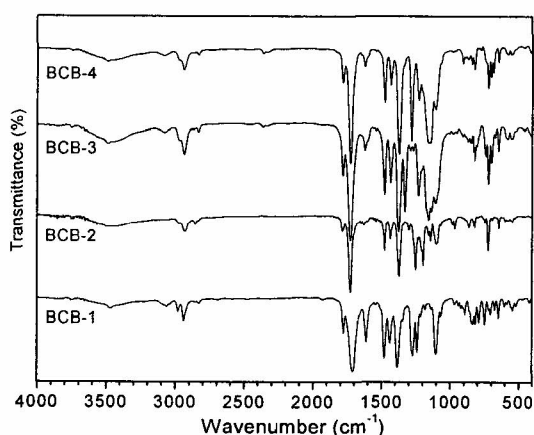


Figure 1. FT-IR spectra of the monomers.

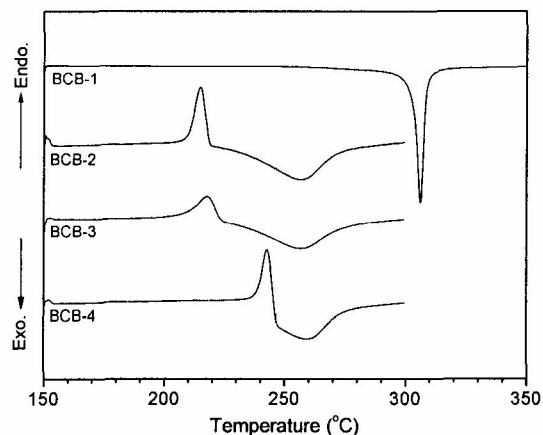


Figure 2. DSC curves of the monomers.

The cure behaviors of the monomers were traced by DSC. The DSC curve of BCB-1 showed no any endothermic peak, suggesting that the monomer has no melting point. In addition, a sharp exothermic peak due to the ring-opening polymerization was observed at $306\text{ }^\circ\text{C}$ for BCB-1. On the contrary, the fluorine-containing BCB monomers gave the sharp endothermic peaks caused by the melting of these monomers. Moreover, these fluorine-containing BCB monomers showed the broad exothermic peaks started at about $230\text{ }^\circ\text{C}$ and reached the peak temperatures around $257\text{ }^\circ\text{C}$, suggesting that these monomers can be easily polymerized at much lower temperature as compared with BCB-1.

The curing cycles of these BCB monomers determined by DSC tracing were $300\text{ }^\circ\text{C}/6\text{ h}$ for BCB-1 and $245\text{ }^\circ\text{C}/2\text{ h}$, $260\text{ }^\circ\text{C}/4\text{ h}$ for the other BCB monomers. The thermal properties of cured BCB resins were evaluated by thermal gravimetric analysis (TGA) and dynamic mechanical analysis (DMA), and the results are summarized in Table 1. It is indicated that the cured BCB resins have good thermal stability with the initial decomposition temperatures in nitrogen higher than $400\text{ }^\circ\text{C}$ and the glass transition temperatures over $340\text{ }^\circ\text{C}$. 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.

Table 1. Thermal properties of the cured BCB resins ^a

Sample	TGA			DMA	
	T _d (°C)	T ₅ (°C)	R _w (%)	G' _{onset} (°C)	tanδ (°C)
BCB-1	404	404	43	366	407
BCB-2	497	504	53	357	406
BCB-3	448	495	43	348	394
BCB-4	431	482	50	340	390

^a T_d: The onset decomposition temperature; T₅: The temperature at 5% of weight loss; R_w: The residual weight retention at 700 °C; G'_{onset}: The onset temperature of storage modulus curve; tanδ: The temperature at the peak of loss tangent curve.

Table 2. Water absorption and dielectric properties of the cured BCB resins ^a

Sample	Water Absorption (%)		ε (1MHz)	tanδ
	I	II		
BCB-1	0.67	0.85	3.2	3.83×10 ⁻³
BCB-2	0.55	0.72	3.0	1.95×10 ⁻³
BCB-3	0.47	0.61	2.8	1.37×10 ⁻³
BCB-4	0.41	0.53	2.7	1.05×10 ⁻³

^a Water absorption: I: Immersion in water at room temperature for 24 h; II: Immersion in boiling water for 24 h; ε: Dielectric constant at 1MHz; tanδ: Dissipation factor.

The water absorption and the dielectric properties of the BCB resins were estimated (Table 2). 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 1.95-3.83×10⁻³. 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.

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