Electronic Supplementary Information

Cyanate ester resins with superior dielectric, mechanical, and flame retardant properties by introducing fluorinated hyperbranched polyaryletherketone

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Materials

Bisphenol A dicyanate ester (BADCy, density 1.171 g/cm^3, molar mass 278.31 g/mol) resin was received from Jiangsu Wuqiao Resin Factory Co., Ltd. (Jiangsu, China). Bisphenol AF (BPAF, 98%), N-Methylpyrrolidone (NMP, ≥99.0%), and benzyl triethyl ammonium chloride (TEBAC, >98.0%) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Difluorobenzophenone (DFBP, 99%), phloroglucinol (PG, ≥99.0%) and epichlorohydrin (ECH, >99.0%) were all purchased from Macklin Reagent Co., Ltd. (Shanghai, China). Anhydrous potassium carbonate (K_2CO_3, >99.0%) and sodium hydroxide (NaOH, >99.0%) were both bought from Komeo Chemical Reagent Co., Ltd. (Tianjin, China). All the chemicals were used as received without further treatment.

Methods

^{1}H nuclear magnetic resonance (NMR): ^{1}H NMR spectra of the samples was measured by Bruker Avance 400 MHz NMR instrument (Bruker, Germany) with tetramethylsilane (TMS) containing $CDCl_3$ as a solvent.

Fourier transform infrared spectroscopy (FT-IR): FT-IR spectra of the samples were measured on Bruker Tensor 27 infrared spectrometer (Bruker, Germany) applying potassium bromide (KBr) tablet compression method with the test wave number range of 4000~400 cm^{-1}.

Size exclusion chromatography (SEC): The number average molar mass (M_n), weight average molar mass (M_w), and molar mass distribution (PDI) of the samples were determined using waters1515 (Waters Technology Co., China.) gel permeation chromatography using tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 mL min^{-1} (35°C). The column system was calibrated with polystyrene standards (molar mass

ranging from 1100 to 138600 g mol^{-1}). Samples were diluted to a concentration about 10 mg mL^{-1} and filtered through 0.45 μm Nylon syringe filters before injection.

Differential scanning calorimetry (DSC): The curing process of *m*-BADCy resin was measured by DSC1 of Mettler-Toledo (Mettler, Switzerland) at heating rates of 5°C/min, 10°C/min, 15°C/min, and 20°C/min under nitrogen atmosphere. The weight of each sample used was 5~10 mg.

Thermal gravimetric analysis (TGA): TGA was performed by STA 449F3 (NETZSCH Co., Germany) thermal gravimetric analyzer. The test temperature range was 40~800°C, and the heating rate was 10°C/min under argon atmosphere. The mass was about 5 mg for each sample.

Scanning electron microscopy (SEM): Scanning electron microscopy was performed on a VEGA3-LMH equipment (TESCAN Co., Czech Republic) to analyze the fracture morphology of the resin. The scanning voltage was 20 kV and the sample was sprayed with gold before testing.

Limit oxygen index (LOI): The flame retardant properties of sample was tested by ZR-01 type oxygen index tester (Qingdao shanfang Instrument Co., China) according to ASTM D2863/77 standard. The size of the sample was 80 mm×10 mm×4 mm.

Vertical combustion test (UL-94): The flame retardant properties of sample was tested by ZR-02 horizontal and vertical combustion tester (Qingdao shanfang Instrument Co., China) according to ASTM D635-77 standard. The size of the sample was 125 mm×13 mm× 3 mm.

Conical calorimeter: The flame retardant properties of sample was tested by the conical calorimeter 6810 (VOUCH Co., China) according to ISO 5660-1: 2005 standard. The heat flux was 50 KW/m^2, and the sample size was 100 mm× 100 mm× 3 mm.

Dielectric properties: Dielectric constant (ε) and dielectric loss tangent (tanδ) values of the samples were measured using a Novocontrol Technologies Alpha-N high resolution dielectric analyzer (Novocontrol, Germany) at room temperature. The corresponding dimension of the specimens was 15 mm×15 mm×1 mm. A layer of conductive silver paste was coated on the surface of the sample before testing, and then the sample was dried at 40°C for two hours. The ε values in the X-band frequency range (8.2~12.4 GHz) of the samples were measured using a MS4644A vector network analyzer (Anritsu Corp., Japan) according to ASTMD5568-08 at room temperature. The corresponding dimension of the specimens was 22.86 mm×10.14 mm×3 mm.

Mechanical properties: The flexural strength of the samples was tested by SANS2CMT5105 electronic universal testing machine (Shenzhen New Sansi Co., China) according to ISO 178-2010 standard. The impact strength of the samples was tested by XCJ-40 impact testing machine (Chengde Materials Testing Co., China) according to ISO 179-2010 standard. The sample sizes for flexural and impact strength tests were 80 mm×15 mm×4 mm and 80 mm×10 mm×4, respectively.

$$In\frac{\beta}{T_p^2} = In\frac{AR}{E} - \frac{E}{RT_p} \qquad \text{(Equation S1)}$$

$$lg\beta = lg\frac{AE}{RG(a)} - 2.315 - 0.4567\frac{E}{RT_p} \qquad \text{(Equation S2)}$$

$$\frac{d(In\beta)}{d(1/T_p)} \approx \frac{-E}{nR} \qquad \text{(Equation S3)}$$

Where, β is the heating rate, K·min^{-1}; T_p is peak temperature, K; A is the frequency factor, min^{-1}; R is the ideal gas constant, 8.314 J·mol^{-1}·K^{-1}; E is the apparent activation energy, kJ·mol^{-1}; G(a) is a function related to the conversion rate, n is the order of reaction.

$$A = \frac{2\pi d\varepsilon \tan\delta}{\lambda(\delta - \sin^2\theta)^{1/2}} \qquad \text{（Equation S4）}$$

$$|\Gamma|^2 = \left[\frac{(\varepsilon - \sin^2\theta)^{\frac{1}{2}} - \varepsilon\cos\theta}{(\varepsilon - \sin^2\theta)^{\frac{1}{2}} + \varepsilon\cos\theta}\right]^2 \qquad \text{（Equation S5）}$$

$$A + |T|^2 + |\Gamma|^2 = 1 \qquad \text{（Equation S6）}$$

Where, A represents energy loss; d is the thickness of the wave-permeable material; λ is the wavelength of electromagnetic waves; θ represents the incidence angle of electromagnetic wave through the material surface.

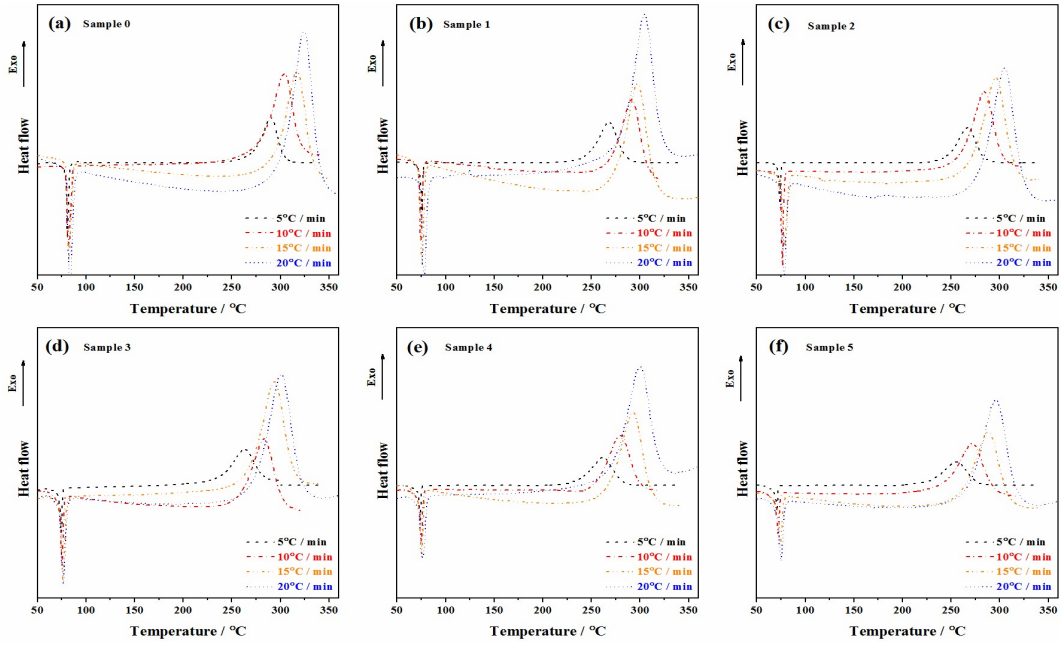


Figure S1. DSC curves of unmodified BADCy and *m*-BADCy resins at different heating rate

Table S1 Peak temperatures of DSC curves of the curing reaction for unmodified BADCy and *m*-BADCy resins at different heating rate

Samples	Peak temperature/°C			
	5°C/min	10°C/min	15°C/min	20°C/min
Sample 0	289.8	303.5	316.9	323.8

Sample 1	268.1	291.4	297.2	304.9
Sample 2	267.2	284.8	295.9	303.8
Sample 3	263.3	283.8	294.5	300.6
Sample 4	262.0	281.0	293.6	299.2
Sample 5	255.7	272.1	289.0	297.5

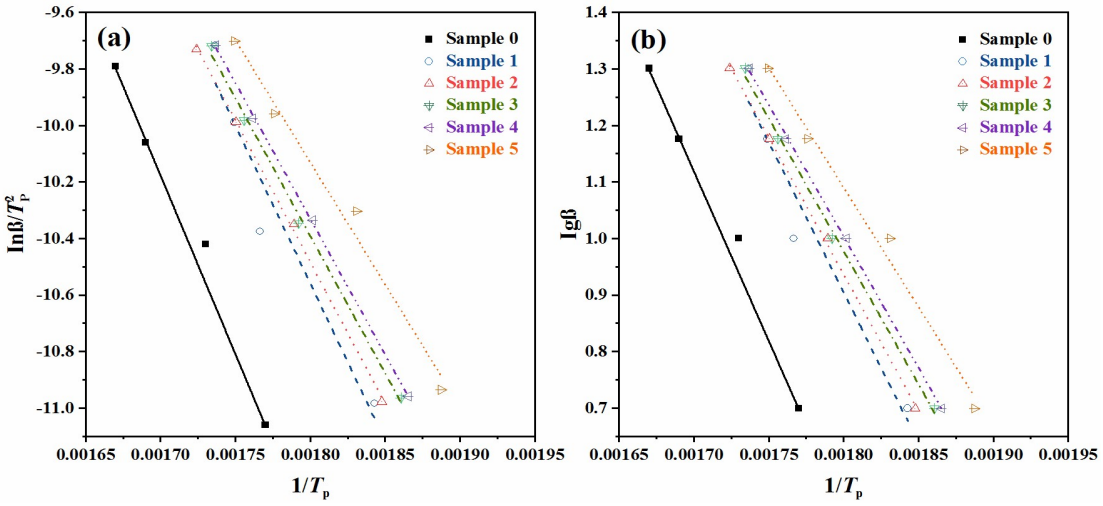


Figure S2. Kinetic curves of the curing reaction for unmodified BADCy and *m*-BADCy resin calculated by Kissinger (a) and Ozawa (b) method

Table S2 Apparent activation energy and reaction order of unmodified BADCy and *m*-BADCy resins

Samples	**Apparent activation energy/kJ·mol^{-1}**		**Reaction order**
	Kissinger	**Ozawa**	**n**
Sample 0	105.1	109.3	0.91
Sample 1	92.7	97.2	0.91
Sample 2	87.2	88.3	0.90
Sample 3	80.9	85.7	0.90
Sample 4	79.9	84.8	0.90
Sample 5	72.0	77.1	0.89

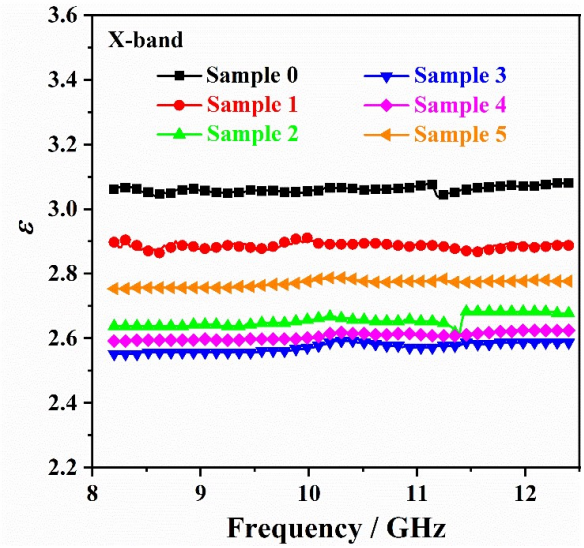


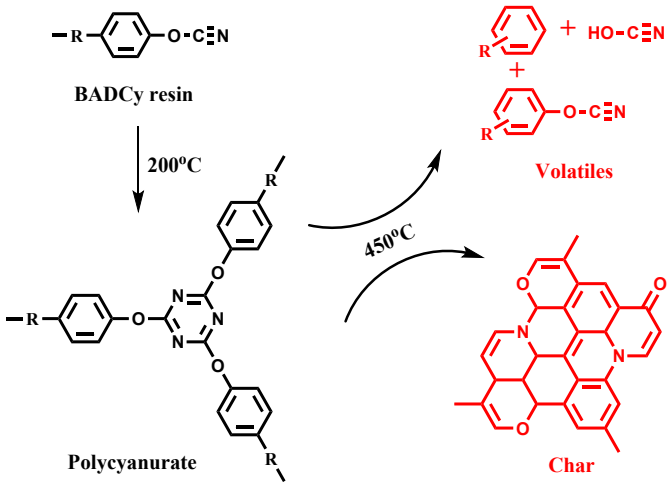
Figure S3. The dielectric constant (ε) of unmodified BADCy (Sample 0) and *m*-BADCy (Sample 1-5) resins in X-band frequency range (8.2~12.4 GHz).

Unmodified BADCy.mp4

Multimedia component S1

m-BADCy with 20 wt% HBPAEK.mp4

Multimedia component S2



Scheme S1. Schematic diagram of polymerization and thermal degradation of BADCy resin