High performance polycyanurate network derived from 4,4'-biscyanato-2,2'-trifluoromethylbiphenyl

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Experimental

Materials

2,2'-Bis(trifluoromethyl)benzidine was purchased from ChinaTech (Tianjin) Chemical Co., Ltd. (Tianjin, China). Bisphenol A dicyanate (BADCy), bisphenol E dicyanate (BEDCy), and bisphenol M dicyanate (BMDCy) were obtained from Yangzhou Techia Material Co., Ltd (Yangzhou, China). All the other chemicals were obtained from J&K Scientific (Beijing, China). All the reagents were used as received.

Synthesis of Monomer

2,2'-Bis(trifluoromethyl)-4,4'-dihydroxybiphenyl

This compound was prepared according to a literature procedure [1], yield: 74%. M.P.: 149 °C (DSC), lit.[1]: 152-152.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26–7.23 (d, 2H), 7.22–7.16 (d, 2H), 7.06–7.00 (dd, 2H), 5.28–5.20 (s, 2H).

4,4'-Biscyanato-2,2'-trifluoromethylbiphenyl

2,2'-Bis(trifluoromethyl)-4,4'-dihydroxybiphenyl (32.22 g, 0.10 mol), cyanogen chloride (21.51 g, 0.35 mol), and dichloromethane (250 mL) were placed into a 500-mL, three-necked flask equipped with a magnetic stirrer, an addition funnel, and nitrogen inlet and outlet. The mixture was cooled to -78 °C by an acetone-dry ice bath, and then triethylamine (30.36 g, 0.30 mol) was added dropwise over a period of 30 minutes. The mixture was stirred at -78 °C for 2 hours under nitrogen, and then warmed to ambient temperature. The white precipitate was removed by filtration, and the filtrated was concentrated by rotary evaporation to afford TFMBDCy as white powder. The crude product was further purified by recrystallization from 1,4-dioxane (yield: 85%). Single crystal was grown from its 1,4-dioxane solution by slow evaporation at room temperature. M.P.: 149 °C (DSC). FT-IR (cm^{-1}): 2290 (asymmetric C≡N stretching), 2250 (symmetric C≡N stretching), 1320 (C–F stretching). ^1H NMR (400 MHz, $CDCl_3$): δ 7.74–7.70 (d, 2H), 7.62–7.56 (dd, 2H), 7.46–7.40 (d, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 152.4, 134.2, 134.0, 132.0-131.2 (q), 125.5-119.0 (q), 117.9, 114.1, 107.5. ^{19}F NMR (376 MHz, $CDCl_3$): -61.6.

Polycyanurate preparation

CE monomers (BADCy and TFMBDCy) were melted in a pre-heated stainless steel mold, and degassed at 150 °C in vacuum for 3 hours. The monomers were then cured at 180 °C for 1 h, 200 °C for 1 h, 220 °C for 1 h, and 250 °C for 2 h to afford the corresponding polycyanurates.

Characterization

FT-IR was carried out on a Bruker VERTEX 70 spectrometer. ^1H, ^{19}F, and ^{13}C NMR spectra were obtained in $CDCl_3$ on a Bruker-400 spectrometer. The X-ray crystallographic data were collected on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The crystal structure was analyzed using a SHELXTL program and refined using full matrix least-squares techniques. The purity of the monomers was determined using a Shimadzu SPD-15C HPLC equipped with a Shimpack VP-ODS column and a UV/Vis detector (at 254 nm). A mixture of acetonitrile and water (60:40, v/v) was used as the eluent at a flowrate of 1.2 mL min^{-1}. DSC was recorded on a DSC Q2000 (TA Instruments) in nitrogen. Thermogravimetric analysis (TGA) was carried out on a TGA Q50 (TA Instruments) 60 100 to 800 °C in air, with a heating rate being 10 °C min^{-1}. Membrane density (ρ) was determined by using a density balance (FA2104J, Shanghai) at an accuracy of 0.1 mg. FFV was determined from:

$$FFV = 1 - \frac{1.3\rho V_w}{M}$$

where M was the molar mass (g mol^{-1}) of the repeat unit, V_w denotes the van der Waals volume calculated by a literature method [2-3].

Dynamic mechanical analysis (DMA) was performed on a Q850 DMA (TA Instruments) from 50 to 400 °C with a heating rate of 3 °C min^{-1} and a frequency of 1.0 Hz. Rheological measurements were conducted on an AR2000ex rheometer (TA Instruments). Tensile, flexural, and compression properties were determined on an Instron material testing system (Model 5982). Unnotched impact strength was measured by using a cantilever beam impact testing machine (JJ-20, Changchun, China). SEM was conducted on a XL-30ESEM FEG microscope (Mico FEI Philips, Eindhoven, the Netherlands)) with an operating voltage of 25 kV. The specimens were fractured at ambient temperature, and coated with a fine gold layer prior to SEM measurements. Dielectric properties were measured by using an Agilent impedance analyzer (Agilent Technologies, USA). Polycyanurates discs (thickness: 1 mm, diameter: 12 mm) were immersed in DI water at 85 °C for 96 hours, and water uptake was determined by their weights before and after immersion [4].

Table S1. Comparison of polycyanurates from TFMBDCy and other existing CE resins

Monomer	TFMBDCy [a]	BADCy	BEDCy [a]	BMDCy [a]	DCPDCy [b]	Phenolic CE [c]
Tensile strength (MPa)	64	53	66	63		
Tensile Modulus (GPa)	3.1	3.1	3.1	3.1		
Elongation at break (%)	2.8	1.8				
Flexural strength (MPa)	150	149	166	152		
Flexural modulus (GPa)	3.2	3.2	3.2	3.2		
Compression strength (MPa)	203	155		156		
Impact strength (KJ m^{-2})	20	15		20		
T_g (°C)	372	310	259	190	265	300-400
$T_{5\%}$ in N_2 (°C)	444	430	405	411		
Dielectric constant	2.6	2.9	3.2	2.7	2.8	3.1
Dielectric loss	0.0025	0.005	0.009	0.003-0.004	0.003	0.006
Water uptake (%)	1.9	2.5	2.7	0.7	1.4	3.8

[a] This study.

[b] Dicyclopebtadienylbisphenol dicyanate, from lit. [5].

[c] From lit. [5].

Reference

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2 W.M. Lee, *Polym. Eng. Sci.* 1980, **20**, 65-69.
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4 C. A. Corley, A. J. Guenthner, C. M .Sahagun, K. R. Lamison, J. T. Reams, M. K. Hassan, S. E. Morgan, S. T. Lacono, J. M. Mabry, *ACS Macro. Lett.* 2014, **3**, 105−109.
5 M. R. Kessler, Cyanate ester resins, *in Wiley Encyclopedia of Composites 2nd Edition*, ed. L. Nicolais and A. Borzacchiello, John Wiley & Sons, Hoboken, NJ, 2012, pp. 658-672.

List of Contents for Supplementary Materials

Figure S6. Representative stress-strain curves of BADCy and TFMBDCy-derived polycyanurates

Figure S7. SEM images of the fracture surfaces for BADCy (right) and TFMBDCy-derived (left) polycyanurates

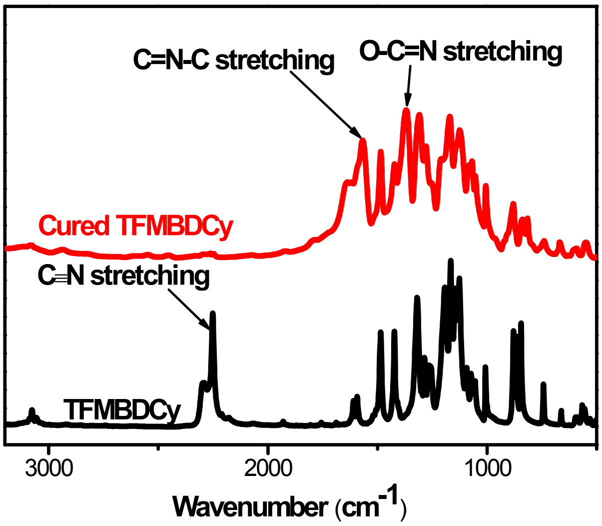

Figure S1. FT-IR spectra of TFMBDCy and its cured resin

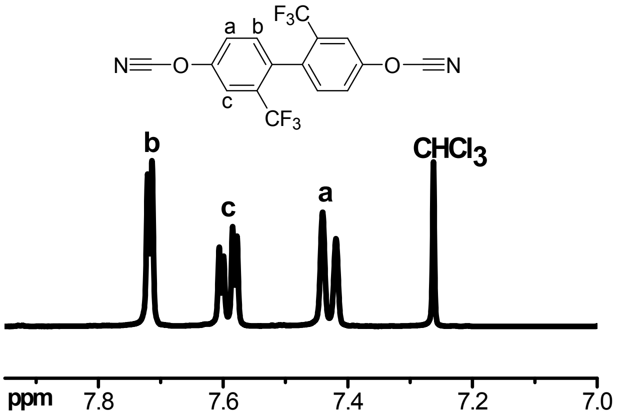

Figure S2. ^{1}H NMR spectrum of TFMBDCy

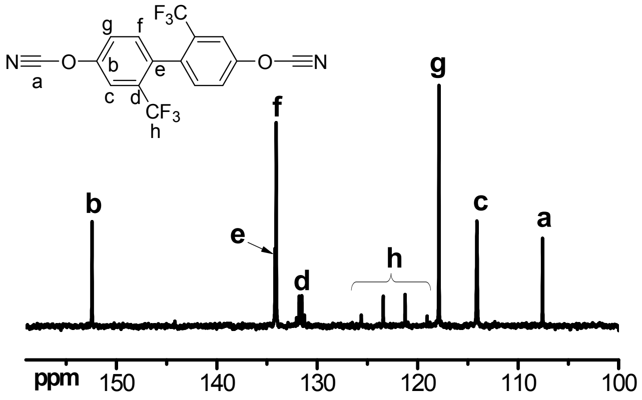

Figure S3. ^{13}C NMR spectrum of TFMBDCy

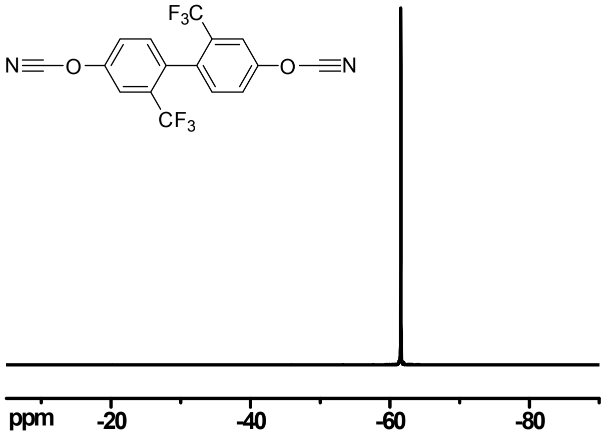

Figure S4. ^{19}F NMR spectrum of TFMBDCy

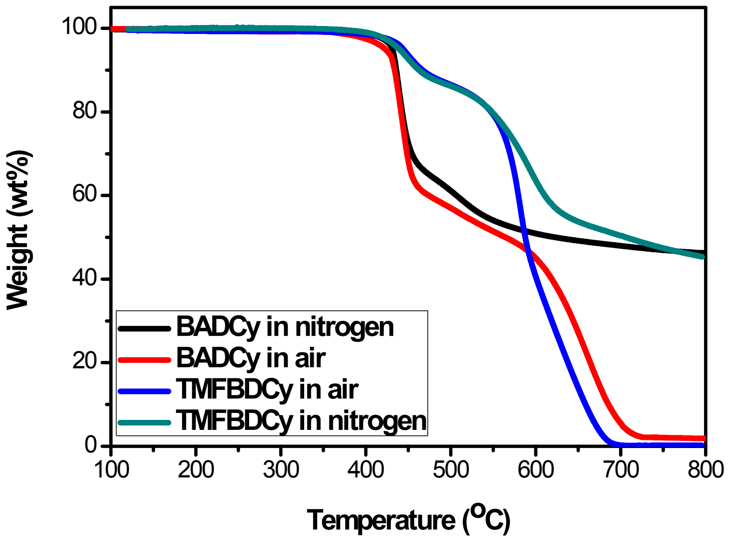

Figure S5. TGA profiles for TMFBDCy- and BADCy-derived thermosets

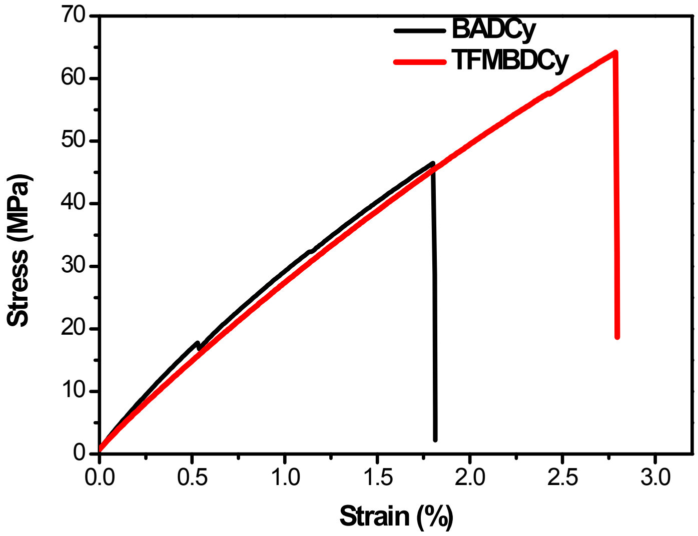

Figure S6. Representative stress-strain curves of BADCy and TFMBDCy-derived polycyanurates

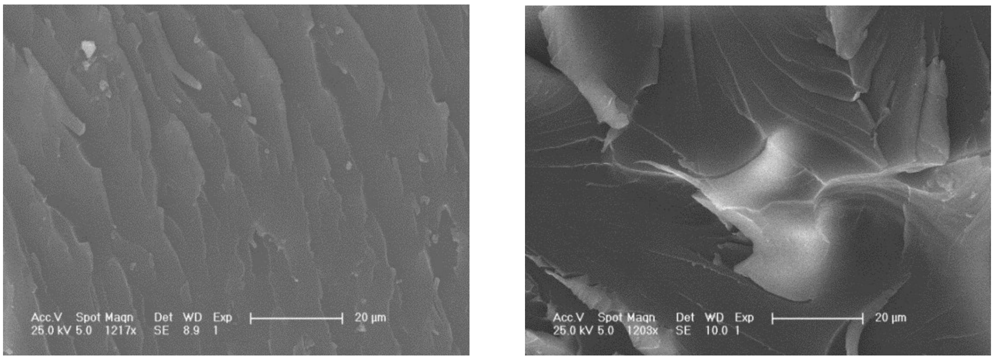

Figure S7. SEM images of BADCy (right) and TFMBDCy-derived (left) polycyanurates