

Supporting Information

Characterization.

¹H nuclear magnetic resonance (NMR) spectra are determined on a Varian Unity Inova 400 instrument, using deuterated dimethyl sulfoxide-d⁶ (DMSO-d⁶) as solvent.

Fourier transform infrared (FT-IR) spectra was recorded on a Thermo Nicolet Nexus 470 FT-IR spectrometer through attenuated total reflectance (ATR) method in the range of 500-4000 cm⁻¹.

In situ IR spectra are using EQUINOX55 Fourier transform IR spectrometer from 4000 to 500 cm⁻¹ at a resolution of 4 cm⁻¹ by 32 scans.

The geometries of these three molecules are optimized under the framework of density functional theory (DFT) with PBE0 functional and def 2SVP basis set. In order to describe the dispersion interaction, the DFT-D3 dispersion correction method is used in all calculations. After the structural optimization, single point calculations for these optimized structures with PBE0functional and def 2TZVP basis set are performed. All calculations are performed using Gaussian 16 program. The electrostatic surface potential (ESP) and surface extrema points are calculated using Multiwfn program and then rendered using VMD program.

Rheological analyses are performed on a TA Instruments AR2000 rheometer. 25 mm diameter flat parallel disposable aluminum plates with a 1 mm gap setting are used for oscillation measurements (strain of 0.02 N, frequency of 1 Hz). The all samples are measured at a heating rate of 3 C/min.

Differential scanning calorimetric (DSC) measurements are performed on a METTLER DSC 822 instrument in aluminum pans under anitrogen atmosphere at flow of 50 ml/min. All samples are heated from 25 to 400°C at a rate of 10°C/min.

Thermal stability studies are carried out on a METTLER TGA/ SDTA851 instrument under a nitrogen or air at flow of 50 ml/min. Be-tween 5 and 10 mg of sample is weighted in open aluminum oxide pan. The samples are scanned from 30 to 800 °C at a ramp rate of 10 °C/min.

STA-FTIR are carried out on a Netzsch STA449F5-Nicolet IS 20-Agilent 8890-5977B instrument under a nitrogen at flow of 50 ml/min. The samples are scanned from 50 to 800 °C at a ramp rate of 10 °C/min.

Dynamic mechanical analysis (DMA) was carried out with a TA Instrument (TA Q800) in a single cantilever mode. All the samples were tested with frequency of 1 Hz and a heating rate of 3 °C min⁻¹ from 25 to 250 °C under air atmosphere.

Synthesis of 1,2-bis(4-hydroxyphenyl)-o-carborane (BHCB) monomers. The *preparation of* compounds 1,2-bis(4-Methoxyphenyl)-o-carborane, are conducted as the method reported by references. The synthetic route is shown in Scheme 1. The 1000mL flask is evacuated and filled with nitrogen for three times. 5.62 g (46 mmol) decaborane is dissolved in 500mL xylene, then 100mL acetonitrile is added in the solution. The reaction is heated to reflux for 4h. The reaction mixture is heated to reflux for 16 h after 6.19 g (26 mmol)1,2-bis(4-Methoxyphenyl) acetylene is added. The orange-red solution is formed without gas bubbles

released from the solution. The solvent is then removed by distillation from product, 1,2-bis (4-Methoxyphenyl)-o-carborane (BMCB), is purified by crystallization from n-heptane. The yield is 63%. BMCB: ¹H NMR (400 MHz, DMSO-d₆) δ 7.44 (d, J = 9.0 Hz, 4H), 6.78 (d, J = 8.9 Hz, 4H), 3.69 (s, 6H) in **Figure S2**.

2.67g (7.5 mmol) BMCB and 24mL dry dichloromethane are added to Shrek-flask which filled with nitrogen. The Shrek-flask are wrapped with aluminum foil and placed in an ice-water mixture for refrigeration. 30mmol boron tribromide is injected Shrek-flask. The reaction is stirred for 24h in an airtight environment at room temperature then reaction mixture is poured into ice water. The resulting white precipitate is collected by suction filtration. The yield is 98%. BHCB: ¹H-NMR (400 MHz, DMSO-d₆) δ 9.92 (s, 2H), 7.28 (d, J = 8.5 Hz, 4H), 6.65 - 6.49 (m, 4H) in **Figure S3**.

Synthesis of 1,2-bis(4-phenyl)-o-carborane (BPCB) monomers. The 1000mL flask is evacuated and filled with nitrogen for three times. 5.62 g (46 mmol) decaborane is dissolved in 500mL xylene, then 100mL acetonitrile is added in the solution. The reaction is heated to reflux for 4h. After the reaction system is cooled to room temperature, 4.63 g (26 mmol) 1,2-bis(4-phenyl) acetylene is added. Then, the reaction mixture is heated to reflux for 16 h. The orange-red solution is formed without gas bubbles released from the solution. The yield is 59% BPCB: ¹H-NMR (400 MHz, DMSO-d₆) δ 7.58 - 7.46 (m, 4H), 7.36 -7.29 (m, 2H), 7.24 (dd, J = 8.4, 6.9 Hz, 4H) in Figure S4.

Synthesis of 1,2-bis(4-bromophenyl)-o-carborane (BBCB) monomers. The 1000mL flask is evacuated and filled with nitrogen for three times. 5.62 g (46 mmol) decaborane is dissolved in 500mL xylene, then 100mL acetonitrile is added in the solution. The reaction is heated to reflux for 4h. After 8.73 g (26 mmol) 1,2-bis(4-bromophenyl) acetylene is added, the reaction mixture is heated to reflux for 20 h. The orange-red solution is formed without gas bubbles released from the solution. The yield is 55%. BBCB: ¹H NMR (400 MHz, DMSO-d₆) δ 7.15 – 7.06 (m, 2H), 7.02 – 6.90 (m, 2H) in Figure S5.

Preparation of the blends. All blends (MPN/DDS, MPN/BHCB, MPN/BPCB and MPN/BBCB) are prepared by dissolving the compound in DMAC. And the solution is stirred for 2h at room temperature to obtain a homogenous mixture. Then the solution is poured into a large amount of water. The resulting yellow precipitate is collected by suction filtration. After drying, a uniform mixture is obtained. The appropriate addition amount (20%-50%) of BHCB curing agent is obtained from Figure S6, here we uniformly select the minimum addition amount of 20wt%. In order to control the variables, we take the molar ratio of carborane in the 20.0wt% BHCB curing agent as the standard and add 18.0wt% BPCB and 27.6wt% BBCB respectively to ensure that each carborane curing agent system has the same molar amount of carborane cage. MPN blends with different hydroxyl-containing structures (11.3wt% BP, 13.9wt% BPA and 16.3wt% BHS) in the same way and same standard as the above method.

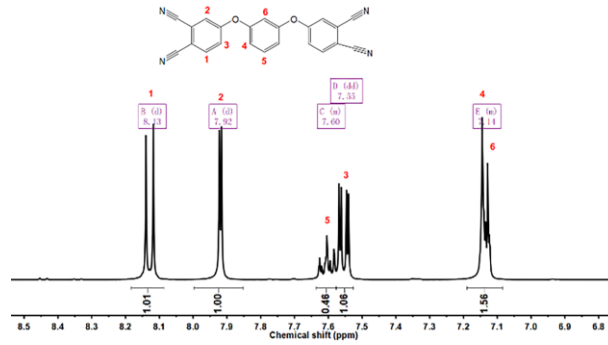


Figure S1. $^1\text{H-NMR}$ structural characterization of BHCBC monomer.

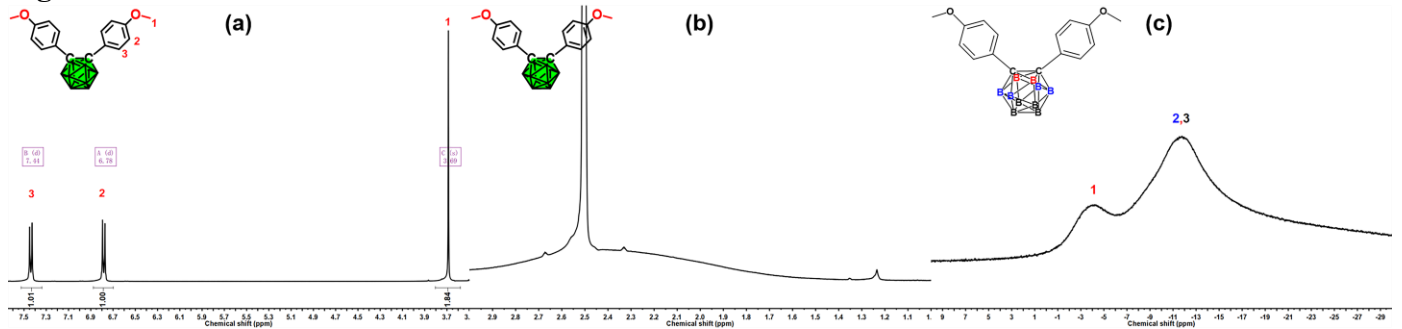


Figure S2. Structural characterization of BMCB monomer. (a) $^1\text{H-NMR}$; (b) $^{11}\text{B-NMR}$.

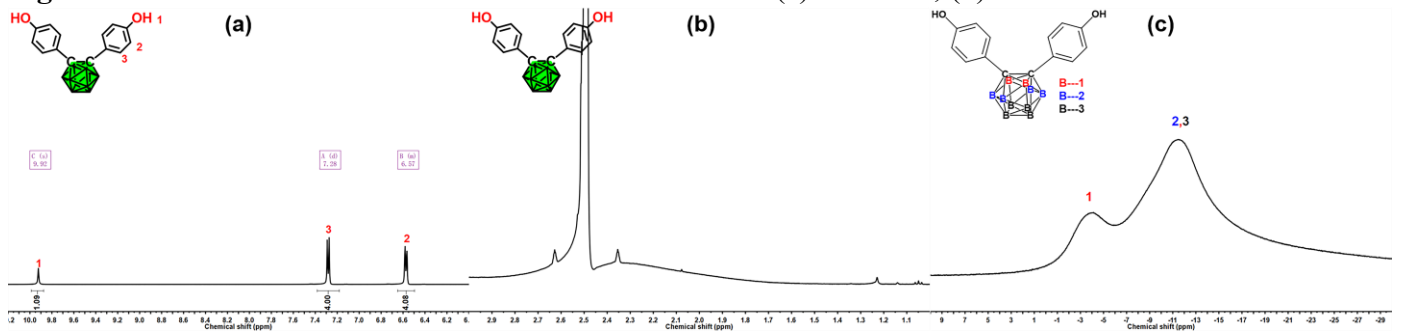


Figure S3. Structural characterization of BHCBC monomer. (a) $^1\text{H-NMR}$; (b) $^{11}\text{B-NMR}$.

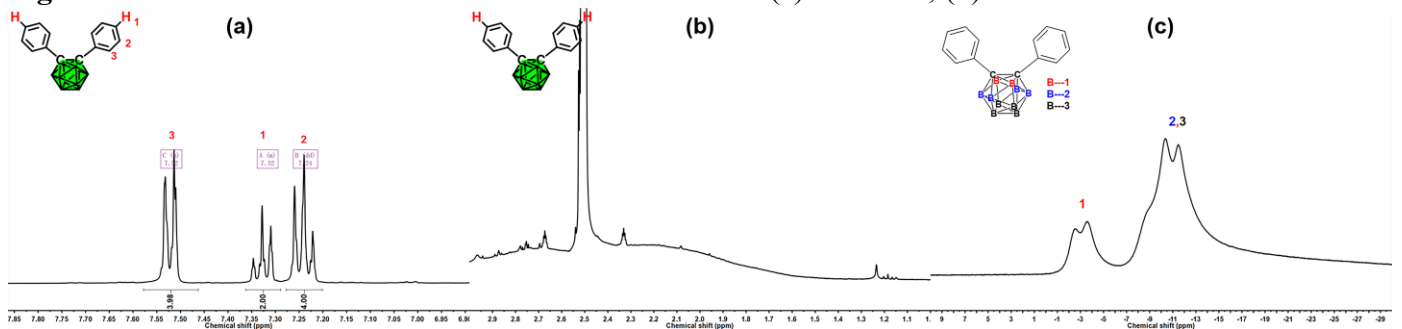


Figure S4. Structural characterization of BPCBC monomer. (a) $^1\text{H-NMR}$; (b) $^{11}\text{B-NMR}$.

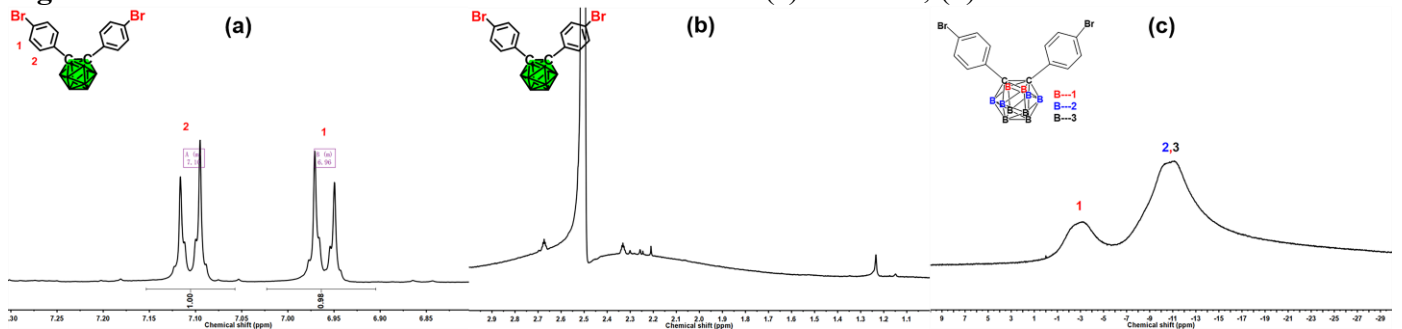


Figure S5. Structural characterization of BBCBC monomer. (a) $^1\text{H-NMR}$; (b) $^{11}\text{B-NMR}$.

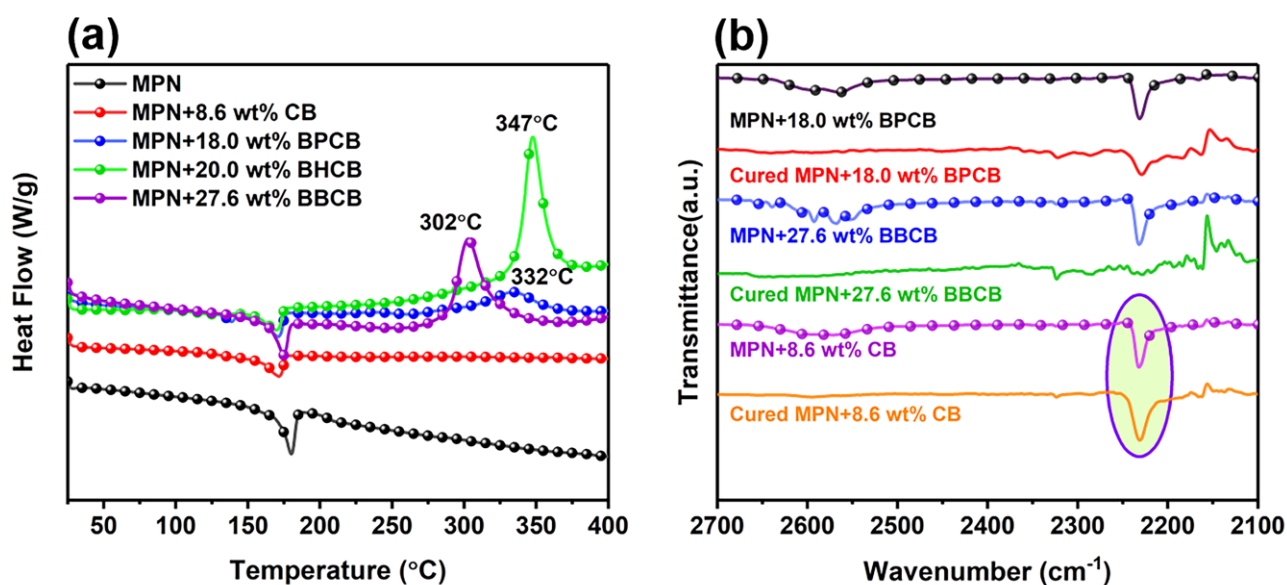


Figure S6. DSC curves. (a) MPN, MPN /CB, MPN /BHCB, MPN /BPCB and MPN /BBCB; (b) Enlarged figure of FI-IR spectra on cyano groups and boron hydrogen bond.

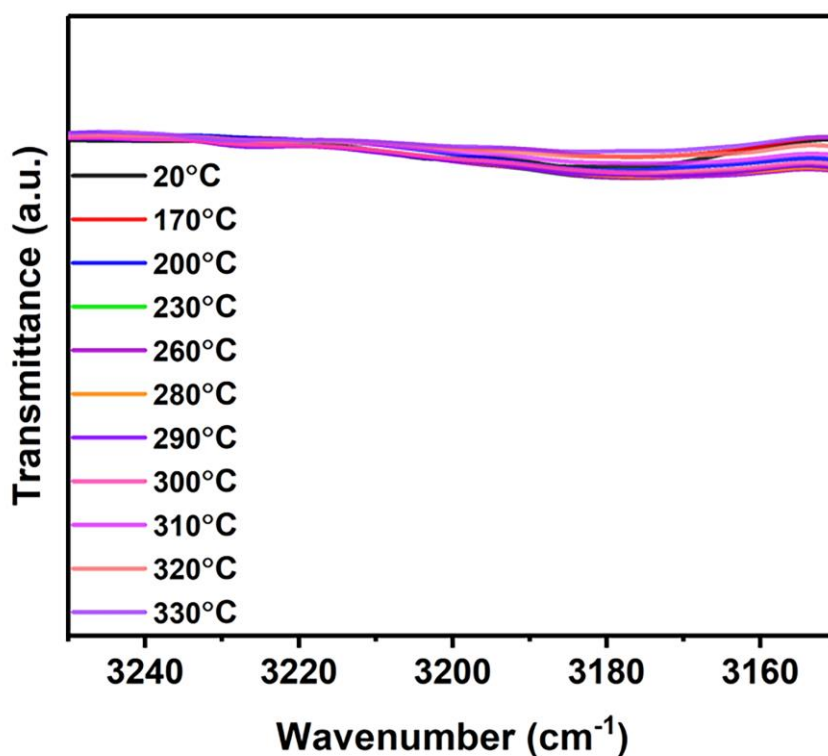


Figure S7. 3150 cm^{-1} -3250 cm^{-1} partial zoom-in of in situ infrared test curve to observe B-OH changes.

In order to prepare soluble thermosetting resins that can detect the state of crosslink network formation, we propose a method for preparing soluble B-staged resins using rheological viscosity detection. This way detects the viscosity of the system by a rheometer as shown in Fig S8 and let as many curing agents as possible participate slowly in the reaction with cyano groups at the lowest possible temperature (Generally set as the complete melting temperature of the system) so that the further growth of the segment is slow.

Under the premise that the reactivity can be controlled, temperature is increased after the curing agent reaction is completed to obtain a B-stage resin with a viscosity of 10 Pa.s that can be completely dissolved in DMSO-d6.

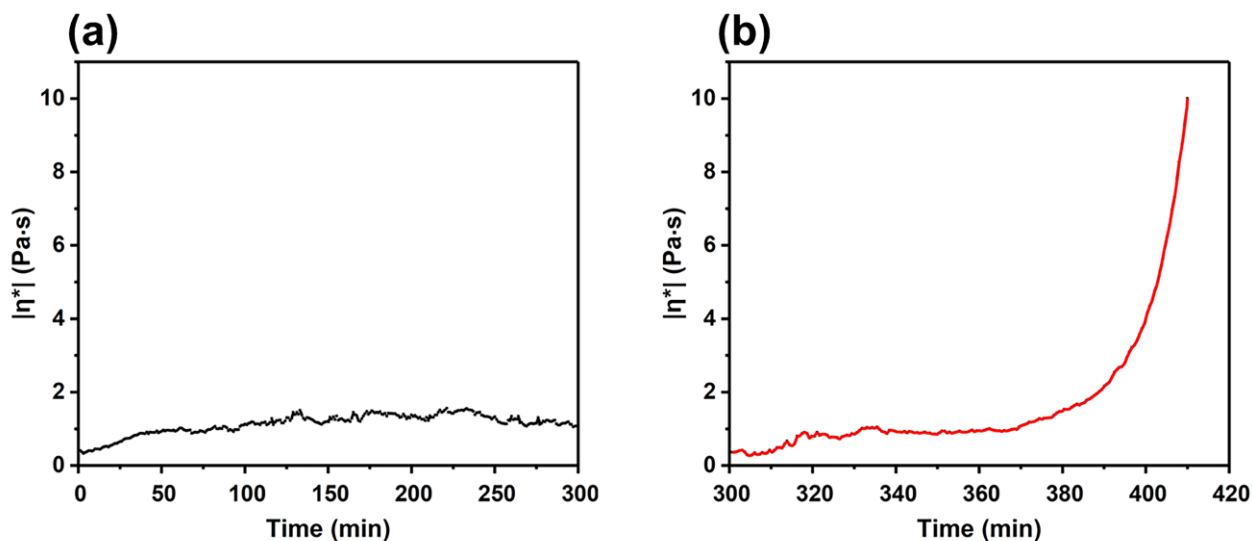


Figure S8. Rheological protocol for preparation of soluble B-Staged cures. (a) Maintain the first stage of heating near the melting point; (b) then increase the temperature to 20°C to promote the slow occurrence of solidification.

Table S1.
Curing schedule

	Curing procedure
a	Uncured
b	300°C/ 30min; 320°C/ 120min
c	300°C/ 30min; 320°C/ 120min; 340°C/120min; 360°C/120min
d	300°C/ 30min; 320°C/ 120min; 340°C/120min; 360°C/120min; 380°C/ 480min
e	300°C/ 30min; 320°C/ 120min; 340°C/120min; 360°C/120min; 380°C/ 480min; 450°C/ 120min

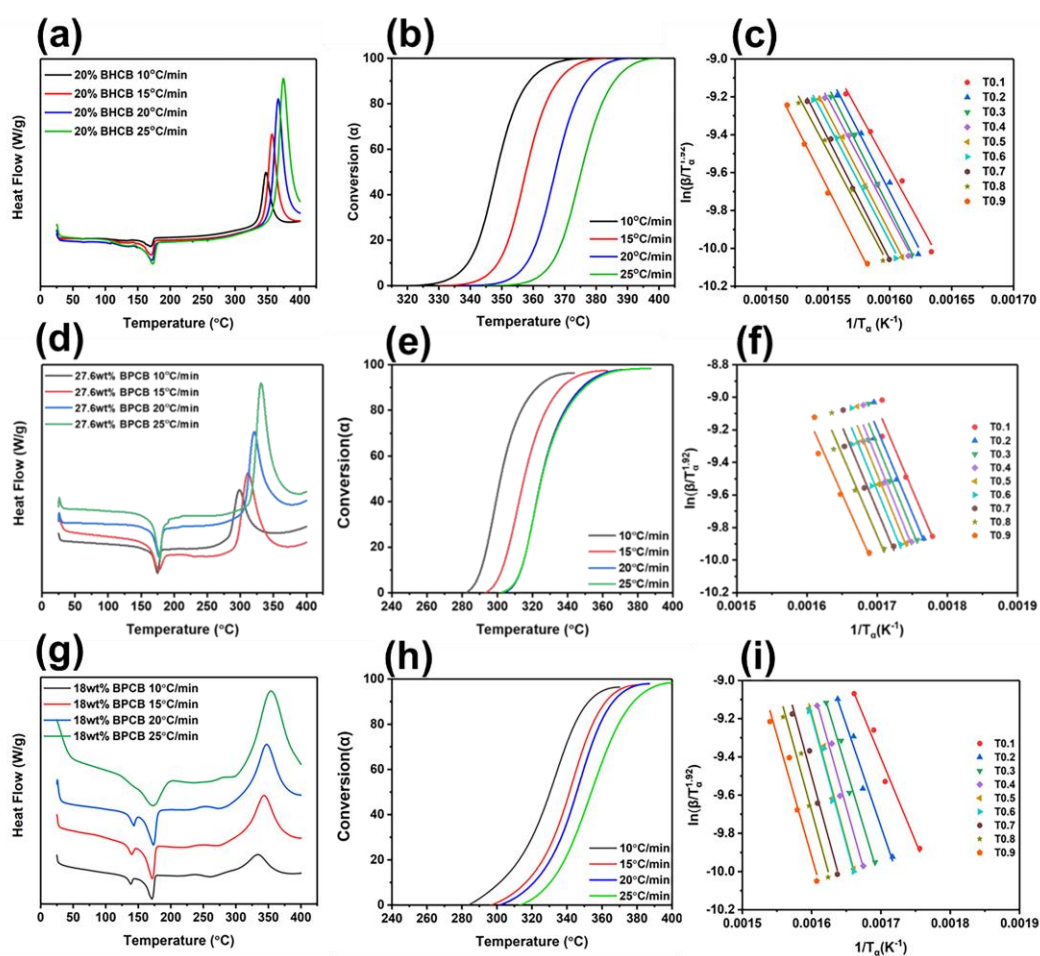


Figure S9. Curing kinetic curve. (a) DSC curves of MPN/BHCB system at various heating rates; (b) Plots of conversion α vs temperature of MPN/BHCB system; (c) Plots of $\ln(\beta_i/T_{\alpha,i}^{1.92})$ vs $1/T\alpha$ of MPN/ BHCB system; (d) DSC curves of MPN/BPCB system at various heating rates; (e) Plots of conversion α vs temperature of MPN/BPCB system; (f) Plots of $\ln(\beta_i/T_{\alpha,i}^{1.92})$ vs $1/T\alpha$ of MPN/ BPCB system; (g) DSC curves of MPN/BBCB system at various heating rates; (h) Plots of conversion α vs temperature of MPN/BPCB system; (i) Plots of $\ln(\beta_i/T_{\alpha,i}^{1.92})$ vs $1/T\alpha$ of MPN/ BBCB system.

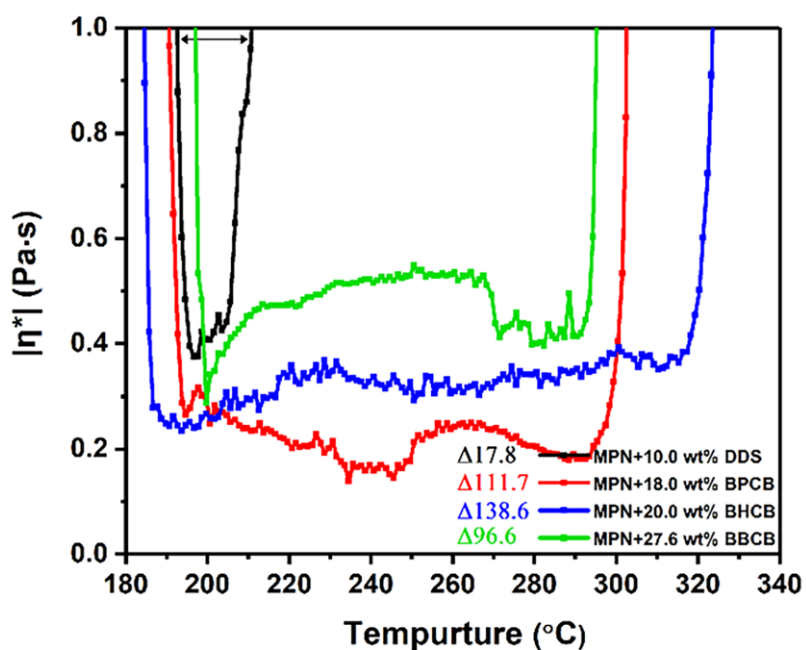


Figure S10. The rheological behavior of MPN blends containing different carborane-based curing agents (BPCB, BHCB and BCB) and control group of MPN/DDS.

Table S2. TGA data in N₂ for the cured MPN systems.

Samples	$T_{d5\%}$ (°C)	$T_{d10\%}$	C_{y800} (%)
MPN/DDS	507	549	76
MPN/BPCB	560	612	80
MPN/BHCB	549	636	82
MPN/BBCB	582	676	85

Table S3. TGA data in Air for the cured MPN systems.

Samples	$T_{d5\%}$ (°C)	$T_{d10\%}$	C_{y800} (%)
MPN/DDS	506	557	33
MPN/BPCB	550	595	64
MPN/BHCB	530	607	69
MPN/BBCB	574	656	83

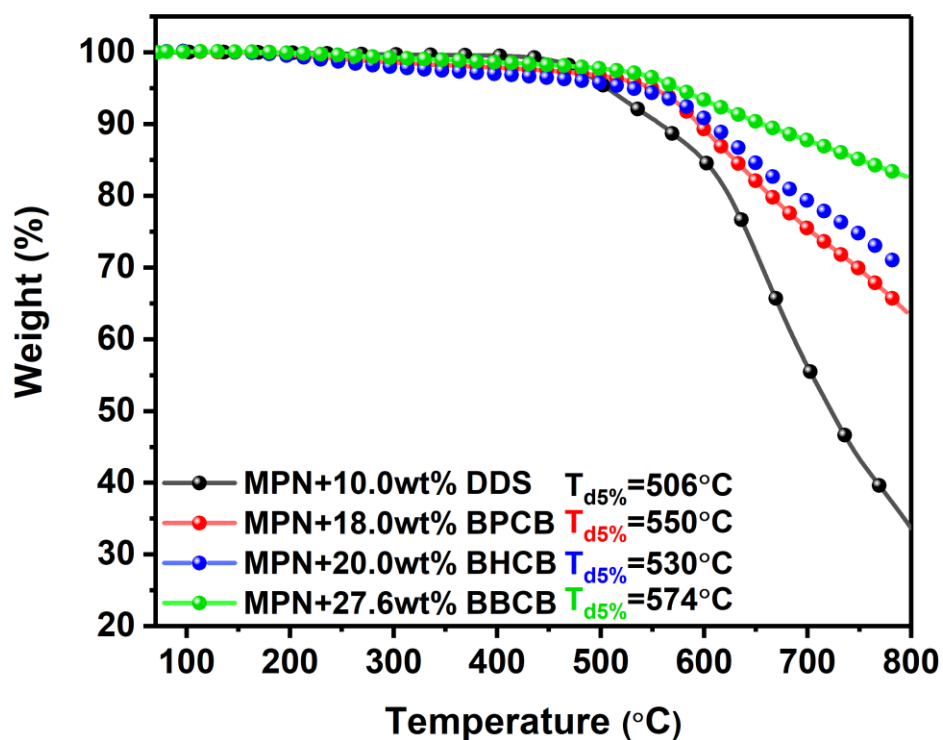


Figure S11. TGA test curve of MPN blend system containing different carborane-based curing agents (BPCB, BHCB and BBCB) and control group of MPN/DDS in Air atmosphere.

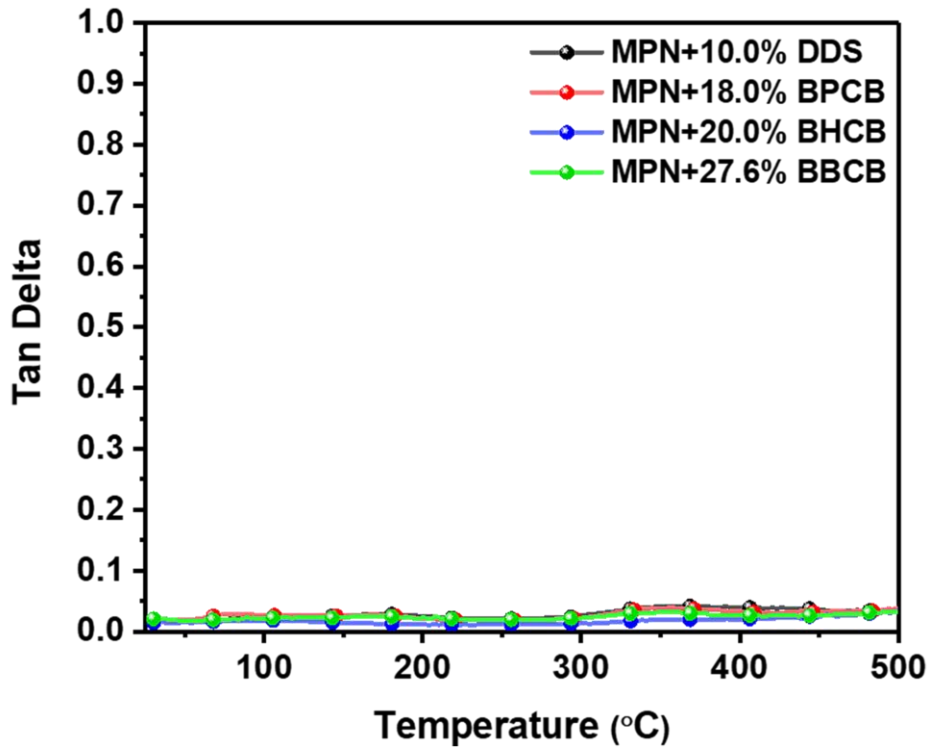


Figure S12. DMA test curve of MPN blends.

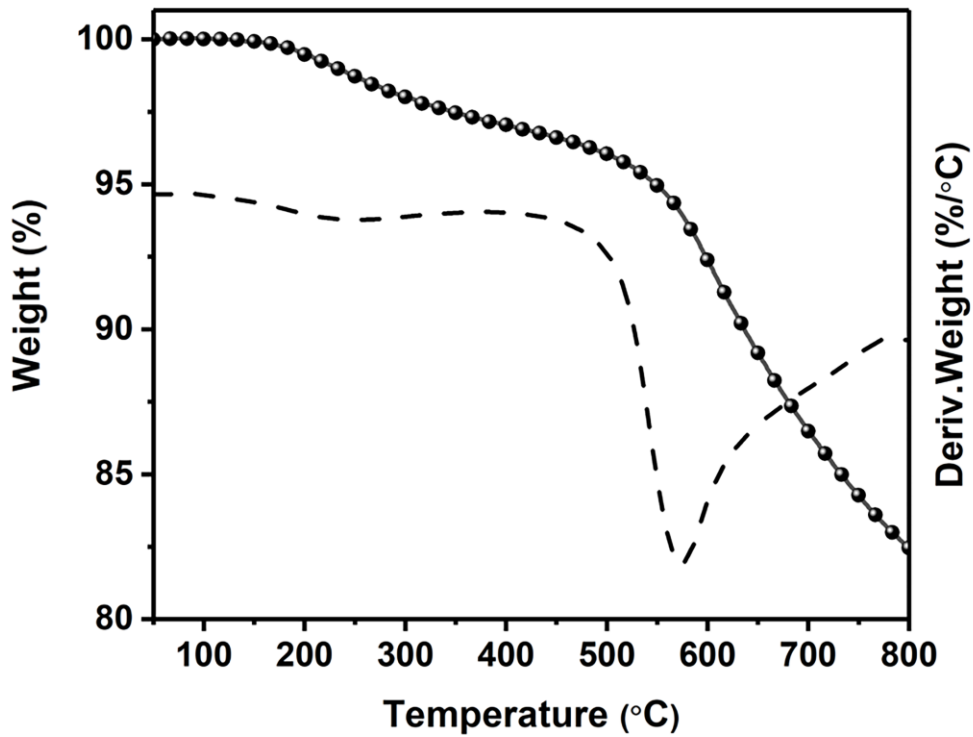


Figure S13. TGA test curve and DTG curve of MPN/BHCB cured product.