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Cross-Linked Porous Polyurethane Materials Featuring Dodecaborate Clusters as Inorganic Polyol Equivalents

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Supporting Information (SI)

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General Considerations

Dry-box manipulations were carried out under an atmosphere of dinitrogen in a Vacuum Atmospheres NexGen dry-box. Acetonitrile was dried prior to use by sparging with argon, and then loaded on a SciMatCo Solvent Purification System. Acetonitrile was then collected and stored over activated 4 Å molecular sieves in a dry-box under dinitrogen atmosphere.

Materials

Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received. The following chemicals were purchased from commercial vendors: 1,4-phenylene diisocyanate (Sigma Aldrich), pentaerythritol (Sigma Aldrich), *p*-tolyl isocyanate (Oakwood).

Cesium and $[N^{n}Bu_4]^+$ salts of $[B_{12}(OH)_{12}]^{2-}$ were synthesized by previously reported methods.[1]

Microwave synthesis

Microwave reactions were carried out using a CEM Discover SP microwave synthesis reactor. 10 ml reaction vials were used for all reactions and sealed with silicone/PTFE caps. Flea micro PTFE-coated stir bars were used in the vials with magnetic stirring set to high and 15 seconds of premixing prior to the temperature ramping. All microwave reactions were carried out at 100-120 °C with the pressure release limit set to 250 psi (no reactions exceeded this limit to trigger venting) and the maximum wattage set to 250W.

Synthesis of non-cross-linked urethanes

The preparation of the microwave reaction was performed in an inert atmosphere dry-box. In a 10 ml glass microwave vial, *p*-tolyl isocyanate (244 mg, 1.83 mmol) in acetonitrile (1 ml) was added to a stirring suspension of $[N^{n}Bu_4][B_{12}(OH)_{12}]$ (25 mg, 0.0305 mmol) in acetonitrile (0.5 ml). The reaction vial was sealed with a PTFE/silicone cap and then brought outside of the dry-box. The mixture was heated at 100 °C with stirring in the microwave for 2 hours. The excess acetonitrile was removed by rotary evaporation and the excess starting reagents were removed through a slurry-packed silica gel column with 3:1 (v/v) hexane:ethyl acetate. The excess solvent was evaporated by rotary evaporation, the residue was dried under high vacuum.

Synthesis of 1

The preparation of the microwave reaction was performed in an inert atmosphere dry-box. In a 10 ml glass microwave vial, 1,4-phenylene diisocyanate (59 mg, 0.366 mmol) in acetonitrile (1 ml) was added to a stirring suspension of $[N^{n}Bu_4][B_{12}(OH)_{12}]$ (50 mg, 0.0611 mmol) in acetonitrile (0.5 ml). The reaction vial was sealed with a PTFE/silicone cap and then brought outside of the dry-box. The mixture was heated at 120 °C with stirring in the microwave for 2 hours. The reaction mixture was transferred to a 20 ml glass scintillation vial. The NCO/OH ratio of 2 and 3 were used to produce allophanate linkages.

Note: The gelation time can be shortened by using a 1,4-diazabicyclo[2.2.2]octane (DABCO) as a catalyst without affecting the structure and thermal stability of the product (Fig. S6, S7).

Synthesis of 2

The preparation of the microwave reaction was performed in an inert atmosphere dry-box. In a 10 ml glass microwave vial, 1,4-phenylene diisocyanate (118 mg, 0.734 mmol) in acetonitrile (2 ml) was added to a stirring suspension of pentaerythritol (50 mg, 0.367) in acetonitrile (0.5 ml). The reaction vial was sealed with a PTFE/silicone cap and then brought outside of the dry-box. The mixture was heated at 120 °C with stirring in the microwave for 2 hours. The product was washed with ethanol and vacuum dried on a lyophilizer.

Instrumentation

^{1}H solution NMR spectra were recorded in $(CD_3)_2CO$-*d*6 on AV 400 spectrometers in ambient conditions and referenced internally to residual solvent resonances in deuterated solvents (δ 2.05 for $(CD_3)_2CO$-*d*6). ^{13}C NMR spectra were obtained on AV 500 spectrometers with a cryoprobe.

Infrared (IR) spectra were obtained with a PerkinElmer Spectrum One instrument equipped with a universal ATR assembly.

Scanning electron microscopy (SEM) images were obtained with a field-emission SEM (JEOL JSM 6700F).

Thermogravimetric analysis (TGA) was carried out on a PerkinElmer Pyris Diamond TG/DTA under a constant flow of Argon (200 mL/min). Samples were heated in alumina oxide trays from 25 °C to 1000 °C at 10 °C/min.

^{11}B and ^{13}C solid-state magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra were obtained on a 600 MHz (14.1 T) Bruker AVANCE III HD spectrometer using a 3.2 mm HXY MAS probe. The MAS frequency used was 20 kHz for ^{11}B and 18 kHz for ^{13}C. The ^{11}B background signal from the MAS probe was suppressed using the EASY sequence.[2] The ^{11}B chemical shift was indirectly referenced to $BF_3O(CH_2CH_3)_2$ in $CDCl_3$ by using $Cs_2[B_{12}(OH)_{12}]$ (δ=-17.4 ppm).[3] The RF field for the ^{11}B central transition selective pulse was 66 kHz.

Mass spectrometry data was acquired using a Thermo Scientific Q-Exactive Plus instrument with a quadrupole mass filer and Orbitrap mass analyzer.

Supercritical CO_2 activation was carried out on as Tousimis™ Samdri® PVT-30 critical point dryer. The solvent contained in the polymer gel was firstly exchanged with ethanol overnight and then with liquid CO_2 for 10 hours. Then, the sample was taken beyond the critical point of CO_2 (T= 31 °C; P= 1071 psi) and slowly vented overnight.

N_2 isotherms were measured at 77 K on a micromeritics Tristar after activation at 40 °C under vacuum 4 h.

Micro Combustion Calorimetry (MCC)

1 and **2** were tested using Micro Combustion Calorimetry (MCC).[4] In MCC, a 3-5 mg sample is pyrolyzed under anaerobic conditions (N_2 atmosphere). The volatiles are then premixed with O_2 and the N_2-fuel-O_2 mixture enters an annular reactor where the fuel is fully oxidized (complete combustion products). Using O_2 consumption calorimetry methods,[5] the heat release rate is obtained. Integration of the heat release rate curve provides the heat of combustion of the sample. The values for the heat of combustion were normalized by the initial sample mass. Solid residue is measured in order to provide char yield data. For the current work, duplicate samples of **1** and **2** were tested. In MCC, the sample was heated at the standard heating rate of 1 °C/s, and the combustor temperature was 925 °C.

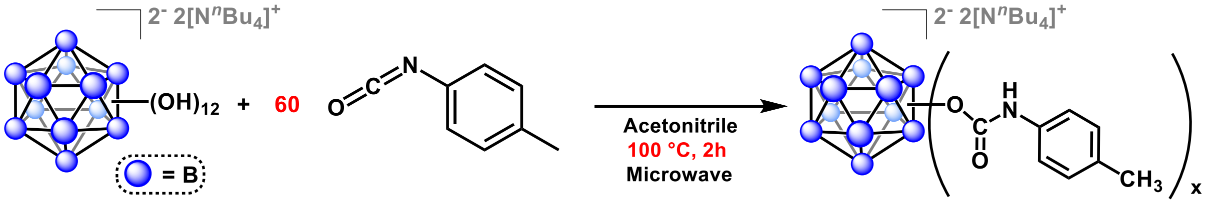


Figure S1. Synthetic route to produce non-cross-linked urethane linkages using $[N^{n}Bu_4]_2[B_{12}(OH)_{12}]$ and *p*-toly isocyanate.

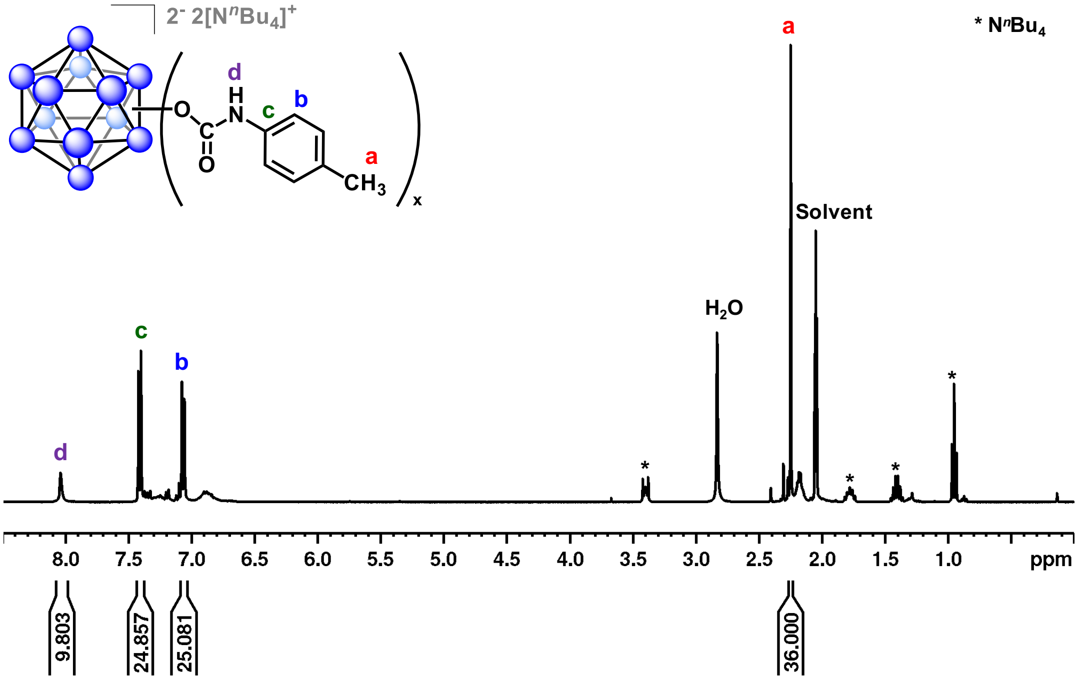


Figure S2. ^{1}H NMR spectrum of the test reaction of *p*-tolyl isocyanate with $[N^{n}Bu_4]_2[B_{12}(OH)_{12}]$ in $(CD_3)_2CO$. Peaks associated with the product are observed, indicating formation of urethane linkages.

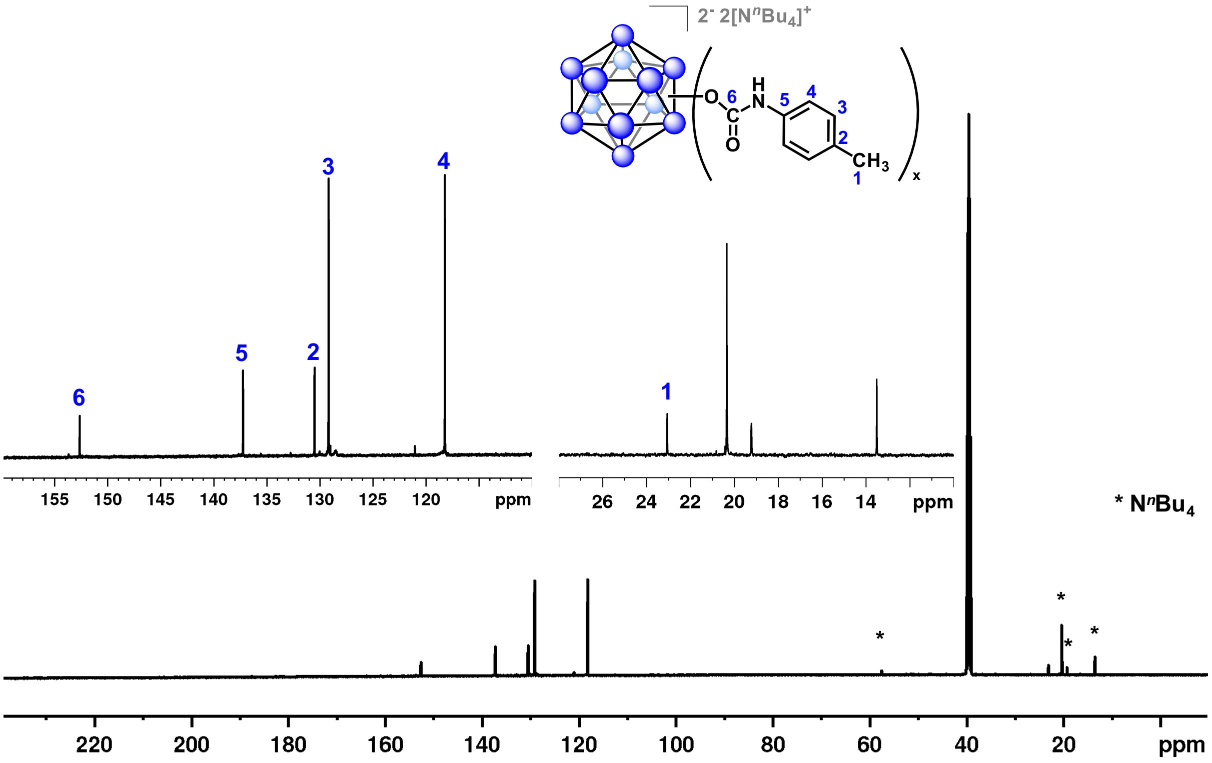
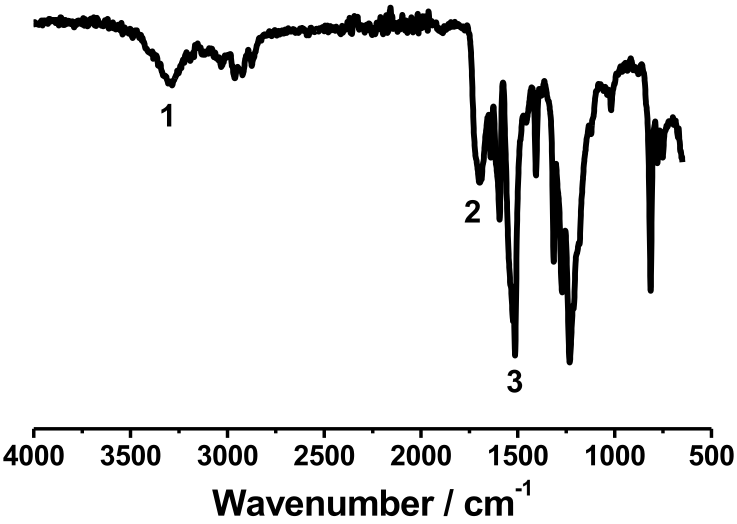


Figure S3. ^{13}C NMR spectrum of the test reaction of *p*-tolyl isocyanate with $[N^{n}Bu_4]_2[B_{12}(OH)_{12}]$ in $(CD_3)_2SO$. Peaks associated with the product are observed, indicating formation of urethane linkages.



	Functional group	Absorption (cm^{-1})
1	N-H stretching	3286
2	C=O stretching	1699
3	C-N stretch coupled with N-H bending	1517

Figure S4. FT-IR spectrum of the test reaction of *p*-tolyl isocyanate with $[N^{n}Bu_4]_2[B_{12}(OH)_{12}]$

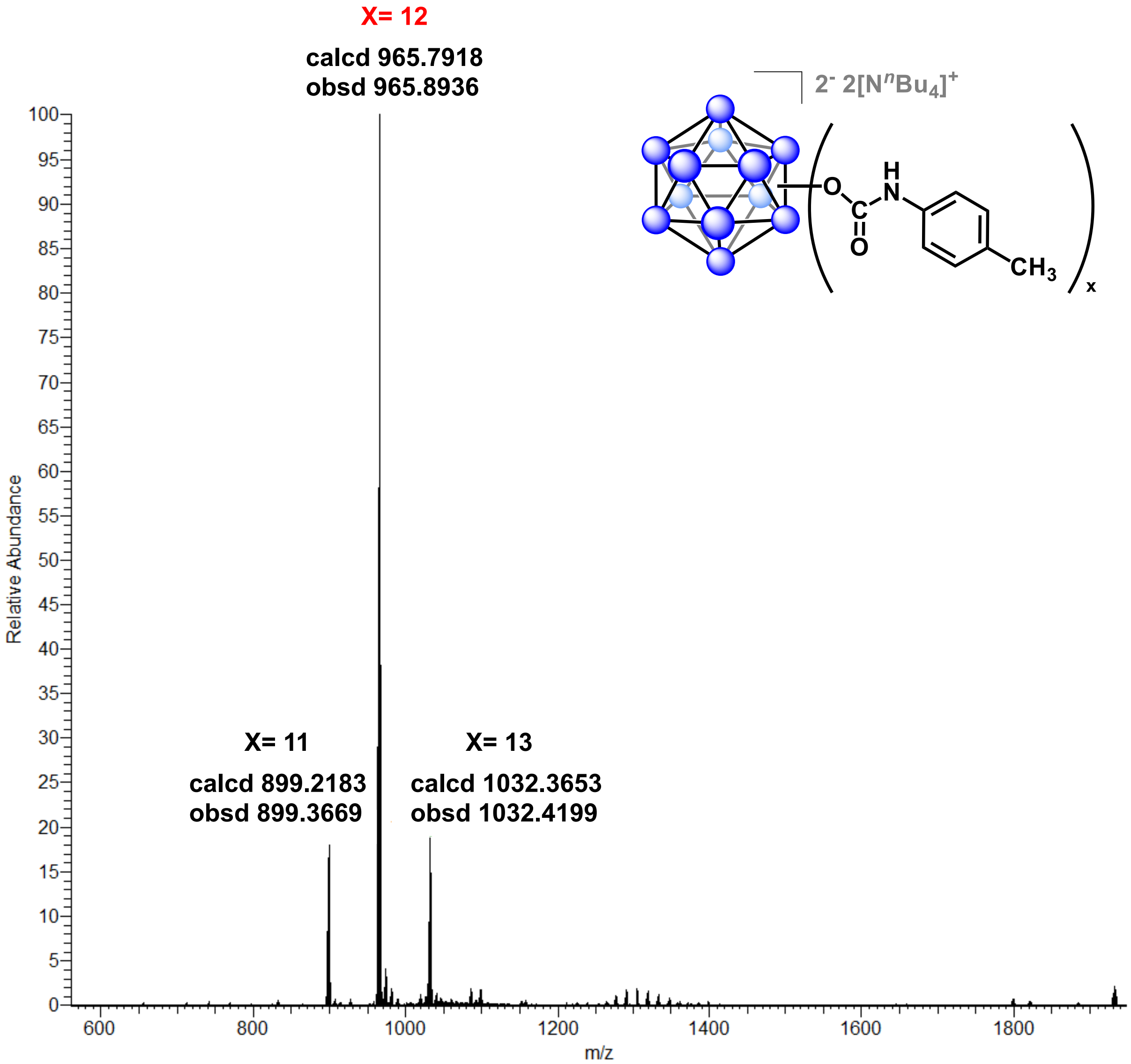
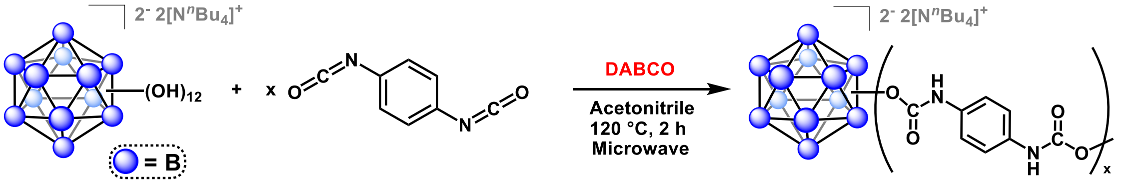


Figure S5. ESI-HRMS of the test reaction of *p*-tolyl isocyanate with $[N^nBu_4]_2[B_{12}(OH)_{12}]$, supporting the complete substitution of $[B_{12}(OH)_{12}]^{2-}$ clusters. The over-substituted compound (X=13) represents the presence of an allophanate linkage in the product which arises from the reaction of the amine of a urethane linkage with an excess isocyanate substrate.



	Catalyst	Gelation time
Trial 1	None	24 h
Trial 2	5.6 mg DABCO	2 h

Figure S6. Synthetic route to produce the cross-linked polyurethane materials using 1,4-diazabicyclo [2.2.2] octane (DABCO) as a catalyst.

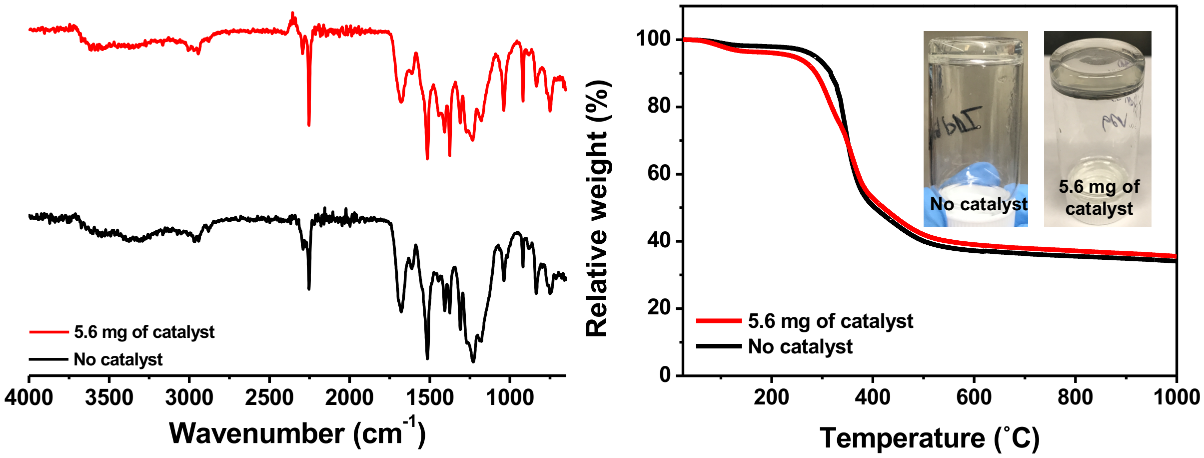


Figure S7. (a) FT-IR spectra and (b) TGA results of the polyurethane gel depending on the use of catalysts. While the use of the catalyst affects the gelation time, there was no noticeable change in the structure and the thermal properties of the cross-linked polyurethane gels.

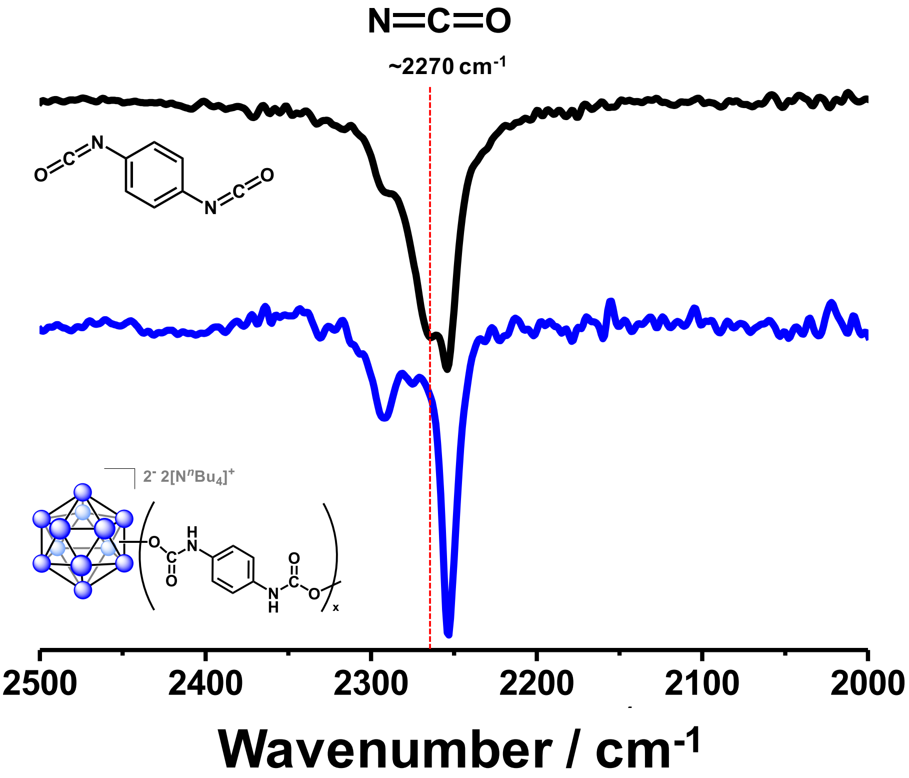


Figure S8. FT-IR spectra of **1** and 1,4-phenylene diisocyanate in acetonitrile. The absence of the peak at 2270 cm^{-1}, which corresponds to the free isocyanates, indicates the complete reaction of $[N^{n}Bu_4]_2[B_{12}(OH)_{12}]$ with 1,4-phenylene diisocyanate. The sharp peak at 2240 cm^{-1} arises from the solvent, CH_3CN.

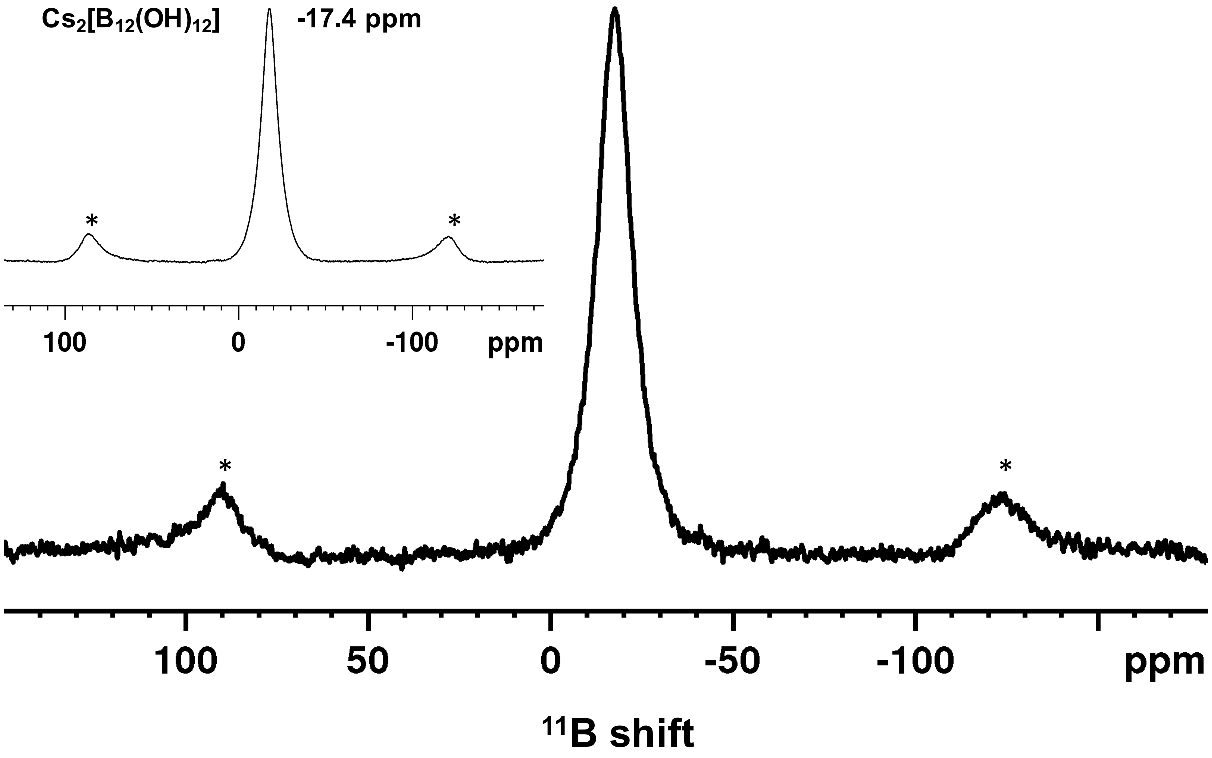


Figure S9. Solid-state 1D single-pulse ^{11}B MAS NMR of **1** and reference $Cs_2[B_{12}(OH)_{12}]$ (inset).

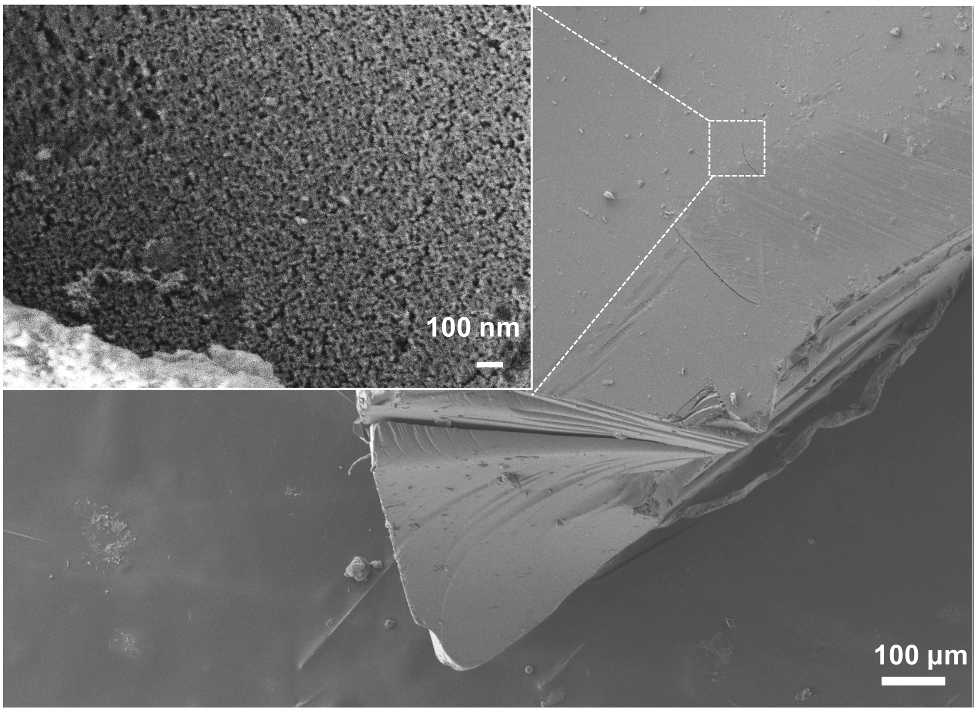
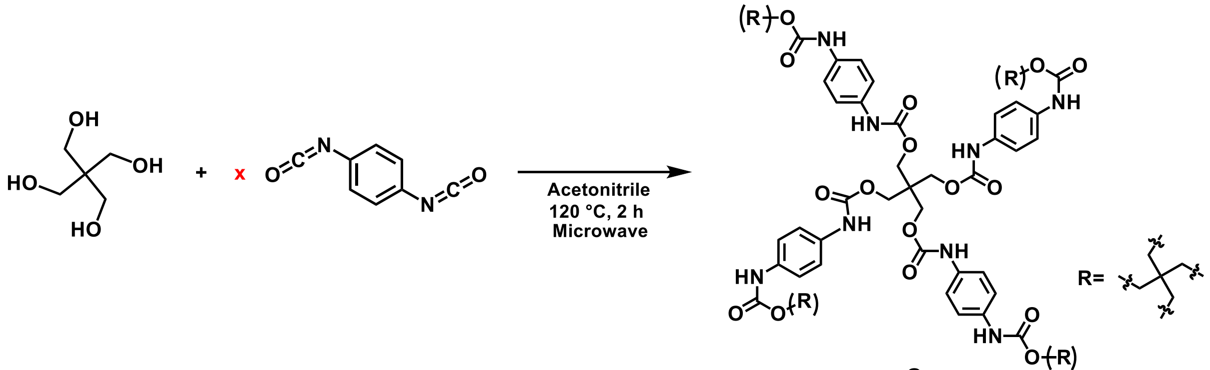
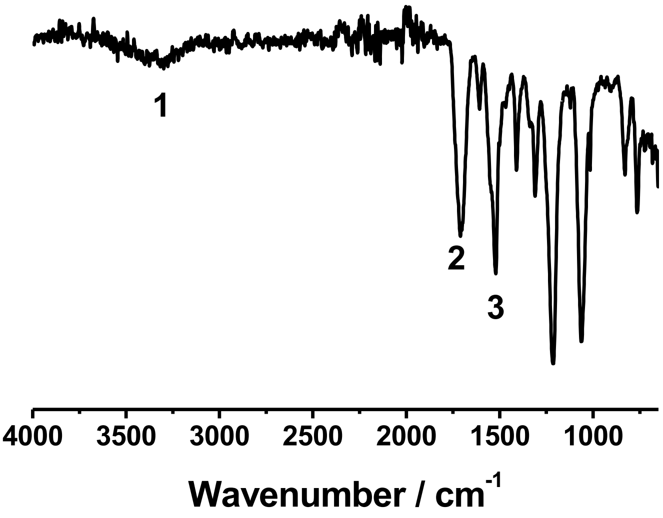


Figure S10. SEM image of **1** after supercritical CO_2 activation.



2

Figure S11. Synthetic route to produce **2** utilizing pentaerythritol as a cross-linker.



	Functional group	Absorption (cm^{-1})
1	N-H stretching	3300
2	C=O stretching	1698
3	C-N stretch coupled with N-H bending	1520

Figure S12. FT-IR spectrum of **2**, confirming the formation of the urethane linkage in **2**.

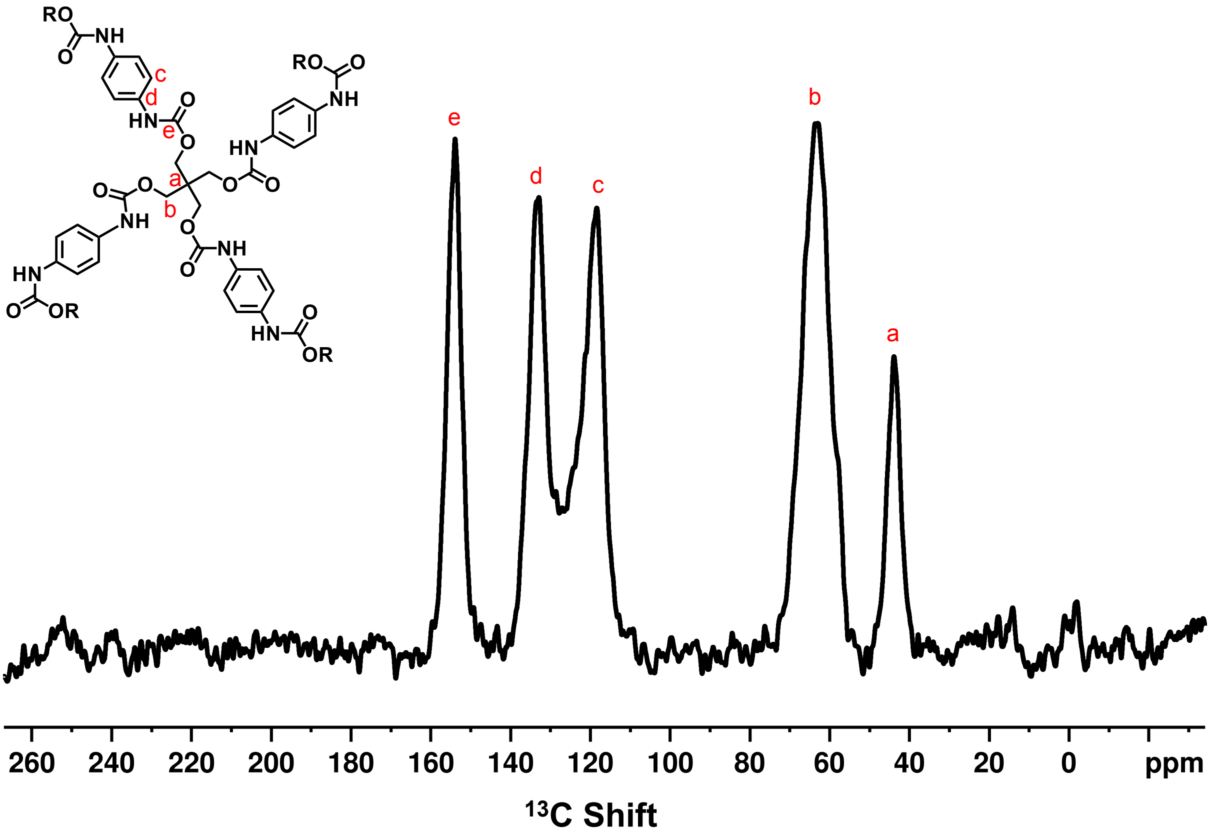
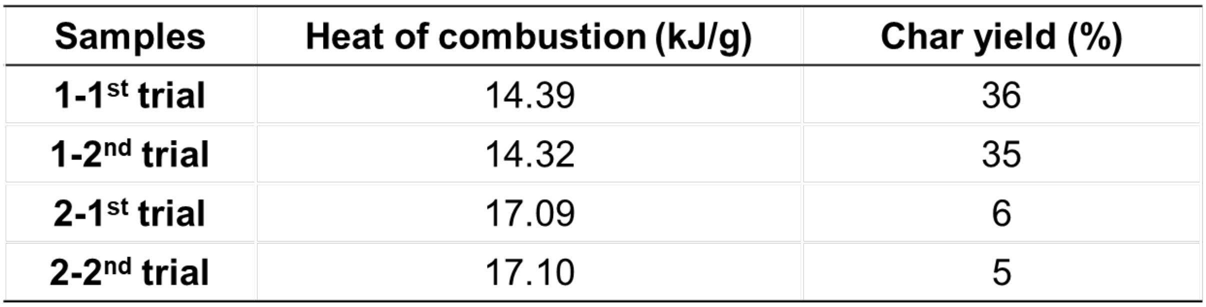


Figure S13. Solid-state 1D single-pulse ^{13}C NMR of **2**. Peaks associated with the product can be observed.

Samples	**$T_{d\ 5\%}$(°C)**	**$T_{d\ max}$ (°C)**	**Residue (%)**
1	286	346	35.0
2	218	303	2.9

Table 1. TGA results of **1** and **2** at the heating rate of 10 °C/min in Ar. $T_{d5\%}$ denotes the temperature at 5 % weight loss; T_{dmax} refers to the temperature at the maximum decomposition; residue % denotes the weight of the char residue at 800 °C.



Samples	**Heat of combustion (kJ/g)**	**Char yield (%)**
1-1st trial	14.39	36
1-2nd trial	14.32	35
2-1st trial	17.09	6
2-2nd trial	17.10	5

Table 2. Micro combustion calorimetry (MCC) test results. The tests were duplicated.

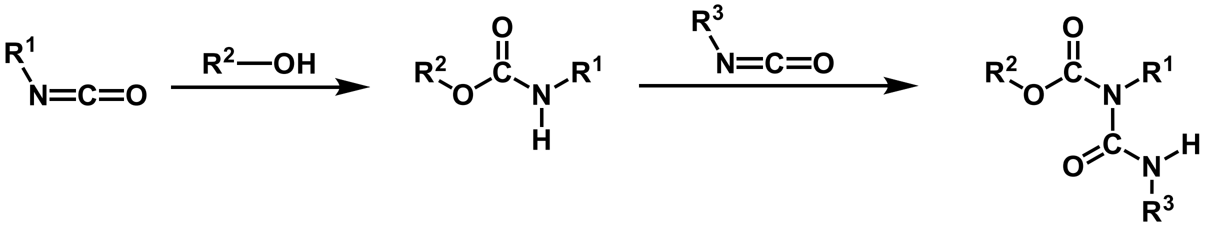


Figure S14. Synthetic route to create allophanate linkages in the polymer network.

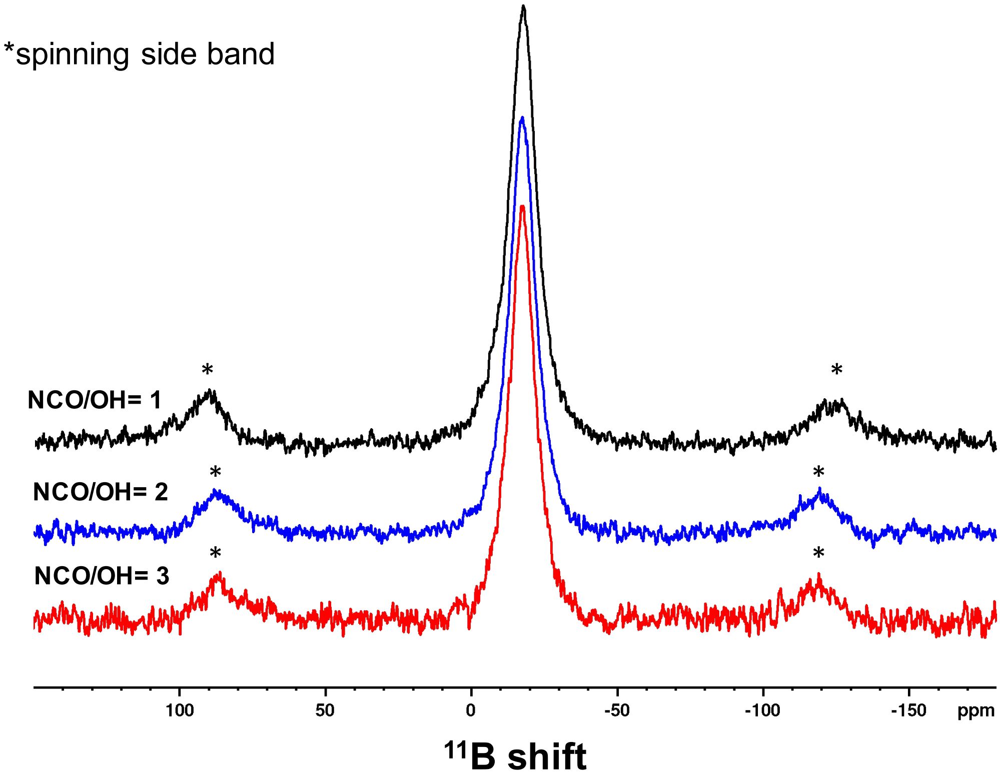


Figure S15. Solid-state 1D single-pulse ^{11}B NMR of the cross-linked polyurethane materials obtained from different ratios of NCO/OH.

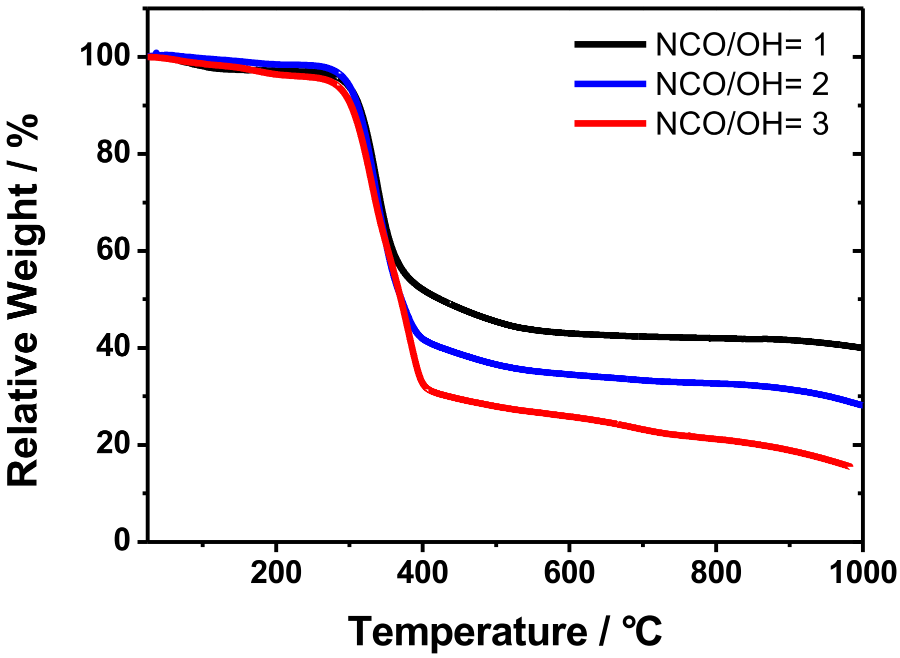


Figure S16. TGA of the cross-linked polyurethane materials obtained from different ratios of NCO/OH.

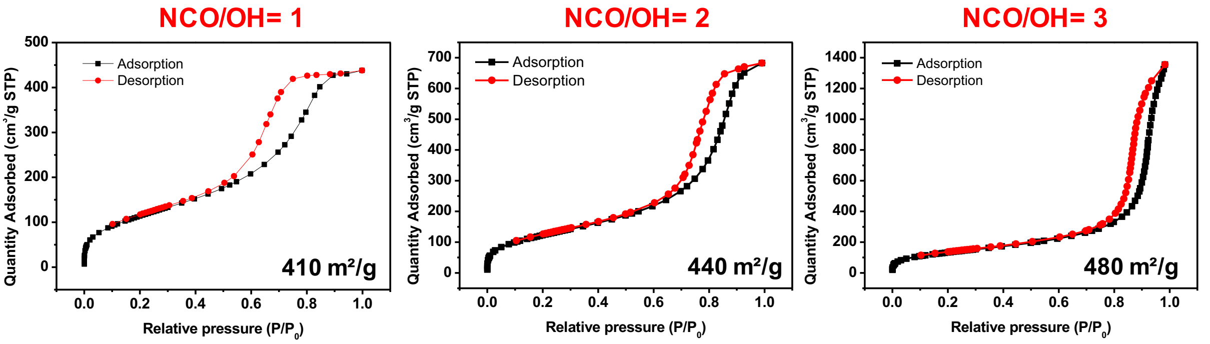


Figure S17. N_2 adsorption and desorption isotherms at 77 K of the cross-linked polyurethane materials obtained from different ratios of NCO/OH.

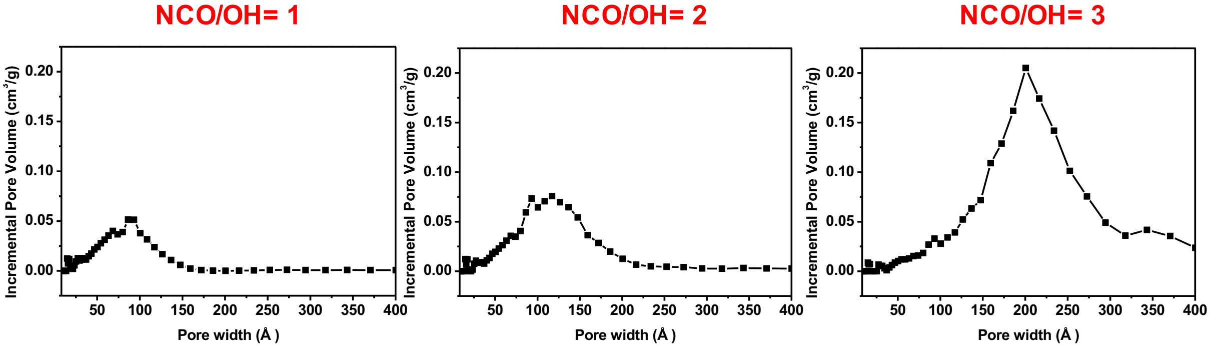


Figure S18. Pore size distribution of the cross-linked polyurethane materials obtained from different ratios of NCO/OH.

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