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Cross-linked porous polyurethane materials featuring dodecaborate clusters as inorganic polyol equivalents†

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We report the discovery that a perhydroxylated dodecaborate cluster ($[B_{12}(OH)_{12}]^{2-}$) can act as an inorganic polyol, serving as a molecular cross-linker in the synthesis of polyurethane-based materials. We further demonstrate how the inherent robustness of the utilized boron cluster can effectively enhance the thermal stability of the produced polyurethane materials incorporating $[B_{12}(OH)_{12}]^{2-}$ building blocks compared to analogous polymers made from carbon-based polyols. Ultimately, this approach provides a potential route to tune the chemical and physical properties of soft materials through incorporation of polyhedral boron-rich clusters into the polymer network.

Since the discovery of the vulcanization of natural rubber, cross-linking has been essential in polymer chemistry to improve the thermal, physical and mechanical properties of synthetic macromolecules.¹ Specifically, adding cross-linkers to polymer chains can affect several features in polymers such as elasticity, solubility, and mechanical strength, depending on the cross-linker density and its chemical nature.^{2–4} Over the past several decades, researchers have developed numerous cross-linking approaches including the use of linker agents that can interact with the polymer chains in a non-covalent and covalent manner. The latter approach was previously shown to increase chemical and physical stability in polymer networks due to the robust and irreversible nature of covalent cross-linking agents.^{5–7}

Polyurethanes represent one of the most extensively studied classes of polymers due to their versatile properties offering a

wide range of applications ranging from rigid foam insulation panels to high performance adhesives.^{8–10} Polyurethanes are prepared *via* condensation of diisocyanates and polyols to form urethane linkages. Consequently, the chemical and physical properties of polyurethanes can be altered by employing different types of isocyanates and polyols. In addition, covalent cross-linking has been shown to play an important role in determining the properties of polyurethane materials.^{11,12} Recently, bio-derived polyols obtained from vegetable oils have attracted significant interest as cross-linkable polyols, with the potential to replace petroleum-based polyols. Although these bio-based polyols exhibit reduced impacts on the environment, the lower reactivity of their hydroxyl groups relative to the primary hydroxyl groups in the petroleum-based polyols and high flammability of the resulting bio-based polyurethanes necessitate significant structural modifications to bio-derived polyols.^{14,15} While a vast amount of research has been carried out on organic-based polyols such as glycerol (**I**), pentaerythritol (**II**) and castor oil (**III**) (Fig. 1a),^{13–15} surprisingly, there has been no reported effort in assessing purely inorganic-based molecular polyols for producing cross-linked polyurethanes. In this work, we introduce a perhydroxylated dodecaborate cluster, $[B_{12}(OH)_{12}]^{2-}$, (referred to as **IV**)¹⁶ as an inorganic polyol equivalent, which serves as a hyper cross-linker possessing multiple cross-linking sites to generate porous polymers.⁶ We show that upon reaction with a model diisocyanate linker, boron-rich **IV** can form multiple urethane linkages to produce a porous polyurethane-based material with enhanced thermal stability compared to an analogue containing a carbon-rich cross-linker.

Our group recently developed a “molecular cross-linking” approach to create hierarchical hybrid metal oxide materials using **IV**.¹⁷ Based on these observations, we envisioned that the molecular cross-linking approach can be further expanded to organic molecules to form densely cross-linked polymeric networks.^{18–21} Specifically, we hypothesized that **IV** can be a suitable polyol system that can potentially react with isocyanates to generate urethane linkages. Given that the molecular scaffold of **IV** can withstand harsh thermal and oxidizing conditions,^{22–24}

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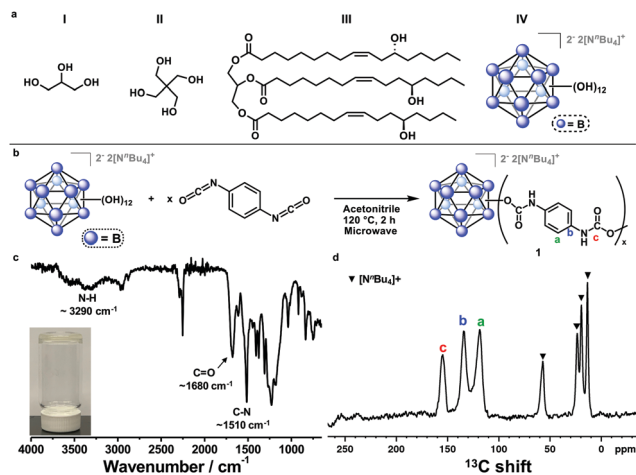


Fig. 1 (a) Overview of existing polyols for the synthesis of polyurethane materials: glycerol (I); pentaerythritol (II); castor-oil (III), and, in this work, a dodecaborate cluster (IV), (b) synthetic route to produce densely cross-linked polyurethanes, utilizing the polyhedral boron cluster $[N^{\text{I}}Bu_4]_2[B_{12}(OH)_{12}]$ as a robust inorganic polyol, (c) FT-IR and (inset) photo of **1**, (d) solid-state 1D single-pulse ^{13}C MAS NMR of **1**.

we further hypothesized that cross-linking these clusters in polyurethane materials would enhance thermal stability and potentially improve other properties of the resulting polymeric materials. To test our hypothesis, we conducted a model reaction between IV and *p*-tolyl isocyanate using a bench-top microwave reactor (see ESI†). When 60 equivalents of *p*-tolyl isocyanate were mixed with IV and heated for 2 hours at 100 °C in acetonitrile, a complete substitution of the starting cluster material was observed by nuclear magnetic resonance (NMR) spectroscopy, Fourier-transform infrared spectroscopy (FT-IR), and electrospray ionization mass spectrometry (ESI-MS) (see ESI†). This model experiment suggested that B-OH groups in IV could indeed behave as competent nucleophiles to form urethane linkages with isocyanates. We then performed condensation polymerizations utilizing 1,4-phenylene diisocyanate (PDI) with IV to ascertain whether this cluster can be used as a polyol equivalent in the synthesis of a model polyurethane-based material (Fig. 1b). We used stoichiometric amounts of functional groups (NCO:OH = 1:1) to produce the cross-linked polymer, **1**. The reaction produced a viscous mixture and a gel (referred to herein as **1**) was formed within 24 hours, suggesting the likely formation of a cross-linked polymer network (Fig. 1c inset and ESI†). The FT-IR spectrum of **1** displayed the characteristic features of N-H (3290 cm^{-1}), C=O (1680 cm^{-1}), and C-N stretching (1510 cm^{-1}) coupled with N-H bending, which corroborated the formation of the urethane linkage (Fig. 1c).²⁵ More importantly, there was no unreacted isocyanate present in the product based on the absence of a peak at 2270 cm^{-1} , corresponding to the free isocyanate (ESI†). Further structural characterization of **1** was obtained using 1D solid-state ^{11}B and ^{13}C magic-angle-spinning (MAS) NMR spectroscopy. The 1D ^{11}B MAS NMR spectrum of **1** showed a sharp signal at -17 ppm , which can be assigned to intact B_{12} -based clusters (ESI†). The ^{13}C MAS NMR showed four signals at 13.3, 19.2, 23.3, and 57.0 ppm

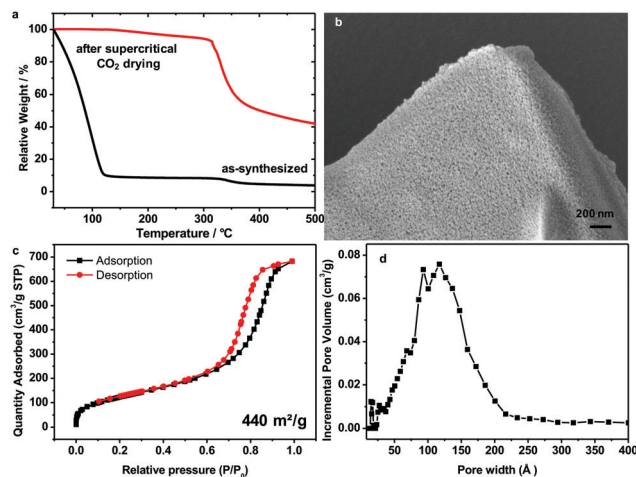


Fig. 2 (a) TGA results of **1**, (b) SEM image, (c) N_2 adsorption and desorption isotherms at 77 K, (d) pore size distribution of **1** following supercritical CO_2 activation.

corresponding to the alkyl carbon-based resonances of the butyl groups in $[N^{\text{I}}Bu_4]^+$ cation. Two signals in the aromatic carbon region (118.6 and 134.2 ppm) arise from the aryl ring in PDI, and the characteristic peak at 154.7 ppm can be assigned to the carbonyl group in the urethane linkage (Fig. 1d). These combined structural characterizations of the material validate the successful formation of cross-linked polyurethane networks and the incorporation of IV into the polymer. The thermal stability of **1** was investigated using thermogravimetric analysis (TGA). The TG curve of the as-synthesized gel showed a significant weight loss (90%) around 80 °C due to the trapped solvent, acetonitrile, suggesting a highly porous network of the gel (Fig. 2a). The hypothesized porous morphology of the material **1** prompted us to collect N_2 isotherm at 77 K which then was used for Brunauer-Emmett-Teller (BET) surface area and pore size distribution calculations. For this analysis, we activated the polymer gel using a supercritical CO_2 drying method to avoid a collapsing of the structure upon solvent removal (ESI†).²⁶ The shape of the N_2 isotherm in Fig. 2c is representative of a Type IV isotherm, indicating a mesoporous structure with a calculated BET surface area of $440\text{ m}^2\text{ g}^{-1}$ (Fig. 2c). The surface morphology obtained by scanning electron microscopy (SEM) and the pore size distribution obtained from N_2 isotherm further confirmed the mesoporous structure of the material (Fig. 2b and d). We then examined the thermal stability of the dried polymer using TGA and observed the decomposition of urethane groups at 330 °C (Fig. 2a). This result demonstrates the notably enhanced thermal stability of material **1** compared to the reported thermal decomposition temperature range (120–250 °C) for polyurethanes obtained using organic polyols.²⁷

We then compared the thermal behavior of **1** with an analogue (referred to herein as **2** and see ESI†) containing carbon-rich cross-linker II. The TGA and the derivative thermogravimetric (DTG) results showed that **1** possesses higher initial and maximum decomposition temperatures and % residual mass at 800 °C than **2**, highlighting the enhanced thermal stability of **1** in comparison

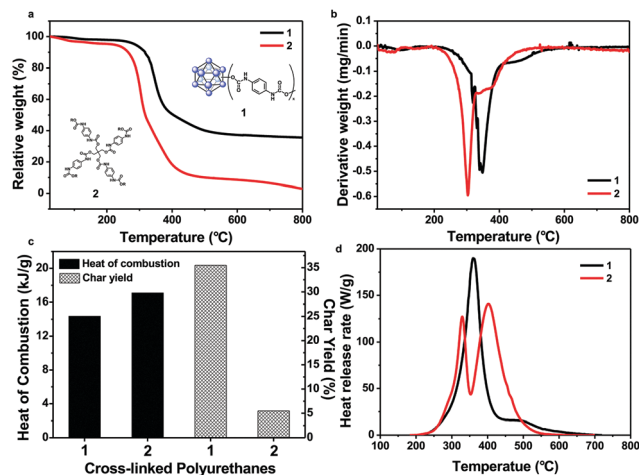


Fig. 3 (a) Thermogravimetric, (b) derivative thermogravimetric results of **1** and **2**, (c) micro combustion calorimetry (MCC) results, (d) comparison of heat release rate of **1** and **2**.

to organic cross-linked analogue **2** (Fig. 3a, b and ESI[†]). These improved thermal properties of **1** can be attributed to the robust cross-linker, **IV**, present in **1** which provides more cross-linking sites than **II**, and consequently results in a higher density of cross-linking.^{28,29} Flammability has been a major issue in the polyurethane industry for certain applications such as polyurethane-based memory foams as they are highly combustible and produce toxic chemicals. Therefore, many efforts have been made to improve the thermal combustion properties of polyurethane foams by physically blending additive type flame-retardants³⁰ or incorporating reactive type flame-retardants, which interact with the polymer during the pyrolysis, into the polymeric network through copolymerization.³¹ In general, polyurethanes copolymerized with flame-retardant monomers exhibit improved thermal stability compared to those with additive types since they form robust covalent bonds with urethane linkages. Given the enhanced thermal stability of **1**, we hypothesized **IV** could function as a flame-retardant polyol in this system. The potential competence of **IV** as a flame-retardant monomer was investigated through micro combustion calorimetry (MCC). In a MCC test, the sample is pyrolyzed at a linear heating rate of 1 °C s^{-1} in a N_2 atmosphere and the volatiles are premixed with O_2 , resulting in a complete combustion of the material.³² MCC results show a drastically higher char yield for **1** compared to **2**, along with a corresponding decrease in heat of combustion for **1** (Fig. 3c). The two-peak heat release rate behavior of **2** is also eliminated, resulting in a single, higher heat release rate peak for **1** (Fig. 3d). The increased char yield, along with the decrease in heat of combustion suggest that, at this heating rate, **1** may offer improved condensed phase flame retardancy. However, given the potential dependence of the char yield on the heating rate, this flame retardancy effect should be characterized at higher heating rates that are more representative of realistic fire scenarios. Nevertheless, for applications where the initial heating rate is on the order of 1 °C s^{-1} or lower, **1** shows promising performance as a char-forming fire retardant material.

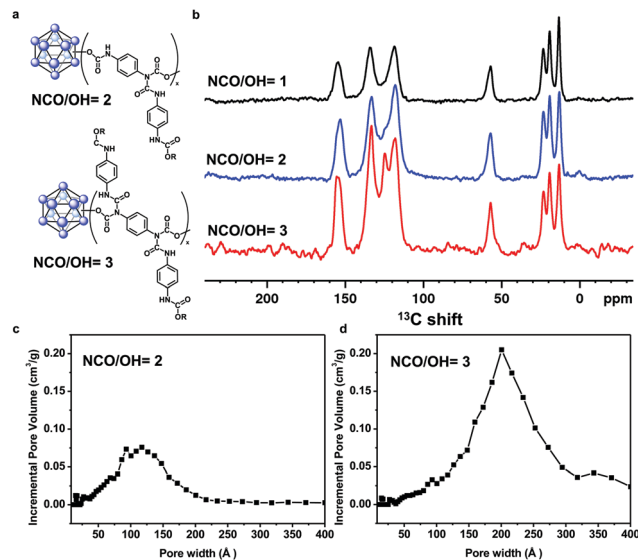


Fig. 4 (a) Branched polymers which possess allophanate linkages, (b) solid-state 1D single pulse ^{13}C MAS NMR of the branched polymers. (c and d) Pore size distribution of the branched polyurethanes shown in (a).

Finally, in the synthesis of polyurethanes, the presence of excess isocyanates can create allophanate linkages in which the newly formed secondary amine of a urethane linkage reacts with an isocyanate substrate (ESI[†]).³³ We envisioned the surface area and the pore size of the resulting polymer could be tailored by introducing allophanates into the network as they form branched structures. Accordingly, we prepared three different cross-linked polyurethanes by employing various ratios of isocyanates to polyol hydroxyl groups (NCO/OH) (Fig. 4a). The formation of allophanate linkages was confirmed through ^{13}C MAS SSNMR. As more diisocyanates are employed, the shoulder around 120 ppm appears more prominent, indicating an increased amount of aromatic carbon close to the allophanate linkages (Fig. 4b and ESI[†]). Moreover, the gradual increase in the intensity of the $\text{C}=\text{O}$ carbon signal (154 ppm) from NCO/OH = 1 to 3 further suggests the formation of allophanate linkages. Indeed, the material containing more allophanate groups, which possesses more branched structures with fewer cross-linkers, exhibits increased surface area and pore sizes (Fig. 4c, d and ESI[†]). This modification of the polyurethane structure demonstrates the value of **IV** to generate polyurethane materials that possess porous structures and to potentially alter their thermal properties (ESI[†]).³⁴

In summary, we have reported a new class of cross-linked porous polyurethanes utilizing polyhedral boron clusters as an inorganic polyol equivalent. The incorporation of these building blocks into the polyurethane results in a porous morphology and enhanced thermal stability of the material compared to analogous polymers produced from carbon-based polyols. These results highlight the value of the molecular cross-linking with the dodecaborate cluster as a novel and effective strategy to alter the chemical and physical properties of polymeric materials. This work further showcases how molecular main group chemistry can be harnessed to improve the properties of polymeric materials.^{35–45}

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Conflicts of interest

There are no conflicts to declare.

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