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Fully Aromatic High Performance Thermoset via Sydnone−Alkyne Cycloaddition

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Supporting Information

ABSTRACT: We have developed an efficient synthetic platform for the preparation of a new class of high performance thermosets based on the 1,3-dipolar cycloaddition of a bifunctional sydnone with a trifunctional alkyne. These processable materials possess outstanding thermal stability, with $T_{d5\%}$ of 520 °C and a weight loss of <0.1% per day at 225 °C (both in air). Key to this performance is the stability of the starting functional groups that allows for reactive B-staging via simple thermal activation to give fully aromatic and highly cross-linked polypyrazole-based thermosets.

Growth in the aerospace and microelectronic industries increasingly requires the development of lightweight materials with excellent chemical, thermal, and mechanical robustness.[1] Thermoset polymers, as densely cross-linked networks of organic repeat units, offer a modular and flexible synthetic approach to such materials also allowing desired properties to be tuned via the macromolecular structure.[2] Specifically, rigid networks with high contents of aromatic units[3] lead to increased heat resistance and improved thermomechanical properties with fully aromatic high performance thermosets (HPTs) offering significant promise.[4] However, the synthesis of fully aromatic structures is a major challenge since it requires the efficient formation of aromatic connecting points between aryl monomers without using metal catalysts.

To address the criteria of efficient and noncatalytic chemistry, cycloaddition reactions were selected for thermoset formation. In contrast to polycondensations that are prevalent in thermoset synthesis,[4c] cycloaddition reactions avoid the formation of significant side products with the most successful example being the use of cyclopentadienone-based $4 + 2\pi$ cycloaddition chemistry for the formation of Dow's low-*k* semiconductor dielectric SiLK materials.[4d] In this study our attention was directed to 1,3-dipolar cycloadditions, which have generated significant interest within the organic synthesis and bioconjugation communities due to their high efficiency, tolerance to functionality, mild reaction conditions, and fast reaction rates.[5] Despite the potential of 1,3-dipolar cycloadditions, their application toward HPT development is underexplored with only a limited number of nonaromatic thermosets being prepared using azide−alkyne click chemistry.[6]

This study aims to translate the efficiency of 1,3-dipolar cycloadditions to the formation of *fully aromatic* thermosets with outstanding thermal properties.[7] Upon approaching this task, we were drawn to alternative 1,3-dipoles such as the mesoionic heterocycles of münchnones[8] and sydnones.[9] Their cycloaddition with alkynes produce aromatic pyrrole[10] or pyrazole units.[9] Especially the stable (*N*-phenyl) sydnones have been established as unusual but promising cycloaddition substrates for pyrazole formation.[11] Based on these considerations, we focused on the reaction of multifunctional sydnones with multifunctional alkynes to produce fully aromatic cross-linked materials[12,13] containing highly thermally stable pyrazole cross-linking points (Scheme 1a).[12] This unique ability to access robust aromatic linkages under catalyst-free conditions with the generation of CO_2 as the only side product illustrates the utility of sydnone chemistry for the preparation of high performance materials.[14] In addition, this approach allows considerable flexibility in molecular design due to the synthetic versatility inherent in either the alkyne or the sydnone monomers.

The synthetic strategy is based on the reaction of a bifunctional sydnone **BS** with a trifunctional alkyne **TA** to produce the fully aromatic thermoset **TS**, consisting of aryl/pyrazole units (Scheme 1b). **TA** was prepared using literature procedures and **BS** was obtained in good yield from 1,4-diaminobenzene. Significantly, both synthetic approaches were scalable to 10+ gram scales from readily available starting materials (see SI).[15] Initially the respective monomers were either mixed in solution or melt processed; however, significant phase separation was observed and low cross-reactivity obtained. To guarantee high cross-linking densities, a prepolymer approach was developed. This efficient B-staging strategy involves two steps: (1) the preparation of partially cross-linked, soluble oligomers with retention of reactive sydnone and alkyne units and (2) processing and final curing of the oligomers at elevated temperatures to produce the fully cross-linked thermoset (Scheme 2).

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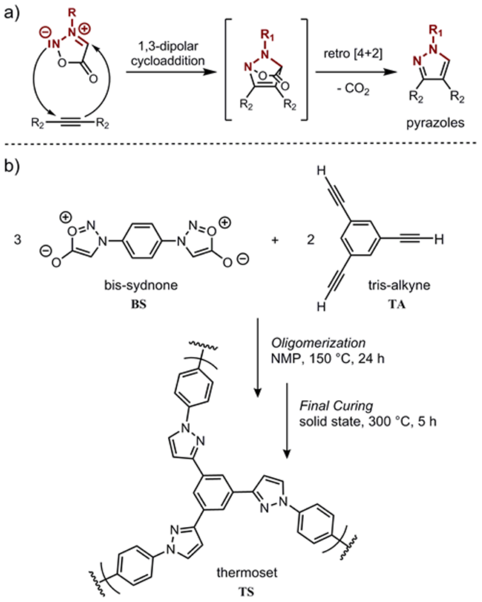
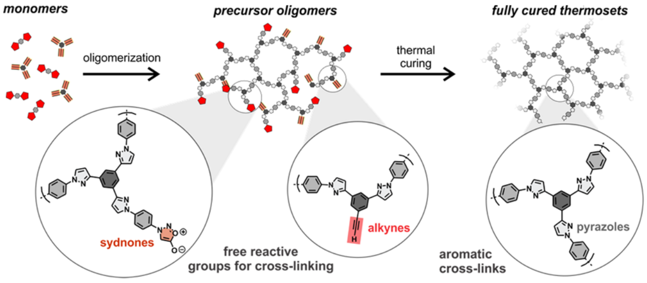
Scheme 1. (a) Exemplary Cycloaddition Reaction of Sydnones and Symmetric Alkynes to Give Aromatic Pyrazoles; (b) Synthetic B-Staging Pathway to the Formation of New Pyrazole-Based Thermoset TS via Cycloaddition Reaction of Bis-sydnone BS with Tris-alkyne TA[a]



[a]Note: only 3-substituted pyrazole units are shown. Potential 4-substitued isomers are omitted for clarity.

Scheme 2. Schematic Representation of the B-Staging Approach for the Preparation of a Pyrazole-Based High Performance Thermoset Reaction of Bis-sydnones with Tris-alkyne Gives Oligomers with Free Reactive Groups Available for Final Thermal Curing



The development of suitable reaction conditions for both the initial oligomerization and subsequent curing was critical in this B-stage strategy. For oligomerization, maintaining solubility and reactivity was achieved by optimizing the time and temperature of the solution reaction between bis-sydnone **BS** and tris-alkyne **TA**. It was found that reaction times between 15 and 24 h at T = 150 °C give essentially a quantitative yield of soluble oligomers **OL** with molecular weights of ~4 kDa (determined by GPC, see SI). Increases in reaction time and temperature ($T > 180$ °C) lead to higher molecular weight, partially cross-linked materials. At lower reaction temperatures ($T < 120$ °C), minimal coupling was observed with high amounts of unreacted monomer still present. The formation of pyrazoles was observed by comparing ^{1}H NMR spectra of **OL** and model compound **MO** (see SI). Additional studies on **MO** (see SI) suggest that the ratio between the 3- and 4-substituted regioisomers is around 10:1 in the oligomers, as suggested by the literature.[16] It was important for thermoset formation that unreacted sydnone and alkyne functional groups are retained in the soluble oligomers even after isolation and prolonged storage in either solution or the solid state. The presence of these unreacted groups was confirmed by solution state ^{1}H and solid state ^{13}C NMR spectroscopy (^{1}H NMR, see SI; ^{13}C NMR, see Figure 2). This retention of reactivity coupled with a wide processing window and reproducible molecular weight control for the oligomer formation allows high solid content solutions and melt processable systems to be used for the preparation of fully cross-linked thermosets.

The final step in this process requires the optimization of curing conditions for thermoset formation. For enhanced thermal stability, the highest degree of cross-linking, i.e., the maximum conversion of reactive groups, is required. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) studies were therefore performed on the oligomeric precursor **OL** to fully understand the relationship between curing conditions and functional group conversion. DSC analysis revealed the existence of a broad exothermic peak between 170 and 390 °C, which can be attributed to the exothermic cross-linking reaction (see SI). These observations were further supported by TGA experiments on **OL**, which showed a series of consecutive weight losses starting at lower temperatures prior to the onset of final degradation at ~500 °C (see SI). Assuming that weight loss is due to CO_2 generation upon cycloaddition to give pyrazole-based cross-linking units, these results indicate that the final curing of **OL** to a fully cross-linked thermoset **TS** occurs over a broad temperature range starting at ca. 170 °C.

In systematically optimizing this curing protocol, monitoring the CO_2 evolution from oligomers **OL** was studied in detail using thermal gravimetric analysis–mass spectrometry (TGA–MS). Precured oligomer films (60 °C for 24 h) were analyzed following heating profiles at 150, 200, 250, and up to 300 °C for 5 h each. As shown in Figure 1, CO_2 evolution and corresponding weight loss were observed at the beginning of each temperature increase with CO_2 evolution decreasing at each stage.

These findings suggest that for a constant curing temperature, the formation of a cross-linked network decreases chain mobility, therefore hindering further reactions. Increasing the temperature increases chain mobility and enables further cross-linking.[17] After

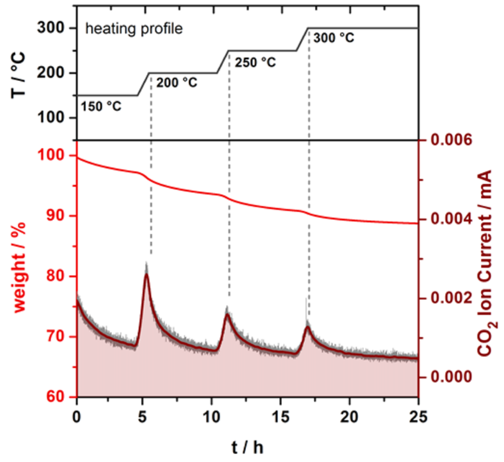


Figure 1. Analysis of thermoset curing by TGA–MS under nitrogen atmosphere. The stepped heating protocol of the thermal curing of **OL** can be correlated to the evolution of CO_2 and the corresponding weight loss.

the final heating step (up to 300 °C for 5 h), TGA showed no further weight loss prior to onset of degradation, indicating complete cross-linking. As a result, the optimized cure conditions for thermoset **TS** involve initial drop-casting of oligomer films from *N*-methyl-2-pyrrolidone (NMP) and removal of residual solvent. Films and bulk samples were then fully cured by subsequent annealing at 150, 200, 250, and up to 300 °C for 5 h.

While TGA and TGA–MS serve as experimental tools to indirectly determine final curing, solid-state ^{13}C NMR was employed to evaluate the reactive moieties in both the oligomeric prepolymer, **OL**, and the final thermoset, **TS**. As can be seen in Figure 2, distinct peaks can be observed for the starting bis-sydnone, **BS**, and tris-alkyne, **TA**, at ~95 ppm (a) and ~85 ppm (b,c), respectively. After initial B-staging, these peaks decrease in intensity for **OL** and disappear for the fully cured thermoset **TS**. Significantly, this disappearance is coincident with the appearance of new resonances at 150 and 105 ppm corresponding to the pyrazole cross-linking units (see SI for spectral data of pyrazole model compound). Further support for this sequence of reactions is obtained from Fourier transform infrared (FT-IR) measurements, which show the reduction and eventual disappearance of the carbonyl stretch for the sydnone units at ~1750 cm^{-1} on going from monomer to thermoset (see SI). This combination of characterization methods demonstrates the robustness of the proposed sydnone-alkyne cross-linking chemistry for pyrazole-based thermosets.

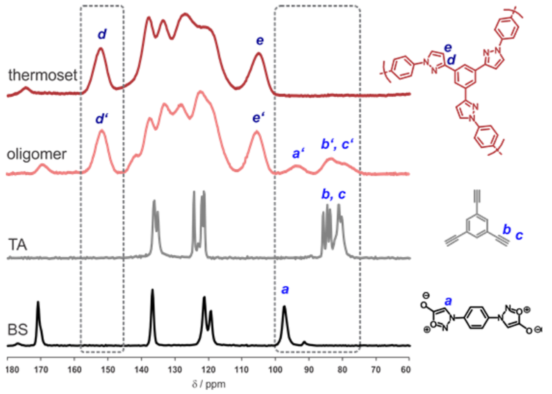


Figure 2. Solid-state ^{13}C NMR comparison of thermoset **TS** with oligomer **OL** and monomers (**BS** and **TA**) reveals the presence of free reactive groups in the oligomeric precursor and their disappearance upon complete cross-linking via formation of pyrazoles.

Having developed a facile and efficient process for the formation of fully aromatic thermosets, their thermal and mechanical properties were investigated. As expected, the thermal stability of **TS** was exceptionally high with $T_{\mathrm{d5\%}}$ observed at 520 °C (Figure 3a) (60% char at 800 °C in N_2; see SI)). Of particular note is the thermal stability in air with $T_{\mathrm{d5\%}}$ greater than 500 °C and negligible long-term weight loss of 0.003 wt %/h (0.072 wt %/day) after aging at 225 °C for over 45 days (Figure 3b). To put this performance in context, conventional polybenzoxazines ($T_{\mathrm{d5\%}} \approx 300$ °C)[18] and polyimide thermosets ($T_{\mathrm{d5\%}} \approx 450$ °C) show significant long-term weight loss at elevated temperatures over much shorter time periods,[19] clearly demonstrating the potential of sydnone–alkyne thermosets for high performance applications.

To illustrate the mechanical performance of these materials, dynamic mechanical analysis (DMA) showed enhanced temperature-dependent storage modulus (E'), loss modulus (E''), and tan δ of **TS** (Figure 4). E' at room temperature was observed to be 3.3 GPa, highlighting the high stiffness of **TS** with only marginal changes being observed up to ~500 °C.[20] The broad peak in tan δ and E'' at ~90 and 70 °C can be assigned to β transitions due to the presence of loose chain ends and network irregularities in these cross-linked structures.[21] Similarly, the maxima of tan δ and E'' reveal a very high T_g approaching 480 °C for **TS**. All of these properties are improved when compared to benchmark thermosetting polyimides such as PETI-5 (249 °C)[19] and TriA-PI (343 °C).[22]

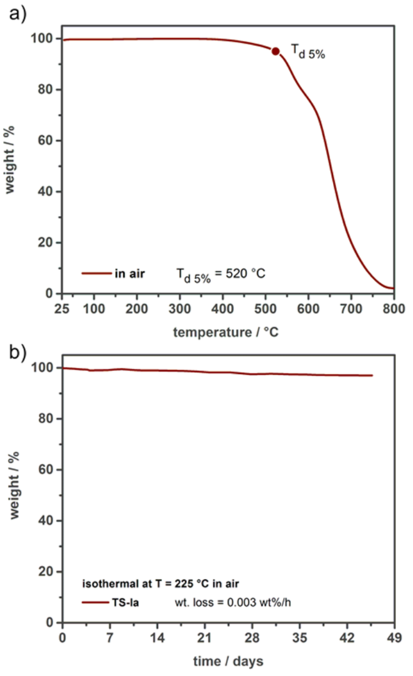


Figure 3. (a) Thermogravimetric analysis (TGA) of **TS** in air. (b) Isothermal TGA of **TS** at 225 °C over 47 days in air.

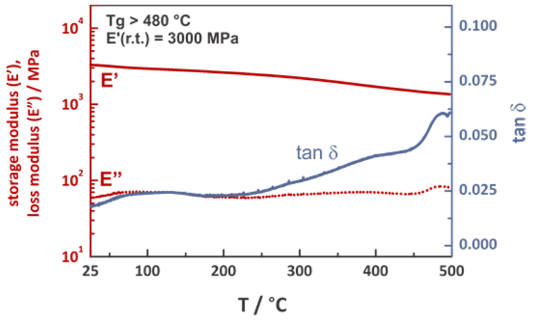


Figure 4. Dynamic mechanical analysis of free-standing films of **TS**. Temperature dependence of storage modulus (E'), loss modulus (E''), and tan δ for the determination of T_g.

Thermomechanical analysis (TMA) of free-standing films of **TS** (see SI) reveals a macroscopic thermal expansion coefficient (CTE) of 47.5 μm/(m·°C) over a temperature range of 25–350 °C. This low thermal expansion is required for dimensional stability in high performance materials and is comparable with commercial poly(benzoxazine) and polyimide materials, which have CTEs of ~24 to 43 μm/(m·°C).[23] Additionally, it was interesting to observe the unexpectedly high adhesion of the thermoset to a variety of substrates. For example, a lap shear adhesion strength of ~2.6 MPa was obtained for aluminum substrates. Given the fully aromatic structure, this is assigned to the nitrogen-rich pyrazole cross-linking units.[24] Finally, the synthetic versatility of this new approach enables a range of thermoset architectures to be obtained by simply changing the molecular structure of the monomers. As shown in Figure 5, varying the combination of four readily accessible monomers (see SI) allows the preparation of four different thermosets (**TS** to **TS-c**), which all show exceptional heat resistance with $T_{d5\%}$ values exceeding 430 °C.

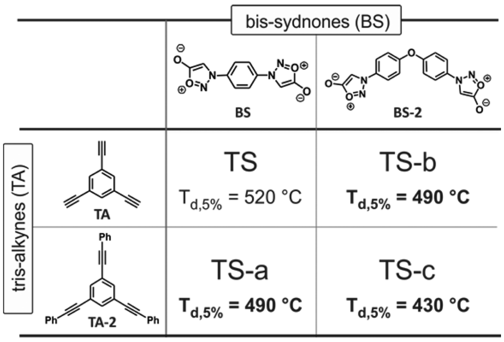


Figure 5. Expanding the sydnone–alkyne cross-linking strategy to different monomers: Investigated monomer combinations to give pyrazole-based thermosets and their respective $T_{d5\%}$ values in air.

In summary, the highly efficient cycloaddition of bifunctional sydnones with trifunctional alkynes represents a facile synthetic approach to a new family of *fully aromatic* thermosets based on pyrazole cross-linking units. Exceptionally high thermal and mechanical performance clearly illustrates the successful translation of efficient cross-linking chemistry and functional group stability to final material properties under standard processing conditions. The availability of alternative monomers demonstrates the potential of this tunable thermoset platform as a high performance matrix for advanced technologies.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b03381.

> Detailed synthetic procedures and characterization data for the new compounds and additional experimental results (PDF)

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Notes

The authors declare no competing financial interest.

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