Ring Opening Metathesis Polymerization (ROMP) of the Dewar Isomer of 1,2-Azaborinine, a B-N Isostere of Benzene

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ABSTRACT: The successful polymerization of the Dewar isomer of an azaborinine heterocycle is reported. Controlled ring-opening metathesis polymerization was accomplished with Grubbs and Hoveya-Grubbs 2nd generation catalysts (G2, HG2), as well as a *Z*-selective Ru catalyst (HGM2001). The structure of the polymers containing 4-membered B-N heterocycles was verified by GPC, multinuclear and 2D NMR. Differences in regiochemistry of polymers derived from G2/HG2 *versus* the *Z*-selective catalyst HGM2001 were substantiated by 2D NOESY, FT-IR and Raman analyses. The incorporation of B-N heterocycles into these polymer structures is promising as a route to functional polymers that contain polar side groups.

First synthesized in 1963 by van Tamelen,[1] Dewar benzene consists of two fused strained cyclobutenes. Suitably substituted derivatives are promising as energy storage materials due to the reversibility of the Dewar benzene formation. For example, hexafluorobenzene is selectively and in high yield photoisomerized to its high energy Dewar isomer, whereas the Dewar isomer of hexamethylbenzene is sufficiently stable to release thermal energy only on demand (Figure 1a).[2] Dewar benzene derivatives have also been utilized in holographic 3D-information storage, taking advantage of quantum-amplification effects of the photoisomerization,[3] and they have been embedded into polymers to achieve new reconfigurable materials that undergo main-chain structural transformations via valence isomerization.[4] The materials discussed above consist solely of carbon atoms in their backbone, and heteroaromatic analogs of Dewar benzene remain exceedingly rare.[5]

Heteroarenes with B-N units embedded in the aromatic framework provoke ever increasing interest due to the extensive applications that are emerging in biochemistry and pharmacology, materials science, and catalysis.[6] The isosteric replacement of C=C for B-N units in benzene to furnish 1,2-azaborinines has proved to be a particularly effective approach. Importantly, azaborinines exhibit significant differences in the aromatic delocalization from benzene. As a consequence, they present distinct reactivity at different ring positions that allows for selective functionalization.[6] In a remarkable recent development, Bettinger and Liu discovered that 1,2-dihydro-1-*tert*-butyldimethylsilyl-2-mesityl-1,2-azaborinine (**A**) undergoes photoconversion into the corresponding Dewar valence isomer (**B**) upon irradiation with UV light (> 280 nm) (Figure 1b).[7] The kinetically stable isomer **B** can be converted back to **A** by a thermal electrocyclic ring-opening reaction that requires an activation energy of (27.0 ± 1.2) kcal mol^{-1} (half-life of 25 min at 100 ºC). In the presence of Wilkinson's catalyst, the ring-opening occurs rapidly and exothermically even at room temperature. Pursuing new synthetic pathways that take advantage of the facile formation of highly functional BN-Dewar benzene derivatives, Liu and coworkers also developed a strategy to 1,2-substituted cyclobutane derivatives via hydrogenation and subsequent ring-opening of the 4-membered B-N heterocycle.[8]

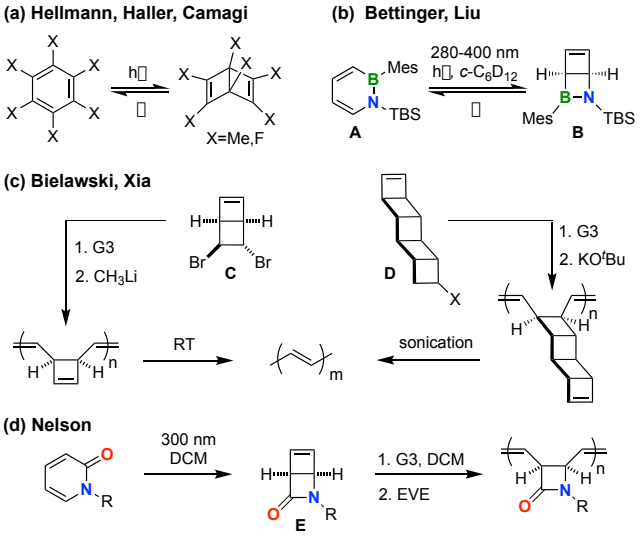

Figure 1. (a) Synthesis of Dewar benzenes by photolysis and thermal reversion; (b) photoisomerization of **A** to the Dewar isomer **B** (TBS = *t*-butyldimethylsilyl, Mes = 2,4,6-trimethylphenyl); (c) examples of ROMP of strained cyclobutenes **C** and **D**; (d) ROMP of heterocyclic Dewar isomer **E** (G3 = Grubbs 3rd generation catalyst, EVE = ethyl vinyl ether).

Inspired by these results, we hypothesized that the presence of a strained cyclobutene ring system in BN Dewar

isomers may provide an avenue to new classes of highly functionalized polyolefins via ring-opening metathesis polymerization (ROMP). Although relatively less studied, ROMP of strained cyclobutenes is well established and typically accomplished using Grubbs 2nd (G2), Grubbs 3rd (G3), or Hoveyda-Grubbs 2nd (HG2) generation catalysts.[5b, 9] For instance, Bielawski and coworkers reported the ROMP of a dibromo derivative of Dewar benzene, which upon MeLi-triggered elimination rapidly converted into *trans*-poly(acetylene) (Figure 1c).[10] More recently, Xia and coworkers demonstrated the ROMP synthesis of poly(ladderane)s and poly(benzoladderene)s that could be mechanochemically transformed into polyacetylene derivatives.[11] Different from these polymeric materials, in which rearrangements are triggered by ring-opening of cyclobutene or unzipping of multiple fused rings, the ROMP of pyridinones has recently been shown to result in functional polymers that incorporate 4-membered lactam heterocycles (Figure 1d).[5b] Similarly, we anticipated that ROMP of BN-Dewar isomers could offer access to a novel class of polyolefins that retain the four-membered heterocycle containing an amine and a borane moiety. Here we report the first synthesis of poly(BN-Dewar benzene)s *via* Ru-catalyzed ROMP of a bicyclic azaboretidine and their structural corroboration by multinuclear and two-dimensional NMR, GPC, FTIR and Raman experiments. The new approach to highly functionalized polyolefins that is presented here is very attractive as the B-N heterocycles can potentially be further elaborated into amine, hydroxyl and other polar functional groups through postmodification[12] approaches that involve B-C and/or B-N bond cleavage.[8]

Figure 2. (a) ROMP Synthesis of polymer **2** with different Ru catalysts (^{R}Py = 3-bromopyridine, Mes = mesityl); (b) representative GPC-RI trace for polymer obtained with Grubbs G2; (c) first order kinetic plot for ROMP of Dewar isomer **1** ([M_0] = 0.3 M) with 1 mol% G2 / HG2; conversion determined by ^{1}H NMR integration (average of 2 runs).

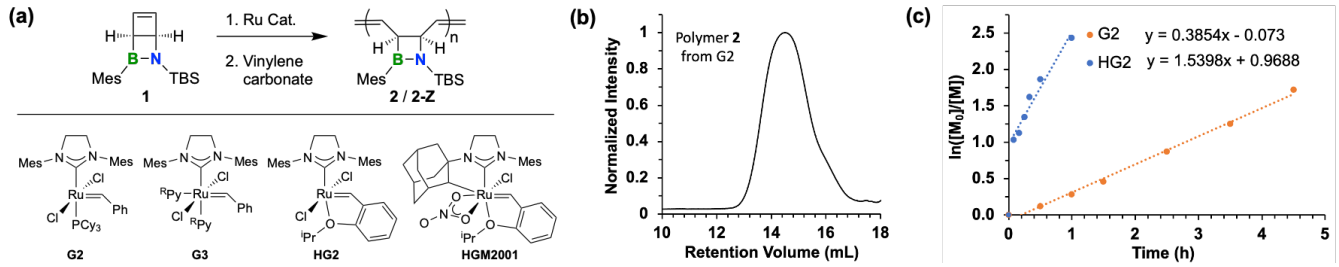

Table 1. Conditions for ring-opening metathesis polymerization (ROMP) of Dewar isomer 1.

Entry	Catalyst	Feed ratio	[1] (M)	Solvent	*T* / t (ºC / h)	Conv (%)	M_n [a] (Da)	M_w [a] (Da)	*Đ* [a]	DP_n
1 [b]	G3	50:1	0.1	C_6D_6	r.t. / 120	47%	4300	7500	1.74	14
2 [b]	G3	50:1	0.1	CD_2Cl_2	0 / 48	51%	5200	8700	1.67	17
3 [c]	G2	100:1	0.1	C_6H_6	r.t. / 9	92%	8100	14400	1.76	26
4 [c]	HG2	100:1	0.1	C_6H_6	r.t. / 7	>99%	6000	9200	1.54	19
5 [c]	G2	100:1	0.3	C_6H_6	r.t. / 4.5	80%	9600	18000	1.88	31
6 [c]	HG2	100:1	0.3	C_6H_6	r.t. / 1	93%	7100	10400	1.45	23
7 [c]	HGM2001	100:1	0.1	C_6H_6	r.t. / 24	31%	8600	12300	1.42	28

[a] Analyzed by gel permeation chromatography with refractive index (GPC-RI) detection relative to narrow polystyrene standards; *Đ* = M_w / M_n. [b] Conversion estimated for the crude product based on ^{1}H NMR integration of the *t*-butyl H NMR signal of the residual monomer relative to the *t*-butyl H signal of the polymer; GPC analysis of crude product in THF. [c] Conversion estimated for the crude product based on ^{1}H NMR integration of the olefinic signals of the residual monomer relative to anisole as a reference; GPC analysis of isolated product in THF.

The Dewar isomer **1** was prepared as previously reported by photoisomerization of B-mesityl-N-(*t*-butyldimethylsilyl)azaborinine (**A**) as described in Figure 1b.[7] To preclude any thermal reversion to the azaborinine, the monomer was stored in a freezer at –28 ºC prior to use. We explored different generations of Grubbs and Hoveyda-Grubbs catalysts for the ROMP of monomer **1** (Figure 2a). The monomer conversion was determined by ^{1}H NMR integration and the results are summarized in Table 1. Grubbs 3rd generation catalyst (G3) is one of the most widely used ruthenium catalysts for ROMP. In comparison to 2nd generation catalysts (G2, HG2), G3 exhibits very fast initiation rates, which typically enables the formation of polymers with very narrow dispersities and excellent control over their molecular weights.[13] However, G3 was found to be not very effective at converting Dewar isomer **1** to polymer **2**. At 0.1 M monomer concentration in benzene or dichloromethane, G3 gave only low monomer conversion even after very long reaction times at either room temperature or 0 ºC (Table 1, entry 1, 2), and conversions were even lower when using THF as the solvent. This contrasts the successful controlled polymerization of other cyclobutene derivatives reported in the literature.[10] A possible reason could be that the pyridine base that is liberated during the initiation

step interferes by binding to the boron centers.[15] However, no change in chemical shift was observed in the ^{1}H or ^{11}B NMR spectra when monomer **1** was treated with an equimolar amount of pyridine. Another possibility is that the initiation step is very fast, as expected, but the stability of the initial ring-opening product and the propagating species in its resting state is insufficient. An indication that this is the case comes from an ^{1}H NMR experiment in which the monomer was mixed with G3 in a 10:1 molar ratio in C_6D_6. Upon mixing the color of the solution immediately changed from yellow-green to orange-brown. An NMR spectrum taken within <10 mins showed that the carbene proton of G3 disappeared completely and multiple new peaks arose in the region from -16 to -20 ppm (Figure S1a). These peaks gradually disappeared with longer reaction times. This is indicative of very rapid but unselective initiation and insufficient selectivity/stability of the propagating species. G2 and HG2, which do not contain unhindered basic pyridine ligands, are known to exhibit improved thermal stability, as well as oxygen- and moisture-tolerance.[16] Although G2 and HG2 are usually not suitable for living polymerization due to the slow initiation and small initiation/propagation rate ratio (k_i/k_p), they have been successfully applied to the polymerization of cyclobutenes when other catalysts gave poor results.[15, 17] An ^{1}H NMR analysis after 10 mins of mixing **1** and G2/HG2 in a 10:1 molar ratio in C_6D_6 again revealed complete disappearance of the carbene proton of the catalyst with formation of several new peaks. The new carbene peaks were present almost exclusively in the region of 17.5 to 18.5 ppm, indicating more selective formation of isomeric propagating species with G2 and HG2 (Figure S1b,c). Indeed, performing the ROMP of **1** at room temperature with either G2 or HG2 in a 100:1 molar ratio proved to be more effective, resulting in higher monomer conversion (>90%) over a shorter time period of 7-9 hours (Table 1, entry 3-4). As seen in Table 1, entries 5-6, higher monomer concentration (0.3 M) promoted propagation, further shortening the reaction time to 4.5 h. HG2 consistently gave slightly higher conversions, indicating a faster rate of polymerization. The use of HGM2001, which is a *Z*-selective catalyst, yielded polymers with an increased number of *cis*-linkages than G2 and HG2 (*vide infra*). Remarkably, an ^{1}H NMR analysis after 10 mins of mixing **1** and HGM2001 in a 10:1 molar ratio showed the formation of only two broad overlapping peaks at ca. 15.5 ppm, suggesting far superior regio- and stereoselectivity in the initiation and propagation steps (Figure S1d). However, only 31% conversion was achieved over 24 hours at room temperature when using a 100:1 molar ratio of 1 to HGM2001 (Table 1, entry 7). An increase of the reaction temperature to 50 °C did not significantly increase the monomer conversion but led to competing cycloreversion to the azaborinine **A** (not observed at RT, see Table S1).

The polymerizations were quenched with a large excess of vinylene carbonate (VC),[18] the volatiles removed in vacuo, and the polymers isolated by repeated precipitation from benzene into MeCN. Polymers **2** and **2-Z** showed good thermal stability as established by thermogravimetric analysis (TGA), revealing an onset of decomposition of ca. 200 °C (Figure S2). DSC analysis of **2** did not reveal a clear glass transition (T_g) within the range of -20 to +180 °C (Figure S3), most likely because the relatively rigid structure of the polymer results in a T_g above the accessible temperature range. The molecular weight distributions were analyzed by gel permeation chromatography (GPC) in tetrahydrofuran (THF) with a refractive index detector (GPC-RI) relative to narrow polystyrene (PS) standards. GPC-RI analysis for the polymer obtained with G2 (1 mol%) at 0.1 M monomer concentration (entry 3) gave a monomodal molecular weight (MW) distribution with a number average molecular weight of M_n = 8100 Da and a dispersity ($Đ$) of 1.76 (Figure 2b). Similar results were obtained for HG2 (entry 4) and HGM2001 (entry 7) (Figure S4). The theoretically predicted molecular weights are significantly higher (31100 at 100% conversion), but the GPC-RI data are likely an underestimation because of the use of structurally different narrow PS standards. Indeed, molecular weights derived from GPC-LS detection were significantly higher (Figure S5). Attempts to further verify the chain lengths and distributions by MALDI-TOF MS with various matrices and ionizing agents proved unsuccessful.

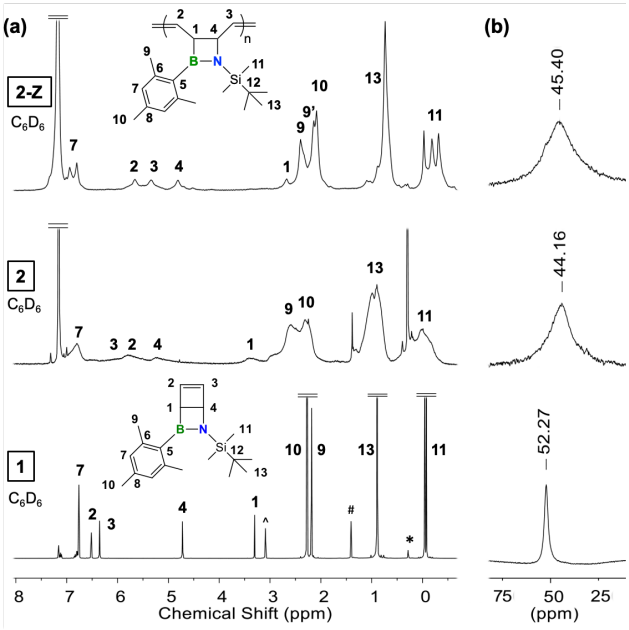

Figure 3. (a) ^{1}H and (b) ^{11}B NMR spectra of monomer (bottom) and polymer (top) prepared with G2 in C_6D_6.; * H_2O, # grease, ^ MeOH.

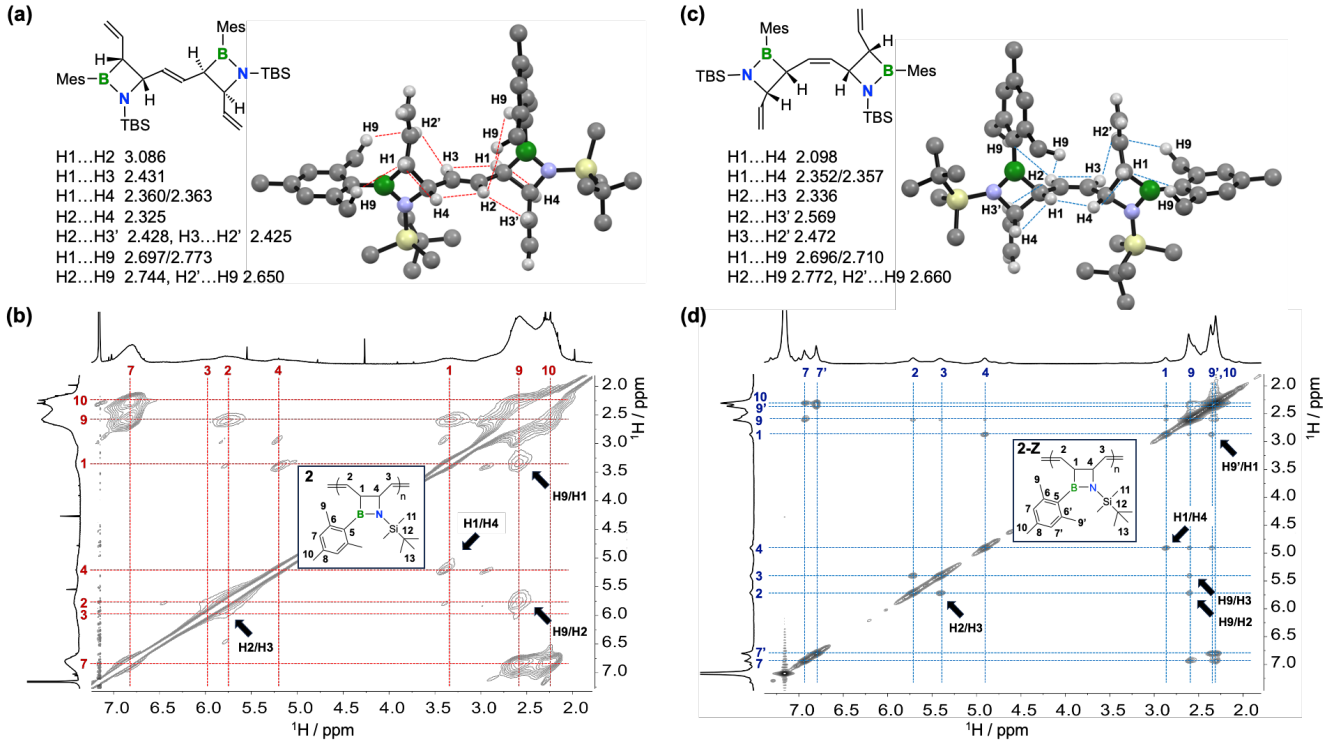

Figure 4. (a) Structure (with relative stereochemistry indicators) of head-to-tail *trans*-vinylene bridged model dimer and H…H bond distances; (b) section of ^{1}H-^{1}H NOESY spectrum of polymer **2** obtained using G2 in C_6D_6; (c) structure of head-to-tail *cis*-vinylene bridged model dimer and H…H bond distances; (d) section of ^{1}H-^{1}H NOESY spectrum of polymer **2-Z** obtained using HGM2001 in C_6D_6. Only relevant H atoms are displayed, and interatomic distances are given in Angstrom.

To further study the controlled nature of the ROMP of **1** with G2 and HG2 as catalysts we carried out kinetic experiments at 0.3 M monomer concentration (Table 1, entries 5, 6 and Figure 2c). At room temperature in benzene the monomer conversion reached 80% within 4.5 hours for G2 and 93% within 1 hour for HG2. The conversion of Dewar isomer **1** with G2 followed first-order kinetics as illustrated by a linear plot of $\ln([M_0]/[M])$ *vs* time that gave a calculated $k_{obsd,G2}$ = 0.38 M^{-1} s^{-1}. Meanwhile, HG2 showed first-order kinetics but very fast conversion over the first 5 minutes, followed by faster first-order kinetics than for G2 with $k_{obsd,HG2}$ = 1.54 M^{-1} s^{-1} (Figure 2c). This suggests that HG2 is more effective in promoting the polymerization than G2. However, G2 showed better first-order kinetic behavior, thus we chose G2 as catalyst in the subsequent studies.

The chemical structure of the new polymers was confirmed by ^{1}H, ^{11}B, and two-dimensional (2D) NMR spectroscopy. The disappearance of the characteristic olefinic group signals and pronounced peak broadening in the ^{1}H NMR spectra clearly indicated successful ROMP of the strained cyclobutene rings in Dewar isomer **1** (Figure 3a). In the ^{11}B NMR spectra of both **2** and **2-Z**, a significant upfield shift from ca. 53 to 45 ppm and concomitant peak broadening provided further evidence for the successful polymerization (Figure 3b). An upfield shift is frequently observed upon polymerization of borane monomers as a result of shielding effects of the neighboring groups along the polymer chain.[19] To further confirm the connectivity between the four-membered BN-heterocycles and vinylene groups in the polymer main chain, heteronuclear single-quantum correlation (HSQC), heteronuclear multiple-quantum correlation (HMBC), and nuclear Overhauser effect spectroscopy (NOESY) NMR data were acquired. The HSQC and HMBC data of **2** and **2-Z** showed the expected cross peaks for the mesityl and *tert*-butyldimethylsilyl groups (Figures S10-11, S15-16). The backbone protons of polymers **2** and **2-Z** in the range from 2.7-6.5 ppm could be assigned based on a NOESY NMR analysis (Figure 4) and supported by DFT methods. To gain insights into the relative distances between protons we optimized the geometry of head-to-tail model dimers with vinyl end groups, having either a *cis*- and *trans*-vinylene linker. The methine protons H1 and H4 were assumed to retain the *syn* configuration that is seen in the Dewar-azaborinine precursor **1** and only one of the possible diastereomers is illustrated (relative stereochemistry of C atoms in the B-N heterocycles). The calculated Gibbs free energy was higher for the isomer with a *cis*-olefin linkage by 20.8 kJ mol^{-1} relative to that with a *trans*-olefin linkage, which suggests that formation of *trans*-linkages is thermodynamically more favorable (Table S2). The structure of the *trans*-isomer is displayed in Figure 4a, illustrating some of the closest intramolecular H···H distances. The distances in this model dimer were then used to assign the NOESY spectrum of the polymer (Figure 4b and Table S3). The allylic methine protons H1 and H4 are expected more upfield than H2 and H3. The upfield signal at 3.4 ppm was assigned to H1 as it shows the expected intense NOE peak at 3.4/2.6 ppm due to its proximity to the boron-bound mesityl group (H9). The *ortho*-mesityl protons (H9) are also in close proximity to H2

resulting in another dominant cross peak at 5.8/2.6 ppm. A third strong cross-peak at 3.4/5.2 ppm is attributed to the NOE between H1 and H4 which are in adjacent positions and share the same orientation. Finally, the assignment of H3 at 6.0 ppm is based on an NOE peak with H2 at δ = 6.0/5.8 ppm. The separation of H2 and H3 within a single *trans*-vinylene unit is large, but H2 comes in close contact to H3' in the next vinylene repeating unit and *vice versa*. Additional weaker NOE peaks indicated the presence of a relatively smaller number of *cis*-vinylene linkages, or possibly some head-to-head defects (Figure S12). For polymer **2-Z** which was prepared with HGM2001 as a *Z*-selective catalyst, the ^{1}H NMR signals were much sharper than those of **2** and appeared at different chemical shifts (Figure 4c,d and Table S3). The presence of a dominant set of sharp signals in the region from 2.5-5.5 ppm allowed for unequivocal assignment of all the protons within the B-N heterocycles and vinylene linkers. The NOE peaks were in excellent agreement with the proposed head-to-tail structure with *cis*-linkages. Notably, the mesityl protons were split into two sets suggesting that rotation about the B-C bond is hindered. Collectively, these data suggest the presence of predominantly but not exclusively *trans*-linkages for polymer **2** (the exact E/Z ratio is difficult to determine because the ^{1}H NMR signals are heavily broadened) and a highly regioregular structure with dominant formation of *cis*-linkages for polymer **2-Z** (>90% Z).

The structural integrity of the four-membered BN-heterocycles was further verified by comparison of the FT-IR spectra of the monomer and the polymers (Figure 5a, for full spectra see Figure S20). As expected, poly(1,2-azaborinine)s **2** and **2-Z** displayed very similar spectral features. The individual IR bands were assigned based on comparisons with results from theoretical calculations (B3LYP/6-31g(d)) on monomer **1** and the *trans*- and *cis*-vinylene-linked head-to-tail model dimers (Table S4), as well as previously reported experimental data for **1**.[7, 20] Strong B-N stretching modes were observed for both the monomer and polymers (ca. 1354 / 1360-1361 cm^{-1}). The characteristic C-H bending modes in the BN heterocycle of **1** (ca. 1179, 1136 and 979 cm^{-1}), as well as the C-B (ca. 1038 cm^{-1}) and C-N stretching modes (ca. 1252 cm^{-1}) are also seen in the poly(1,2-azaborinine)s **2** (1250, 1041 cm^{-1}) and **2-Z** (1250, 1034 cm^{-1}) with some peak broadening, further confirming the integrity of the BN- heterocycle. The C-B stretch for **2-Z** is shifted slightly to lower wavenumbers as also predicted computationally. For monomer **1**, an additional set of strong bands was found at 1275, 1228, 1158, 1120-1106 and 941-883 cm^{-1} and assigned to C-H bending modes in the cyclobutene ring. The disappearance of these bands in poly(1,2-azaborinines) **2** and **2-Z** confirms the ring opening of the cyclobutene ring during polymerization.

While the NMR features for poly(1,2-azaborinine)s **2** and **2-Z** are distinct, very similar FT-IR features were seen for the isomeric polymers as illustrated above. To further verify the preferential incorporation of *cis*-linkages for polymer **2-Z** we also acquired Raman data for both polymers. Because of the different selection rules, Raman is uniquely able to distinguish between *E*- and *Z*-olefin incorporation into the backbone of polymers such as poly(butadiene) rubbers of polynorbornene.[21] Raman spectra were acquired by excitation with a 785 nm laser. The region for the olefinic signals is illustrated in Figure 5b. The bands for the C=C stretching modes are expected around 1640-1680 cm^{-1} and those for the olefinic C-H bending in the region of 1250-1320 cm^{-1}.[21-22] While differences in the intensity of the bands in these regions are apparent for **2** and **2-Z**, signal overlap prevented a quantitative analysis. Nevertheless, collectively, the NMR, IR and Raman data strongly support the unique structure with four-membered B-N heterocycles embedded in the backbone of a ROMP-derived polyolefin.

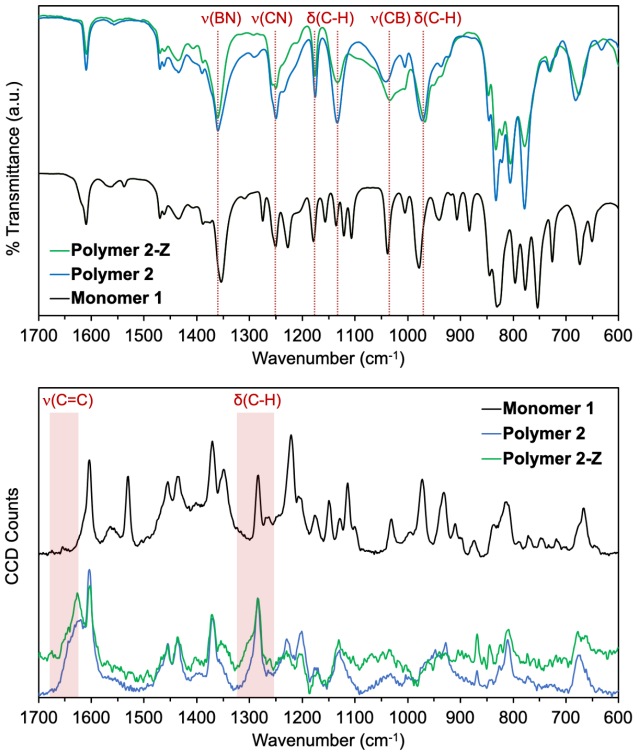

Figure 5. Sections of (top) FT-IR and (bottom) Raman spectra of monomer **1**, poly(1,2-azaborinine)s **2** and **2-Z**.

In conclusion, we have successfully synthesized the first example of a Dewar-azaborine polymer (**2**) by ROMP of Dewar isomer **1** with Grubbs and Hoveya-Grubbs 2nd generation catalysts, as well as a *Z*-selective catalyst. While several azaborinine-derived polymers have recently been reported as analogs of common carbon-based polymers such as polyphenylene, polystyrene, and polyvinyl naphthalene,[12b, 19a, 23] the structure of polymers **2** and **2-Z** containing 4-membered B-N heterocycles is unprecedented. Successful formation of **2** was verified by GPC, 2D NMR, and FT-IR, and the differences in regiochemistry for the *Z*-selective catalyst were further evaluated by 2D NOESY and Raman measurements. Recent studies by Klausen, Ouchi and others demonstrate the great promise of polymers with B substituents and B-N units in the pursuit of novel polyolefins with polar functional groups through post-

polymerization modification methods.[12c, 23h, 24] In a similar vein, we anticipate that the presence of the B-N four-membered rings may be exploited in the preparation of new functional polymers that contain both amine and hydroxyl side groups via chemoselective organoborane oxidation[8] and/or hydrogenation of the double bonds in the backbone.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental data and synthetic procedures (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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