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Expanding the ROMP Toolbox: Synthesis of Air-Stable Benzonorbornadiene Polymers by Aryne Chemistry

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Abstract

Benzonorbornadiene polymers synthesized by ring-opening metathesis polymerization (ROMP) are typically prone to oxidation at the benzylic/allylic position under ambient conditions. Accordingly, the use of benzonorbornadiene polymers in practical applications has remained limited. In this manuscript, we report the synthesis of poly(benzonorbornadiene) polymers using a strategic blend of benzyne chemistry and ROMP. Through a comparative study, we show that substitution at the benzylic/allylic position prevents oxidative deformation, yet does not inhibit polymerization by common ruthenium catalysts with good control over molecular weight dispersity. We expect the benzyne/ROMP reaction sequence will allow easy access to air-stable benzonorbornadiene polymers for various applications.

Graphical Abstract

INTRODUCTION

Since its original discovery, ring-opening metathesis polymerization (ROMP) has enabled ready access to well-defined polymers for numerous industrial applications including drug delivery,^{1, 2} electronic materials,^{3, 4} and nanostructures.^{5, 6} This process typically relies on strained monomers, such as norbornene and cyclopentene, to provide the thermodynamic

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driving force necessary to achieve ring opening and promote polymerization. In particular, norbornene and its related analogues have proven to be ideal substrates for ROMP. The energy stored as ring strain (~27.2 kcal/mol) allows for facile ring opening and promotes the subsequent polymerization, while substituents prevent the secondary metathesis of the polymer backbone.⁷ In fact, norbornenes are the most frequently used substrates for ROMP.⁸

Despite the widespread utility of norbornenes in various synthetic applications, norbornadienes fused to a benzene ring, or benzonorbornadienes, have been rarely investigated. As a result, the potential utility of the resulting polymers have been largely overlooked. El-Saafin and Feast first reported the synthesis of poly(benzonorbornadiene) (**1**, Figure 1) in 1982.^{9, 10} In their study, this polymer was found to be susceptible to oxidation under ambient conditions. Molecular oxygen was thought to facilitate oxidation of the benzylic/allylic position, which then led to intermolecular cross-linking, chain scission, and the ultimate formation of ill-defined materials. Similar studies on related systems by the groups of Grubbs¹¹ and Schrock^{12, 13} further suggested that polymers containing a C–H bond at the readily oxidized benzylic/allylic position undergo rapid decomposition, rendering the polymers unstable and of limited utility.

To evade the problem of poly(benzonorbornadiene) stability, one approach is to chemically alter the resulting polymer to essentially mask the troublesome functional groups, thus avoiding the undesired reactivity (Figure 1, *Solution A*). In fact, the Swager group opted to hydrogenate the olefins in the benzonorbornadiene polymer backbone to give **2**, in order to prevent oxidation and improve polymer solubility.¹⁴ This strategy proved effective for further electrochemical polymerization and cross-linking of the polymers to form target conducting materials. However, the hydrogenation reaction was shown to change the polymer properties such as glass transition temperatures and oxidation onset values.

An alternative solution for the synthesis of air-stable poly(benzonorbornadiene) involves substituting the benzylic/allylic position that is otherwise prone to oxidation with an unreactive substituent (R = alkyl group) (Figure 1, *Solution B*). Ideally, the substituents would be introduced prior to ROMP, thus allowing for the synthesis of polymers without further chemical modification. Such a strategy would not only complement the approach taken by Swager, but could also allow for the potential utilization of the intact double bonds for post-polymerization modification.^{15–18} To test this general strategy, we envisioned accessing substituted polymers **3** (Figure 1) via ROMP of monomers **4**. The success of this approach hinged on the development of an efficient route to access various monomers **4**. For this purpose, we sought to utilize the Diels–Alder trapping of benzyne (**5**) with cyclic dienes **6**. Although historically avoided due to their high reactivity, arynes have been recently employed in chemical synthesis,^{19–42} albeit with only limited applications in polymer chemistry.^{43–46} Herein, we report the use of a benzyne annulation/ROMP reaction sequence to furnish well-defined poly(benzonorbornadiene) derivatives, including two that are stable to oxidation.

RESULTS AND DISCUSSION

The benzonorbornadiene monomers **M1–M4** were easily synthesized using the commercially available benzyne precursor **7**,⁴⁷ as summarized in Table 1. Whereas **M3** and **M4** would later be used to access air-stable polymers, the less substituted monomers, **M1** and **M2**, were targeted for comparative purposes. Silyltriflate **7** was exposed to CsF in the presence of cyclic diene trapping partners in acetonitrile at 60 °C. This simple protocol promotes an elimination reaction to give the benzyne intermediate (**5**), which is subsequently trapped in Diels–Alder cycloadditions to give monomers **M1–M4** in excellent yields. Several features of this approach should be noted: (a) the reactions are operationally trivial to perform and generally do not require the rigorous exclusion of water or oxygen; (b) the benzyne trapping allows for the formation of two new carbon–carbon bonds and two tertiary stereocenters in a single transformation, and (c) purification of the desired monomers is straightforward using chromatography.

The results of polymerization studies are shown in Table 2. Monomers **M1–M3** were readily polymerized using the first-generation Grubbs catalyst in toluene at room temperature (entries 1–9) at various monomer to catalyst ratios. Initially we observed that ROMP of benzonorbornadiene **M1** resulted in polymers **P1** with moderate dispersities ($\bar{M}_w/\bar{M}_n = 1.60 - 1.73$, Supporting information Figure S1b). Based on the aforementioned precedents, we suspected that polymers **P1** were highly sensitive to molecular oxygen and readily oxidized at the benzylic/allylic position when exposed to air. Since the polymers were stored in the freezer and thus exposed to ambient oxygen prior to analysis, we theorized that this was the origin of the observed molecular weight distributions. To test this hypothesis, we took freshly polymerized samples directly from the glove box and dissolved them in chloroform immediately before analyzing by gel permeation chromatography (GPC). Even with this precaution, the traces of **P1** exhibited shoulder peaks (Figure 2a); however the dispersities of the polymers ($\bar{M}_w/\bar{M}_n = 1.15 - 1.20$, Table 2) were much smaller than those of the stored samples. It is also interesting to observe that the molecular weight of **P1** decreased after incubation in air (Table S1) suggesting chain scission. El-Saafin and Feast had postulated that molecular oxygen reacts at the benzylic/allylic of poly(benzonorbornadiene) to produce peroxy radical and that oxidation of the polymer both degrades and cross-links the polymer;⁹ the GPC data for **P1** supports this hypothesis.

The oxygen-containing analogue **M2** resulted in ill-defined polymers with high dispersities even when analyzed right after polymerization (Figure S1c). The light scattering (LS) trace significantly differed from the refractive index (RI) trace and showed larger molecular weight species that eluted prior to the main peak (Figure S1c). It should be noted that LS is more sensitive to higher molecular weight species than RI,^{48–50} and thus the high molecular weight shoulder is more pronounced in the LS trace. Continued exposure of the sample to air resulted in further deformation of the LS trace, and a second distinct peak appeared near the 10 min mark on the chromatogram (Figure S1d). Comparison of **P1** and **P2** GPC traces suggested that **P2** underwent more significant oxidation (Figure S1a vs. S1c), suggesting that **P2** is especially prone to oxidation and will likely oxidize immediately upon contact with air. To compare the relative oxidation potentials of **P1** and **P2**, energies of monomer units were computed by density functional theory (DFT) calculations.⁵¹ Results show that

the oxidation potential of **P2** is 0.238 V higher than that of **P1**, which supports the experimental observation that **P2** oxidizes more readily than **P1** (see Calculation of Oxidation Potential section in the Supporting Information).

It was also noted that the main peaks from the **P2** chromatogram had higher dispersity values (Figure 2b, $\bar{M}_w/\bar{M}_n = 1.83 - 2.00$) than those observed for freshly **P1** (Figure 2a, $\bar{M}_w/\bar{M}_n = 1.15 - 1.20$). It has been previously reported that monomer **M2** is roughly 19 times more reactive than monomer **M1**.⁵² Assuming similar rate of initiation (k_i) for the first-generation Grubbs catalyst in the ROMP of **M1** and **M2**, this increased reactivity likely leads to high propagation rate (k_p) and low k_i/k_p ratio that consequently results in the observed higher dispersities for **M2**.

Whereas the unsubstituted polymers **P1** and **P2** were highly susceptible to oxidation, polymers **P3** and **P4** (bearing alkyl substituents at the benzylic/allylic positions) did not exhibit such discrepancy between RI and LS traces, suggesting that benzylic substitution effectively prevents oxidation. For the dimethyl-substituted monomer **M3**, the substitution attenuates the reactivity of the system, allowing for well-controlled polymerizations with narrow dispersity ($\bar{M}_w/\bar{M}_n = 1.14 - 1.17$) for all molecular weights tested (Figure 2c). Effective polymerization of monomer **M4** required the use of the more reactive third-generation Grubbs catalyst and higher reaction temperatures (60 °C) (Table 2, entries 10–12) to give polymers with low dispersity values (Figure 2d, $\bar{M}_w/\bar{M}_n = 1.07 - 1.12$).

In order to verify that alkyl substitution at the benzylic/allylic positions results in polymers that are stable to oxidation, we analyzed polymers **P1–P4** by elemental analysis (Table 3). Benzonorbornadiene polymer **P1** was detected to contain 0.37 oxygen atoms per repeat unit. This represents direct evidence for the incorporation of oxygen to the polymer once it is exposed to air. Similarly, oxabenzonorbornadiene polymer **P2** was found to contain 1.32 oxygen atoms per repeat unit. The instrumental error in the measurement of oxygen is 0.30%. The data indicates that both unsubstituted polymers have higher oxygen-content than we would normally expect (>30% more oxygen). In stark contrast, polymers **P3** and **P4** both contained the expected number of oxygen atoms per repeat unit, suggesting that substitution at the benzylic/allylic positions successfully suppressed the oxidation pathway.

To further confirm the oxidation of **P1** and **P2**, the polymer samples were subjected to Fourier-transform infrared spectroscopy (FT-IR) analysis (Figure 3). Upon oxidation and incorporation of an OH group, the FT-IR spectrum is expected to show a broad alcohol or peroxide O–H stretch in the 3600–3200 cm^{-1} range. Polymer **P1** shows a small broad peak at 3400 cm^{-1} (Figure 3a), in good agreement with the IR spectrum previously reported for the poly(benzonorbornadiene).¹⁰ The same indicative stretch (3400 cm^{-1}) is more pronounced in polymer **P2** (Figure 3b), and it is completely absent in the cases of polymers **P3** and **P4** (Figure 3c and 3d). Taken together with the elemental analysis data, these experimental findings confirm that benzonorbornadiene monomers with benzylic/allylic substitution give air-stable polymers.

Having determined the relative stability to oxygen of non-substituted (**P1** and **P2**) and substituted (**P3** and **P4**) polymers, we measured the glass transition temperatures (T_g) by

dynamic scanning calorimetry (DSC) (Figure 4). Polymers **P1** and **P3** each have a high T_g (**P1**: 155.40 °C and **P2**: 151.99 °C), whereas the diethyl-substituted polymer **P4** has a lower T_g (93.58 °C). This drastic decrease in glass transition temperature, related to the longer alkyl substituent (methyl vs. ethyl), has been previously attributed to the internal plasticization effect.^{53,54} Longer alkyl substituents are thought to disrupt intermolecular interactions between polymer chains, thereby reducing the thermal barrier required to reach the glass transition threshold. For polymer **P2** (Figure 4b), Schrock and coworkers have previously reported a T_g of 167 °C.¹³ Interestingly, we do not observe a T_g in the –50 to 250 °C range. We suspect that the polymer cross-linked through the oxidation pathway prior to analysis, which would restrict polymer chain motion that causes the onset of glass transition.⁵⁵ As cross-linking would make the microstructure of the polymer highly heterogeneous, the glass transition of the polymer may be altered to different extents, ultimately leading to broadening of T_g such that it is not detectable.

CONCLUSIONS

We have successfully demonstrated an efficient approach for the synthesis of air-stable benzonorbornadiene polymers. Monomers were synthesized in high yields using benzyne Diels–Alder reactions involving a commercially available benzyne precursor. Subsequently, ruthenium-based Grubbs catalysts were used to promote ROMP, giving polymers with good control over molecular weight dispersity. This approach complements more commonly used strategies for handling unstable materials, such as post-polymerization modifications. We anticipate that this report will stimulate further efforts to utilize arynes in the synthesis of polymers, in addition to benzonorbornadiene polymers in materials applications.

EXPERIMENTAL SECTION

Materials and Methods

Unless stated otherwise, reactions were conducted in flame-dried glassware under an atmosphere of nitrogen using anhydrous solvents (freshly distilled or passed through activated alumina columns). All commercially obtained reagents were used as received unless otherwise specified. Cesium fluoride (CsF) was obtained from Strem Chemicals and stored on the bench-top at ambient temperature under an N₂ atmosphere. 2-(Trimethylsilyl)phenyl trifluoromethanesulfonate, dicyclopentadiene, and 2,5-dimethylfuran were obtained from Sigma Aldrich. Furan was obtained from Alfa Aesar. First-generation and second-generation Grubbs catalysts were obtained from Materia Inc. Third-generation Grubbs catalyst was synthesized from second-generation catalyst according to literature.⁵⁶ Reaction temperatures were controlled using an IKAmag temperature modulator and, unless stated otherwise, reactions were performed at room temperature (rt, approximately 23 °C). Thin-layer chromatography (TLC) was conducted with EMD gel 60 F254 pre-coated plates (0.25 mm) and visualized using a combination of UV light and potassium permanganate staining. Silicycle Siliacflash P60 (particle size 0.040–0.063 mm) was used for flash column chromatography. ¹H NMR spectra were recorded on Bruker spectrometers (at 400 MHz, or 500 MHz) and are reported relative to deuterated solvent signals. Data for ¹H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and

integration. ^{13}C NMR spectra were recorded on Bruker spectrometers (at 125 MHz) and are reported relative to deuterated solvent signals. Data for ^{13}C NMR spectra are reported in terms of chemical shift and, when necessary, multiplicity, and coupling constant (Hz). IR spectra were recorded on a Perkin-Elmer 100 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). High-resolution mass spectra were obtained on Waters LCT Premier with ACQUITY LC and Thermo ScientificTM Exactive Mass Spectrometers with DART ID-CUBE.

Analytical Techniques

Gel permeation chromatography (GPC) was conducted on a Shimadzu HPLC Prominence-i system equipped with a UV detector, Wyatt DAWN Heleos-II Light Scattering detector, Wyatt Optilab T-rEX RI detector, one MZ-Gel SDplus guard column, and two MZ-Gel SDplus 100 Å 5 μm 300 $\times$ 8.0 mm columns. Chloroform (CHCl_3) at 40 $^\circ\text{C}$ was used as the eluent (flow rate: 0.70 mL/min). For polymers **P1**, **P3**, and **P4**, dn/dc was calculated by the Astra 6.0 software and used for calculation of molecular weights. For **P2**, near-monodisperse poly(styrene) standards (Polymer Laboratories) were employed for calibration and molecular weights were calculated from refractive index. Infrared absorption spectra were recorded on a PerkinElmer FT-IR equipped with an ATR accessory. Elemental analysis was conducted through Midwest Microlab, Inc., on an Exeter Analytical CE-440. For each polymer series, equal amounts of samples were combined from all equivalents (50, 150, and 300 equiv) and submitted for analysis. The samples were vacuum dried overnight prior to the elemental analysis. Differential scanning calorimetry was conducted on a DSCQ200 calorimeter (TA Instruments) equipped with a RSC 90 electric freezing machine, using approximately 5 mg of dried polymer sample (150 equiv as the representative sample) in an aluminum pan under a dry nitrogen flow at a heating/cooling rate of 10 $^\circ\text{C}/\text{min}$, with a total of two cycles from -80 to 200 $^\circ\text{C}$.

Representative Procedure: Cyclopentadiene Diels-Alder monomer **M1** (Table 1, Entry 1)

Cyclopentadiene was purified as follows: a 250 mL round bottom flask containing a stir bar was attached to a Vigreux column. The Vigreux column was fitted with a short-path distillation head, which in turn, was connected to a Schlenk tube. The apparatus was flame-dried, and then the 250 mL round bottom flask was charged with dicyclopentadiene (100 mL). The apparatus was purged with N_2 , and the 250 mL round bottom flask was heated to 220 $^\circ\text{C}$. After several hours, approximately 50 mL of cyclopentadiene was collected in the Schlenk tube, which was submerged in a -78 $^\circ\text{C}$ bath (acetone/dry ice). The distillate was stored at -80 $^\circ\text{C}$.

To a stirred solution of silyltriflate **7** (500 mg, 1.68 mmol) and cyclopentadiene (705 μL , 8.38 mmol, 5 equiv) in CH_3CN (17 mL) was added CsF (1.3 g, 8.38 mmol, 5 equiv). The reaction vessel was sealed and placed in an aluminum heating block maintained at 60 $^\circ\text{C}$ for 16 h. After cooling to 23 $^\circ\text{C}$, the reaction mixture was filtered over silica gel (EtOAc eluent). Evaporation under reduced pressure afforded the crude **M1**. The crude residue was further purified by column chromatography (hexanes) to afford **M1** (239 mg, 99% yield) as a colorless oil: Spectral data matched those previously reported.⁵⁷

Representative Procedure: Polymerization P1 (50 equiv) (Table 2, Entry 1)

A 1-dram vial containing a magnetic stir bar was flame-dried under reduced pressure, and then allowed to cool under N₂. The vial was charged with monomer **M1** (20.0 mg, 0.14 mmol, 50 equiv), and the vial was flushed with N₂. The vial was taken into a glove box and the monomer was dissolved in toluene (100 μ L).

In the glovebox, a separate vial was charged with Grubbs first-generation catalyst (5.9 mg) and toluene (230 μ L). A 90 μ L aliquot of the resulting solution (2.3 mg Grubbs 1st gen. cat., 2.8 μ mol, 1 equiv) was then added to the monomer **M1** solution while stirring vigorously. The reaction mixture was allowed to stir at 23 °C for 24 h. The vial was then removed from the glove box and the reaction was quenched with ethyl vinyl ether (10 μ L, 0.1 mmol). The polymer was then precipitated by dropwise addition into a scintillation vial containing 15 mL of MeOH kept at –20 °C. The precipitated polymer was recovered and freeze-dried from benzene to afford **P1** (50 equiv). ¹H NMR (400 MHz, CD₂Cl₂) δ : 7.56–6.93 (4H), 5.88–5.41 (2H), 4.35–4.09 (1H), 3.93–3.60 (1H), 2.74–2.43 (1H), 1.92–1.64 (1H). *M_n* (MALS): 5.8 kDa, η = 1.73.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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References

1. Callmann CE, Barback CV, Thompson MP, Hall DJ, Mattrey RF, Gianneschi NC. Therapeutic Enzyme-Responsive Nanoparticles for Targeted Delivery and Accumulation in Tumors. *Adv Mater.* 2015; 27:4611. [PubMed: 26178920]
2. Liao L, Liu J, Dreaden EC, Morton SW, Shopsowitz KE, Hammond PT, Johnson JA. A convergent synthetic platform for single-nanoparticle combination cancer therapy: ratiometric loading and controlled release of cisplatin, doxorubicin, and camptothecin. *J Am Chem Soc.* 2014; 136:5896. [PubMed: 24724706]
3. Rutenberg IM, Scherman OA, Grubbs RH, Jiang W, Garfunkel E, Bao Z. Synthesis of polymer dielectric layers for organic thin film transistors via surface-initiated ring-opening metathesis polymerization. *J Am Chem Soc.* 2004; 126:4062. [PubMed: 15053568]
4. Long TM, Swager TM. Molecular design of free volume as a route to low- κ dielectric materials. *J Am Chem Soc.* 2003; 125:14113. [PubMed: 14611248]
5. Yoon KY, Lee IH, Kim KO, Jang J, Lee E, Choi TL. One-pot in situ fabrication of stable nanocaterpillars directly from polyacetylene diblock copolymers synthesized by mild ring-opening metathesis polymerization. *J Am Chem Soc.* 2012; 134:14291. [PubMed: 22920217]
6. Miyake GM, Piunova VA, Weitekamp RA, Grubbs RH. Precisely Tunable Photonic Crystals From Rapidly Self-Assembling Brush Block Copolymer Blends. *Angew Chem Int Ed.* 2012; 51:11246.
7. Schleyer, PvR, Williams, JE., Jr, Blanchard, K. Evaluation of strain in hydrocarbons. The strain in adamantane and its origin. *J Am Chem Soc.* 1970; 92:2377.

8. Leitgeb A, Wappel J, Slugovc C. The ROMP toolbox upgraded. *Polymer*. 2010; 51:2927.
9. El-Saafin IF, Feast WJ. Metathesis polymerization of arylpolycyclic olefins. *J Mol Catal*. 1982; 15:61.
10. El-Saafin, IF. PhD Dissertation. Durham University; 1981. Ring-opening polymerization of some aryl substituted polycyclic alkenes.
11. Cannizzo LF, Grubbs RH. Block copolymers containing monodisperse segments produced by ring-opening metathesis of cyclic olefins. *Macromolecules*. 1988; 21:1961.
12. Bazan G, Khosravi E, Schrock RR, Feast W, Gibson V, O'Regan M, Thomas J, Davis W. Living ring-opening metathesis polymerization of 2, 3-difunctionalized norbornadienes by Mo (: CHBu-tert)(NC6H3Pr-iso2-2, 6)(OBu-tert) 2. *J Am Chem Soc*. 1990; 112:8378.
13. Bazan GC, Oskam JH, Cho HN, Park LY, Schrock RR. Living ring-opening metathesis polymerization of 2, 3-difunctionalized 7-oxanorbornenes and 7-oxanorbornadienes by Mo (CHCMe2R)(NC6H3-iso-Pr2-2, 6)(O-tert-Bu) 2 and Mo (CHCMe2R)(NC6H3-iso-Pr2-2, 6)(OCMe2CF3) 2. *J Am Chem Soc*. 1991; 113:6899.
14. Kang HA, Bronstein HE, Swager TM. Conductive block copolymers integrated into polynorbornene-derived scaffolds. *Macromolecules*. 2008; 41:5540.
15. Wolfberger A, Rupp B, Kern W, Griesser T, Slugovc C. Ring Opening Metathesis Polymerization Derived Polymers as Photoresists: Making Use of Thiol-ene Chemistry. *Macromol Rapid Commun*. 2011; 32:518. [PubMed: 21433209]
16. Durmaz H, Butun M, Hizal G, Tunca U. Postfunctionalization of polyoxanorbornene via sequential Michael addition and radical thiol-ene click reactions. *J Polym Sci, Part A: Polym Chem*. 2012; 50:3116.
17. van Hensbergen JA, Burford RP, Lowe AB. Post-functionalization of a ROMP polymer backbone via radical thiol-ene coupling chemistry. *J Polym Sci, Part A: Polym Chem*. 2013; 51:487.
18. Lowe AB. Thiol-ene "click" reactions and recent applications in polymer and materials synthesis: a first update. *Polym Chem*. 2014; 5:4820.
19. Kauffmann T. The Hetarynes. *Angew Chem, Int Ed Engl*. 1965; 4:543.
20. Reinecke MG. Hetarynes. *Tetrahedron*. 1982; 38:427.
21. Pellissier H, Santelli M. The use of arynes in organic synthesis. *Tetrahedron*. 2003; 59:701.
22. Wenk HH, Winkler M, Sander W. One century of aryne chemistry. *Angew Chem Int Ed*. 2003; 42:502.
23. Sanz R. Recent applications of aryne chemistry to organic synthesis. A review. *Org Prep Proced Int*. 2008; 40:215.
24. Bronner SM, Goetz AE, Garg NK. Understanding and modulating indolyne regioselectivities. *Synlett*. 2011; 2011:2599.
25. Tadross PM, Stoltz BM. A comprehensive history of arynes in natural product total synthesis. *Chem Rev*. 2012; 112:3550. [PubMed: 22443517]
26. Gampe CM, Carreira EM. Arynes and cyclohexyne in natural product synthesis. *Angew Chem Int Ed*. 2012; 51:3766.
27. Bhunia A, Yetra SR, Biju AT. Recent advances in transition-metal-free carbon-carbon and carbon-heteroatom bond-forming reactions using arynes. *Chem Soc Rev*. 2012; 41:3140. [PubMed: 22278415]
28. Yoshida H, Takaki K. Aryne insertion reactions into carbon-carbon σ -bonds. *Synlett*. 2012; 23:1725.
29. Dubrovskiy AV, Markina NA, Larock RC. Use of benzyne for the synthesis of heterocycles. *Org Biomol Chem*. 2013; 11:191. [PubMed: 23132413]
30. Wu C, Shi F. A closer look at aryne chemistry: details that remain mysterious. *Asian J Org Chem*. 2013; 2:116.
31. Goetz AE, Garg NK. Enabling the use of heterocyclic arynes in chemical synthesis. *J Org Chem*. 2014; 79:846. [PubMed: 24410270]
32. Goetz AE, Shah TK, Garg NK. Pyridynes and indolynes as building blocks for functionalized heterocycles and natural products. *Chem Commun*. 2015; 51:34.

33. Shah TK, Medina JM, Garg NK. Expanding the Strained Alkyne Toolbox: Generation and Utility of Oxygen-Containing Strained Alkynes. *J Am Chem Soc.* 2016; 138:4948. [PubMed: 26987257]
34. Medina JM, Mackey JL, Garg NK, Houk K. The role of aryne distortions, steric effects, and charges in regioselectivities of aryne reactions. *J Am Chem Soc.* 2014; 136:15798. [PubMed: 25303232]
35. Bronner SM, Mackey JL, Houk K, Garg NK. Steric effects compete with aryne distortion to control regioselectivities of nucleophilic additions to 3-silylarynes. *J Am Chem Soc.* 2012; 134:13966. [PubMed: 22876797]
36. Bronner SM, Goetz AE, Garg NK. Overturning indolyne regioselectivities and synthesis of indolactam V. *J Am Chem Soc.* 2011; 133:3832. [PubMed: 21351773]
37. Picazo E, Houk K, Garg NK. Computational predictions of substituted benzyne and indolyne regioselectivities. *Tetrahedron Lett.* 2015; 56:3511. [PubMed: 26034336]
38. Im GYJ, Bronner SM, Goetz AE, Paton RS, Cheong PHY, Houk K, Garg NK. Indolyne experimental and computational studies: Synthetic applications and origins of selectivities of nucleophilic additions. *J Am Chem Soc.* 2010; 132:17933. [PubMed: 21114321]
39. Goetz AE, Garg NK. Regioselective reactions of 3, 4-pyridynes enabled by the aryne distortion model. *Nat Chem.* 2013; 5:54. [PubMed: 23247178]
40. Bronner SM, Bahnck KB, Garg NK. Indolynes as electrophilic indole surrogates: fundamental reactivity and synthetic applications. *Org Lett.* 2009; 11:1007. [PubMed: 19178159]
41. Cheong PHY, Paton RS, Bronner SM, Im GYJ, Garg NK, Houk K. Indolyne and aryne distortions and nucleophilic regioselectivities. *J Am Chem Soc.* 2010; 132:1267. [PubMed: 20058924]
42. Medina JM, McMahon TC, Jiménez-Osés G, Houk K, Garg NK. Cycloadditions of cyclohexynes and cyclopentyne. *J Am Chem Soc.* 2014; 136:14706. [PubMed: 25283710]
43. Mizukoshi Y, Mikami K, Uchiyama M. Aryne polymerization enabling straightforward synthesis of elusive poly (ortho-arylene) s. *J Am Chem Soc.* 2015; 137:74. [PubMed: 25459083]
44. Ihara E, Kurokawa A, Koda T, Muraki T, Itoh T, Inoue K. Benzyne as a monomer for polymerization: Alternating copolymerization of benzyne and pyridine to give novel polymers with o-phenylene and 2, 3-dihydropyridine units in the main chain. *Macromolecules.* 2005; 38:2167.
45. Ito S, Takahashi K, Nozaki K. Formal aryne polymerization: use of [2.2. 1] oxabicyclic alkenes as aryne equivalents. *J Am Chem Soc.* 2014; 136:7547. [PubMed: 24828624]
46. Sibi, MP., SS, Zimmermann, N., Serum, E., Ma, G., Moorthy, R., Kalliokoski, K. Novel monomers from biomass. U S Patent. 2016022943. Jun 16. 2016
47. Himeshima Y, Sonoda T, Kobayashi H. Fluoride-induced 1, 2-elimination of o-trimethylsilylphenyl triflate to benzyne under mild conditions. *Chem Lett.* 1983; 12:1211.
48. MacRury T, McConnell M. Measurement of the absolute molecular weight and molecular weight distribution of polyolefins using low-angle laser light scattering. *J Appl Polym Sci.* 1979; 24:651.
49. Podzimek S. The use of GPC coupled with a multiangle laser light scattering photometer for the characterization of polymers. On the determination of molecular weight, size and branching. *J Appl Polym Sci.* 1994; 54:91.
50. Ganachaud F, Monteiro MJ, Gilbert RG, Dourges MA, Thang SH, Rizzardo E. Molecular weight characterization of poly (N-isopropylacrylamide) prepared by living free-radical polymerization. *Macromolecules.* 2000; 33:6738.
51. Roth HG, Romero NA, Nicewicz DA. Experimental and Calculated Electrochemical Potentials of Common Organic Molecules for Applications to Single-Electron Redox Chemistry. *Synlett.* 2016; 27:714.
52. Amir-Ebrahimi V, Rooney JJ. The remarkable activity of 7-oxa-benzonorborene in metathesis copolymerization using Ru-based initiators. *J Mol Catal A: Chem.* 2004; 212:107.
53. Simril V. Internal plasticization: The effect of chemical structure. *J Polym Sci.* 1947; 2:142.
54. Khosravi E, Feast W, Al-Hajaji A, Leejarkpai T. ROMP of n-alkyl norbornene dicarboxyimides: from classical to well-defined initiators, an overview. *J Mol Catal A: Chem.* 2000; 160:1.
55. Jenekhe SA, Roberts MF. Effects of intermolecular forces on the glass transition of polymers. *Macromolecules.* 1993; 26:4981.

56. Love JA, Morgan JP, Trnka TM, Grubbs RH. A practical and highly active ruthenium-based catalyst that effects the cross metathesis of acrylonitrile. *Angew Chem Int Ed.* 2002; 41:4035.
57. Wang BY, Turner DA, Zujoví T, Hadad CM, Badji JD. The Role of Chirality in Directing the Formation of Cup-Shaped Porphyrins and the Coordination Characteristics of such Hosts. *Chem Eur J.* 2011; 17:8870. [PubMed: 21678514]

Figure 1.
Possible solutions to poly(benzonorbornadiene) oxidation problem

Figure 2. SEC-MALS Chromatograms of unsubstituted polymers (a) **P1** and (b) **P2** show broad overlapping peaks. Chromatograms of substituted polymers (c) **P3** and (d) **P4** show well-defined peaks.

Figure 3.
FT-IR spectra: (a) **P1**, (b) **P2**, (c) **P3**, and (d) **P4**

Figure 4. DSC curves for polymers **P1–P4**, (a) **P1**, (b) **P2** (not detected), (c) **P3**, and (d) **P4**

Table 1Benzonorbornadiene monomers **M1–M4** synthesized by aryne chemistry

Entry	Trapping agent	Product	Yield
1			<i>M1</i> 99%
2			<i>M2</i> 94%
3			<i>M3</i> 99%
4			<i>M4</i> 91%

Table 2

ROMP of monomers **M1–M4** using Grubbs catalysts

Entry	Catalyst	Monomer	[M]/[I]	<i>M_n</i> (theo)	<i>M_n</i>
1	G1	M1	50	7.1 kDa	11.8 kDa
2	G1	M1	150	21.3 kDa	31.6 kDa
3	G1	M1	300	42.6 kDa	53.0 kDa
4	G1	M2	50	7.2 kDa	15.7 kDa ^a
5	G1	M2	150	21.6 kDa	38.4 kDa ^a
6	G1	M2	300	43.3 kDa	50.6 kDa ^a
7	G1	M3	50	8.6 kDa	5.4 kDa
8	G1	M3	150	25.8 kDa	25.2 kDa
9	G1	M3	300	51.7 kDa	54.0 kDa
10	G3	M4	50	10.0 kDa	17.4 kDa
11	G3	M4	150	30.0 kDa	46.4 kDa
12	G3	M4	300	60.1 kDa	162.0 kDa

^aMajor peak calculated from RI trace

Table 3Elemental analysis data for polymers **P1–P4**

Polymer	Element	% observed	# of atoms per unit observed	# of atoms per unit theoretical
P1	Carbon	88.70	11	11
	Hydrogen	7.27	10.74	10
	Oxygen	3.96	0.37	0
P2	Carbon	80.38	10	10
	Hydrogen	5.58	8.27	8
	Oxygen	14.14	1.32	1
P3	Carbon	83.54	12	12
	Hydrogen	7.09	12.14	12
	Oxygen	9.46	1.02	1
P4	Carbon	83.89	14	14
	Hydrogen	7.93	15.77	16
	Oxygen	8.08	1.01	1