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Benzoladderene Mechanophores: Synthesis, Polymerization, and Mechanochemical Transformation

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Supporting Information Placeholder

ABSTRACT: We have previously reported a polymechnanophore system, poly(ladderene), which underwent dramatic bond rearrangement in response to mechanical force to yield semiconducting polyacetylene. Herein, we report the scalable synthesis of benzoladderenes as new mechanophore monomers. Ring-opening metathesis polymerization of benzoladderenes yielded homopolymers and block copolymers with controlled molecular weights and low dispersity. The resulting nonconjugated poly(benzoladderene) can be mechanochemically transformed into conjugated poly(*o*-phenylenehexatrienylene) up to 40-45% using sonication. These benzoladderenes and their resulting polymers are easier to synthesize than the poly(ladderene) system and allow access to force-activated conjugated structures beyond polyacetylene.

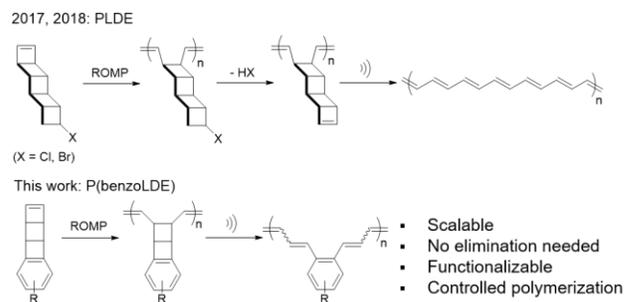
Polymer mechanochemistry has rapidly advanced over the past decade through the discovery of force-induced reactivities that are unique from thermal and photochemical pathways and the development of unprecedented force-responsive polymers.¹ Embedding properly designed mechanochemically active motifs, termed mechanophores, in polymers can induce nondestructive chemistry and complex mechanical response of materials, rather than simple bond scission and mechanical failure. Exciting reported mechanochemical responses include coloration,² luminescence,³ crosslinking,⁴ depolymerization,⁵ small molecule release,⁶ catalysis,⁷ and mechanically gated activation.⁸ Most examples of polymer mechanochemistry involve sparse incorporation of mechanophores into a mechanochemically inert polymer. The relatively low content of mechanophore limits the magnitude of mechanical response of the materials. Thus, a polymechnanophore system is highly desired to achieve significant mechanical transformation along a polymer chain.⁹

We recently designed an unprecedented mechanophore monomer, ladderene (LDE), that undergoes efficient ring-opening metathesis polymerization (ROMP) to form poly(ladderene) (PLDE). Force-triggered unzipping of PLDE

converted a series of strained σ bonds to π bonds, thus transforming a non-conjugated polymer to a semiconducting polymer (polyacetylene).¹⁰ Direct polymerization of LDE mechanophore, facile mechanochemistry of PLDE, and dramatic changes of polymer properties upon mechano-activation hold great promise for a new generation of force-responsive polymers. However, the synthesis of [5]-chloro/bromoladderene monomer is arduous and limited to small milligram quantities,¹⁰⁻¹¹ and the derivatization of ladderene is also difficult, limiting our ability to functionalize the resulting polymers. Moreover, in order to establish continuous conjugation upon activation, an HCl/HBr elimination step was required to generate a terminal olefin on each repeat unit after ROMP. This elimination often resulted in some polymer backbone truncation, broadening the MW distribution.^{10, 12}

In order to overcome these issues and access other force-activated conjugated structures, we sought alternative designs of LDE-based monomers. We were drawn to an interesting benzoladderene (benzoLDE) structure first reported by Pettit in 1967, resulting from the cycloaddition between $\text{Fe}(\text{CO})_3$ stabilized cyclobutadiene and benzocyclobutadiene.¹³ We envisioned that 1) P(benzoLDE) would allow mechanochemical generation of new conjugated polymers; 2) the terminal benzo group would avoid the post-polymerization elimination as required for PLDE; 3) polymer

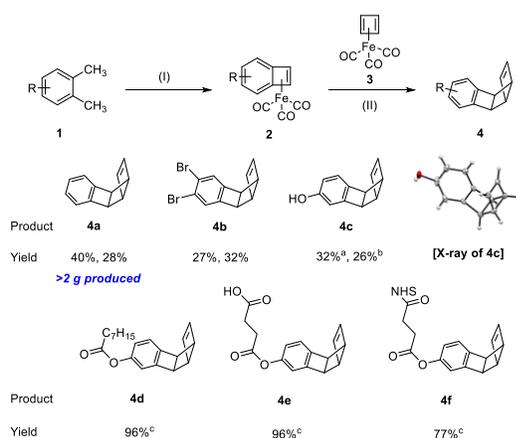
Scheme 1. Designs of mechanochemically generated conjugated polymers.



substitution may be achieved by derivatizing the benzo group (Scheme 1). Optimizing and expanding Pettit's original synthesis,¹³ we synthesized several benzoLDEs via a four-step sequence. *o*-xylene derivatives were first brominated to yield $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-*o*-xylenes, which were treated with sodium iodide to undergo intramolecular cyclization followed by reduction with $\text{Fe}_2(\text{CO})_9$ to afford the benzocyclobutadiene- $\text{Fe}(\text{CO})_3$ complexes. BenzoLDEs were then synthesized via Diels-Alder reaction between cyclobutadiene and benzocyclobutadiene that were liberated when treating their corresponding $\text{Fe}(\text{CO})_3$ complexes with $\text{Pb}(\text{OAc})_4$ (Scheme 2). The involved reactions are all scalable at gram quantities. An exclusively *endo* configuration of the Diels-Alder adduct was obtained as evidenced by both $^1\text{H-NMR}$ spectroscopy (Figure S15) and single crystal structure (insert in Scheme 2), thus forming a *syn* ladder configuration. We also synthesized dibromo- and acetoxy-benzoLDEs at similar yields to the benzoLDE. The acetoxy group was readily hydrolyzed to afford hydroxy-benzoLDE, which gave us a convenient phenol group to carry out simple derivatization. For demonstration, a long alkyl chain was introduced onto the benzoLDE, which could enhance the solubility of the mechanically generated conjugated polymers; a carboxylic acid and an activated NHS ester were installed to enable further modification. Despite their high strain, these benzoLDEs did not undergo any detectable decomposition for several weeks upon storage under ambient conditions. Attempts to synthesize strongly electron-withdrawing substituents, such as $-\text{NO}_2$, or changing the benzene to an electron-poor pyridine failed to generate the corresponding $\text{Fe}(\text{CO})_3$ complexes.

Cyclic olefins with *endo* configuration are generally less

Scheme 2. Synthesis of Benzoladderene Monomers.



Conditions: (I) NBS, CCl_4 , $h\nu$, 85 °C; NaI, EtOH, 85 °C; then $\text{Fe}_2(\text{CO})_9$, benzene, 65 °C. (II) $\text{Pb}(\text{OAc})_4$, pyridine, 0 °C. ^aDMF was used as the solvent. ^bAcetoxy substituted product was hydrolyzed directly. ^cYield of derivatization from 4c. Insert is the single crystal structure of 4c.

reactive towards ROMP due to the steric hindrance.¹⁴ Therefore, we first carried out a kinetics experiment, monitored by $^1\text{H-NMR}$ spectroscopy, to probe the ROMP reactivity of *endo* benzoLDE initiated by the 3rd generation Grubbs catalyst (G_3). Delightfully, the monomer conversion reached 95% in 10 min at 1 M concentration and room temperature in CHCl_3 . BenzoLDE conversion was found to

follow clean first-order kinetics, illustrated by a linear plot of $\ln([M])/[M]_0$ vs time with a calculated $k_{\text{obsd}} = 4.5 \pm 0.1 \text{ M}^{-1} \text{ s}^{-1}$ (Figure S2). Gel permeation chromatography (GPC) analysis of polymerization solution showed a narrowly dispersed peak with dispersity (D) of 1.16 with the expected MW, suggesting the controlled nature of ROMP of benzoLDE. However, significant peak broadening was observed when the polymerization was prolonged after full monomer conversion (Figure 1a), which suggested potential secondary metathesis along the polymer backbone after ROMP. This was quite unexpected, because we have previously observed that the backbone olefins of PLDE are considerably shielded and could not engage any detectable secondary metathesis, and it is

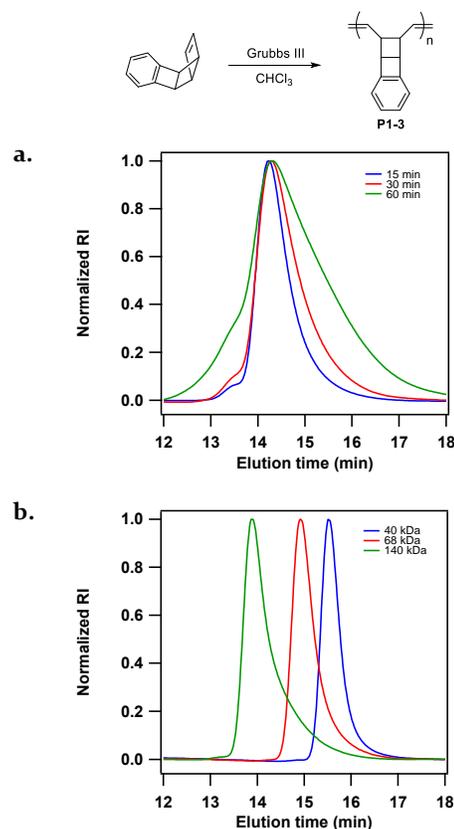


Figure 1. ROMP of benzoladderene: (a) The broadening GPC traces of P(benzoLDE) after full monomer conversion. Conditions: $[M]_0 = 1 \text{ M}$, $[M/\text{G}_3] = 500:1$ at room temperature. The times in legend are the total times allowed for ROMP. (b) GPC traces of P(benzoLDE) with different MWs obtained at 0 °C. Conditions: $[M]_0 = 2 \text{ M}$, $[M/\text{G}_3] = 1000:1$ (green trace **P1**); $[M]_0 = 1 \text{ M}$, $[M/\text{G}_3] = 500:1$ (red trace **P2**); $[M]_0 = 1 \text{ M}$, $[M/\text{G}_3] = 250:1$ (blue trace **P3**). Reaction quenched at > 95% monomer conversion.

reasonable to expect that the backbone olefins of P(benzoLDE) are similarly shielded, if not more. It is known that metal species such as $\text{Cu}(\text{I})$ and $\text{Ag}(\text{I})$ could effectively trigger ring-opening of fused cyclobutanes¹⁵ and [3]ladderdiene with a *syn*-configuration undergoes faster isomerization to form cyclooctatetraene than the *anti*-stereoisomer upon heating.¹⁶ Therefore, we suspected that a

Table 1. ROMP of Benzoladderenes^a

Polymer	BenzoLDE	[M/G ₃] ₀	[M] ₀ (M)	M _n theory (kDa)	M _n MALLS (kDa) ^d	Đ
P1	4a	1000	2 ^c	154	140	1.14
P2	4a	500	1	77.0	68.3	1.06
P3	4a	250	1	38.5	40.4	1.03
P4	4d	1000	2 ^c	296	317	1.19
P5	4d,4b (2:1) ^b	150	1	45.2	50.8	1.04
P6	4d,4f (2:1) ^b	150	1	48.0	41.4	1.04

^aPolymerization was performed at 0 °C in chloroform.

^bCopolymerization of 4b or 4f was performed due to the poor solubility of their homopolymers. ^cHigher monomer concentration promoted propagation and improved the control of ROMP when targeting DP = 1000 (Figure S3).

^dDetermined by GPC MALLS analysis in THF.

minute extent of cyclobutane ring-opening in P(benzoLDE) may occur during or after ROMP via either thermal or catalyzed processes, generating unhindered backbone olefins susceptible to secondary metathesis. The UV-vis spectra of the isolated ROMP polymer showed weak absorption around 270 nm (Figure S8-9), suggesting the presence of a small amount of bis-butadienyl benzene species,¹⁷ although this ring-opened species was not detectable by ¹H-NMR spectroscopy even at high polymer concentrations. As a comparison, this minute ring-opening side reaction was never observed in the PLDE synthesis using ladderene with all *anti*-configuration, suggesting that either the *syn*-configuration or the benzo-fusion of ladderane may account for the side reaction.

In order to suppress the ring-opening and secondary metathesis, we carried out ROMP either at 0 °C or at room temperature in the presence of 15 equiv. weakly coordinating 3-bromopyridine and quenched the polymerization at nearly complete conversion (Figure S4-5). Running ROMP at 0 °C was found more effective at suppressing the side reactions, and we obtained narrowly dispersed polymers, **P1** – **P3**, with MWs ranging from 40 to 140 kDa and Đ < 1.2, controlled by the monomer-to-catalyst ratio (Figure 1b and Table 1). ROMP of the functionalized benzoLDE monomers also resulted in well-controlled polymers (Table 1). Due to the relatively poor solubility of the homopolymers of **4b** and **4f**, their copolymers with **4d** were synthesized (Figure S6).

Living ROMP of benzoLDE enabled us to synthesize well-defined block copolymers (BCPs) by simple sequential monomer additions. As a demonstration, we chose norbornene (NBE-1) first as the simplest monomer. A triblock copolymer P(NBE-1)-*b*-P(benzoLDE)-*b*-P(NBE-1) was synthesized via stepwise addition of NBE-1, benzoLDE, and NBE-1 to **G3** at 0 °C with targeted degrees of polymerization (DPs) of 400, 200 and 400, respectively (Figure 2a). The time for carrying out each block synthesis was chosen to be 10, 10, and 15 min, respectively, in order to reach quantitative conversion for NBE-1 and ~95% conversion for benzoLDE. GPC analysis showed clean and complete shifts of narrow and symmetric peaks to lower elution times as each block was successfully extended from the preceding block (Figure 2b). Unlike PLDE, elimination under strongly basic conditions is not needed for P(benzoLDE), so almost any norbornene derivatives containing a wide range of functional groups can be used for the BCP synthesis. To this end, we demonstrated three other types of substituted NBEs that are commonly used

for living ROMP, NBE-2, NBE-3, and NBE-4, all of which yielded well-controlled monomodal triblock copolymers with benzoLDE (Figure S7). The quality of these synthesized BCPs is significantly improved over our previously reported BCPs using bromoladderene, where the PLDE-appended Ru complex at the chain end has limited stability when monomer is depleting.¹² Thus, benzoLDE greatly expands the scope of stress-responsive BCPs that can be synthesized.

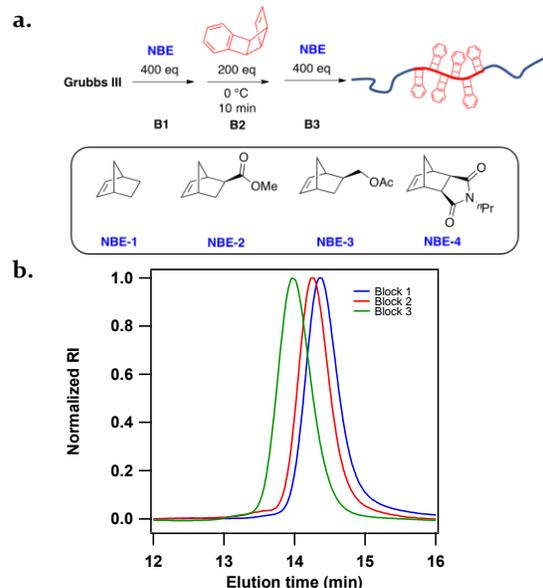


Figure 2. (a) Synthesis of P(NBE)-*b*-P(benzoLDE)-*b*-P(NBE) triblock copolymers using norbornenes with different functional groups. (b) GPC traces of P(NBE-1), P(NBE-1)-*b*-P(benzoLDE) and P(NBE-1)-*b*-P(benzoLDE)-*b*-P(NBE-1), respectively.

Next, we investigated the mechanoactivation of P(benzoLDE) under ultrasonication using a dilute solution of **P1** ($M_n = 140$ kDa, DP ~ 1000) in THF. After only 2 min of sonication, the initially colorless **P1** solution turned light yellow and the color became more intense as sonication time was increased. Aliquots removed at regular intervals were analyzed by UV-vis spectroscopy. A peak around 380 nm with an onset of absorption at 460 nm was observed, which were attributed to the mechanochemically generated poly(*o*-phenylene-hexatrienylene) structure. The observed peak and onset of absorption are close to those reported for poly(*p*-phenylene-hexatrienylene), which is a regioisomer of our generated conjugated polymer and was previously synthesized by polycondensation.¹⁸ The absorption intensity continued to grow throughout the course of sonication without any shift of the absorption maximum (Figure 3). The generated poly(*o*-phenylene-hexatrienylene) in solution is stable for at least several days when stored in dark under air. We subjected P(benzoLDE)s with different MWs to identical sonication condition and polymers with higher MWs changed color much more rapidly (Figure S10), confirming the mechanochemical nature of the activation.

The solution of activated P(benzoLDE) remained clear and homogenous throughout sonication, which enabled us to further analyze their MW evolution over the course of sonoactivation by GPC (Figure S11). The refractive index (RI) traces showed a rapid decrease in intensity of the original

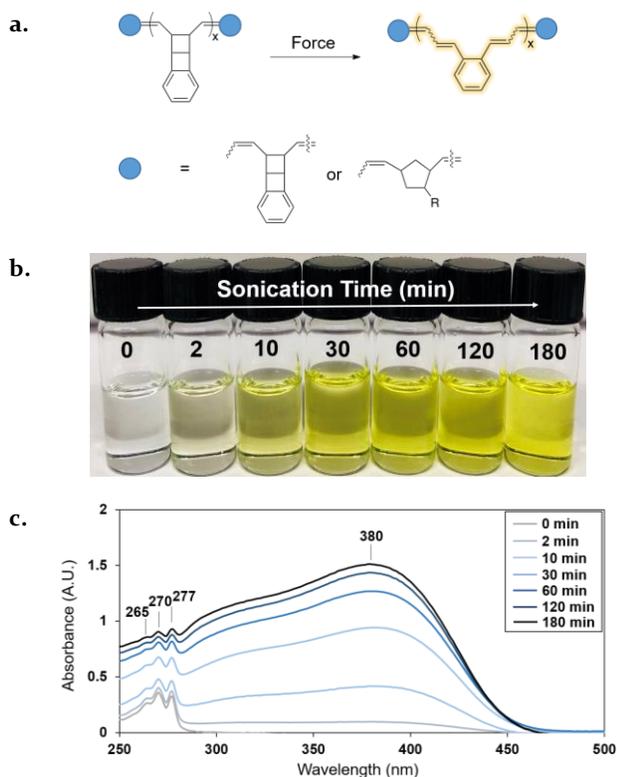


Figure 3. (a) Mechanochemical formation of conjugated poly(*o*-phenylene-1,3,5-hexatrienylene). *Trans*- and *cis*-configurations may be present in the formed double bonds. (b) Photographs of sonicated **P1** solution at different sonication times. (c) UV-vis absorption spectra of sonicated **P1** solution at different sonication times.

polymer peak within 10 mins along with a significant peak broadening. As the sonication time increased, a high MW peak was observed, which corresponds to the nanoscale aggregation of the formed conjugated structure. Different from our previous GPC analysis on the activation PLDE block copolymers,¹² the high and low MW peaks had similar relative intensity of RI/UV signals, suggesting relatively even distribution of the generated conjugated block in the aggregates and the more solubilized fraction, as a result of weaker aggregation of poly(*o*-phenylene-hexatrienylene) than the mechanically generated polyacetylene in our previous reports. Mechanoactivation of P(NBE)-*b*-P(benzolDE)-*b*-P(NBE) block copolymer gave similar profiles to that of the homopolymer, but no aggregation was detected by GPC analysis (Figure S13), presumably due to the relatively long soluble P(NBE) end blocks.

Despite the weak aggregation, solution NMR spectroscopy of the isolated activated polymer still did not show any signals from the conjugated poly(*o*-phenylene-hexatrienylene) structure. Therefore, we used cross-polarization magic-angle spinning (CP-MAS) ¹³C solid-state NMR spectroscopy to quantify the degree of activation on the isolated polymer **P1** after 180 min of sonication. The spectra of activated polymer showed a diminution in carbon resonances at 46 and 41 ppm (*sp*³ carbons on cyclobutane) with a concomitant increase in a broad peak in the range of 150 – 115 ppm (*sp*² carbon). Based on the changes in the integration of *sp*² and *sp*³ carbon signals,

the degree of activation was determined to be 40-45% (Figure S14).

In summary, we have demonstrated the scalable synthesis of several benzoladderenes and their controlled ROMP to generate a new family of polymechanophores and their BCPs. Facile mechanochemical activation was achieved to generate a new conjugated polymer without a post-polymerization elimination step required for PLDE. The scalable synthesis and functionalizability of benzoladderenes and their controlled polymerization expand the unique family of polymechanophores with dramatic response to mechanical force.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Synthetic procedures, ¹H and ¹³C NMR spectra, additional UV-Vis Spectra, GPC traces, and single crystal structure

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Notes

The authors declare no competing financial interests.

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