JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Subscriber access provided by The University of Melbourne Libraries

Article

Bicyclohexene-peri-naphthalenes: Scalable Synthesis, Diverse Functionalization, Efficient Polymerization, and Facile Mechanoactivation of Their Polymers

Jinghui Yang, Matias Horst, Sabrina H. Werby, Lynette Cegelski, Noah Z. Burns, and Yan Xia

J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/jacs.0c06454 • Publication Date (Web): 30 Jul 2020

Downloaded from pubs.acs.org on July 31, 2020

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Bicyclohexene-peri-naphthalenes: Scalable Synthesis, Diverse Functionalization, Efficient Polymerization, and Facile Mechanoactivation of Their Polymers

Jinghui Yang, Matias Horst, Sabrina H. Werby, Lynette Cegelski, Noah Z. Burns, Yan Xia*

Department of Chemistry, Stanford University, Stanford, California, 94305, United States

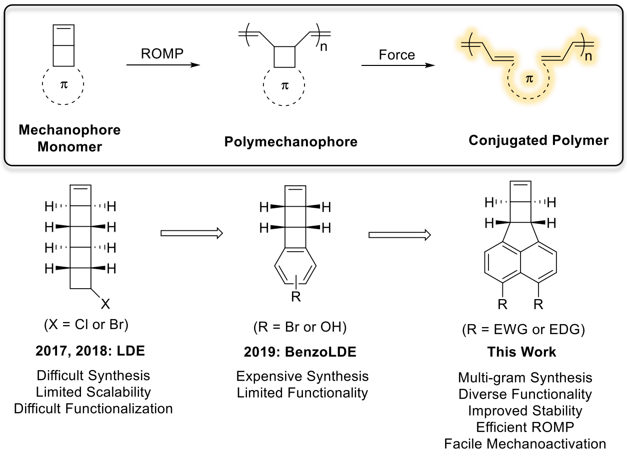
ABSTRACT: Pursuing polymers that can transform from a non-conjugated to a conjugated state under stress to significantly change their properties, we developed a new generation of ladder-type mechanophore monomers, *bicyclo[2.2.0]hex-5-ene-peri-naphthalene* (BCH-Naph), that can be directly and efficiently polymerized. BCH-Naphs can be synthesized in multi-gram quantities using readily available chemicals and functionalized with a wide range of electron-rich and electron-poor substituents, allowing tuning of the optoelectronic and physical properties of mechanically generated conjugated polymers. Efficient ROMP of BCH-Naphs yielded ultrahigh molecular weight polymechanophores with controlled MWs and low dispersity. The resulting poly(BCH-Naph)s can be mechanically activated into conjugated polymers using ultrasonication, grinding, and even simple stirring of the dilute solutions, leading to changes in absorption and fluorescence. Poly(BCH-Naph)s represent an attractive polymechanophore system to explore multifaceted mechanical response in solution and solid states, owing to the synthetic scalability, functional diversity, efficient polymerization, and facile mechanoactivation.

INTRODUCTION

The advent of polymer mechanochemistry has led to the development of various so-called mechanophores that are embedded in polymer backbones to respond to mechanical force and manifest in many force-activated functions, such as coloration,[1-3] luminescence,[4-7] self-strengthening,[8-9] self-demolishing,[10] gated degradation,[11-12] release of small molecules[13-15] and active catalyst.[16] Fundamentally, these developments have advanced our understanding on force-coupled chemical reactions. For instance, mechanical force has been shown to bias reaction pathways,[17] accelerate or suppress reaction rates,[18] stabilize reaction intermediate,[19] and induce dynamic effect.[20] Mechanophores are commonly incorporated sparsely into a mechanically inert polymer backbone.[21-24] The low content of mechanophores in a polymer chain often limits the magnitude of overall force response of a material and can make quantitative analysis of mechanochemical activation difficult. Alternatively, these limitations may be overcome by developing polymechanophore systems,[25] where every repeat unit is a mechanophore. Direct and controlled polymerization of mechanophores would significantly facilitate the synthesis of polymechanophores. In pursuit of polymers that dramatically change their intrinsic material properties under stress, we proposed mechanochemical transformation of non-conjugated polymers to conjugated polymers through continuous rearrangement of a series of strained σ bonds to π bonds (Scheme 1). The first example of such polymers was polyladderenes, which can be activated to form polyacetylene with long conjugation length.[26] A terminal cyclobutene ring in the ladderene design enabled direct ring-opening metathesis polymerization (ROMP) of mechanophore, leading to polymechanophores with relatively controlled molecular weights (MWs) and the synthesis of their block copolymers.[27]

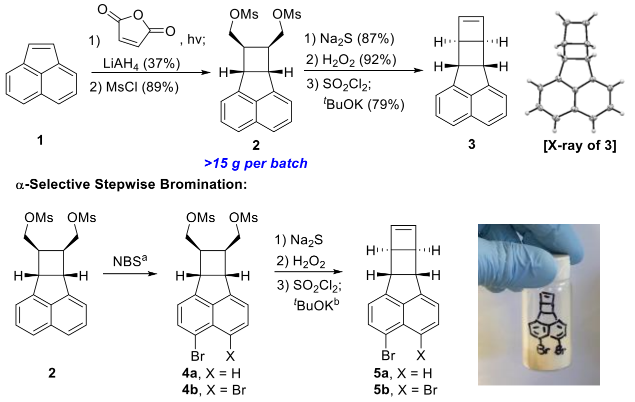
After our initial success with polyladderene, we sought new mechanophore monomers that are scalable in synthesis and can generate diverse conjugated structures with variable optoelectronic properties. As a result, we

Scheme 1. Design of polymechanophores that transform from a non-conjugated state to a conjugated state in response to mechanical force.



recently developed benzoladderenes (benzoLDEs), which can be synthesized at gram quantities and allow incorporation of certain simple functionalities.[28] BenzoLDEs overcame some of the synthetic challenges in chloro/bromo-ladderenes and their polymerization.[26-27] However, the synthesis of benzoLDEs still involves the use of not-easily-accessible intermediates, such as iron-carbonyl stabilized cyclobutadiene and benzocyclobutadiene, and we could not synthesize benzoLDE with electron withdrawing moieties due to the extreme instability of iron-carbonyl stabilized electron-poor benzocyclobutadiene.[28] BenzoLDEs, though stable under ambient conditions, can undergo thermal ring opening in refluxing $CDCl_3$ with a $t_{1/2} = 3$ h as measured by ^1H-NMR spectroscopy. Further, ROMP of benzoLDEs was found to result in a minute amount of ring-opened species, which caused chain transfer if the polymerization was run at room temperature or prolonged.[28]

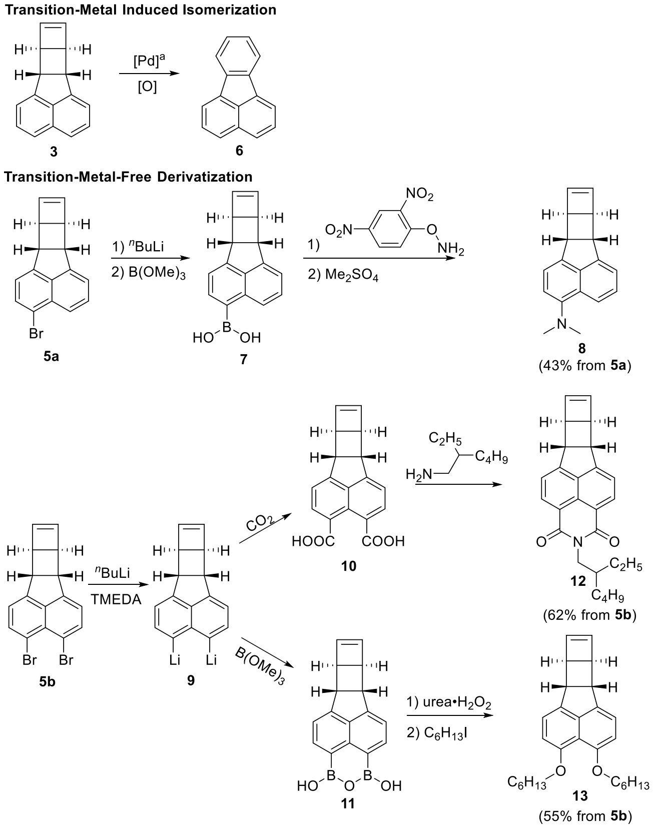
Scheme 2. Synthesis of BCH-Naph and its brominated derivatives.



[a]mono-bromination (>90% yield) or di-bromination (>85% yield) was selectively achieved using 1.05 or 2.10 equiv. NBS. [b]yields in cyclobutene formation were similar to unsubstituted BCH-NaPh (see SI for details).

Herein, we report a new generation of mechanophore monomers, *bicyclo[2.2.0]hex-5-ene-2,3-peri-naphthalene* (BCH-Naph), with many advantages over our previous systems. BCH-Naphs can be synthesized in multi-gram quantities from readily available starting materials and with a range of electron-rich or electron-poor substituents. ROMP of BCH-Naph is easy, controlled, and remarkably efficient, leading to ultra-high MW polymechanophores with degrees of polymerization (DPs) up to 10,000 and narrow dispersity. BCH-Naphs also exhibit much improved thermal stability with minimal change (<5% based on NMR spectroscopy) upon heating at 100 °C for 1 h. Excitingly, besides mechanochemical activation in solution by ultrasonication or in solid state by grinding, we found that the ultrahigh MW poly(BCH-Naph) can even be mechanochemically activated by simple rapid stirring of their solutions, opening new avenues for the applications of polymechanophores.

Scheme 3. Derivatization of BCH-Naph using transition-metal free methods



[a]$Pd(OAc)_2$ (5 mol%), toluene, 60 °C, 8 h.

RESULTS AND DISCUSSIONS

Acenaphthylene is relatively cheap and commercially available, and it can undergo efficient photochemical [2+2] cycloaddition with maleic anhydride to form a four-membered ring.[29] Thus, we devised a synthetic route to a family of BCH-Naphs, where the fused naphthalene motif is expected to become part of the conjugated polymer backbone upon mechanochemical activation.

Table 1. ROMP of BCH-Naphs.[a]

Entry	Polymer	Monomer	$[M/G3]_o$	$[M]_o$ (M)	$M_{n,theory}$ (kDa)	$M_{n,MALLS}$ (kDa)[b]	Conversion (%)[c]	Đ[d]
1	**P1**	**3**	250	0.5	51.1	61.8	>95	1.03
2	**P2**	**3**	500	0.5	102	119	>95	1.04
3	**P3**	**3**	1000	0.5	204	187	>95	1.11
4	**P4**	**3**	3000	1	613	689	>95	1.07
5	**P5**	**3**	5000	1	1021	1208	>95	1.11
6	**P6**	**3**	10000	1	2043	1716	>95	1.10
7	**P7**	**8**	1000	0.5	247	440	>95	1.32
8	**P8**	**12**	1000	0.5	386	418	>95	1.04
9	**P9**	**13**	1000	0.5	405	448	>95	1.11
10	**P10**	**12**, **13** (1:1)	1000	0.5	395	378	>95	1.07

[a] ROMP was run in reagent grade $CHCl_3$ under air at room temperature. [b] Determined by GPC MALLS analysis in THF. [c] Determined by ^{1}H-NMR spectroscopy. [d] Dispersity determined based on calibration with PS standards.

As outlined in Scheme 2, photochemical [2+2] cycloaddition of acenaphthylene and maleic anhydride at 1:2.7 mole ratio in dibromomethane was performed in decagram scales by irradiation using a medium-pressure mercury lamp. The crude cycloadduct was subsequently reduced by $LiAlH_4$ to diol, which was then mesylated to give dimesylate **2** in > 15 g per batch. Two-fold substitution of **2** with Na_2S followed by oxidation with H_2O_2 led to the formation of five-membered cyclic sulfoxide, which then underwent α chlorination with SO_2Cl_2 and an atypical Ramberg-Bäckland olefination, developed by Burns and coworkers,[30] to yield BCH-Naph **3**. **3** was formed exclusively as an *exo* isomer as evidenced by single crystal structure (Scheme 2). All the reaction steps from intermediate **2** were scalable and gave very high yields. We next developed strategies to introduce various substituents to BCH-Naph. We found that bromination of **2** by *N*-bromosuccinimide (NBS) resulted in selective bromination at α positions of the naphthalene and could be carried out in a stepwise fashion. Thus, 1-bromomesylate **4a** and 1,8-dibromomesylate **4b** were synthesized in > 85% yields using 1.05 or 2.1 equiv. NBS, respectively. **4a** and **4b** were then converted to 1-bromo-BCH-Naph **5a** and 1,8-dibromo-BCH-Naph **5b**, respectively, in similarly high yields.

Aryl bromides are commonly derived via transition-metal catalyzed cross-coupling reactions. However, the presence of Pd catalyst triggered the isomerization of the bicyclohexene unit in BCH-Naph to cyclohexadiene, which was rapidly oxidized to form fluoranthene.[31] Therefore, we sought transition-metal-free reactions to introduce functional groups to BCH-Naph (Scheme 3). Lithium halogen exchange is an extremely fast and efficient reaction, transforming aryl halides to reactive aryl lithium species under mild conditions.[32] Aryl lithium can be subsequently quenched by a range of electrophiles to install substituents. Gratifyingly, both 1-bromo-BCH-Naph and 1,8-dibromo-BCH-Naph could be cleanly converted to lithiated species using *n*-BuLi under mild conditions. 1-

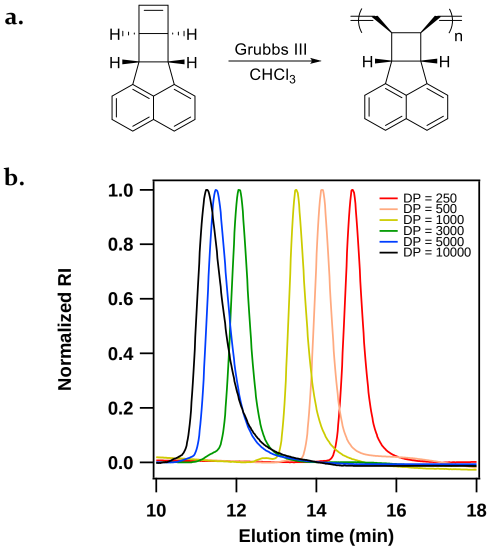


Figure 1. (a) ROMP of BCH-Naph **3** (The specified stereochemistry refers to that of the repeating unit, but not the polymer tacticity). (b) GPC traces of synthesized poly(BCH-Naph)s showing the ROMP was controlled and efficient over a wide range of DPs.

lithium-BCH-Naph was quenched by trimethyl borate to yield BCH-Naph boronic acid **5**, which could then be transformed to electron-rich dimethylamino-BCH-Naph **8** using *O*-(2,4-dinitrophenyl)hydroxyamine under conditions developed by Kürti,[33] followed by methylation. Interestingly, when using hydroxylamine-*O*-sulfonic acid for amination,[34] partial hydrogenation of the cyclobutene presumably by *in situ* generated diimide was observed (Figure S1). Similarly, 1,8-dilithium-BCH-Naph **9** could be quenched by CO_2 to generate BCH-Naph dicarboxylic acid **10** or treated with trimethyl borate to generate BCH-Naph diboronic acid **11**. **10** was then treated with alkylamine to yield an electron-poor BCH-Naph imide **12**, and **11** was oxidized by urea hydrogen peroxide[35] followed by alkylation to generate an electron-rich dialkoxy-BCH-Naph **13**. All the derivatization of BCH-Naphs was in good yields and can potentially be conducted in gram scales.

We next investigated ROMP of BCH-Naphs using the fast-initiating third generation Grubbs catalyst (**G3**). Due to the favored *exo* configuration, BCH-Naphs underwent extremely fast and efficient ROMP. Narrowly dispersed polymers up to DP of 10,000 were obtained within 10 min at room temperature with full monomer conversion under air using non-degassed reagent grade chloroform as the solvent (Figure 1). The polymer MW scaled linearly with the monomer to catalyst ratio and no chain transfer was observed, as evidenced by the unchanged GPC traces even when the polymerization was prolonged to 30 min (Figure S2). These ultrahigh DPs (> 5000) are usually challenging to achieve in controlled polymerizations, but thanks to the efficient ROMP of these very active BCH-Naph monomers, we have synthesized these polymechanophores with ultra-high DPs at ease. In the ROMP of benzoLDE, we have previously observed a small degree of cyclobutane ring-opening to generate bis-butadienyl benzene, which resulted in broadening of MW distribution when the polymerization was carried out at room temperature or prolonged.[28] In contrast, no such side reaction was observed in the ROMP of BCH-Naph. Previous study on *anti*- and *syn*-[3]-ladderdienes indicated that the latter undergoes faster isomerization to form cyclooctatetraene than the *anti*-stereoisomer upon heating,[36] which may also explain the observed higher stability of *exo*-BCH-Naph compared to our previously synthesized *endo*-benzoLDE.

We also synthesized narrowly dispersed homopolymers and random copolymers of imide- and dialkoxy-BCH-Naph **12** and **13** via their controlled ROMP under ambient conditions (Figure S3). ROMP of dimethylamino-BCH-Naph **8** gave broader MW distribution and higher-than-expected MW (Figure S3), presumably due to amine coordination with the Ru catalyst, which is known to broaden MW distribution in ROMP of norbornene-based monomers.[37]

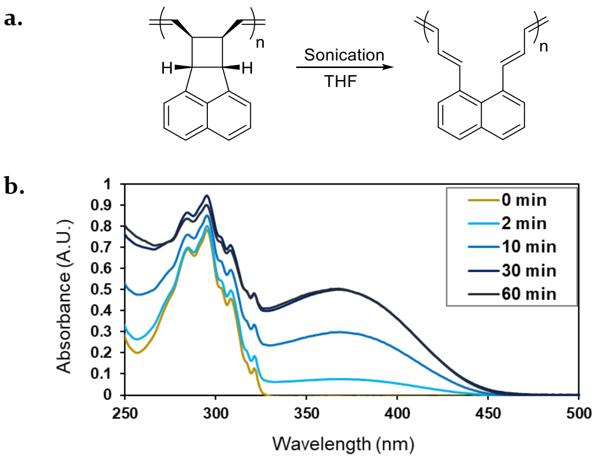


Figure 2. (a) Mechanochemical transformation of poly(BCH-Naph) to a conjugated polymer (sonication was performed using a 1 mg/mL polymer solution). (b) Changes in UV-Vis absorption spectra during the course of sonoactivation of **P3** (polymer solution was diluted in THF to a concentration of 0.02 mg/mL before UV-Vis measurement).

With all these polymers in hand, we investigated their mechanochemical activation under ultrasonication conditions. Ultrasonication is known to produce radicals by solvent sonolysis,[38-40] the sono-radicals may react with the generated unsaturated polymers, leading to a small extent of covalent crosslinking of polymer chains. Therefore, we added a common radical scavenger, butylated hydroxytoluene (BHT), at 1 mM to 1 mg/mL polymer solutions in THF before sonication. All the polymer solutions rapidly turned from nearly colorless to colored in 2 min of sonication due to the formation of conjugated polymers. All the colored solutions remained transparent during the course of sonoactivation without noticeable macroscopic aggregation. To track the changes in optical properties, aliquots were removed at regular time intervals and analyzed by UV-Vis spectroscopy. For all the polymers, an absorption peak in the visible light region emerged and continuously increased in intensity with increasing sonication time, and reached maximum after about 1 h of sonication (Figure 2 and 3). Our calculation suggested that the generated poly(*peri*-hexatrienylene naphthalene) has non-planar conformations that limit the conjugation length (Figure S16-17). The substituents on BCH-Naph affected the absorption of the mechanochemically generated polymers, leading to visually different colors from yellow to orange (Figure 3). Comparing the absorption onset wavelength of the generated polymers, the unsubstituted poly(BCH-Naph) exhibited an onset of 442 nm, and the absorption onset red-shifted to 453, 481, and 531 nm for the dialkoxy, dimethylamine, imide substituted poly(BCH-Naph)s, **P9**, **P7**, **P8**, respectively (Figure S9). Interestingly, the generated polymer from the random copolymer **P10** of electron-rich dialkoxy and electron-poor imide BCH-Naphs exhibited slightly red-shifted absorption with an onset at 556 nm, as compared to that from the homopolymers of either constituent monomers, **P8** and **P9**. This observation agrees with commonly observed bathochromic shift for donor-acceptor type of conjugated polymers due to the reduction of band gap.[41]

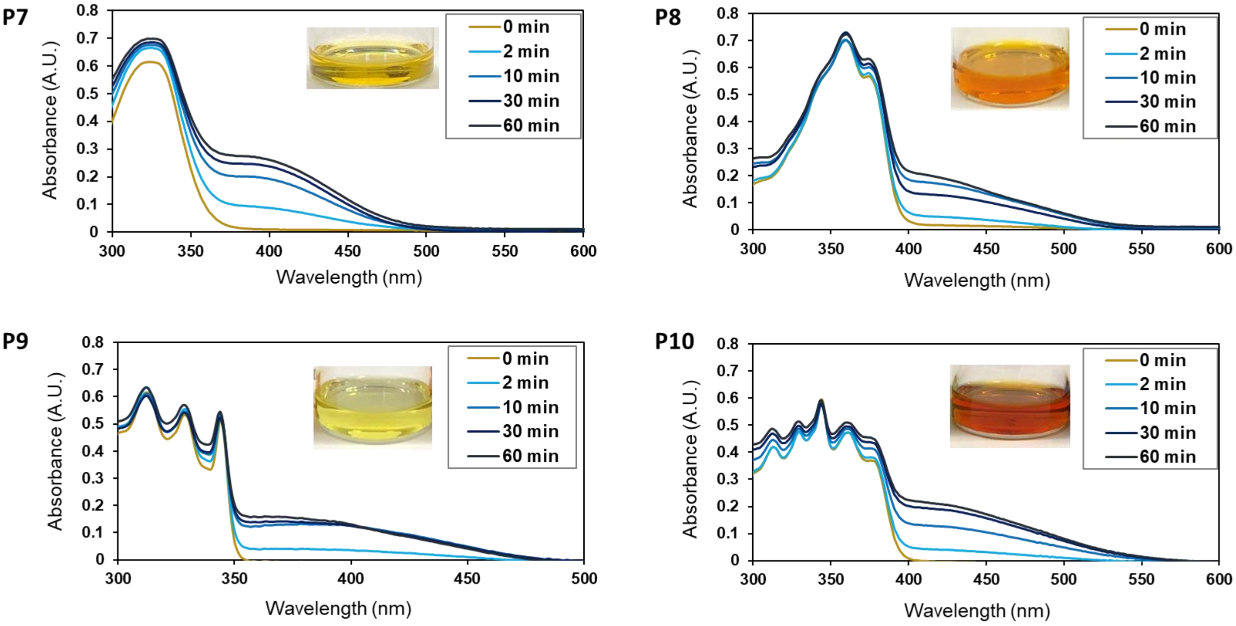


Figure 3. UV-Vis absorption spectra change during the sonication of **P7-10** (polymer solution was diluted in THF to a concentration of 0.02 mg/mL before measurement). The inset shows the photograph of activated polymer solution.

Solution ^{1}H NMR spectroscopy of the activated polymers showed increased intensity of peaks in the olefinic and aromatic region, and was used to quantify the degree of mechanoactivation. Based on the relative integration of olefinic/aromatic vs aliphatic protons, we determined the activation ratio to be 35% for **P3** after sonication for 2 h (Figure S56). This activation ratio agreed with the solid-state ^{13}C NMR spectroscopy, which revealed 39 % activation for **P3** based on the relative ratio of sp^3 and sp^2 carbon resonances (Figure S7). This activation ratio is similar to what we have previously determined for polyladderenes and poly(benzoLDE)s at the same DP (1000) and sonication time (2 h), suggesting their similar mechanochemical reactivity. Sonicating shorter polymer **P2** (DP = 500) and **P1** (DP = 250) for 2 h resulted in 19% and no activation, respectively (Figure S54-55). This strong MW dependence of activation further confirms the mechanochemical nature of the observed activation. Notably, in the absence of BHT during sonoactivation, the activated polymers could not be redissolved after precipitation, precluding their analysis by solution ^{1}H NMR spectroscopy, presumably due to partial chemical crosslinking caused by the radicals generated by ultrasonication.

The changes in polymer MW and MW distribution during sonication were monitored by GPC analysis. The refractive index (RI) traces showed a rapid decrease of the original polymer peak and appearance of broad lower MW peak(s) as expected from sonochemical chain cleavage (Figure S5). Again, the GPC analysis showed the expected chain length dependence of the rate of chain cleavage (Figure S5). Polymers that exhibit turn-on or change of fluorescence upon mechanical activation are of particular interest,[42-44] since fluorescence detection is much more sensitive than absorption detection. Interestingly, the poly(BCH-Naph imide) **P8** exhibited distinct fluorescence upon activation. Under 360 nm excitation, **P8** showed an emission peak around 467 nm, but after 60 min of sonication, a broad emissions peak emerged around 554 nm, changing the emission color from blue to yellow (Figure 4a). Further, a clear fluorescence turn-on can be achieved when these two solutions were excited at 500 nm, a wavelength that only the activated polymer absorbed (Figure S10). The turn-on fluorescence is a useful feature for sensitive detection of stress.

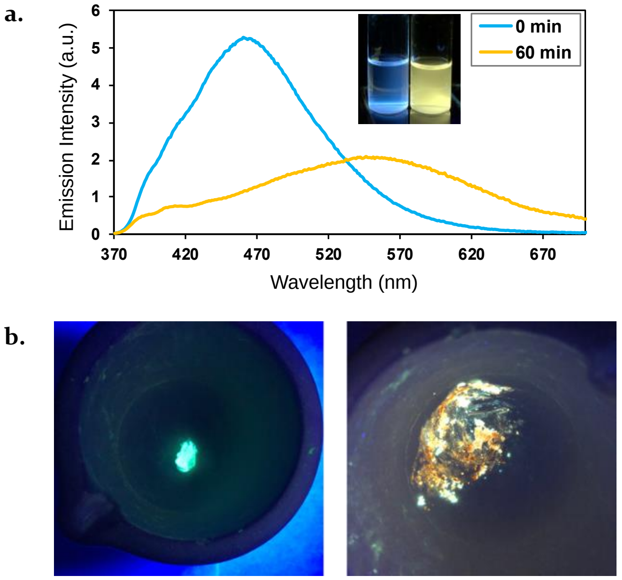


Figure 4. (a) Change in fluorescence spectrum (excitation at 360 nm) for **P8** before and after 60 min of sonication. The inset shows photographs of the two solutions under 365 nm irradiation. (b) Solid-state mechanoactivation of **P8** by grinding. Photographs were taken under 365 nm UV irradiation.

Ultrasonication has been the predominant activation method for polymer mechanochemistry and has allowed the exciting advancement of mechanochemistry in the past decade. But strong ultrasound is not commonly used in most polymer applications. Polymer behavior in common flow fields has been a topic of interest for many technical applications of polymers for over 80 years.[45] However, more practical elongational flows other than strong ultrasound are typically unable to activate mechanophores, presumably due to the challenge to synthesize ultrahigh molecular weight mechanophore-containing polymers that can accumulate enough force to activate mechanophores as pointed out by Moore and coworkers.[40] To our delight, for the ultrahigh molecular weight poly(BCH-Naph) **P6** (M_n = 1.7 MDa, DP = 10,000), we observed its mechanoactivation by simply rapidly stirring the dilute polymer solution (5 mg/mL in THF stirring at 1500 rpm)! The polymer solution turned from colorless and clear to yellow and slightly opaque after stirring for 30 h under nitrogen (Figure 5a). UV-Vis spectroscopy of the stirred solutions showed the same absorption profile as observed from sonoactivation (Figure 5b). The activation ratio after 30 h of stirring was estimated to be about 6% based on the absorption intensity of activated polymer at 368 nm, taking into account of the slow degradation of the generated conjugated polymer over this period of time (Figure S14). In comparison, stirring the same polymer solution at slower stirring speed (500 rpm) or stirring a lower molecular weight polymer **P3** (DP = 1000) under the same speed (1500 rpm) did not result in any noticeable

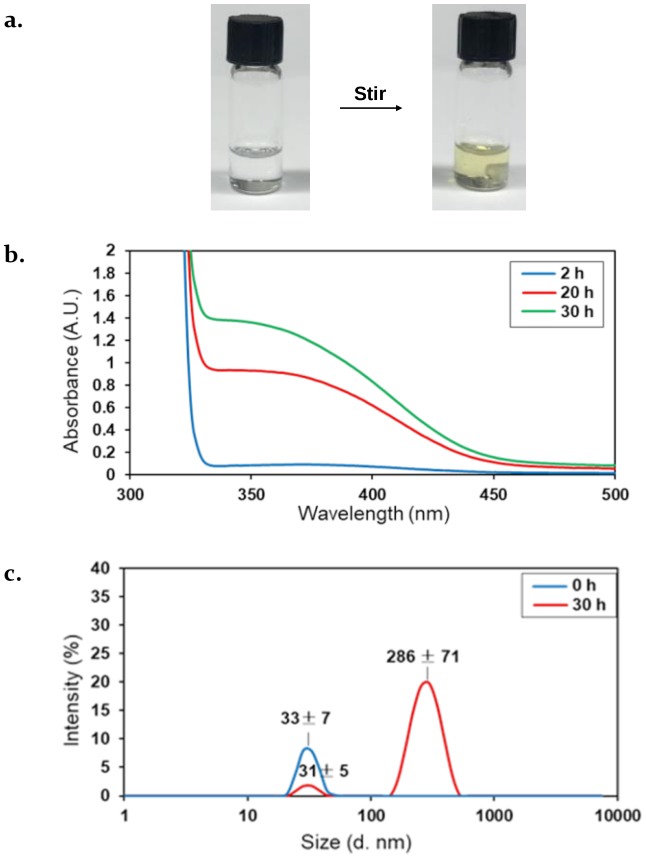


Figure 5. Mechanoactivation of **P6** upon rapid stirring of its solution (5 mg/mL) at 1500 rpm. (a) Photographs of **P6** solution before and after stirring for 30 h. (b) UV-Vis absorption spectra of **P6** solution at different times of stirring (polymer was diluted in THF to a concentration of 0.5 mg/mL to take the absorption measurements). (c) Dynamic light scattering analysis of **P6** solution, showing the formation of large aggregates after stirring.

change of solutions (Figure S11-12), confirming the mechanochemical nature of the observed stirring activation. Dynamic light scattering measurements of the stirred solution of **P6** indicated the formation of large aggregates with D_h peaked around 286 nm (Figure 5c). The stir-activated sample could not be analyzed by GPC because the formed large aggregates prevented polymer solution from being filtered. In contrast, when the same polymer solution was activated using ultrasonication, no such large aggregates were observed and the polymer MWs continued to decrease during the course of sonoactivation (Figure S5), due to the inevitable rapid chain scission under ultrasonic conditions. The remarkably high reactivity of ROMP of BCH-Naphs enabled the synthesis of ultrahigh molecular weight polymechanophores that can experience high enough force for mechanoactivation in a relatively weak elongational flow. This surprising observation opens exciting opportunities to manipulate the rheology of solutions or viscous media using shear-responsive polymechanophores under different types of shear flow.[45-46]

We were also able to achieve mechanoactivation in solid state using uncrosslinked poly(BCH-Naph)s. Grinding poly(BCH-Naph) **P3** (DP = 1000) in a mortar turned the white polymer to strongly colored within tens of seconds (Figure S13). Interestingly, the activated polymer was unable to be redissolved in THF or $CHCl_3$ even at higher temperatures, despite the high solubility of the precursor polymer. The insolubility of activated polymer may be attributed to the aggregation of activated domains, which served as strong physical crosslinks. Solid-state activation of poly(BCH-Naph imide) **P8** (DP = 1000) was also achieved through grinding, and the significant change in polymer fluorescence upon activation allows clear visualization of the activation process (Figure 4b). In this preliminary study, although we could not quantify the degree of activation due to the insolubility of the activated polymers, we demonstrated solid-state activation for these polymechanophores with ladder-type repeat units even in their glassy state. We plan to tune the physical properties of these polymechanophores via different substituents and crosslink them in different ways to systematically investigate their solid-state mechanical response in the future.

CONCLUSIONS

We report a new generation of ladder-type mechanophore monomers, BCH-Naphs, with significant advantages over our previous systems. BCH-Naphs with a range of electron-rich or electron-poor substituents can be synthesized in multi-gram quantities using cheap, commercially available chemicals and allows tuning of the optoelectronic and physical properties of mechanically generated polymers. Due to the favorable *exo* configuration, BCH-Naphs and its derivatives can undergo efficient ROMP to yield ultrahigh MW polymechanophores with controlled MWs and low dispersity. We demonstrated mechanoactivation of the synthesized poly(BCH-Naph)s using ultrasonication, grinding, and even simple stirring of the dilute solutions, leading to changes in absorption and fluorescence as well as microscopic aggregation. Poly(BCH-Naph)s represent an attractive polymechanophore system to explore multifaceted mechanical response in different physical states, owing to the synthetic scalability, functional diversity, and efficient and controlled polymerization of BCH-Naphs, as well as facile mechanoactivation of poly(BCH-Naph)s.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:
Detailed descriptions of synthetic procedures, ^1H and ^{13}C NMR spectra of new compounds and polymers, additional UV-Vis spectra, fluorescence spectra, GPC analysis, and crystallographic data for BCH-Naph **3**.

AUTHOR INFORMATION

Corresponding Author

* yanx@stanford.edu

ORCID

Jinghui Yang: 0000-0002-6957-6265
Matias Horst: 0000-0002-9794-5355
Lynette Cegelski: 0000-0002-0978-1814
Yan Xia: 0000-0002-5298-748X

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was supported by the U.S. Army Research Office under grant number W911NF-15-1-0525. J. Y. is supported by a Stanford Graduate Fellowship. M. H. is supported by a National Defense Science and Engineering Graduate Fellowship. S.W. is supported by an NSF Predoctoral Fellowship. L.C. acknowledges support from the NSF CAREER/PECASE Award 1453247. Single-crystal X-ray diffraction experiments were performed at beamline 12.2.1 at the Advanced Light Source (ALS). The ALS is supported by the Director, Office of Science, Office of Basic Energy Science, of the U.S. Department of Energy under contract no. DE-AC02-05CH11231. GC-MS data were collected at the Vincent Coates Foundation Mass Spectrometry Laboratory of Stanford University. Computation was performed on the Sherlock cluster at the Stanford Research Computing Center.

REFERENCES

(1) Davis, D. A.; Hamilton, A.; Yang, J.; Cremar, L. D.; Van Gough, D.; Potisek, S. L.; Ong, M. T.; Braun, P. V.; Martinez, T. J.; White, S. R.; Moore, J. S.; Sottos, N. R. Force-induced activation of covalent bonds in mechanoresponsive polymeric materials. *Nature* **2009**, *459*, 68-72.
(2) Robb, M. J.; Kim, T. A.; Halmes, A. J.; White, S. R.; Sottos, N. R.; Moore, J. S. Regioisomer-Specific Mechanochromism of Naphthopyran in Polymeric Materials. *J. Am. Chem. Soc.* **2016**, *138*, 12328-12331.

(3) Imato, K.; Kanehara, T.; Nojima, S.; Ohishi, T.; Higaki, Y.; Takahara, A.; Otsuka, H. Repeatable mechanochemical activation of dynamic covalent bonds in thermoplastic elastomers. *Chem. Commun.* **2016**, 52, 10482-10485.

(4) Chen, Y.; Spiering, A. J.; Karthikeyan, S.; Peters, G. W.; Meijer, E. W.; Sijbesma, R. P. Mechanically induced chemiluminescence from polymers incorporating a 1,2-dioxetane unit in the main chain. *Nat. Chem.* **2012**, *4*, 559-562.

(5) Göstl, R.; Sijbesma, R. P. π-Extended Anthracenes as Sensitive Probes for Mechanical Stress. *Chem. Sci.* **2016**, *7*, 370-375.

(6) Sagara, Y.; Karman, M.; Seki, A.; Pannipara, M.; Tamaoki, N.; Weder, C. Rotaxane-Based Mechanophores Enable Polymers with Mechanically Switchable White Photoluminescence. *ACS Cent. Sci.* **2019**, 5, 874-881.

(7) Filonenko, G. A.; Sun, D.; Weber, M.; Müller, C.; Pidko, E. A. Multicolor Organometallic Mechanophores for Polymer Imaging Driven by Exciplex Level Interactions. *J. Am. Chem. Soc.* **2019**, *141*, 9687-9692.

(8) Ramirez, A. L.; Kean, Z. S.; Orlicki, J. A.; Champhekar, M.; Elsakr, S. M.; Krause, W. E.; Craig, S. L. Mechanochemical strengthening of a synthetic polymer in response to typically destructive shear forces. *Nat. Chem.* **2013**, 5, 757-761.

(9) Wang, J.; Piskun, I.; Craig, S. L. Mechanochemical Strengthening of a Multi-mechanophore Benzocyclobutene Polymer. *ACS Macro Lett.* **2015**, *4*, 834-837.

(10) Diesendruck, C. E.; Peterson, G. I.; Kulik, H. J.; Kaitz, J. A.; Mar, B. D.; May, P. A.; White, S. R.; Martinez, T. J.; Boydston, A. J.; Moore, J. S. Mechanically triggered heterolytic unzipping of a low-ceiling-temperature polymer. *Nat. Chem.* **2014**, *6*, 623-628.

(11) Hsu, T.; Zhou, J.; Su, H.; Schrage, B. R.; Ziegler, C. J.; Wang, J. A Polymer with "Locked" Degradability: Superior Backbone Stability and Accessible Degradability Enabled by Mechanophore Installation. *J. Am. Chem. Soc.* **2020**, *142*, 2100-2104.

(12) Lin, Y.; Kouznetsova, T. B.; Craig, S. L. Mechanically Gated Degradable Polymers. *J. Am. Chem. Soc.* **2020**, *142*, 2105-2109.

(13) Diesendruck, C. E.; Steinberg, B. D.; Sugai, N.; Silberstein, M. N.; Sottos, N. R.; White, S. R.; Braun, P. V.; Moore, J. S. Proton-coupled mechanochemical transduction: a mechanogenerated acid. *J. Am. Chem. Soc.* **2012**, *134*, 12446-12449.

(14) Larsen, M. B.; Boydston, A. J. "Flex-activated" mechanophores: using polymer mechanochemistry to direct bond bending activation. *J. Am. Chem. Soc.* **2013**, *135*, 8189-8192.

(15) Hu, X.; Zeng, T.; Husic, C. C.; Robb, M. J. Mechanically Triggered Small Molecule Release from a Masked Furfuryl Carbonate. *J. Am. Chem. Soc.* **2019**, *141*, 15018-15023.

(16) Piermattei, A.; Karthikeyan, S.; Sijbesma, R. P. Activating catalysts with mechanical force. *Nat. Chem.* **2009**, *1*, 133-137.

(17) Hickenboth, C. R.; Moore, J. S.; White, S. R.; Sottos, N. R.; Baudry, J.; Wilson, S. R. Biasing reaction pathways with mechanical force. *Nature* **2007**, *446*, 423-427.

(18) Akbulatov, S.; Tian, Y.; Huang, Z.; Kucharski, T. J.; Yang, Q.; Boulatov, R. Experimentally Realized Mechanochemitry Distinct from Force-accelerated Scission of Loaded Bonds. *Science* **2017**, *357*, 299-303.

(19) Lenhardt, J. M.; Ong, M. T.; Choe, R.; Evenhuis, C. R.; Martinez, T. J.; Craig, S. L. Trapping a Diradical Transition State by Mechanochemical Polymer Extension. *Science* **2010**, *329*, 1057-1060.

(20) Chen, Z.; Zhu, X.; Yang, J.; Mercer, J. A. M.; Burns, N. Z.; Martinez, T. J.; Xia, Y. The Cascade Unzipping of Ladderane Reveals Dynamic Effects in Mechanochemistry. *Nat. Chem.* **2020**, *12*, 302-309.

(21) Li, J.; Nagamani, C.; Moore, J. S. Polymer mechanochemistry: from destructive to productive. *Acc. Chem. Res.* **2015**, *48*, 2181-2190.

(22) Brown, C. L.; Craig, S. L. Molecular engineering of mechanophore activity for stress-responsive polymeric materials. *Chem. Sci.* **2015**, *6*, 2158-2165.

(23) Boulatov, R. *Polymer Mechanochemistry*; Springer: Berlin, 2015.

(24) Larsen, M. B.; Boydston, A. J. Investigations in Fundamental and Applied Polymer Mechanochemistry. *Macromol. Chem. Phys.* **2016**, *217*, 354-364.

(25) Bowser, B. H.; Craig, S. L. Empowering mechanochemistry with multi-mechanophore polymer architectures. *Poly. Chem.* **2018**, *9*, 3583-3593.

(26) Chen, Z.; Mercer, J. A. M.; Zhu, X.; Romaniuk, J. A. H.; Pfattner, R.; Cegelski, L.; Martinez, T. J.; Burns, N. Z.; Xia, Y. Mechanochemical unzipping of insulating polyladderene to semiconducting polyacetylene. *Science* **2017**, *357*, 475-479.

(27) Su, J. K.; Feist, J. D.; Yang, J.; Mercer, J. A. M.; Romaniuk, J. A. H.; Chen, Z.; Cegelski, L.; Burns, N. Z.; Xia, Y. Synthesis and Mechanochemical Activation of Ladderene–Norbornene Block Copolymers. *J. Am. Chem. Soc.* **2018**, *140*, 12388-12391.

(28) Yang, J.; Horst, M.; Romaniuk, J. A. H.; Jin, Z.; Cegelski, L.; Xia, Y. Benzoladderene Mechanophores: Synthesis, Polymerization, and Mechanochemical Transformation. *J. Am. Chem. Soc.* **2019**, *141*, 6479-6483.

(29) Shields, J. E.; Gavrilovic, D.; Kopecky, J.; Hartmann, W.; Heine, H. G. Photochemical cycloadditions of maleic anhydride and some derivatives to acenaphthylene. New route to pleiadienes. *J. Org. Chem.* **1974**, *39*, 515-520.

(30) Mercer, J. A. M.; Cohen, C. M.; Shuken, S. R.; Wagner, A. M.; Smith, M. W.; Moss, F. R.; Smith, M. D.; Vahala, R.; Gonzalez-Martinez, A.; Boxer, S. G.; Burns, N. Z. Chemical Synthesis and Self-Assembly of a Ladderane Phospholipid. *J. Am. Chem. Soc.* **2016**, *138*, 15845-15848.

(31) Bishop, K. C. Transition metal catalyzed rearrangements of small ring organic molecules. *Chem. Rev.* **1976**, *76*, 461-486.

(32) Rappoport, Z.; Marek, I. *The Chemistry of Organolithium Compounds*; John Wiley & Sons: Chichester, U.K., 2006.

(33) Zhu, C.; Li, G.; Ess, D. H.; Falck, J. R.; Kürti, L. Elusive Metal-Free Primary Amination of Arylboronic Acids: Synthetic Studies and Mechanism by Density Functional Theory. *J. Am. Chem. Soc.* **2012**, *134*, 18253-18256.

(34) Voth, S.; Hollett, J. W.; McCubbin, J. A. Transition-Metal-Free Access to Primary Anilines from Boronic Acids and a Common $^{+}NH_2$ Equivalent. *J. Org. Chem.* **2015**, *80*, 2545-2553.

(35) Gupta, S.; Chaudhary, P.; Srivastava, V.; Kandasamy, J. A chemoselective ipso-hydroxylation of arylboronic acids using urea-hydrogen peroxide under catalyst free condition. *Tetrahedron Lett.* **2016**, *57*, 2506-2510.

(36) Case, R. S.; Dewar, M. J. S.; Kirschner, S.; Pettit, R.; Slegier, W. Possible intervention of triplet states in thermal reactions of hydrocarbons. Rearrangements of cyclobutadiene dimers and analogous compounds. *J. Am. Chem. Soc.* **1974**, *96*, 7581-7582.

(37) Sutthasupa, S.; Sanda, F.; Masuda, T. ROMP of Norbornene Monomers Carrying Nonprotected Amino Groups with Ruthenium Catalyst. *Macromolecules* **2009**, *42*, 1519-1525.

(38) Riesz, P.; Berdahl, D.; Christman, C. L. Free Radical Generation by Ultrasound in Aqueous and Nonaqueous Solutions. *Environ. Health Perspect.* **1985**, *64*, 233-252.

(39) Suslick, K. S. Sonochemistry. *Science* **1990**, *247*, 1439-1445.

(40) Caruso, M. M.; Davis, D. A.; Shen, Q.; Odom, S. A.; Sottos, N. R.; White, S. R.; Moore, J. S. Mechanically-Induced Chemical Changes in Polymeric Materials. *Chem. Rev.* **2009**, *109*, 5755-5798.

(41) van Mullekom, H. A. M.; Vekemans, J. A. J. M.; Havinga, E. E.; Meijer, E. W. Developments in the chemistry and band gap engineering of donor–acceptor substituted conjugated polymers. *Mat. Sci. Eng. R Rep.* **2001**, *32*, 1-40.

(42) Ducrot, E.; Chen, Y.; Bulters, M.; Sijbesma, R. P.; Creton, C. Toughening Elastomers with Sacrificial Bonds and Watching Them Break. *Science* **2014**, *344*, 186-189.

(43) Sagara, Y.; Karman, M.; Verde-Sesto, E.; Matsuo, K.; Kim, Y.; Tamaoki, N.; Weder, C. Rotaxanes as Mechanochromic Fluorescent Force Transducers in Polymers. *J. Am. Chem. Soc.* **2018**, *140*, 1584-1587.

(44) Kato, S.; Ishizuki, K.; Aoki, D.; Goseki, R.; Otsuka, H. Freezing-Induced Mechanoluminescence of Polymer Gels. *ACS Macro Lett.* **2018**, *7*, 1087-1091.

(45) Nguyen, T. Q.; Kausch, H. H. *Dynamics of Flexible Polymer Chains in Elongational Flow: Theory and Experiment*; Springer: Berlin, 1999.

(46) Fox, N. W.; Rognin, E.; Baumann, C.; Aljohani, T. A.; Göstl, R.; Daly, R. Going with the Flow: Tunable Flow-Induced Polymer Mechanochemistry. *Adv. Funct. Mater.* **2020**, *30*, 2002372.

TOC Graphic