ACS Macro Letters

Letter

pubs.acs.org/macroletters

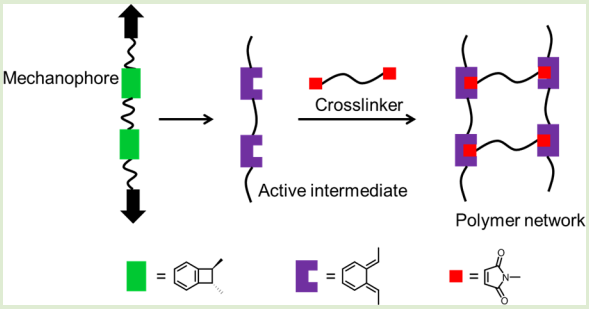
Mechanochemical Strengthening of a Multi-mechanophore Benzocyclobutene Polymer

Junpeng Wang, Ilya Piskun, and Stephen L. Craig*

Department of Chemistry, Duke University, Durham, North Carolina 27708, United States

Supporting Information

ABSTRACT: The mechanical stresses that materials experience during use can lead to aging and failure. Recent developments in covalent mechanochemistry have provided a mechanism by which those stresses can be channeled into constructive, rather than destructive, responses, including strengthening in materials. Here, the synthesis and mechanical response of a polymer containing multiple benzocyclobutene (BCB) mechanophores along its backbone are reported. When solutions of the BCB polymer were exposed to the normally destructive elongational flow forces generated by pulsed ultrasonication, the number of intermolecular bond-forming reactions was greater than the number of bond-breaking reactions, leading to a net increase in polymer molecular weight. The molecular weight increase could be turned into gelation by introducing a bismaleimide cross-linker that reacts with the *ortho*-quinodimethide intermediate generated by mechanically assisted ring opening of the BCB mechanophores and using polymer concentrations in excess of the critical overlap concentration. Unlike a previous mechanically induced gelation of a mechanophore-based polymer, the BCB cross-linking requires no ionic components and represents an attractive, second platform for stress-strengthening materials.



The inevitable stress that almost all materials experience during use leads in many cases to bond breakage, materials aging, and failure, as is reflected in both polymer solutions[1] and solid state polymers.[2] To solve this problem, biological materials have evolved to have the ability to remodel and become stronger in response to otherwise destructive forces.[3,4] This form of mechanical adaptation has provided significant inspiration to current synthetic polymer chemistry efforts. Our group has recently demonstrated that the activation of multiple *gem*-dibromocyclopropane (*g*DBC) mechanophores[5] embedded along a polybutadiene backbone turns otherwise destructive chemical responses into constructive responses.[6] When the polymer was exposed to large forces, through either pulsed ultrasonication of polymer solutions or the extrusion of bulk materials, the *g*DBCs undergo electrocyclic ring-opening reactions to form 2,3-dibromoalkenes that react intermolecularly with carboxylate nucleophiles. The number of intermolecular bond-forming reactions exceeds the number of bond-breaking reactions and leads to a cross-linked polymer network.[6] While the *g*DBC system represents an important first example of mechanophore-based self-strengthening, the ultimate utility of the approach will depend on the ability to create mechanophore-based systems that match the demands of a particular application. To that end, we sought to develop multi-mechanophore polymers that might overcome the relatively low reactivity of the 2,3-dibromoalkene,[6] the irreversibility of *g*DBC ring opening in the absence of cross-linking, and the presence of ionic reactants.

Because of the substantial recent activity in the realm of covalent polymer mechanochemistry,[7−9] and especially the exploration of mechanophore design and synthesis,[5,10−16] there already exists a library of viable candidates for this form of mechanochemical strengthening. We chose to employ the mechanophore benzocyclobutene (BCB), which Moore and coworkers demonstrated can be mechanically activated to an *ortho*-quinodimethide (*o*QDM) that reacts intermolecularly in the absence of chain scission[5] and which inspired much of our previous approach in the *g*DBC system. The highly reactive *o*QDM intermediate participates in Diels−Alder reactions and [4 + 4] dimerizations[17] and can be accessed from BCB at high temperatures. Because of this reactivity, BCB has a distinguished history of use in a variety of roles in the synthesis and fabrication of polymeric materials,[18] including as an end-capping group,[19,20] a monomer for Diels−Alder polymerization,[21−24] and a latent cross-linker.[25−28] The high reactivity of *o*QDM and the reversibility of the mechanophore make BCB an excellent candidate for developing mechanochemically strengthened polymers, a fact that undoubtedly motivated the earlier work by Moore. While a single BCB incorporated along a polymer backbone was able to activate and react intermolecularly without chain scission, however, extension to

Received: July 1, 2015
Accepted: July 17, 2015
Published: July 20, 2015

DOI: 10.1021/acsmacrolett.5b00440
ACS Macro Lett. 2015, 4, 834−837

multi-mechanophore polymers and their subsequent cross-linking has not been reported.

Here we report that multi-BCB polymer **1** (Figure 1a), synthesized as reported previously,[29] can function as an

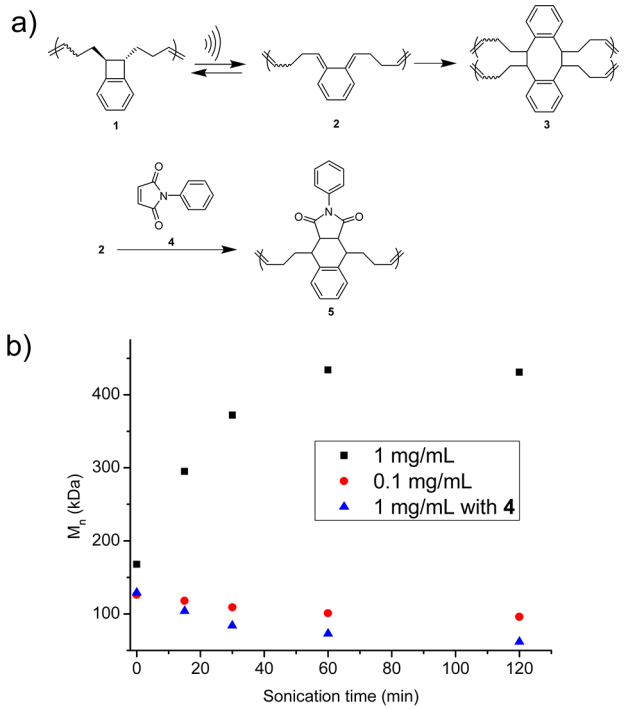


Figure 1. (a) Mechanochemical activation of poly(BCB), **1**, generates *o*QDM intermediates (**2**), which either close back to **1** or cross-link through multiple avenues. (b) Molecular weights of the polymer with time as it is sonicated at concentrations of 1 mg/mL (black squares), 0.1 mg/mL (red circles), and 1 mg/mL with **4** (blue triangles).

mechanochemical strengthening system. When a 1 mg/mL THF solution of polymer **1** is subjected to pulsed ultrasonication (30% amplitude, 11.9 W/cm^2; conditions we have employed previously[30]), the behavior differs from that of previously reported multi-mechanophore polymers[11,14,15,30] in that the molecular weight of the polymer increased as it was sonicated (Figure 1b). The increase in molecular weight suggests a reaction between the *o*QDMs on different polymer chains (Figure 1a). Support for intermolecular cross-linking is found in sonication of **1** at a lower concentration (0.1 mg/mL) and led to a decrease in molecular weight (Figure 1b), consistent with the importance of interchain reactions to the molecular weight increase. Further, the addition of *o*QDM trap *N*-phenylmaleimide **4** suppressed the cross-linking of **1**, even at the higher concentration of 1 mg/mL.

The mechanical activation of BCB has been demonstrated previously,[5,29] and support for mechanical formation of *o*QDM here was found by sonicating solutions of two different molecular weights of polymer **1** (95 kDa and 16 kDa) in the presence of *N*-pyrenemaleimide **6** (Figure 2a).[5] The UV intensity of the resulting polymer **7** was used as an indication of *o*QDM formation and reaction. As expected for a mechanochemical process, BCB activation depends strongly on molecular weight;[7] the sonicated 95 kDa polymer **1** was significantly more UV active than the 16 kDa polymer (Figure 2b) under identical conditions.

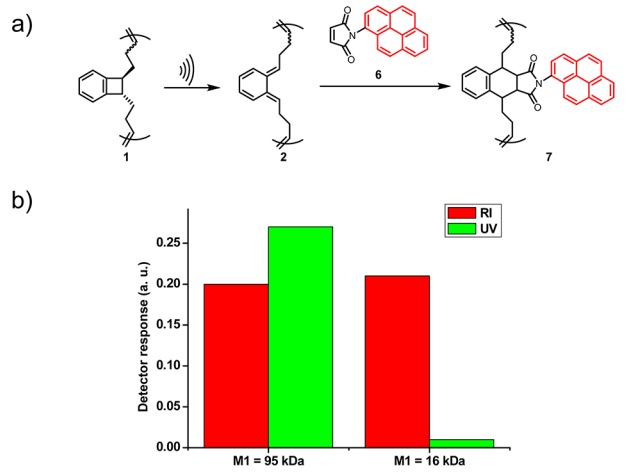


Figure 2. Experimental characterization of the mechanical reactivity of BCB-containing polymer **1**. (a) BCB is mechanically activated to *ortho*-quinodimethide to form polymer *o*QDM, which reacts with *N*-pyrene-maleimide **6** via a Diels–Alder reaction to form UV-active adduct **7** (concentration of the polymer: 1 mg/mL; concentration of **6**: 5 mM.) (b) The intensity of the refractive index (red) and UV (green) of **7** when 95 kDa (left) and 16 kDa (right) of **1** was sonicated.

Given the observed molecular weight increases, we wondered whether polymer **1** might gel if sonicated above its critical overlap concentration (8.4–17.6 mg/mL for 16–95 kDa **1**, as calculated from radii of gyration),[6,31] but no gelation was observed at initial concentrations of 25 mg/mL. When the same concentration of polymer was sonicated together with bismaleimide cross-linker **8** (14 mM, Figure 3a), however, the solution gelled *in situ* during the sonication (Figure 4). The gelation of **1** + **8**, rather than **1** alone, is attributed to two possible contributions. First, the rate of reaction between BCB polymers is not as high as for reaction with maleimide. When the polymer is sonicated at 1 mg/mL with non-cross-linking maleimide, the intermolecular reaction was suppressed, indicating that the reaction of *o*QDM with maleimide is faster than the intermolecular reaction between two *o*QDMs. Because gelation is always in competition with scission, the faster reaction might be necessary for gelation. Second, **8** is less soluble than **1** (faint cloudiness in the initial solution), and it is possible that aggregation helps accelerate the gelation and/or retard the chain scission processes. Nonetheless, the gelation response is much faster than observed in the previous *g*DBC system (several hours after sonication ended).[6] Although **8** is poorly soluble, the insoluble product **9** is confirmed as a cross-linked gel first by its insolubility in a range of common organic solvents (see Supporting Information). Second, when **9** was extensively washed with methanol to remove unreacted small molecules, characterization by FTIR (Figure 3b) was consistent with covalent incorporation of the bismaleimide into the polymer (the appearance of C=O stretch at 1700 cm^{-1}, the disappearance of maleimide C–N–C stretch at 1141 cm^{-1}, and the appearance of succinimide C–N–C stretch at 1180 cm^{-1}).[32] Third, frequency sweep experiments are also consistent with the formation of a covalent polymer network; the storage modulus increases by over 3 orders of magnitude upon gelation, in substantial excess of the loss modulus (see Supporting Information).

The BCB polymer **1** therefore represents only the second multi-mechanophore, self-strengthening polymer yet reported.

DOI: 10.1021/acsmacrolett.5b00440
ACS Macro Lett. 2015, 4, 834–837

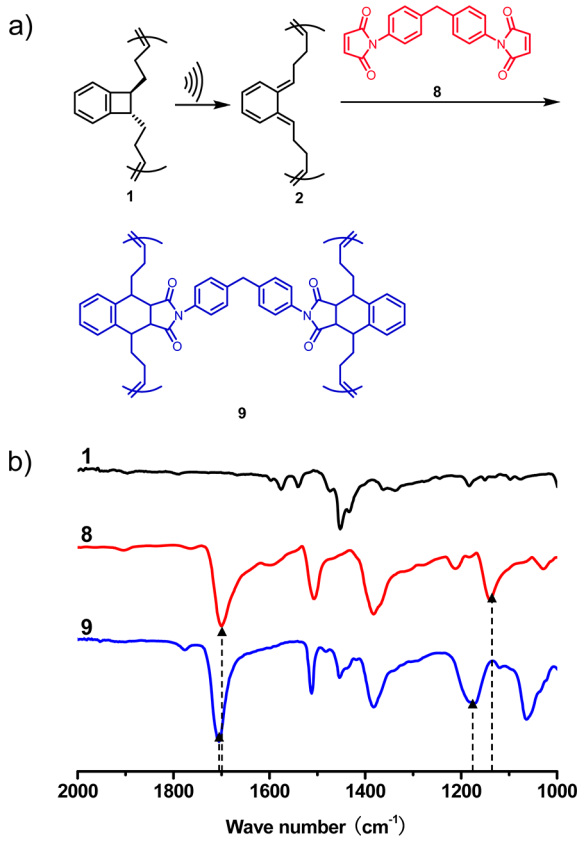


Figure 3. Mechanochemical strengthening process and characterization of benzocyclobutene (BCB) polymer. (a) When **1** is sonicated, BCB is mechanically activated to *o*QDM, which reacts with bismaleimide **8** via a Diels–Alder reaction to form polymer network **9**. (b) FTIR spectra overlay of **1**, **8**, and **9**. The dashed lines designate the C–N–C stretch peaks of maleimide in **8** at 1141 cm^{-1} and succinimide in **9** at 1180 cm^{-1}.

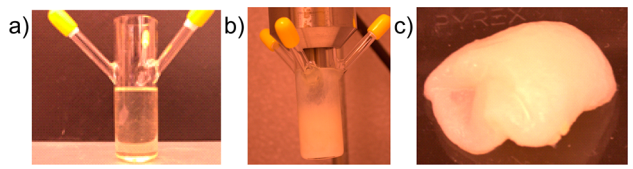


Figure 4. Solution of 25 mg/mL **1** + **8** before (a) and after (b) sonication and following removal from the Suslick vessel (c).

Relative to the initial *g*DBC system, **1** exhibits more efficient *in situ* mechanochemical strengthening as a consequence of the highly reactive *o*QDM that is generated mechanochemically. In addition, unlike *g*DBC, when the force dissipates, unreacted *o*QDM undergoes ring closure to re-form BCB (Figure 1a), and its mechanical activation therefore represents a potentially less perturbative influence on initial material properties compared to the *g*DBC system. Finally, we note that the reactivity reported here, whether simply between BCB polymers or with *N*-substituted maleimides, does not involve ionic species as was previously required for the *g*DBC—a factor that has substantial advantages in a range of potential polymer applications. In fact, BCB itself is already used as a latent cross-linker,[25−28] and the results presented here lend additional support to the idea of BCB acting as a useful stress-triggered agent for polymer property enhancement. Such developments in mechanochemically strengthening materials complement, and might be combined with, other applications of covalent polymer mechanochemistry, including those in stress-sensing,[10,13,33−35] catalysis,[12,36,37] small molecule and acid release,[16,34,38] and soft devices.[39]

■ ASSOCIATED CONTENT

Supporting Information

Sonication experiments; IR and GPC-MALS characterization; rheology (PDF). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00440.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: stephen.craig@duke.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This material is based on work supported by the Army Research Office and Army Research Lab under grant W911NF-15-0143, with partial support for I.P. from the ACC and the National Science Foundation under Grant No. DMR-1121107 as part of the NSF Triangle MRSEC REU program of Duke University, UNC, and NC State. We thank J. Moore for inspiring conversations and Z. Kean for technical assistance with the rheological measurements.

■ REFERENCES

(1) Odell, J. A.; Keller, A. *J. Polym. Sci., Part B: Polym. Phys.* **1986**, *24*, 1889.
(2) Zhurkov, S. N.; Korsukov, V. E. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 385.
(3) Watson, G. M.; Mire, P. *J. Neurocytol.* **2001**, *30*, 895.
(4) Keckes, J.; Burgert, I.; Fruhmann, K.; Muller, M.; Kolln, K.; Hamilton, M.; Burghammer, M.; Roth, S. V.; Stanzl-Tschegg, S.; Fratzl, P. *Nat. Mater.* **2003**, *2*, 810.
(5) Hickenboth, C. R.; Moore, J. S.; White, S. R.; Sottos, N. R.; Baudry, J.; Wilson, S. R. *Nature* **2007**, *446*, 423.
(6) Ramirez, A. L. B.; Kean, Z. S.; Orlicki, J. A.; Champhekar, M.; Elsakr, S. M.; Krause, W. E.; Craig, S. L. *Nat. Chem.* **2013**, *5*, 757.
(7) Caruso, M. M.; Davis, D. A.; Shen, Q.; Odom, S. A.; Sottos, N. R.; White, S. R.; Moore, J. S. *Chem. Rev.* **2009**, *109*, 5755.
(8) Kean, Z. S.; Craig, S. L. *Polymer* **2012**, *53*, 1035.
(9) Ribas-Arino, J.; Marx, D. *Chem. Rev.* **2012**, *112*, 5412.
(10) 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. *Nature* **2009**, *459*, 68.
(11) Lenhardt, J. M.; Black, A. L.; Craig, S. L. *J. Am. Chem. Soc.* **2009**, *131*, 10818.
(12) Piermattei, A.; Karthikeyan, S.; Sijbesma, R. P. *Nat. Chem.* **2009**, *1*, 133.
(13) Chen, Y.; Spiering, A. J. H.; Karthikeyan, S.; Peters, G. W. M.; Meijer, E. W.; Sijbesma, R. P. *Nat. Chem.* **2012**, *4*, 559.
(14) Klukovich, H. M.; Kean, Z. S.; Ramirez, A. L. B.; Lenhardt, J. M.; Lin, J.; Hu, X.; Craig, S. L. *J. Am. Chem. Soc.* **2012**, *134*, 9577.
(15) Kean, Z. S.; Niu, Z.; Hewage, G. B.; Rheingold, A. L.; Craig, S. L. *J. Am. Chem. Soc.* **2013**, *135*, 13598.
(16) Larsen, M. B.; Boydston, A. J. *J. Am. Chem. Soc.* **2013**, *135*, 8189.
(17) Klundt, I. L. *Chem. Rev.* **1970**, *70*, 471.
(18) Kirchhoff, R. A.; Bruza, K.; Carriere, C.; Rondan, N. *Makromol. Chem., Macromol. Symp.* **1992**, *54−55*, 531.
(19) Tan, L.-S.; Arnold, F. E. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 1819.
(20) Upshaw, T. A.; Stille, J. K.; Droske, J. P. *Macromolecules* **1991**, *24*, 2143.

DOI: 10.1021/acsmacrolett.5b00440
ACS Macro Lett. 2015, 4, 834−837

(21) Tan, L.-S.; Arnold, F. E. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 3159.
(22) Tan, L.-S.; Arnold, F. E.; Soloski, E. J. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 3103.
(23) Hahn, S. F.; Martin, S. J.; McKelvy, M. L. *Macromolecules* **1992**, *25*, 1539.
(24) Hahn, S. F.; Martin, S. J.; McKelvy, M. L.; Patrick, D. W. *Macromolecules* **1993**, *26*, 3870.
(25) Markoski, L. J.; Walker, K. A.; Deeter, G. A.; Spilman, G. E.; Martin, D. C.; Moore, J. S. *Chem. Mater.* **1993**, *5*, 248.
(26) Walker, K. A.; Markoski, L. J.; Moore, J. S. *Macromolecules* **1993**, *26*, 3713.
(27) Blomberg, S.; Ostberg, S.; Harth, E.; Bosman, A. W.; Van Horn, B.; Hawker, C. J. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1309.
(28) Ryu, D. Y.; Shin, K.; Drockenmuller, E.; Hawker, C. J.; Russell, T. P. *Science* **2005**, *308*, 236.
(29) Wang, J.; Kouznetsova, T. B.; Niu, Z.; Ong, M. T.; Klukovich, H. M.; Rheingold, A. L.; Martinez, T. J.; Craig, S. L. *Nat. Chem.* **2015**, *7*, 323.
(30) Lenhardt, J. M.; Ong, M. T.; Choe, R.; Evenhuis, C. R.; Martinez, T. J.; Craig, S. L. *Science* **2010**, *329*, 1057.
(31) Francis, R. S.; Patterson, G. D.; Kim, S. H. *J. Polym. Sci., Part B: Polym. Phys.* **2006**, *44*, 703.
(32) Luo, Z.; Wei, L.; Liu, F.; Zhao, T. *Eur. Polym. J.* **2007**, *43*, 3461.
(33) Ducrot, E.; Chen, Y.; Bulters, M.; Sijbesma, R. P.; Creton, C. *Science* **2014**, *344*, 186.
(34) Gossweiler, G. R.; Hewage, G. B.; Soriano, G.; Wang, Q.; Welshofer, G. W.; Zhao, X.; Craig, S. L. *ACS Macro Lett.* **2014**, *3*, 216.
(35) Kean, Z. S.; Hawk, J. L.; Lin, S.; Zhao, X.; Sijbesma, R. P.; Craig, S. L. *Adv. Mater.* **2014**, *26*, 6013.
(36) Groote, R.; Jakobs, R. T. M.; Sijbesma, R. P. *Polym. Chem.* **2013**, *4*, 4846.
(37) Kean, Z. S.; Akbulatov, S.; Tian, Y.; Widenhoefer, R. A.; Boulatov, R.; Craig, S. L. *Angew. Chem., Int. Ed.* **2014**, *53*, 14508.
(38) Diesendruck, C. E.; Steinberg, B. D.; Sugai, N.; Silberstein, M. N.; Sottos, N. R.; White, S. R.; Braun, P. V.; Moore, J. S. *J. Am. Chem. Soc.* **2012**, *134*, 12446.
(39) Wang, Q.; Gossweiler, G. R.; Craig, S. L.; Zhao, X. *Nat. Commun.* **2014**, *5*, 4899.

DOI: 10.1021/acsmacrolett.5b00440
ACS Macro Lett. 2015, 4, 834−837