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Mechanophore-Linked Addition Polymers

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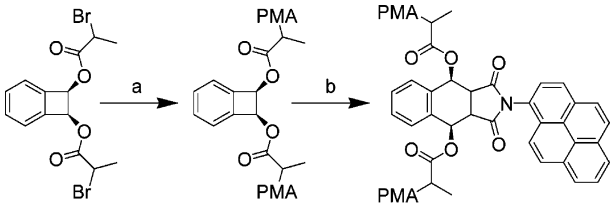
There is growing interest in the use of mechanical energy to alter the molecular and supramolecular structure of polymers to create stress-responsive materials.[1a−l] Chemical reactions that are accelerated by force remain poorly understood, and there is a need for the rapid discovery of new mechanophores (i.e., stress-sensitive units). Screening putative mechanophores, however, is a slow process that requires a high molecular weight polymer having a single testable unit positioned near the midpoint of the chain, the location where stress under elongation is greatest. Here we show that the required mechanophore-linked addition polymers are easily prepared using bifunctional initiators and a living polymerization method. The approach is demonstrated with benzocyclobutene[1k] and spiropyran mechanophores that undergo stress-induced 4π and 6π electrocyclic ring opening, respectively. Mechanophore-linked addition polymers thus show considerable promise for rapidly identifying new mechanophores and will lead to a greater, molecular-level understanding of mechanochemical transduction in polymeric materials.

Single electron transfer living radical polymerization (SET-LRP)[2] was employed for the synthesis of mechanophore-linked polymers, as this method has been shown to generate high molecular weight macromolecules with narrow polydispersity indices (PDIs). *cis*-1,2-Bis(α-bromopropionyloxy)-1,2-dihydrobenzocyclobutene (**1**), capable of initiating bidirectional SET-LRP, was synthesized and used to produce a series of benzocyclobutene (BCB)-linked PMAs (Scheme 1). Polymerizations were performed at room temperature in DMSO with Cu(0) catalyst and a hexamethylated tris(2-aminoethyl)amine (Me_6TREN) ligand. Low (18 kDa), medium (91 kDa), and high (287 kDa) molecular weight BCB-linked PMAs (PMA−BCB−PMA) with PDIs around 1.3 were synthesized and used to investigate the ultrasound-induced electrocyclic ring opening reaction. Mechanochemical activation was analyzed by trapping the intermediate *ortho*-quinodimethide with UV-active *N*-(1-pyrene)-maleimide via cycloaddition (Scheme 1).[1k] PMA end-functionalized with a BCB unit (PMA−BCB) was prepared as a mechanochemical control polymer since ultrasound-generated forces at the chain ends are minimal. Specifically, the monofunctional initiator *cis*-1-acetoxy-2-(α-bromopropionyloxy) 1,2-dihydrobenzocyclobutene was used to produce a PMA−BCB with a PDI of 1.3 and molecular weight of 190 kDa. This control polymer dispels the notion that the chemical changes are thermally induced, rather than the result of mechanical force.

The BCB-containing polymers and PMA homopolymer were subjected to an acoustic field to probe for mechanical activity. Each polymer was dissolved in CH_3CN with a large excess of *N*-(1-pyrene)maleimide and radical trap 2,6-di-*tert*-butyl-4-methylphenol (BHT) and exposed to pulsed sonication[3] for 45 min under Ar at 6−9 °C. Aliquots were withdrawn at the beginning and end of each experiment and analyzed by analytical gel permeation chromatography (GPC) using a refractive index (RI) detector. The remainder of the sonicated solution was analyzed by preparatory GPC having both UV (set to 345 nm) and RI detectors.

Scheme 1. Synthesis of Benzocyclobutene Mechanophore-Linked Addition Polymer PMA−BCB−PMA and Subsequent Mechanochemical Reaction: (a) Cu(0), Me_6TREN, Methyl Acrylate, DMSO, 25 °C; (b) *N*-(1-Pyrene)maleimide, CH_3CN, BHT, Ar, 8.7 W/cm^2, 6−9 °C



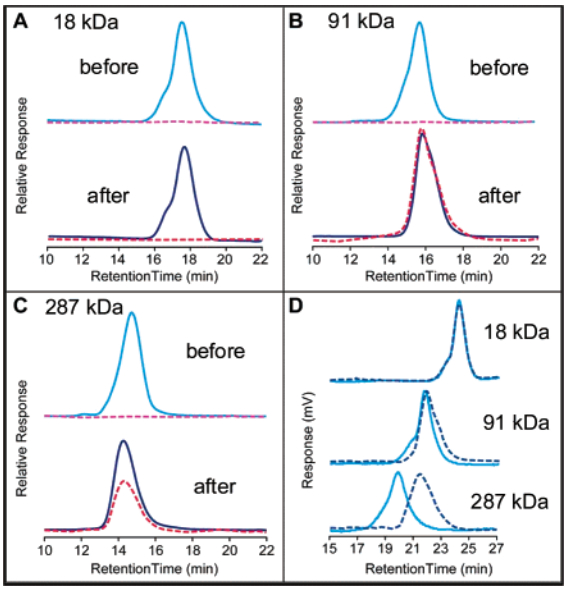


Figure 1. (A−C) Preparatory GPC chromatograms of PMA−BCB−PMA. The upper pair of traces corresponds to analysis before sonication; the lower pair, after sonication. The dotted pink trace is the UV signal; the blue trace is the RI signal. (D) Overlay of the analytical GPC traces before (solid light blue) and after (dotted dark blue) sonication.

No UV signal was present in the GPC trace of the sonicated low molecular weight PMA−BCB−PMA, indicating no reaction (Figure 1A). This low molecular weight polymer exhibited no chain cleavage, as indicated by the superposition of analytical GPC traces collected before and after sonication (Figure 1D). This result is consistent with the findings of Vijayalakshmi and Madras that the lower molecular weight threshold for chain cleavage of PMA by ultrasound is 87 kDa.[4] The GPC trace of the intermediate molecular weight sample (91 kDa) PMA−BCB−PMA exhibited a marked

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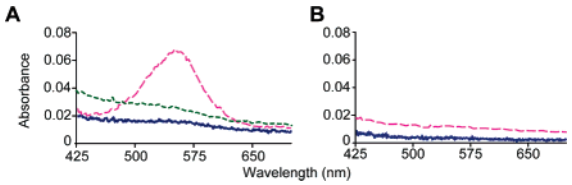
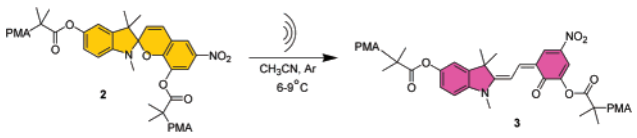


Figure 2. (A) UV spectrum of PMA−SP−PMA in CH_3CN (7.5 mg/mL) before sonication (blue trace), after 18 min pulsed sonication (dashed pink trace), and after 40 min exposure to ambient light (dotted green trace). (B) UV spectrum of end-functionalized PMA−SP control before sonication (blue trace) and after 18 min pulsed sonication (dashed pink trace).

increase in the UV signal following sonication (Figure 1B). These observations together with the appropriate controls[5] suggest that incorporation of *N*-(1-pyrene)maleimide occurs via a mechanochemically induced electrocyclic ring opening of the benzocyclobutene linker and that the reaction is not due to thermal activation, consistent with our previous findings.[1k] Little chain scission was observed with PMA−BCB−PMA of intermediate molecular weight (Figure 1D), indicating that the mechanically induced electrocyclic reaction takes place competitively or possibly in preference to chain scission.[6] The high molecular weight PMA−BCB−PMA sample (287 kDa) also showed a strong UV signal following ultrasound exposure (Figure 1C). Since the RI signal is proportional to the mass of the polymer, while the UV signal is proportional to moles of polymer molecules, a smaller UV/RI ratio is observed for the 287 kDa sample compared to the 91 kDa sample. The final molecular weight of the cleaved polymer was found to be 85 kDa (Figure 1D, trace c), a value near the reported[4] molecular weight threshold for chain scission.[7] Although nearly complete chain scission is observed (Figure 1D), *N*-(1-pyrene)maleimide is still incorporated into the polymer, suggesting that the cycloaddition occurs prior to, or competitively with, chain scission. These observations demonstrate that mechanochemical activation via ultrasound is not limited to the PEG polymers we studied previously.[1k]

The ease of preparing mechanophore-linked addition polymers makes it possible to rapidly screen for new mechanophore activity. First investigated by Tipikin,[8] small molecule spiropyrans have previously been noted to exhibit mechanochromic properties upon grinding. Given this observation, we investigated the potential for ultrasound to cause a stress-induced 6π-electron electrocyclic ring opening of a spiropyran mechanophore (Scheme 2).

Scheme 2. Mechanochemical Ring Opening of PMA−SP−PMA



A spiropyran bisfunctionalized with α-bromo-α-methylpropionyloxy groups was used as a SET-LRP initiator to produce spiropyran-linked PMA **2** (PMA−SP−PMA) having a PDI of 1.2 and molecular weight of 170 kDa. When subjected to pulsed ultrasound under Ar at 6−9 °C, the originally colorless PMA−SP−PMA solution changed to a visible pink hue, indicating a mechanochemical ring opening of the SP mechanophore. Examination of the sonicated solution with a UV spectrophotometer showed a new band centered at 550 nm, corresponding to the open form of spiropyran **3** (Figure 2A).[9] Exposure to ambient light for 40 min at room temperature caused the color to disappear (Figure 2A), consistent with the known photolytic reversion to the closed form **2**.

A monofunctional spiropyran initiator was synthesized and used to prepare an end-terminated polymer (PMA−SP) with a PDI of 1.3 and molecular weight of 183 kDa. In great contrast to PMA−SP−PMA, the sonicated end-functionalized solution was colorless and showed no visible absorption following ultrasound exposure (Figure 2B). These experiments suggest that the observed ring opening for PMA−SP−PMA is mechanically induced and not the result of thermal activation.

In conclusion, we have developed a method for synthesizing mechanophore-linked addition polymers and have demonstrated their value in probing mechanochemical activity. The bidirectional living method used here is capable of placing the mechanophore near the center of the polymer where the ultrasound-generated forces are the largest. Control experiments with terminally linked mechanophores rule out the possibility of thermally induced reactions. We have also established the utility of the PMA backbone as an effective polymer for investigating mechanophores via ultrasound. The value of this method was demonstrated by its application to a spiropyran mechanophore, which underwent a mechanochemical 6π-electron electrocyclic ring opening. A thorough study of the mechanochromic properties of these polymers is now underway and will be reported in due course.

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Supporting Information Available: Procedures, synthesis, further control experiments, and thermal experiments of the SP-functionalized PMAs. This material is available free of charge via the Internet at http://pubs.acs.org.

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(3) Ultrasound conditions: pulse rate = 0.5 s on, 1.0 s off, intensity = 8.7 W/cm^2; frequency = 20 kHz.
(4) Vijayalakshmi, S. P.; Madras, G. *Polym. Degrad. Stab.* **2005**, *90*, 116−122.
(5) When end-functionalized PMA−BCB (190 kDa) and PMA homopolymer (171 kDa) were subjected to ultrasound, no significant changes in the UV signal were observed.
(6) Quantification of chain scission versus ring-opening reaction rates is in progress.
(7) The final molecular weight is less than half of the initial value, suggesting that the polymer chains are cleaved more than once.
(8) Tipikin, D. S. *Zh. Fiz. Kh.* **2001**, *75*, 1876−1879.
(9) The new absorption corresponds to the same λ_{max} as seen upon UV irradiation at 245 nm of PMA−SP−PMA.

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