Retraction for *Journal of Materials Chemistry*:

Selective scission of pyridine–boronium complexes: mechanical generation of Brønsted bases and polymerization catalysts

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The Royal Society of Chemistry hereby wholly retracts this *Journal of Materials Chemistry* article with the agreement of Christopher W. Bielawski, Andrew G. Tennyson and Kelly M. Wiggins (other co-authors could not be reached) due to data fabrication as detailed below. This retraction supersedes the information provided in the Expression of Concern related to this article.

The Royal Society of Chemistry has been contacted by the corresponding author of this article and the Research Integrity Officer at The University of Texas at Austin regarding concerns of scientific misconduct affecting this article. The Research Integrity Officer has informed us that an investigation to ascertain the validity of the work reported has found that scientific misconduct by one of the articles co-authors has taken place as follows: the kinetics data and plots in this article were fabricated. Specifically, the rates and associated data in the Results and Discussion section were fabricated. The data acquired from the kinetics experiments discussed in the Supporting Information section entitled "3. Polymer Chain Scission Experiments: Kinetic Analyses", was fabricated. The data found in Figures 1B, 1C, and 1D, Supplementary Figures S5 and S6, and Supplementary Table S2 was fabricated. In addition, all of the Gel Permeation Chromatographs presented in this article and the accompanying Supplementary Information were smoothed. The signing authors would like to apologise for this and any consequent inconvenience to authors and readers.

Signed: Christopher W. Bielawski, Andrew G. Tennyson and Kelly M. Wiggins, March 2015

Retraction endorsed by Fiona McKenzie, Executive Editor, *Journal of Materials Chemistry*

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PAPER

Selective scission of pyridine–boronium complexes: mechanical generation of Brønsted bases and polymerization catalysts†

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Coupling two pyridine-capped poly(methyl acrylate) (PMA) chains of varying molecular weights to bis(pentafluorophenyl)boron chloride afforded the first examples of boronium-based polymers. Ultrasonication of CH_3CN solutions of these polymers with number average molecular weights (M_n) > 40 kDa induced selective scission of a boron–pyridine bond, affording a two-fold reduction in M_n. The liberated pyridine was used to effect a colorimetric change, *via* a stoichiometric Brønsted acid–base reaction with an indicator, and to catalyze the polymerization of α-trifluoromethyl-2,2,2-trifluoroethyl acrylate. No reduction in M_n, colorimetric response, or polymerization activity were observed (*i*) in the absence of sonication, (*ii*) for polymers with $M_n < 40$ kDa, (*iii*) for a high molecular weight PMA ($M_n =$ 110 kDa) containing a terminal boronium species, or (*iv*) when the boron–pyridine adduct was not covalently linked to a PMA chain. Collectively, these results support the notion that the aforementioned scission processes were induced by an applied mechanical force.

Introduction

Mastication and other methods of mechanical degradation on the physical and chemical properties of polymeric materials have been studied since the 1930s.[1] More recently, ultrasound has received significant attention for its ability to mechanically alter the chemical structures, physical properties and functions of polymeric materials.[2,3] In this technique, solvodynamic shear forces are created when microbubbles form in solution and then collapse under sonication. The solvated polymer segments nearest the collapsing bubbles move at higher velocities than those farther away in a manner that forcibly elongates the polymer chains.[4] For polymers of sufficiently high molecular weight, this tension may facilitate the selective activation of chemical processes at predesignated, centrally located sites – termed mechanophores.[2,3]

Recent advances in ultrasound-induced mechanochemistry have enabled the targeted cleavage of predetermined scissile bonds to release highly reactive moieties.[2,3] For example, Moore reported the generation of cyanoacrylate moieties *via* a mechanically-facilitated electrocyclic ring-opening of cyclobutanes embedded within polymer chains.[5] Applications targeted for these and other mechanically-activated systems range from self-repairing materials and diagnostics[6] to the establishment of fundamentally new chemical reactions.[7]

We[8] and others[9] have been interested in using ultrasound-induced mechanochemistry to activate catalysts for facilitating synthetic transformations, including olefin metathesis and coupling reactions. All of the mechanoresponsive catalysts, termed mechanocatalysts,[9] reported to date feature transition metals,[8,9] which can be complicated by undesired changes in coordination number and redox state leading to premature decomposition.[2,10] To circumvent these design limitations, we sought to prepare a transition metal-free mechanocatalyst by utilizing a p-block, rather than a d-block element. Lewis acid–base pairs comprised of p-block elements are known to form reversible bonds with tunable strengths,[11] and thus may be well suited for mechanoresponsive systems.

An attractive scaffold for p-block based mechanophores are boroniums, which are tetrahedral, four-coordinate, formally cationic boron compounds that feature two coordination sites occupied by neutral ligands (*e.g.*, pyridine) and two occupied by σ-bound anionic substituents. Boroniums have been known for over half a century,[12] and are the most stable of the known classes of boron-based cations.[13] Despite their high stabilities, these species have received surprisingly little attention for use in macromolecular applications. We hypothesized that the coordination of two pyridine-capped polymers to an electron-deficient diaryl boryl fragment would yield a main group-based mechanophore with boron–pyridine bonds capable of undergoing scission under stress. Herein we describe the synthesis of the first boronium-based polymers and demonstrate the mechanically-activated, selective bond-cleavage of a boron–nitrogen bond therein, whereby the liberated pyridine effected stoichiometric Brønsted acid–base reactions and catalyzed anionic polymerizations.

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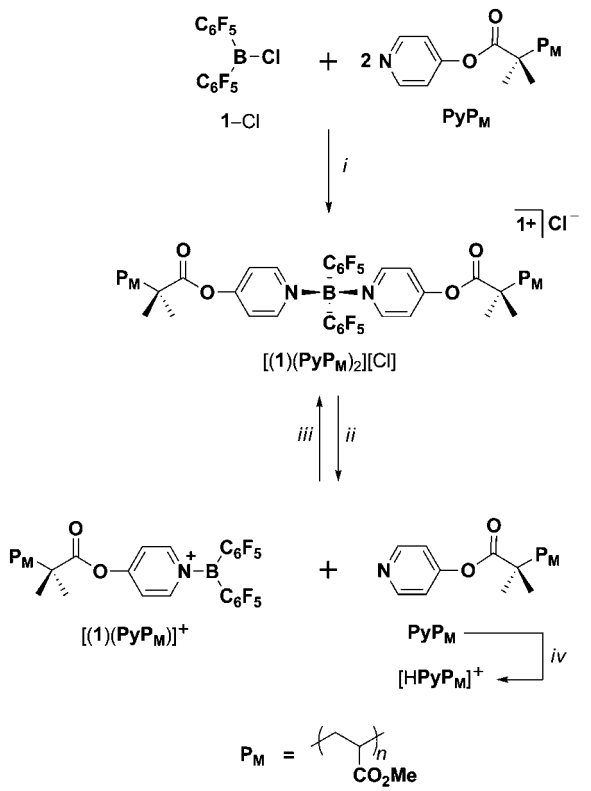
Results and discussion

Mechanoresponsive polymer synthesis and analysis

To access the targeted mechanoresponsive materials, pyridine-capped PMA polymers[8] of varying molecular weights ($\mathbf{PyP_M}$, where M corresponds to the number average molecular weight (M_n) in kDa of the PMA chain $\mathbf{P_M}$) were treated with 0.5 molar equiv of bis(pentafluorophenyl)boron chloride (**1**–Cl).[14] After allowing the reaction to proceed for 12 h at room temperature, the resultant polymer [(**1**)($\mathbf{PyP_M}$)$_2$][Cl] exhibited a M_n value twice that of the starting polymers, as determined by gel permeation chromatography (GPC) (see Step *i* in Scheme 1 and Table 1). As part of a series of control experiments (see below), [(**1**)(**PyPiv**)$_2$][Cl] and end-functionalized derivative [(**2**)($\mathbf{PyP_{110}}$)] were prepared by mixing 4-pyridinyl pivalate (**PyPiv**) with 0.5 molar equiv of **1** and treatment of $\mathbf{PyP_{110}}$ with 1.0 molar equiv of tris(pentafluorophenyl)borane (**2**), respectively (structures not shown).†

To gain additional evidence for pyridine coordination to the boron center in the aforementioned polymers, ^{1}H NMR spectra of a low molecular weight $\mathbf{PyP_M}$ (M_n = 1.7 kDa) were acquired before and after treatment with **1**–Cl or **2**. A downfield shift of the pyridyl *meta*-protons from δ = 7.08 ppm in free $\mathbf{PyP_M}$ to 7.55 ppm was observed upon formation of both [(**1**)($\mathbf{PyP_M}$)$_2$][Cl] and [(**2**)($\mathbf{PyP_M}$)] ($CDCl_3$), consistent with the coordination of the pyridine moiety to an electron-deficient Lewis acid (see Figures S1–S3).† Additionally, a significant upfield shift was observed in the ^{11}B NMR spectrum acquired for [(**1**)($\mathbf{PyP_M}$)$_2$][Cl] (1.48 ppm; $CDCl_3$) when compared to that of **1**–Cl (59.1 ppm), consistent with the rehybridization of the boron nucleus from sp^2 in the free borane to sp^3 in the corresponding boronium salt.[15]



Scheme 1 Synthesis of boronium-based mechanoresponsive reagents and chain scission in response to sonication. Conditions: *i*) CH_2Cl_2, room temperature, 12 h; *ii*) sonication‡ for 4 h at 4 °C of [(**1**)($\mathbf{PyP_M}$)$_2$][Cl] (10 mg) in CH_3CN (10 mL) and *iii*) re-coordination of $\mathbf{PyP_M}$ to boron or *iv*) trapping of $\mathbf{PyP_M}$ with 20 equiv HBF_4 to form [H$\mathbf{PyP_M}$][BF_4].

Table 1 Summary of molecular weight data for chain coupling and scission experiments[a]

			[(**1**)($\mathbf{PyP_M}$)$_2$][Cl]			
			Pre-Sonication		Post-Sonication	
$\mathbf{PyP_M}$	M_n [kDa]	PDI	M_n [kDa]	PDI	M_n [kDa]	PDI
$\mathbf{P_7}$	6.8	1.2	13	1.2	13	1.3
$\mathbf{P_{11}}$	11	1.2	23	1.1	23	1.2
$\mathbf{P_{21}}$	21	1.2	41	1.2	21	1.2
$\mathbf{P_{25}}$	25	1.4	48	1.3	24	1.4
$\mathbf{P_{66}}$	66	1.4	120	1.3	62	1.4

[a] Number and weight average molecular weights (M_n and M_w, respectively) were determined by gel permeation chromatography (GPC; eluent = DMF, 0.1 M LiBr) and are reported relative to polystyrene standards. Polydispersity indices (PDIs) were calculated using the equation PDI = M_w/M_n.

Due to the centrally-positioned mechanophore in [(**1**)($\mathbf{PyP_M}$)$_2$],[2,3,8,9] we expected that sonication‡ of a solution of this material would afford [(**1**)($\mathbf{PyP_M}$)]$^+$ and $\mathbf{PyP_M}$ *via* boron–pyridine bond scission (Step *ii*, Scheme 1). However, upon concentration, the material produced in these experiments resulted in no change in M_n, as determined by GPC, presumably due to recoordination of the liberated pyridine to [(**1**)($\mathbf{PyP_M}$)]$^+$ (Step iii, see Figure S7 for additional details).† It has been previously shown that HBF_4 effectively traps liberated $\mathbf{PyP_M}$,[8] hence we reasoned that the addition of a Brønsted acid to the aforementioned reactions should sequester the $\mathbf{PyP_M}$ as the pyridinium [H$\mathbf{PyP_M}$]$^+$ (Step *iv*). In support of this supposition, we found that sonicating CH_3CN solutions of [(**1**)($\mathbf{PyP_M}$)$_2$][Cl] (where M = 21, 25 and 66) and excess HBF_4 in a Suslick[16] cell immersed in a 4 °C ice bath for 4 h resulted in a two-fold reduction of M_n (see Fig. 1A for M = 66), consistent with the anticipated scission a boron–pyridine bond (see Table 1).‡ To verify that HBF_4 did not induce scission *via* protonation of the pyridyl moieties, a series of control experiments were performed in the absence of sonication (at both 4 and 25 °C) under otherwise identical conditions. Because no change in the M_n values measured for the polymers analyzed occurred during these experiments, we concluded that the aforementioned ultrasound induced reductions in molecular weight arose from mechanically-induced boron–pyridine bond scission processes.

Previous reports have shown that extending polymer chain length increases the rate of mechanophore activation, and that a minimum molecular weight of 20–40 kDa is required for activation to occur.[2,3,8,9] To determine if similar behavior was

‡ General sonication conditions: All sonications were performed on solutions with a final volume of 10 mL in a Suslick cell under a positive pressure of argon. Pulsed ultrasound (1.0 s on, 1.0 s off) was supplied at 23% power (10.1 W cm^2) for 4 h. The external temperature was maintained at 4 °C aided by the use of a cold room and ice–water bath. The internal temperatures of the sonicated solutions were monitored *via* a thermocouple and measured at ≤9 °C.

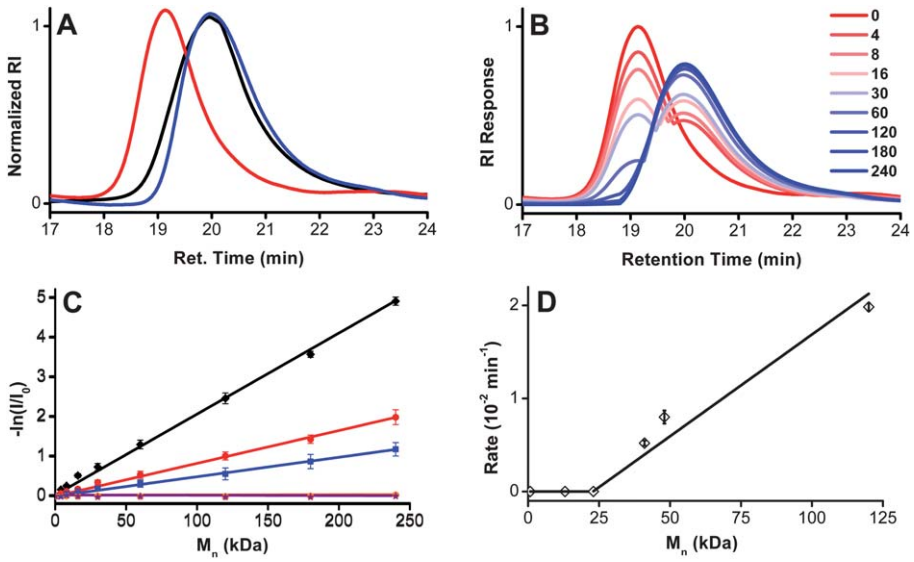


Fig. 1 Representative gel permeation chromatograms (GPCs) and kinetic data for the ultrasound-induced mechanical scission of $[(\mathbf{1})(\mathbf{PyP_M})_2][Cl]$. (**A**) GPC traces of $[(\mathbf{1})(\mathbf{PyP_{66}})_2][Cl]$ before (red) and after (blue) sonication, with $\mathbf{PyP_{66}}$ (black) overlaid for reference.‡ (**B**) Aliquots were removed over the course of the sonication of a solution of $[(\mathbf{1})(\mathbf{PyP_{66}})_2][Cl]$ at timed intervals and analyzed by GPC; the gradual reduction in peak intensity measured at retention time = 19.11 min (($t = 0$, topmost red; $t = 4$–16 min, fading red) was accompanied by the growth of a new peak measured at retention time = 19.87 min ($t = 30$–240 min, darkening blue). All aliquots analyzed consisted of an initial polymer concentration of 4.0 mg mL^{-1}. (**C**) First-order rate plot for the mechanical scission of $[(\mathbf{1})(\mathbf{PyP_M})_2][Cl]$, where M = 66 (black), 25 (red), 21 (blue), 11 (orange) and 7 (purple). I_0 and I correspond to the RI signal intensity for each polymer taken at the peak retention times before sonication and at each time-point t afterward, respectively (*cf.*, Table S2). (**D**) Plot of scission rates determined in (**C**) as a function of the number average molecular weight (M_n) of $[(\mathbf{1})(\mathbf{PyP_M})_2][Cl]$. For **C** and **D**, the data points were calculated from the average of three separate experiments. The error bars shown are the standard deviation.

exhibited by the aforementioned boronium-based polymers, the rate of the change in molecular weight was measured for all of $[(\mathbf{1})(\mathbf{PyP_M})_2][Cl]$ (Fig. 1A–C) and plotted *versus* the initial M_n (Fig. 1D). The kinetics of the observed loss of the peak at the initial M_n were determined by GPC analysis of aliquots removed at timed intervals during the sonication of $[(\mathbf{1})(\mathbf{PyP_M})_2][Cl]$.‡ For the polymers exceeding the minimum molecular-weight threshold ($M_n > 40$ kDa), the refractive index (RI) signal at the peak retention time associated with the initial M_n steadily decreased over 4 h and was accompanied by growth of the signal at the peak retention time associated with $[(\mathbf{1})(\mathbf{PyP_M})]^+$ and $[\mathbf{HPyP_M}]^+$ (for M = 66, see Fig. 1B). Plotting $-\ln(I/I_0)$ *versus* time, where I_0 and I correspond to the RI signal at the peak retention time for $[(\mathbf{1})(\mathbf{PyP_M})_2][Cl]$ before sonication and at each time-point analyzed, respectively, enabled determination of the rate of chain scission.[2,3,8] The polymers above the molecular weight threshold, $[(\mathbf{1})(\mathbf{PyP_{21}})_2][Cl]$, $[(\mathbf{1})(\mathbf{PyP_{25}})_2][Cl]$ and $[(\mathbf{1})(\mathbf{PyP_{66}})_2][Cl]$, were measured to exhibit first-order rates of 0.80, 0.52, and 1.98 $\times$ 10^{-2} min^{-1}, respectively.§ In contrast, no scission was observed for the polymers below the threshold, $[(\mathbf{1})(\mathbf{PyP_7})_2][Cl]$ and $[(\mathbf{1})(\mathbf{PyP_{11}})_2][Cl]$ (Fig. 1C and 1D).

Qualitative colorimetric detection of $\mathbf{PyP_M}$

To confirm that bond scission was occurring at the anticipated boron–pyridine linkage, we performed a series of colorimetric experiments whereby the liberated $\mathbf{PyP_M}$ was detected *via* reaction with an acid–base indicator. We have previously shown that 4-[(4-anilinophenyl)azo]-benzenesulfonic acid (**3**) in its protonated form ($[\mathbf{3H}][BF_4]$) was viable for the qualitative detection of sonochemically-liberated $\mathbf{PyP_M}$, and afforded a deep purple to yellow colorimetric response in the presence of 1 equiv of $\mathbf{PyP_M}$.[8] Employing the same indicator (see Fig. 2A), a purple solution was obtained upon mixing 10 μM $[(\mathbf{1})(\mathbf{PyP_M})_2][Cl]$ with 10 μM $[\mathbf{3H}][BF_4]$ in 10 mL CH_3CN. This solution was subsequently transferred to a Suslick cell, where mechanical chain scission was induced as described above. Sonication of the higher molecular weight polymers ($\mathbf{PyP_M}$; M = 21, 25 and 66) afforded clear, yellow solutions, consistent with the deprotonation of $[\mathbf{3H}][BF_4]$ by free $\mathbf{PyP_M}$ (for M = 66, see Fig. 2B).‡ These yellow solutions returned to their original purple color upon the addition of 1 equiv of HBF_4, which suggested to us that the observed colorimetric response was due to deprotonation of the indicator and not sonochemical degradation. In the absence of sonication, the same solutions remained purple, indicating that thermally-induced or proton-facilitated ligand displacement did not occur. To confirm that this Brønsted acid–base reaction originated *via* a mechanically-induced process, similar colorimetric experiments were performed *via* sonication of: (*i*) polymers below the minimum molecular weight threshold required for mechanical activation, $[(\mathbf{1})(\mathbf{PyP_7})_2][Cl]$ and $[(\mathbf{1})(\mathbf{PyP_{11}})_2][Cl]$ (see Fig. 2C for M = 11); (*ii*) the end-capped derivative $[(\mathbf{2})(\mathbf{PyP_{110}})]$ (Fig. 2D); (*iii*) and a mechanophore model complex $[(\mathbf{1})(\mathbf{PyPiv})_2][Cl]$ (in the presence of 90 kDa PMA) (Fig. 2E). No color change was observed during any of these control experiments. Collectively, these results support the sonochemically-induced mechanical chain scission of $[(\mathbf{1})(\mathbf{PyP_M})_2][Cl]$ at the boron–pyridine bond.

§ The magnitude of the chain scission rates measured for analogous polymers containing pyridine-palladium complexes[8] was approximately double that of the polymers described herein.

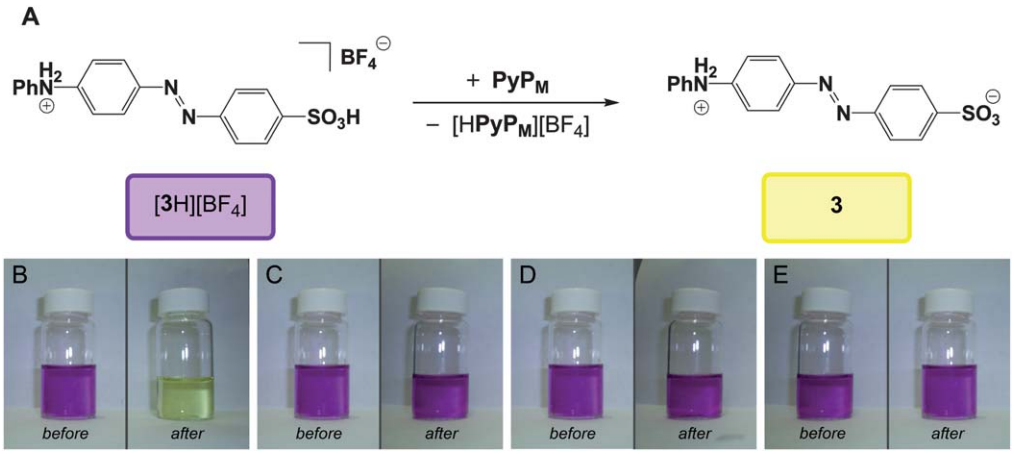
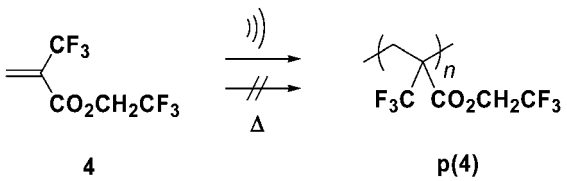


Fig. 2 (**A**) Indicator system employed for the qualitative, colorimetric detection of free $\mathbf{PyP_M}$. (**B**–**E**) Results of colorimetric indicator experiments for [(**1**)($\mathbf{PyP_{66}}$)$_2$][Cl] and selected control experiments. The sonication experiments‡ were performed for 4 h at 4 °C on a 10 mL CH_3CN solution containing 1 equiv of [**3**H][BF_4] with respect to 10 μM analyte: (**B**) [(**1**)($\mathbf{PyP_{66}}$)$_2$][Cl], (**C**) [(**1**)($\mathbf{PyP_{11}}$)$_2$][Cl], (**D**) [(**2**)($\mathbf{PyP_{110}}$)], (**E**) [(**1**)(**PyPiv**)$_2$][Cl] in the presence of 90 kDa PMA. The solution containing [(**1**)($\mathbf{PyP_{66}}$)$_2$][Cl] changed from purple before sonication (before) to yellow afterwards (after) indicating the formation of free $\mathbf{PyP_{66}}$ whereas no color change was observed during any of the control experiments.

Mechanocatalyzed anionic polymerization reactions

Because the sonication of [(**1**)($\mathbf{PyP_M}$)$_2$][Cl] generated $\mathbf{PyP_M}$ *in situ*, we reasoned that this species could be utilized to facilitate base-catalyzed reactions.[8] Mechanoresponsive materials are ideally suited for self-healing applications, wherein the initiation of polymerization reactions may induce repair processes;[6,17] therefore, we focused on polymerizations that are initiated by pyridine. Unfortunately most known pyridine-initiated polymerizations (*e.g.*, ring-opening polymerizations) require derivatives with functional groups that enhance nucleophilicity, high monomer concentrations, high catalyst loadings, and/or elevated temperatures,[18] which were not conducive to the constraints inherent to the sonochemical conditions necessary to effect pyridine liberation (*i.e.*, micromolar mechanophore concentration and low temperatures). Recently, Willson reported that pyridine catalyzes the anionic polymerization of α-trifluoromethyl-2,2,2-trifluoroethyl acrylate (**4**), which was found to proceed at −78 °C and at low pyridine loadings (< 0.5 wt%).[19] Sonication of [(**1**)($\mathbf{PyP_{66}}$)$_2$][Cl] and **4** in CH_3CN for 4 h,‡ followed by stirring at 4 °C for 20 h to allow for sufficient chain-growth, resulted in formation of the desired polymer **p(4)** (M_n = 21 kDa, PDI = 1.5) in 49% yield with respect to monomer consumption (Scheme 2).¶ As negative controls, sub-threshold [(**1**)($\mathbf{PyP_7}$)$_2$][Cl], end-capped [(**2**)($\mathbf{PyP_{110}}$)], and small molecule analogue [(**1**)(**PyPiv**)$_2$][Cl] in the presence of 90 kDa PMA were individually subjected to sonication under the same conditions; polymer formation was not observed for any of these experiments. Similarly, no polymer was obtained from a solution of [(**1**)($\mathbf{PyP_{66}}$)$_2$][Cl] and **4** in CH_3CN in the absence of sonication, representing negligible thermal background formation of **p(4)** (*cf.*, Table S4).† Collectively, these results suggested to us that the polymerization of **4** to **p(4)** was activated by mechanical force and was catalyzed by the release of $\mathbf{PyP_{66}}$ from [(**1**)($\mathbf{PyP_{66}}$)$_2$][Cl] during sonication.



Scheme 2 Pyridine catalyzed polymerization of **4** by $\mathbf{PyP_{66}}$ liberated from [(**1**)($\mathbf{PyP_{66}}$)$_2$][Cl] occurred only under ultrasound (see text).

Conclusion

In conclusion, we have synthesized a mechanoresponsive reagent comprised of an electron-deficient boron atom coordinated to two pyridine-capped poly(methyl acrylate)s, effectively producing the first known boronium-based polymer. Ultrasound-induced stress facilitated the selective cleavage of a boron–pyridine bond in polymers of sufficient molecular weight, whereby the liberated pyridine moiety effected stoichiometric Brønsted acid–base reactivity and catalyzed an anionic polymerization reaction. Comprehensive control experiments confirmed that chain cleavage was exclusively the result of ultrasonically-supplied mechanical force. Collectively, our findings demonstrate that mechanophores derived from p-block elements can afford mechanoresponsive materials that exhibit dynamic structures and catalytic functions akin to their d-block analogues. The Lewis acid–base mechanophore and methodology described herein are expected to preclude complications that can arise from organic (*i.e.* irreversible bond formation/

¶ The unoptimized polymerization conditions employed may have led to early termination that curtailed monomer consumption. For example, using $\mathbf{PyP_{66}}$ as the pyridine source and similar conditions to those employed for the sonication reactions described above resulted in the formation of **p(4)** (M_n = 30 kDa; PDI = 1.3) in 50% yield with respect to monomer consumption (see Table S4). Additionally, the liberated boron species did not appear to promote or hamper the polymerization reaction, as evidenced by the similar molecular weights and yields obtained for polymers grown independently using pyridine as an initiator.

cleavage) or transition metal (*i.e.* irreversible changes in coordination number or redox state) systems, and may enable advances in self-healing materials, main group Lewis acid-catalyzed reactions[20] as well as the reversible activation of small molecules for use in energy-response applications.[21]

Acknowledgements

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