RSC Publishing Faraday Discussions

Enhancing Covalent Mechanochemistry in Bulk Polymers Using Electrospun ABA Triblock Copolymers

Journal:	*Faraday Discussions*
Manuscript ID:	FD-ART-01-2014-000001
Article Type:	Paper
Date Submitted by the Author:	08-Jan-2014
Complete List of Authors:	Black, Ashley; Duke University, Chemistry Schmitt, Adam; University of Wisconsin, Department of Chemistry Mahanthappa, Mahesh; University of Wisconsin, Department of Chemistry Craig, Stephen; Duke University, Department of Chemistry

Journal Name

RSCPublishing

COMMUNICATION

Enhancing Covalent Mechanochemistry in Bulk Polymers Using Electrospun ABA Triblock Copolymers†

Cite this: DOI: 10.1039/x0xx00000x

Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

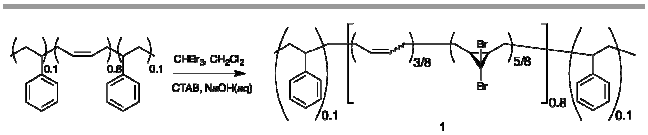
A. L. Black Ramirez,[a] A. K. Schmitt,[b] M. K. Mahanthappa[b] and S. L. Craig[a]

The mechanochemical activation of covalent bonds in bulk polymers is often characterized by low conversions. Here we report that the activation of *gem*-dibromocyclopropane (*g*DBC) mechanophores embedded in a poly(1,4-butadiene) (PB) is enhanced when a central *g*DBC-PB block is flanked by two polystyrene (PS) end blocks in an ABA-type triblock architecture. Electrospinning the PS-(*g*DBC)PB-PS leads to even greater activation in aligned fiber mats under tension.

Covalent polymer mechanochemistry[1] has in recent years provided access to new chemical reactions,[2-8] mechanistic insights,[1, 4, 8-17] and polymer transformations.[1, 2, 18] In bulk polymers, mechanochemical activation has been used as the basis for new classes of responsive polymers that demonstrate stress/strain sensing,[15, 16, 19-23] molecular level remodeling and stress-strengthening,[4, 23-30] and the release of small molecules that are potentially capable of triggering further chemical or material response.[31, 32] These demonstrations of mechanochemical reactivity in the bulk, however, are often limited by low levels of mechanophore activation, particularly in cases where the reactions require large (~nN) forces. For example, we recently reported that *gem*-dibromocyclopropane (*g*DBC) mechanophores[33] embedded in the main chain of poly(1,4-butadiene) (PB) can be activated in the bulk to undergo a ring opening reaction to a 2,3-dibromoalkene product under unconstrained uniaxial compression, but only with very low levels of activation (approximately 0.3%) accompanying dramatic, irreversible deformation of the bulk *g*DBC-PB.[6] Uniaxial tension is even less effective, with no mechanophore activation detected by ^{1}H NMR in films stretched to failure.[6]

The lack of mechanical activity was attributed to the relatively modest stresses achieved during tension, at which point the material presumably fails through the disentanglement of polymer chains. General approaches that can enhance the force-induced reactivity of a given mechanophore, therefore, are highly desirable. One approach is to devise and optimize molecular-level solutions, such as the recently reported "lever arm effect" that is controlled at the level of polymer backbone structure.[8, 34] Here, we consider an alternative strategy, in which mechanophore reactivity is influenced by changes in polymer morphology and macroscopic material structure.

We hypothesized that a cross-linked material would allow for higher stresses and strains to be achieved, improving the magnitude of the forces transduced to individual polymer chains. Because the insolubility of covalently cross-linked systems would challenge quantitative analysis, and because of discouraging exploratory results in covalently cross-linked polymer gels, we turned to triblock thermoplastic elastomers as an attractive strategy for enhanced mechanical properties. Microphase separation between blocks could lead to physical cross-linking in samples that could still be readily dissolved in an appropriate solvent. Because PB has proven to be a useful platform for the *g*DBC mechanophores, we focused our attention on poly(styrene-*b*-1,4-butadiene-*b*-styrene) (SBS) triblocks (Figure 1). The SBS microphase separates into glassy PS and amorphous PB regions, in which the stiff glassy regions act as non-covalent crosslinks that provide high strength and the soft amorphous regions accumulate the large stresses that might trigger mechanochemical activation. We envisioned that incorporating the *g*DBC moiety into the amorphous block would allow for greater



1

Figure 1. Phase transfer catalysed carbene addition to generate mechanophore-rich SBS **1**. Note that the central butadiene-*g*DBC block is random.

force transduction to the mechanophore, relative to that found in pure *g*DBC-PB.

Phase transfer catalyzed dibromocarbene addition (Figure 1) to the alkenes in the PB block of SBS (140 kDa, 30 wt% styrene, Sigma Aldrich) produced a poly(styrene-*b*-(*g*DBC-*ran*-1,4-butadiene)-*b*-styrene) polymer **1** with 50 mol% overall mechanophore content (by ^{1}H NMR), all of which is randomly distributed in the central soft block, and a total molecular weight of 220 kDa as determined by gel permeation chromatography with multi-angle light scattering detection. Films were cast from a 6.5 wt % solution in toluene, from which the solvent was allowed to slowly evaporate under ambient conditions in a fume hood over 7 days, followed by drying under vacuum at ambient temperature for 24 h. Small-angle x-ray scattering (SAXS) was used to characterize the morphologies of the films. Films of **1** adopted a cylindrical phase with a domain spacing

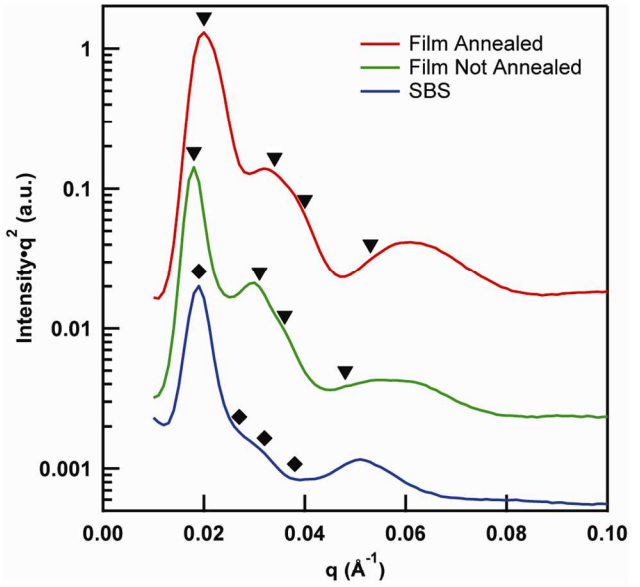


Figure 2. Small-angle X-ray scattering Kratky plot of $q^2I(q)$ v. q of annealed film of modified SBS, non-annealed film of modified SBS, and film of as-received SBS. The film of as-received SBS (bottom) exhibits a spherical morphology (d = 33.1 nm) with observed scattering peaks (q*, √2q*, √3q*, and √4q*) denoted with filled diamonds and a broad, spherical form factor scattering peak centered at q = 0.051 Å^{-1}. The modified SBS films exhibit a cylindrical morphology with a domain spacing of 21.7 nm for the annealed film (20.9 nm for unannealed) as evidenced by the observed scattering peaks (q*, √3q*, √4q*, and √7q*) (filled triangles) and a broad, cylindrical form factor scattering peak centered at q = 0.061 Å^{-1} (q = 0.055 Å^{-1}).

of 21.7 nm, as compared to a spherical morphology, d = 33.1 nm, for the SBS precursor (Figure 2). Uniaxial tensile tests were performed at a constant crosshead velocity of 0.2 mm/s (initial strain rate of ~0.03 s^{-1}). Two types of loading were investigated: single, constant strain to failure, or cyclic loading in which the films is stretched to 700% strain on the initial loading cycle, relaxed to 0% strain, and stretched in increasing increments of approximately 100% in subsequent cycles (800% strain on the second, 900% on the third, etc…).

In contrast to those made from pure *g*DBC-PB, films made from polymer **1** undergo measurable (but still sparse) activation. For both the single strain and cyclic loading cycles, the ^{1}H NMR spectra reveal that approximately 0.2% of the *g*DBC mechanophores are opened to their 2,3-dibromoalkene products (Figure 3). This

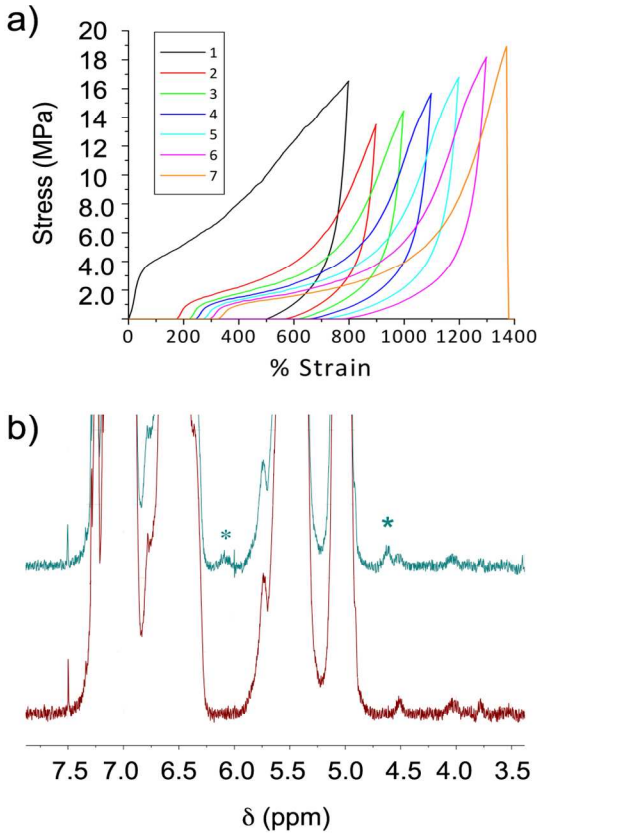


Figure 3. Cyclic loading at increasing strains (a) results in modest but detectable formation of the 2,3-dibromoalkene product of *g*DBC ring opening, indicated by ^{1}H NMR resonances denoted by asterisks at δ = 6.09 and 4.60 ppm (b; red spectrum is of film held in absence of tension, teal spectrum is of film loaded in (a)).

activation, while very small, is not observed in unstretched films and represents an enhancement from the undetectable levels of activation observed previously in pure *g*DBC-PB.[6]

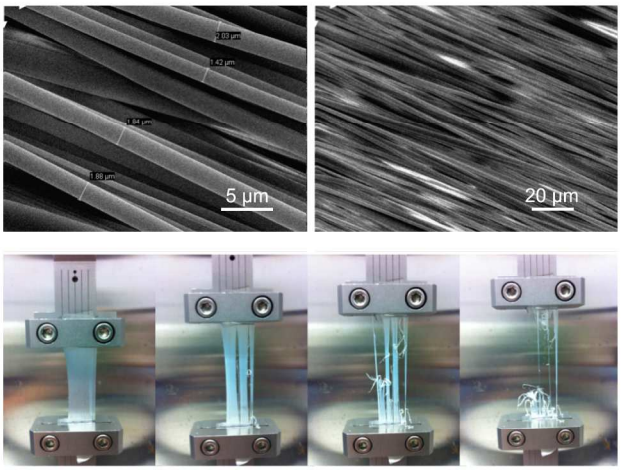


Figure 4. SEM images (top) of electrospun fibers of **1**. Aligned fiber mats (bottom) were subjected to uniaxial tension, and fibers from the gauge section were collected just prior to or after failure for analysis by ^{1}H NMR.

Lee *et al.* previously demonstrated that chain alignment in the direction of strain increases the activation of spiropyran mechanophores embedded in a polyurethane.[35] We wondered whether electrospinning aligned fibers might influence the transduction of force and the associated mechanophore activation in **1**. Polymer **1** was electrospun from a 16 wt % solution in $CHCl_3$ to produce ~2 μm fibers that were collected into aligned mats (Figure 4). These mats, approximately 30 μm thick, were subsequently annealed for 2 h at 70 °C under vacuum.

The mats were again placed in a microstrain analyzer and subjected to a uniaxial strain velocities of 0.2 mm/s, mimicking the conditions employed with the solvent cast films. Whether single strain or cyclic loading cycles were employed, enhanced activation of 1.5% ring opening was observed, roughly a factor of seven times greater than that in the films (Figure 5). Importantly, analysis of the fibers following electrospinning and annealing, but in the absence of applied tension, showed no detectable *g*DBC ring opening during the fabrication of the mats. A similar lack of activation was observed in mats placed in the microstrain analyzer for 1 h but without an applied strain (Figure 5).

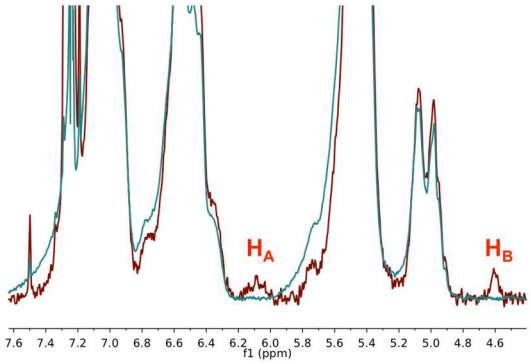


Figure 5. ^{1}H NMR overlay of dissolved fibers after electrospinning and annealing (blue) and then straining to failure at 0.2 mm/sec (red). The resonances indicative of mechanophore activation appear at δ = 6.09 and 4.60 ppm.

Although covalent mechanochemistry has been demonstrated previously in triblock polymer architectures,[36] to the best of our knowledge this is the first quantitative comparison of activity in a homopolymer relative to that same polymer as a block in a triblock copolymer. In addition, this is the first report of incorporating mechanophores into electrospun fibers, and the substantially enhanced activation observed as a result both points to raises interesting questions about the underlying mechanism. The physics at play are undoubtedly complex and beyond the scope of this manuscript, but we consider and briefly evaluate some possible contributions.

First, we note that the mats withstand greater stresses than the films (36 vs. 20 MPa), and loading is typically correlated with activity. When unannealed fiber mats are employed, however, the stress at failure (15 MPa) was comparable to or slightly less than that of the solvent cast films, and enhanced mechanophore activation (relative to the solvent cast films) of 1.2% was observed. The difference in activation is apparently due to factors beyond the actual stress at break. Second, the stress concentration in the mats is undoubtedly different than that in the films, as evidenced by the distribution of failed fibers under tension (Figure 4, bottom). We note, however, that if the strain is stopped as soon as the first fiber fails, total activation across the gauge section is still 1.0%, well above that observed in the solvent cast films after complete failure of the film.

Another, initially counterintuitive, influence might be the extent of ordering in the bulk. We were initially surprised to observe that, in contrast to the solvent cast films, no ordered microphase segregation was observed by SAXS in the fibers (see ESI); there is only a weak correlation hole scattering peak that is symptomatic of the length scale of the block copolymer radius of gyration, and no higher order peaks. The observed lack of ordering with increased activation is contradictory to our original hypothesis and motivation, but there is reason to believe that it might actually be beneficial to have less order. Prior studies of microphase separated copolymers suggest that the weak point in such materials is often the glassy domain.[37] That is, the glassy polystyrene breaks before substantial strain is built up in the amorphous butadiene regions. It is therefore possible that by disrupting microphase separation, as done here by electrospinning, the macroscopic tension ends up being more efficiently built up as tension along the *g*DBC-PB block.

Finally, we point out that electrospinning induces chain alignment with the fiber axis, which is in turn aligned with the tension applied to the fiber mats.[38] Because chain and mechanophore alignment are correlated with mechanochemical activation,[15, 35] this component of the electrospinning process might also contribute to the enhanced reactivity in the fiber mats.

Conclusions

Incorporating mechanophore-rich polybutadiene as the central block of an SBS-based triblock thermoplastic elastomer yields films with better mechanical properties and enhanced mechanochemical responses relative to mechanophore-embedded polybutadiene alone. The enhanced activation suggests some potential advantages for the design of mechanochemically active bulk polymers. A much greater enhancement (a factor of seven beyond that observed in the films), however, is observed when the functionalized triblocks are electrospun into aligned fiber mats. Somewhat surprisingly, the enhanced mechanical activity occurs despite the absence of ordered microphase separation, consistent with earlier reports in which the glassy styrene domains provide a weak point for fracture that might dissipate energy that might otherwise be channelled into mechanophore activation. It is difficult to draw mechanistic conclusions at this time, because a direct comparison between electrospun mats and solvent cast films is compromised by the numerous structural factors that change simultaneously. Nevertheless, the levels of activation observed in these systems motivate further exploration of mechanophore-rich triblock[18] thermoplastics and electrospun fibers as platforms for bulk polymers with covalent mechanochemical activity. Polymer microstructure provides another handle through which to modulate mechanochemical activity, complementing previously noted "lever arm" effects at the single molecule level.[8]

Notes and references

[a] Department of Chemistry, Duke University, Durham, NC, 27708-0346 (USA).
[b] Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706 (USA)

† This material is based upon work supported by the U.S. Army Research Laboratory and the U.S. Army Research Office under grant number W911NF-11-1-0071. A. L. B. R. acknowledges a DoD SMART Fellowship. SAXS data was acquired at the Advanced Photon Source (APS) (Sector 12-ID-B), and we thank Dominic V. Perroni for access to synchrotron beam time through General User Proposal No. 31075 Use of the APS, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory (Argonne, IL), was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.

Electronic Supplementary Information (ESI) available: synthesis, characterization, and additional SAXS data. See DOI: 10.1039/c000000x/

1. M. M. Caruso, D. A. Davis, Q. Shen, S. A. Odom, N. R. Sottos, S. R. White and J. S. Moore. *Chem. Rev.,* 2009, **109**, 5755.
2. C. R. Hickenboth, J. S. Moore, S. R. White, N. R. Sottos, J. Baudry and S. R. Wilson. *Nature,* 2007, **446**, 423.
3. J. M. Lenhardt, M. T. Ong, R. Choe, C. R. Evenhuis, T. J. Martinez and S. L. Craig. *Science,* 2010, **329**, 1057.
4. H. M. Klukovich, Z. S. Kean, S. T. Iacono and S. L. Craig. *J. Am. Chem. Soc.,* 2011, **133**, 17882.
5. J. N. Brantley, K. M. Wiggins and C. W. Bielawski. *Science,* 2011, **333**, 1606.
6. J. M. Lenhardt, A. L. Black, B. A. Beiermann, B. D. Steinberg, F. Rahman, T. Samborski, J. Elsakr, J. S. Moore, N. R. Sottos and S. L. Craig. *J. Mater. Chem.,* 2011, **21**, 8454.
7. K. M. Wiggins and C. W. Bielawski. *Angew. Chem. Intl. Ed.,* 2012, **51**, 1640.
8. H. M. Klukovich, T. B. Kouznetsova, Z. S. Kean, J. M. Lenhardt and S. L. Craig. *Nature Chem.,* 2013, **5**, 110.
9. S. S. Konda, J. N. Brantley, B. T. Varghese, K. M. Wiggins, C. W. Bielawski and D. E. Makarov. *J. Am. Chem. Soc.,* 2013, **135**, 12722.
10. S. Akbulatov, Y. Tian and R. Boulatov. *J. Am. Chem. Soc.,* 2012, **134**, 7620.
11. R. Boulatov. *Nature Chem.,* 2013, **5**, 84.
12. M. J. Kryger, A. M. Munaretto and J. S. Moore. *J. Am. Chem. Soc.,* 2011, **133**, 18992.
13. Z. S. Kean, Z. Niu, G. B. Hewage, A. L. Rheingold and S. L. Craig. *J. Am. Chem. Soc.,* 2013, **135**, 13598.
14. J. Ribas-Arino and D. Marx. *Chem. Rev.,* 2012, **112**, 5412.
15. B. A. Beiermann, S. L. B. Kramer, J. S. Moore, S. R. White and N. R. Sottos. *ACS Macro Lett.,* 2012, **1**, 163.
16. C. K. Lee, B. A. Beiermann, M. N. Silberstein, J. Wang, J. S. Moore, N. R. Sottos and P. V. Braun. *Macromolecules,* 2013, **46**, 3746.
17. R. Groote, B. M. Szyja, E. A. Pidko, E. J. M. Hensen and R. P. Sijbesma. *Macromolecules,* 2011, **44**, 9187.
18. Z. S. Kean, A. L. Black Ramirez and S. L. Craig. *J. Polym. Sci. B Polym. Phys.,* 2012, **50**, 3481.
19. C. M. Kingsbury, P. A. May, D. A. Davis, S. R. White, J. S. Moore and N. R. Sottos. *J. Mater. Chem.,* 2011, **21**, 8381.
20. B. A. Beiermann, D. A. Davis, S. L. B. Kramer, J. S. Moore, N. R. Sottos and S. R. White. *J. Mater. Chem.,* 2011, **21**, 8443.
21. D. A. Davis, A. Hamilton, J. Yang, L. D. Cremar, D. Van Gough, S. L. Potisek, M. T. Ong, P. V. Braun, T. J. Martinez, S. R. White, J. S. Moore and N. R. Sottos. *Nature,* 2009, **459**, 68.
22. Y. Chen, A. J. Spiering, S. Karthikeyan, G. W. Peters, E. W. Meijer and R. P. Sijbesma. *Nature Chem.,* 2012, **4**, 559.
23. S. Karthikeyan and R. P. Sijbesma. *Macromolecules,* 2009, **42**, 5175.
24. B. R. Crenshaw and C. Weder. *Macromolecules,* 2006, **39**, 9581.
25. A. L. Black, J. A. Orlicki and S. L. Craig. *J. Mater. Chem.,* 2011, **21**, 8460.
26. A. L. Ramirez, Z. S. Kean, J. A. Orlicki, M. Champhekar, S. M. Elsakr, W. E. Krause and S. L. Craig. *Nature Chem.,* 2013, **5**, 757.
27. B. R. Crenshaw, M. Burnworth, D. Khariwala, A. Hiltner, P. T. Mather, R. Simha and C. Weder. *Macromolecules,* 2007, **40**, 2400.
28. N. Bruns, K. Pustelny, L. M. Bergeron, T. A. Whitehead and D. S. Clark. *Angew. Chem. Int. Ed. Engl.,* 2009, **48**, 5666.
29. S. Y. Cho, J. G. Kim and C. M. Chung. *Sensor Actuat. B-Chem.,* 2008, **134**, 822.
30. Y. K. Song, K. H. Lee, W. S. Hong, S. Y. Cho, H. C. Yu and C. M. Chung. *J. Mater. Chem.,* 2012, **22**, 1380.
31. C. E. Diesendruck, B. D. Steinberg, N. Sugai, M. N. Silberstein, N. R. Sottos, S. R. White, P. V. Braun and J. S. Moore. *J. Am. Chem. Soc.,* 2012, **134**, 12446.
32. M. B. Larsen and A. J. Boydston. *J. Am. Chem. Soc.,* 2013, **135**, 8189.
33. D. Wu, J. M. Lenhardt, A. L. Black, B. B. Akhremitchev and S. L. Craig. *J. Am. Chem. Soc.,* 2010, **132**, 15936.
34. H. M. Klukovich, Z. S. Kean, A. L. Black Ramirez, J. M. Lenhardt, J. Lin, X. Hu and S. L. Craig. *J. Am. Chem. Soc.,* 2012, **134**, 9577.
35. C. K. Lee, D. A. Davis, S. R. White, J. S. Moore, N. R. Sottos and P. V. Braun. *J. Am. Chem. Soc.,* 2010, **132**, 16107.
36. S. Jiang, L. Zhang, T. Xie, Y. Lin, H. Zhang, Y. Xu, W. Weng and L. Dai. *ACS Macro Lett.,* 2013, **2**, 705.
37. M. K. Mahanthappa, M. A. Hillmyer and F. S. Bates. *Macromolecules,* 2008, **41**, 1341.
38. H. Fong and D. H. Reneker. *J. Polym. Sci.: Part B: Polym. Phys.,* 1999, **37**, 3488.

