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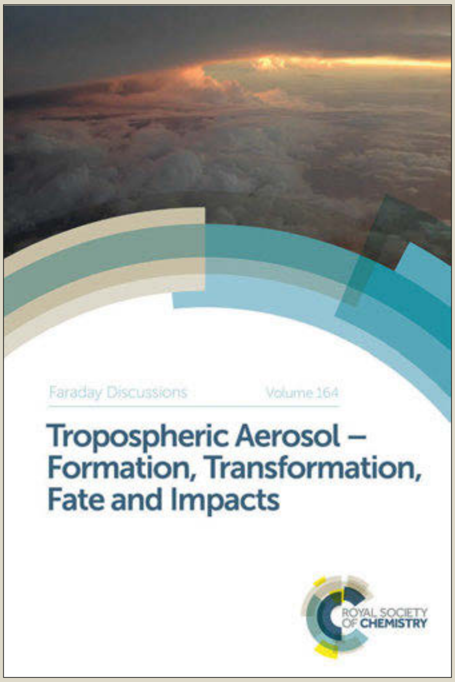

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Mechanochemical production of phenyl cations through heterolytic bond scission

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High mechanical forces applied to polymeric materials typically induce unselective chain scission. For the last decade, mechanoresponsive molecules, mechanophores, have been designed to harness the mechanical energy applied to polymers and provide a productive chemical response. Selective homolysis of chemical bonds was achieved by incorporating peroxide and azo mechanophores into polymer backbones. However, selective heterolysis in polymer mechanochemistry is still mostly unachieved. We hypothesized that highly polarized bonds in ionic species are likely to undergo heterolytic bond scission. To test this, we examined a triarylsulfonium salt (TAS) as a mechanophore. Poly(methyl acrylate) possessing TAS at the center of the chain (PMA-TAS) is synthesized by a single electron transfer living radical polymerization (SET-LRP) method. Computational and experimental studies in solution reveal mechanochemical production of phenyl cations from PMA-TAS. Interestingly, the generated phenyl cation reacts with its counter-anion (trifluoromethanesulfonate) to produce a terminal trifluoromethyl benzene structure that, to the best of our knowledge, is not observed in the photolysis of TAS. Moreover, the phenyl cation can be trapped by the addition of a nucleophile. These findings emphasize the interesting reaction pathways that become available by mechanical activation.

Introduction

Biological systems are able to detect mechanical forces and harness mechanical energy through mechanochemical transduction that utilize complex functional networks.[1] In terms of synthetic mechanoresponsiveness, polymer mechanochemistry has recently gathered significant interest, using mechanical force as an external stimulus to induce chemical reactions leading to new types of smart, functional materials.[2]

Achieving a selective mechanochemical response requires judicious design of force-responsive molecules, called mechanophores. Mechanophores are tethered to polymer chains through a specific chemical bond which transmits the external force to the mechanophore through polymer chain stretching from elongational flow or mechanical deformation. Useful mechanochemical responses such as deformation indicators[3], mechanocatalysis[4] and small molecule release[5] have been reported. The activation processes usually involve chemical bond scission in mechanophores; thus, design the resulting products after bond cleavage is an important factor to exploit in terms of function and response.

Mechanical scission of chemical bonds in homopolymers is mostly homolytic, producing radical species.[6] This response has been amplified synthetically by

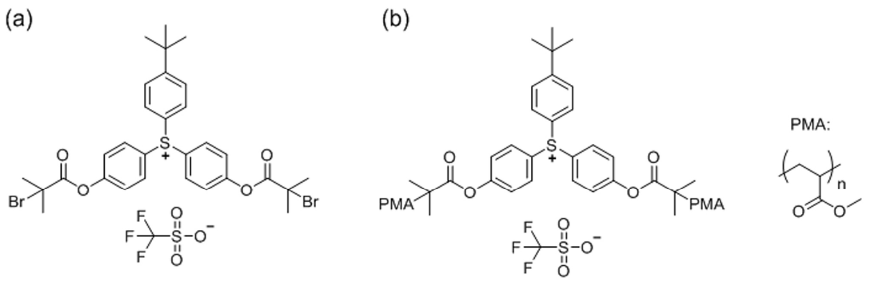


Figure 1. Chemical structures of (a) TAS initiator and (a) PMA-TAS.

introducing strained rings[7] or weak bonds such as peroxide[8a], azo[8b] and disulfide[8c] linkages in polymer backbones. On the other hand, reports regarding heterolytic bond scission are very limited. For example, Sakaguchi *et al*. demonstrated that heterolytic scission of polymers is partially observed when ball-milling bacteria cellulose, poly(vinylidene fluoride) and poly(tetrafluoroethylene) under careful experimental conditions (vacuum, dark, 77 K).[9] Therefore, we designed a new mechanophore with a highly polarized chemical bond that would favor heterolytic bond scission. This new mechanophore could lead to novel reactivity since the generated ionic species (such as phenyl cations and carbocations) may be useful as highly reactive-intermediates in various chemical reactions.

Given our interests in mechanochemical acid production[5a], we investigated a triarylsulfonium salt (TAS, Figure 1) as a mechanophore candidate. TASs are well-known photoacid generators commonly used in photolithography applications.[10] Different mechanisms for the photochemical acid production have been proposed and debated in the literature, but they always involve heterolysis or homolysis of the C-S bond.[10] Here, we investigate the mechanochemical scission of TAS using both computational simulations and sonication experiments in solution.

Experimental

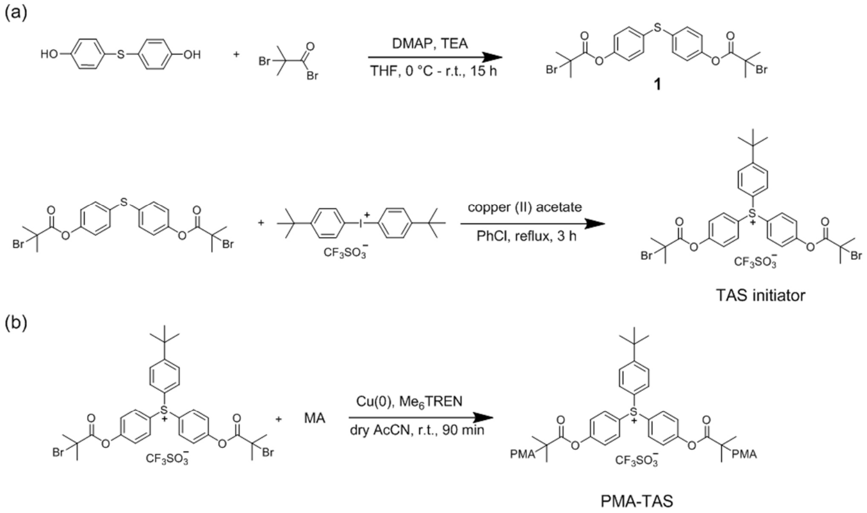
Materials

Unless otherwise stated, all chemical reagents were obtained from commercial suppliers and used without purification. α-Bromoisobutyryl bromide, 4,4’-thiodiphenol, methyl acrylate (MA), Cu(0) powder and tris[2-(dimethylamino)ethyl]amine (Me_6TREN) were purchased from Sigma-Aldrich. Bis(4-*tert*-butylphenyl)iodonium trifluoromethanesulfonate was purchased from TCI. Silica gel 60 (230-400 mesh) was obtained from Silicycle.

Instruments

^1H, ^{13}C and ^{19}F NMR spectra were collected by using a Varian 500 MHz spectrometer in the VOICE NMR laboratory at the University of Illinois; the residual solvent proton was used to reference the chemical shifts.[11] Coupling constants (J) are reported in Hertz (Hz) and splitting patterns are designated as s (singlet), d (doublet), m (multiplet), and br (broad). Electrospray ionization (ESI) and high resolution ESI mass spectra were obtained through the Mass Spectrometry Facility, SCS, University of Illinois. Elemental analysis data were obtained through the Microanalysis Facility, SCS, University of Illinois (CHN Analysis - Exeter Analytical CE 440 and Perkin Elmer 2440, Series II). Gel permeation chromatography (GPC) analyses were carried out in Waters 1515 Isocratic HPLC pump, with a Waters (2707) 96-well autosampler and a series of 4 Waters HR Styragel columns (7.8 X 300mm, HR1, HR3, HR4, and HR5) in THF at 30 °C, coupled to a Waters (2998) Photodiode Array Detector and a Waters (2414) Refractive Index Detector. Polystyrene standard samples (Showa Denko K.K.) were used for standard calibration. Ultrasound sonication experiments were performed on a Vibra Cell 505 liquid processor with a ½" diameter solid horn from Sonics and Materials. The distance between the titanium tip and bottom of the Suslick cell was 1 cm. The Suslick cells were made by the Glass Shop, SCS, University of Illinois. Novacure 2100 (EXFO America, 4000 mW/cm^2, 15 min) was used for UV light irradiation experiments. CoGEF (constrained geometries simulate external force) calculations were conducted in Spartan '10 at the B3LYP/6-31G* level of theory.

Synthesis



Scheme 1. Synthetic routes of (a) TAS initiator and (b) PMA-TAS via SET-LRP.

Thiobis(4,1-phenylene) bis(2-bromo-2-methylpropanoate) (**1**)

In a 100 mL three-neck round-bottom flask equipped with an addition funnel, 4,4'-thiodiphenol (1.00 g, 4.58 mmol) and 4-dimethylaminopyridine (DMAP, 14.0 mg, 0.115 mmol) were dissolved in 20 mL THF and the solution was cooled in an ice bath. Triethylamine (TEA, 1.60 mL, 11.5 mmol) was added and then α-bromoisobutyryl bromide (1.42 mL, 11.5 mmol) in 15 mL THF was added dropwise. After stirring at 0 °C for 1 h, the mixture was allowed to warm to room temperature and stirred overnight. The solids were filtered out and the filtrate evaporated. The obtained solid was dissolved in 30 mL CH_2Cl_2 and washed with saturated $NaHCO_3$ (twice), water and brine (30 mL each). The organic layer was dried over anhydrous magnesium sulfate, filtered, and evaporated to provide **1** as an off-white solid (2.35 g, yield 99 %); ^{1}H NMR(500 MHz, $CDCl_3$, Figure S1): δ/ppm 7.37 (d, *J* = 8.7 Hz, 4H), 7.09 (d, *J* = 8.7 Hz, 4H), 2.06 (s, 12H), ^{13}C NMR (500 MHz, $CDCl_3$) : δ/ppm 170.2, 150.2, 133.5, 132.4, 122.2, 55.3, 30.8, HRMS-ESI (*m/z*): calculated for $C_{20}H_{21}O_4SBr_2$ $[M+H]^+$: 514.9527; found: 514.9531.

Bis(4-((2-bromo-2-methylpropanoyl)oxy)phenyl)(4-(tert-butyl)phenyl)sulfonium trifluoromethanesulfonate (TAS initiator)[12]

Compound **1** (1.03 g, 2.00 mmol), bis(4-*tert*-butylphenyl)iodonium trifluoromethanesulfonate (1.08 g, 2.00 mmol) and Cu(II) acetate (8.7 mg, 0.024 mmol) were weighed in a 50 mL two-neck round-bottom flask equipped with a condenser. Chlorobenzene (20 mL) was added and the mixture was refluxed for 3 h. After cooling to room temperature, the mixture was filtered and the solvent was evaporated to dryness. The product was recrystallized from a 2:8 (v/v) CH_2Cl_2:diethyl ether mixture to provide colorless crystals (346 mg, yield 22 %); ^1H NMR(500 MHz, $CDCl_3$, Figure S2): δ/ppm 7.85 (d , J = 9.0 Hz, 4H), 7.70 (d, J = 4.63 Hz, 4H), 7.51 (d, J = 9.0 Hz, 4H), 2.06 (s, 12H), 1.35 (s, 9H). ^{13}C NMR (500 MHz, $CDCl_3$) : δ/ppm 169.4, 159.6, 155.6, 133.0, 131.2, 129.2, 124.8, 121.9, 120.8, 119.7, 54.9, 35.7, 31.0, 30.5. MS-ESI (*m/z*): calculated for $C_{30}H_{33}Br_2O_4S+$ $[M]^+$: 649.0 and for $CF_3O_3S_-$ $[M]^-$: 149.0. ; found: 649.1 and 149.0, respectively. Elemental analysis: $C_{31}H_{33}Br_2F_3O_7S_2$: calc.% C 46.63, H 4.17: found C 46.38, H 4.05.

PMA-TAS

Poly(methyl acrylate) having a TAS group at the center position (PMA-TAS) was synthesized through a single electron transfer living radical polymerization (SET-LRP)[13] using the functionalized TAS initiator. MA was filtered through basic alumina to remove inhibitor. To a N_2-purged 10 mL Schlenk flask equipped with a Teflon stir bar, Me_6TREN (4.01 μL, 0.0150 mmol), TAS initiator (3.99 mg, 0.00500 mmol) and MA (1.00 mL, 11.1 mmol) were added. Cu(0) powder (0.95 mg, 0.0150 mmol) dispersed in 1.0 mL of dry acetonitrile was injected to the reaction mixture. Three freeze-pump-thaw cycles were applied. The flask was backfilled with N_2 and allowed to stir in a water bath for 90 min at room temperature. The polymerization was quenched by immersing the flask in liquid N_2. The resulting solution was diluted with 10 mL THF and filtered through a pad of silica gel. After concentrating the solution in vacuo, the polymer was precipitated by dropwise addition to stirring methanol. The resulting polymer was collected and dried under vacuum at room temperature. The product was obtained as a colorless solid (269 mg); GPC (THF eluent, polystyrene standard) M_p = 94 kDa, Mw/Mn = 1.10. ^1H NMR (500 MHz, $CDCl_3$, Figure S3): δ/ppm 7.80 (d br, 4H of TAS), 7.69 (s br, 4H of TAS), 7.46 (d br, 4H of TAS), 3.64 (s br, 3H of PMA), 2.39-2.23 (br, 1H of PMA), 1.98-1.39 (m br, 2H of PMA). Low molecular weight PMA-TAS was synthesized in the similar procedure (M_p = 19 kDa, Mw/Mn = 1.17).

Procedure for Sonication Experiments

The general apparatus for sonication experiments has been described in a previous publication.[14] The polymer was dissolved in acetonitrile (10 mg in 10 mL) and transferred to a Suslick cell, which was placed into the collar and screwed to the horn. A N_2 line was introduced into the cell and N_2 was sparged through the system for 30 min prior to any sonication runs, as well as during the run itself. The Suslick cell was cooled with an ice bath throughout the entire sonication in order to maintain a constant temperature of 6 ºC. Pulsed ultrasound (1.0 s on, 2.0 s off, 8.7 W/cm^2) was applied to the system.

Results and Discussion

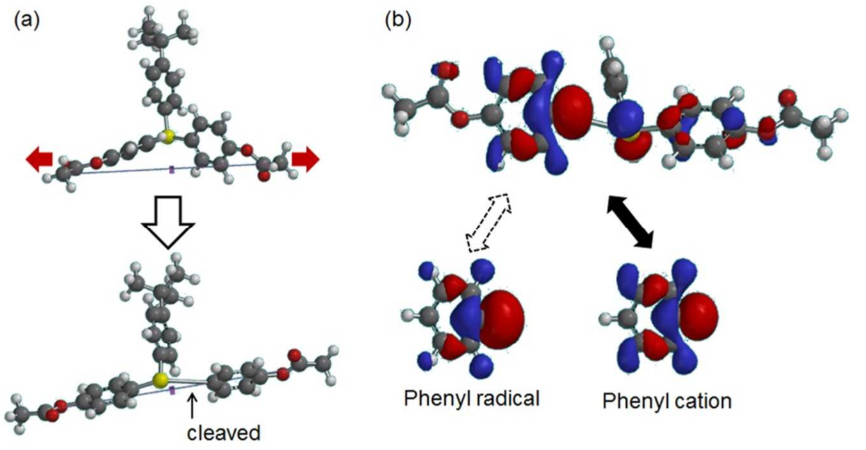


Figure 2. (a) Calculated TAS structure through a CoGEF simulation and (b) calculated LUMO of the cleaved structure compared to the LUMO of phenyl radical and cation. All calculations were done Spartan ’10 at the B3LYP/6-31G* level of theory.

As an initial step, we used CoGEF simulations to predict the mechanochemical reaction.[7c,15] Therein, the simulation is employed to examine effects of induced molecular scale mechanical deformation by artificially constraining the distance between two points (i.e., two atoms at each end of the mechanophore). The CoGEF calculation was applied to a model TAS and revealed that selective scission occurred at the C-S bond in a constrained geometry (Figures 2a and S4). Moreover, the LUMO of the resulting mechanically-cleaved structure was calculated and found consistent with phenyl cation and not with the phenyl radical (Figure 2b).[16] Thus, the DFT calculations support our hypothesis that the polarized bond in TAS undergoes heterolytic C-S scission by mechanical activation to generate a phenyl cation, even given that phenyl cation is 530 kJ/mol more stable than phenyl radical. Homolytic bond scission would produce a diaryl sulfide radical cation, which is 526 kJ/mol less stable than diaryl sulfide; i.e., the energy difference between homolytic and heterolytic bond scission is negligible (energies calculated with addition of acetonitrile solvation using the SM8 solvation model).[17]

We investigated the mechanoresponsiveness of PMA-TAS experimentally by applying solvodynamic shear forces to dilute polymer solutions using an ultrasound horn.[2a,b] GPC analyses of sonicated PMA-TAS indicates the polymer was cleaved approximately in half (Figure S5) and NMR signals pertaining to the aromatic groups of TAS were significantly shifted (Figure S6), indicating that chain scission occurs at the TAS center. For control experiments, TAS initiator itself and its mixture with homo PMA were sonicated under the same conditions. NMR of the sonicated products in both cases showed no significant changes, indicating the reaction is not thermal (Figure S7).

^{19}F NMR measurements revealed structural changes of the resulting product which were unexpected (Figure 3). Before sonication, a single peak at -78.9 ppm was observed, which is ascribable to the trifluoromethanesulfonate counter anion of PMA-TAS. Interestingly, sonication gave rise to a single new peak at -62.5 ppm. After consulting ^{19}F NMR tables, the only plausible assignment would be to a trifluoromethylphenyl group. We confirmed this assignment by preparing 4-(trifluoromethyl)phenyl acetate through simple acetylation of *p*-trifluoromethylphenol with acetic anhydride. ^{19}F NMR analysis showed a peak at -62.3 ppm, very close to the one observed in PMA-TAS after sonication. In contrast, TAS initiator sonicated or photo-irradiated by itself or in the presence of homo PMA exhibited no change in the ^{19}F NMR spectra (Figure S8). Moreover, low-molecular weight PMA-TAS (19 kDa), which did not fragment under sonication conditions (Figure S9), showed no spectral shifts in the ^{19}F and ^{1}H NMR data after sonication (Figures S10 and S11, respectively). Thus, these results point to a trifluoromethyl phenyl terminated product, caused by reaction of the mechanochemical product of TAS with its counter anion, which is the only source of fluoride atoms in the mixture. Furthermore, this product is not observed in the photochemical reaction.

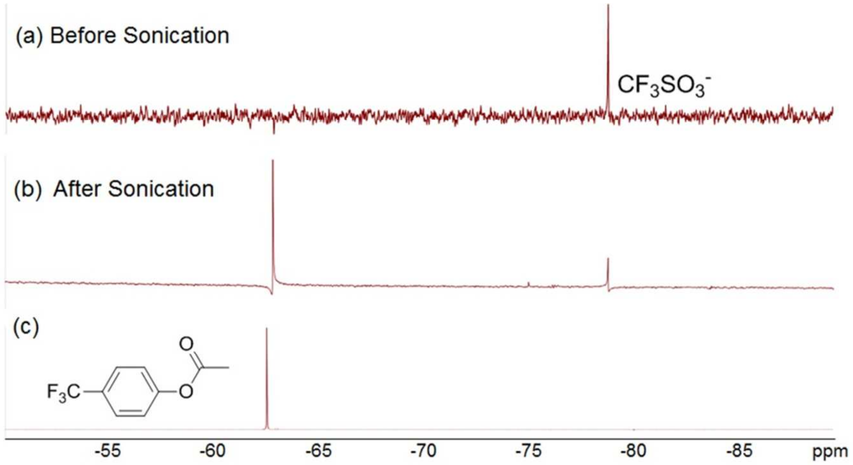
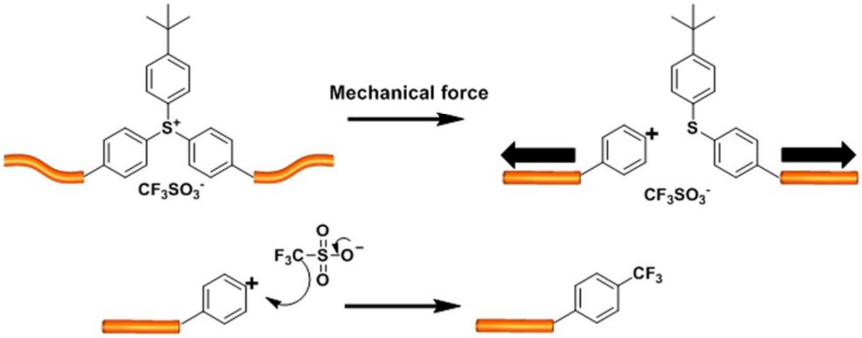


Figure 3. ^{19}F NMR spectra of PMA-TAS (a) before and (b) after sonication and (c) 4-(trifluoromethyl)phenyl acetate as a control compound; solvent:CDCl$_3$, sonication: 60 min in acetonitrile under a N$_2$ atmosphere at 6 °C.



Scheme 2. Proposed reaction mechanism of TAS in the mechanochemically-induced pathway to generate the trifluorotoluene group.

We propose the mechanochemical heterolytic scission of the C-S bond in the TAS moiety creates a phenyl cation, as anticipated by the computational simulation. The generated phenyl cation is an extremely reactive intermediate and is attacked by the trifluoromethanesulfonate to provide the trifluoromethylphenyl structure (Scheme 2).

Importantly, photochemical activation of TAS is proposed to produce phenyl cations, which rapidly react with diphenyl sulfide to give (phenylthio)biphenyls. These biphenyls form through a direct reaction with the generated diphenyl sulfide or via formation of phenyl radical and diphenylsulfinyl radical cation pair.[10] Subsequently, the following proton extraction and transfer reactions result in acid production. While we cannot disprove this mechanism for our system, this reaction would leave the ^{19}F NMR unchanged and, as observed in Figure 3, a significant portion of the fluoride atoms are shifted. A possible explanation for this significant change in the products is that the pulling force employed during sonication causes the generated species to move rapidly apart from each other. Consequently, the produced phenyl cation is not near the diphenyl sulfide by-product for an electron or hydrogen transfer reaction. Therefore, the cation may react with other components present in solution. Thus, in dilute solutions, mechanochemical scission of TAS not only generates phenyl cations through heterolytic bond scission, it also creates a unique product for this reaction system.

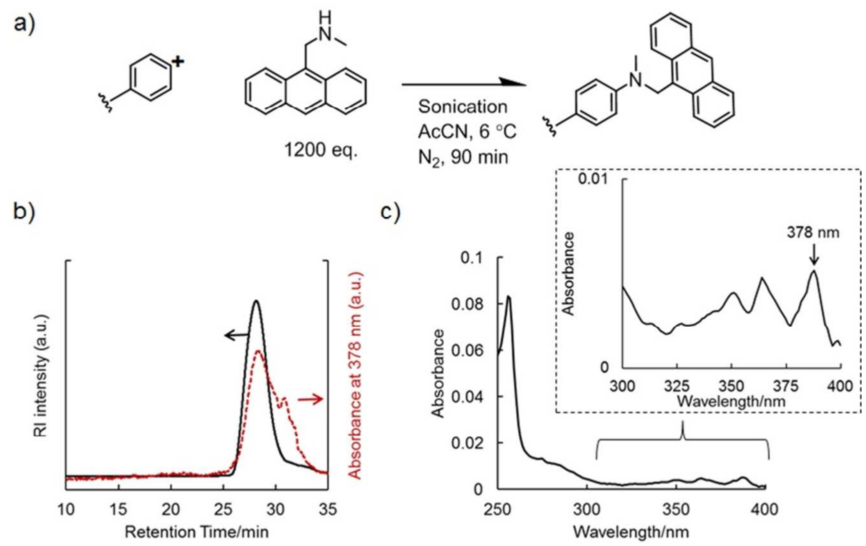


Figure 4. (a) Reaction scheme of phenyl cation with MAMA and GPC analysis results monitoring (b) RI and UV (378 nm) signals (black solid line and red dash line, respectively) and (c) absorption spectrum of the sonicated PMA-TAS with MAMA (retention time 27.5 min). UV absorption data were collected by a PDA detector equipped in the GPC system.

Our hypothesis was also supported by a trapping experiment. Phenyl cation is a high energy intermediate compound in organic chemistry that rapidly reacts with nucleophiles such as amines and alcohols.[18] Based on previous research experiments,[14] we chose 9-(methylaminomethyl) anthracene (MAMA, Figure 4a) as a trapping nucleophile to confirm our reaction mechanism. Sonication of PMA-TAS was repeated under similar conditions, but in the presence of excess amount of the trapping MAMA (1200 eq. molar with respect to the TAS concentration). Figure 4b shows GPC traces of sonicated PMA-TAS in presence of MAMA using RI and photo diode array (PDA) detectors. UV spectrum of the polymer can be seen in Figure 4c. The absorption band of MAMA (Figure S12) was clearly observed in the sonicated PMA-TAS in presence of MAMA. In addition, mixing (no sonication) of

PMA-TAS and MAMA results in no absorbance increase, indicating no nucleophilic attack of MAMA to the TAS (Figure S13). Thus, mechanochemical scission of TAS is necessary to produce a stronger electrophile. These results strongly support our proposed mechanism, and suggest that the mechanochemically generated phenyl cations can be utilized as reactants for chemical reactions with electrophiles. Production of a highly electrophilic reagent will be considerably useful in the design of new mechanochemically triggered responses.

Conclusion

We designed and prepared a new mechanophore that selectively undergoes heterolytic bond scission. CoGEF DFT calculations supported our hypothesis and we prepared PMA-TAS to experimentally study the mechanochemical reaction. Surprisingly, the generated phenyl cations reacted with the counter anion (trifluoromethanesulfonate) to produce a trifluormethylphenyl structure. Although heterolytic scission of C-S bonds in TAS is expected in photochemistry, we observed unique products derived from the polymer mechanochemistry process; herein, the reactive phenyl cation product could react with different solution components and not be limited to reaction with the diphenyl sulfide byproduct. Further studies on this novel mechanochemical reaction are underway in order to elucidate with more detail the mechanism and to direct the reactivity of the phenyl cation. Our efforts will contribute in the development of new mechanochemical self-healing applications utilizing mechanical damage-induced cross-linking/polymerization and mechanical deformation-induced site selective reactions of polymeric materials.

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† Electronic Supplementary Information (ESI) available: NMR data, CoGEF energies and GPC data are included. See DOI: 10.1039/b000000x/

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