WHEN CHEMISTRY MEETS MECHANICS

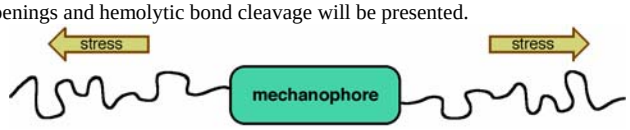
Jeffrey S. Moore, Nancy R. Sottos and Scott R. White

Beckman Institute for Advanced Science and Technology
University of Illinois at Urbana-Champaign
405 North Mathews Avenue
Urbana, IL 61801 USA | Tel: (217) 244-1176

Introduction

Damage-prone regions in polymeric and composite materials are difficult to detect and even harder to mitigate. Damage is preceded by complex spatial and temporal changes in stress state, and it is therefore desirable to utilize these mechanical changes to activate – without human intervention – chemical changes that favorably alter materials properties where and when they are needed. Desirable materials properties brought about in response to high-stress conditions include: (1) signal generation to warn of ensuing failure, (2) molecular structure modification to slow the rate of damage and extend lifetime (e.g., stress-induced crosslinking), and (3) repair of damage to avoid catastrophic failure. Several approaches have been taken to realize these functions including composites that incorporate compartmentalized healing agents and solvents or composites embedded with microvascular networks. These kinetic approaches to healing are triggered by damage in the form of microcracking.

Molecular mechanisms are also needed in which a kinetic barrier can be surmounted by stress-induced activation of a mechanophore – the putitive mechanically active unit. An experimental approach to develop new mechanophores will be presented. Examples involving electrocyclic ring-openings and hemolytic bond cleavage will be presented.

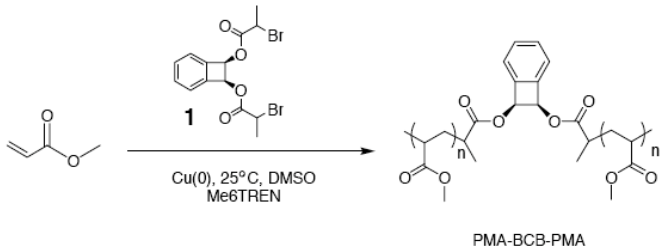


Experimental Section

Ultrasound. Ultrasound experiments were performed on a Vibra Cell 505 liquid processor with a 1/2" diameter replaceable tip titanium probe or solid probe from Sonics and Materials (http://www.sonics.biz/). The distance between the titanium tip and bottom of the Suslick cell was 1 cm. The Suslick cells were made by the School of Chemical Sciences' Glass Shop at the University of Illinois.

A CH_3CN solution of the polymer was placed in an oven-dried Suslick cell that was inserted into a collar, and screwed onto the transducer. A thermocouple and an Ar line were threaded through septa on two of the Suslick cell side arms and placed in contact with the solution, ensuring that they did not touch the probe. The third side arm of the cell was sealed with a plastic screw cap. Ar gas was bubbled through the solution for 30 min prior to each experiment as well as during the experiment. The entire system was cooled in an ice water bath to maintain a temperature of 6-9 °C throughout sonication. The solution was exposed to pulsed ultrasound (0.5 s on, 1.0 s off, 20 kHz, 8.7 W/cm^2).

Mechanophore-Linked Addition Polymers. A freshly opened bottle of ACS grade DMSO from Fischer Scientific was degassed and purged with Ar for 30 min immediately prior to using it for polymerization. BCB initiator (9.76 mg, 0.024 mmol, 1 equiv), Cu(0) (6.14 mg, 0.097 mmol, 4 equiv), and Me6TREN (21.89 mg, 0.095 mmol, 4 equiv) were weighed into aluminum weigh boats using a microbalance and each compound was added to a 10 mL Schlenk flask equipped with a Teflon stir bar. Methyl acrylate (2.0 mL, 22.21 mmol, 925 equiv) and DMSO (1.0 mL) were then added to the Schlenk flask via micropipette (a small amount of the monomer and solvent were used to wash residual initiator and ligand from the weigh boats into the reaction flask). The flask was sealed, the head space was evacuated, and the reaction was submitted to three freeze-pump-thaw cycles. The Schlenk flask was backfilled with Ar and stirred at room temperature in a water bath. Aliquots were periodically withdrawn, dissolved in $CDCl_3$, and the ^{1}H NMR spectrum acquired to determine reaction conversion. Upon completion of the reaction (93% conversion, 55 min), the flask was opened to air and THF (2 mL) was added to the viscous solution. The reaction was filtered through a 0.45 μm nylon filter to remove Cu(0) particles andprecipitated into stirring MeOH. The MeOH was decanted and the polymer was washed 3 times by adding fresh MeOH, stirring for 30 min, and decanting the solvent. The polymer was collected and dried under vacuum. The Mn and Mw/Mn values were determined by analytical GPC with polystyrene standards. Mn = 87.4 kDa, Mw/Mn = 1.3.



PMA-BCB-PMA

Results and Discussion

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 sonication3 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.

No UV signal was present in the GPC trace of the sonicated low molecular weight PMA-BCB-PMA, indicating no reaction. The lowest molecular weight polymers exhibited no chain cleavage, as indicated by the superposition of analytical GPC traces collected before and after sonication. This result is consistent with a lower molecular weight threshold for chain cleavage of PMA by ultrasound. The GPC trace of an intermediate molecular weight sample (91 kDa) PMA-BCB-PMA exhibited a marked increase in the UV signal following sonication. These observations together with the appropriate controls 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.

A spiropyran bisfunctionalized with alpha-bromo-alpah-methylpropionyloxy groups was used as a SET-LRP initiator to produce spiropyran-linked (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. Exposure to ambient light for 40 min at room temperature caused the color to disappear, consistent with the known photolytic reversion to the closed form.

Conclusions

An summary of new chemistries and experimental methods for the development of mechanically responsive materials including self-healing polymers will be presented.

Acknowledgements. This work was supported by the Army Research Office (grant no. W911NF-07-1-0409) by the Air Force Office of Scientific Research (grant no. FA9550-05-1-0346).