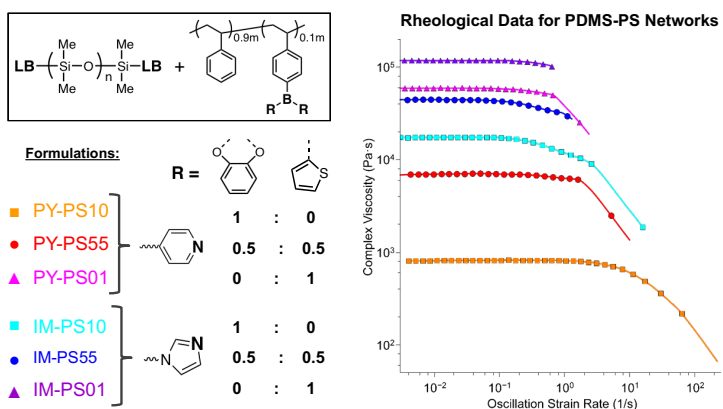


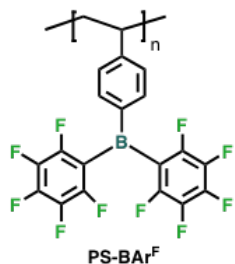
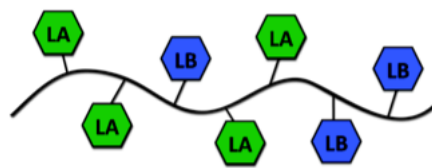
Project D: Sustainable Chemistry: Polymer-Supported Lewis Acids and Pairs

1) Development of Transient Polymer Networks [D1-D2]. The reversibility of Lewis pair interactions presents a largely overlooked motif in the development of supramolecular materials, despite many potential advantages, including the facile tuning of the LA and LB strength. We generated novel TPNs by physically blending immiscible but complementary LB-functionalized telechelic PDMS (as the soft network branches) and LA-functionalized PS (as hard multi-crosslinking points) with the aim of studying the effect of the LP strength on the mechanical properties of the network. Drawing on our earlier work on borane-functionalized PS homopolymers, PS random copolymers bearing tricoordinate organoboranes were conveniently obtained in one pot from 10 mol% SiMe₃-functionalized PS. LB-functionalized ditelechelic PDMS polymers ($M_n = 9600$ Da) were prepared from commercial vinyl-terminated PDMS using thiol-ene “click” chemistries. PDMS/PS blends were then generated by mixing solutions of the selected polymers in stoichiometric ratios and annealed at 60–80 °C, giving rise to perfectly homogeneous, transparent, air and moisture stable (most B centers are tetracoordinate), and viscoelastic gels. Rheology measurements showed a striking 2 orders of magnitude difference in complex viscosity between the network containing the *weakest* LP (BR₂ = BCat (Cat = catecholate), LB = pyridyl, PY; G' > G'') and that containing the *strongest* LP (BR₂ = BTh₂ (Th = 2-thienyl); LB = imidazolyl, IM; G' > G''), while the values for blends from 50:50 mixtures of PS-BTh₂ and PS-BCat were in between those of the TPNs made with only one type of LA. Other viscoelastic parameters such as the relaxation time (3 orders of magnitude difference) and crossover temperatures (66 °C difference) followed a similar trend. The self-healing ability of the networks was observed by allowing the pieces of broken gels to stand at room temperature undisturbed for several days. Those with the weakest LP healed much faster, attributed to the more facile and reversible crosslinking. These findings unequivocally demonstrate that LA-LB pair formation is a highly tunable, versatile and promising tool for supramolecular materials design.



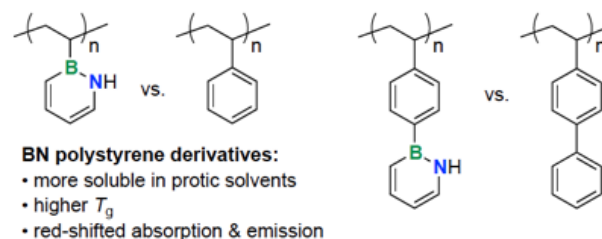
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2) Polymer-supported Catalysts [D3]. The goal of this project is to combine the benefits of metal-free small molecule activation processes with polymer-supported catalyst technologies. Toward this end we prepared polymers that are functionalized with highly electron-deficient main group Lewis acid (LA) sites and/or sterically hindered Lewis basic (LB) donor ligands such as amines, phosphines, and carbenes. Both soluble polymers and functional porous polymeric materials are pursued. The resulting materials are expected to be advantageous in small molecule activation, transition-metal free hydrogenation, hydrosilylation and other organic transformations.

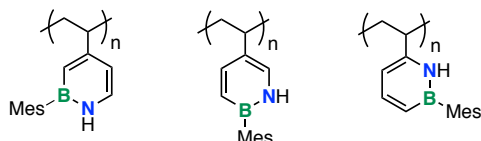


In earlier work we succeeded in the preparation of a highly Lewis acidic polymer containing pentafluorophenyl substituents on boron (PS-BAr^F). This unusual polymer represents a supported analog of the industrially important class of fluorinated organoborane Lewis acid catalysts. However, we found that the polymer is susceptible to hydrolytic/oxidative degradation, complicating applications in catalysis. In current work we are exploring new polymeric materials with more sterically demanding, yet highly electron-deficient pendant groups. The results of these studies will be communicated in due course.

3) Other Related Collaborative Efforts [D4-D6]. A collaboration with Prof. Lothar Weber at the University of Bochum (Germany) has taken advantage of our expertise in the borane functionalization of polystyrene derivatives to prepare new materials that contain functional azaborole moieties pioneered by the Weber group. The photophysical characteristics of the products were studied in depth. More recently, we have pursued azaborinine-substituted polyolefins in conjunction with the group of Shih-Yuan Liu. We found striking differences in the polymerization of vinylazaborinine (BN-St) and styrylazaborinine (BN-VBP) which are attributed primarily to the direct attachment of boron to the vinyl group in BN-St. This suggests that the specific position of B and N in BN-substituted styrene plays an important role and further studies on the polymerization of different isomers are in progress in our laboratories. Another intriguing aspect of the resulting hybrid organic-inorganic polymers is that the physical properties, such as solubility characteristics and thermal behavior, are vastly different from those of PS due to the increased polarity of the side groups and the presence of N-H moieties that are capable of hydrogen bonding interactions. Thus, we anticipate the development of azaborinine-substituted polymers to greatly expand the diversity and functionality of PS materials.



Our earlier observation that the parent BN-PS, while showing unusual solubility and thermal characteristics, is obtained in modest molecular weights prompted us to investigate the effects of placing the B-N moieties in different positions relative to the vinyl group on both the polymerizability and the physical properties of the products. We found that with 2 mol% of AIBN as the initiator, the sterically stabilized mesityl-substituted azaborine polymers are all obtained with high molecular weight. These findings indicate that the NH moiety in *ortho*-position to the vinyl group (present in both the parent vinylazaborine and the monomer 6V-NBMes) is not detrimental to the polymerization process. Copolymerization experiments with styrene revealed that both 4V-NBMes and 6V-NBMes polymerize at a higher rate but 5V-NBMes at a lower rate than styrene. The formation of statistical copolymers was supported by DSC studies that yielded glass transition temperatures in-between those recorded for the homopolymers. A manuscript detailing these results is currently in preparation and to be submitted for publication once comparative studies using mesityl-substituted styrene derivatives as direct analogs are completed.



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