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Frustrated Lewis Pair Polymers as Responsive Self-Healing Gels

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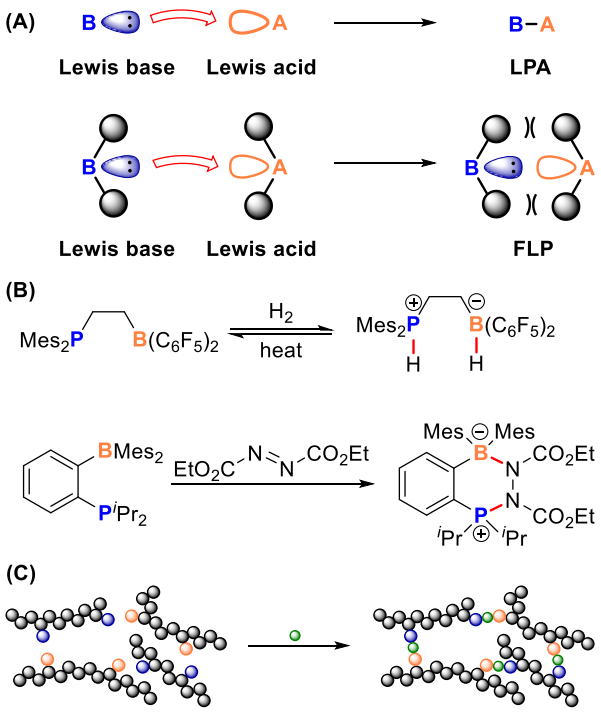
Supporting Information Placeholder

ABSTRACT: Steric bulk prevents the formation of strong bonds between Lewis acids and bases in frustrated Lewis pairs (FLPs), where latent reactivity makes these reagents transformative in small molecule activations and metal-free catalysis. However, their use as a platform for developing materials chemistry is unexplored. Here we report a fully macromolecular FLP, built from linear copolymers that containing either a sterically encumbered Lewis base or Lewis acid as a pendant functional group. The target functional copolymers were prepared by a controlled radical copolymerization of styrene with designer boron or phosphorus containing monomers. Mixtures of the B- and P-functionalized polystyrenes do not react, with the steric bulk of the functional monomers preventing the favorable Lewis acid base interaction. Addition of a small molecule (diethyl azodicarboxylate) promotes rapid network formation, crosslinking the reactive polymer chains. The resulting gel is dynamic, can self-heal, is heat responsive, and can be reshaped by post-gelation processing.

While the formation of new bonds is principally driven by a thermodynamic advantage, bulky reagents can prevent the required close contact necessary for reactivity. This general concept can be applied to the interaction between a Lewis base (an electron pair donor) and a Lewis acid (an electron pair acceptor), creating a frustrated Lewis pair (FLP).[1,2] (Scheme 1A) While conventional Lewis pair adducts can form quite strong bonds, the frustration induced by the steric clashes between acid and base retains the reagents complementary reactivity, promoting activation and catalysis with small molecules like dihydrogen, carbon dioxide, or diethyl azodicarboxylate, DEAD.[2-8] (Scheme 1B)

Polymers with dynamic crosslinks can be reshaped, reprocessed or repaired, giving rise to self-healing and stimuli-responsive materials. Common crosslinking strategies include reversible covalent[9-11], ionic[12,13], or hydrogen bonds[12,14,15], metal coordination[12,16, 17], or even weaker interactions like metal-metal[18] or π-π stacking.[12,19] We wondered if the unique molecular chemistry of FLPs could enable a more specific and triggerable response, where polymers could act as gelators only upon addition of specific small molecules. Establishing an equilibrium between the small molecule and FLP can be shaped by tuning both the sterics and the innate Lewis acidity and basicity of the system. We hypothesized that these interactions would be reversible, providing a new type of dynamic cross-link that could be exploited in stimuli-responsive and self-healing polymer chemistry.

We thus targeted a mixture of linear polymers containing complementary FLP donors and acceptors that can switch the soluble polymers into a gel upon addition of specific small molecules. (Scheme 1C) Although network polymers with Lewis pair adducts are known and a solid Lewis base paired with a solution based Lewis acid acts as a hydrogenation catalyst,[20] an FLP-based responsive network is unprecedented. We now report our first effort of synthesizing poly(FLP)s incorporating linear polymers and their application to gel formation.

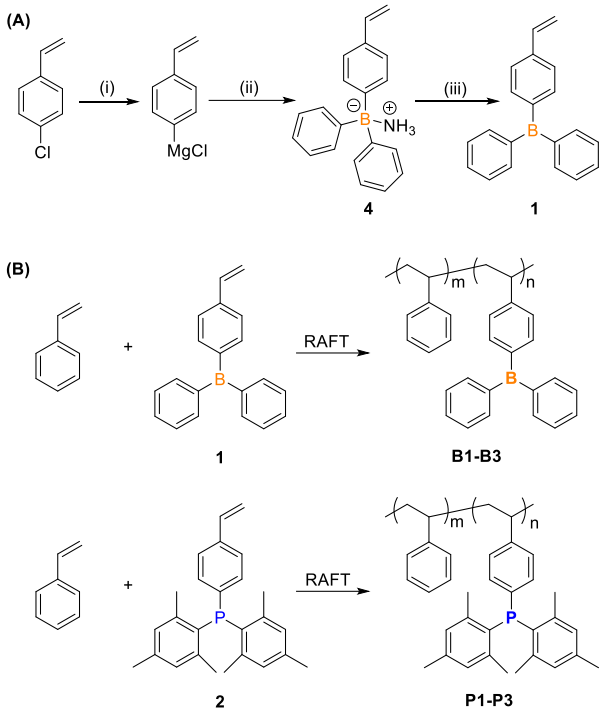


Scheme 1. (A) Comparison of conventional Lewis pair adduct (LPA) and frustrated Lewis pair (FLP); (B) Literature examples of reactions between FLP and dihydrogen/DEAD.[2-8]

(C) Schematic representation of network formation by addition of a small molecule into poly(frustrate Lewis pair)s, orange ball = Lewis acid, blue ball = Lewis base, green ball = DEAD.

In order to target poly(FLP)s, Lewis acidic and basic elements need to be incorporated into polymer chains, either via polymerisation of main-group containing monomers or post-polymerization modification of a parent polymer.[21] The former methodology is more advantageous, as it offers better control over the functional group incorporation, avoiding errors which arise from incomplete modification. In this work, two styryl based monomers, 4-styryl-diphenylborane, **1**, and 4-styryl-dimesitylphosphine, **2**, were designed as the source of FLP functionality. Compared to the more widely used strong Lewis acid tris(pentafluorophenyl)borane, monomer **1** has moderate Lewis acidity, hence could provide the freedom needed to promote the dynamic crosslinking underpinning gel self-healing. The mesitylene group in monomer **2** provides extra basicity and, more importantly, steric hindrance at phosphorus center (4-styryl-diphenylphosphine forms Lewis acid base adducts with **1** in non-coordinating solvents, thus are not ideal FLP partners; see Supporting Information Page S12).

The synthesis of monomer **1** was achieved by reaction of the Grignard derivative of 4-chlorostyrene and a boron precursor, 2-aminoethyldiphenyl borate (**3**, Scheme 2A). An excess of Grignard is used to react with the acidic amine protons in **3** and prevent ethanolamine contamination of the reaction mixture.[22] Quenching by saturated NH_4Cl aqueous solution prevents hydrolysis, forming borane monomer **4**, with NH_3 coordinated to the borane (see SI Figures S4 and S6). Finally, the coordinated NH_3 was removed by treatment with HCl in anhydrous diethyl ether to recover the desired monomer (for the change in chemical shift in ^{11}B NMR see SI Figures S6 and S9). Such a synthetic procedure has advantages, as both **3** and **4** are air-stable, easy to handle, readily purified and amenable to long-term storage. The Lewis acidity of the final monomer, **1**, was tested by the Gutmann-Beckett method.[23-26] The acceptor number (AN) was determined to be 67.6 in CD_2Cl_2, (SI Figure S26) which is comparable to that of triphenylborane (55.0-69.6), but lower than the aforementioned $B(C_6F_5)_3$.[26]



Scheme 2. (A) Synthetic preparation of 4-styryl-diphenylborane, **1**: (i) Mg, THF, reflux 75 min, r.t. 1 h; (ii) 2-aminoethyl diphenylborinate, **3**, THF, -78 °C 1 h, 0 °C 1 h, r.t. 2 h; NH_4Cl (aq) (iii) HCl in Et_2O. (B) Self-initiated RAFT copolymerization of styrene with **1** and **2** using cumyl dithiobenzoate as RAFT agent at 110 °C.

The phosphorus monomer, **2**, was obtained via a similar route, reacting styrylmagnesium chloride with dimesitylphosphorus halide.[27-29] With monomers in hand, their reactivity as FLPs was explored. Mixing equimolar amounts of **1** and **2** in toluene confirmed no significant reaction between the Lewis acid base pair, evidenced by NMR spectroscopy. However, a mixture of **1**, **2** and the azo bridge **DEAD** (5.0 eq.) dissolved in toluene produced a rapid reaction. (Figure 1) Both ^{31}P and ^{11}B NMR spectra show monomer binding with **DEAD**. In the ^{31}P NMR spectrum, a **2•DEAD** adduct is seen as a broad peak at 25.8 ppm, as assigned by **DEAD•2** NMR studies, alongside the desired **1•DEAD•2** adduct indicated by broad peaks at 44.3 and 32.4 ppm for the two crosslink isomers. The ^{11}B NMR spectrum also confirms binding, with **1•DEAD•2** resonances appearing at 6.4 ppm. The broad product peaks in both phosphorus and boron NMR spectra confirms the dynamic exchange between boron monomer and **2•DEAD** adduct. Binding is efficient, as no free boron resonances are observed.

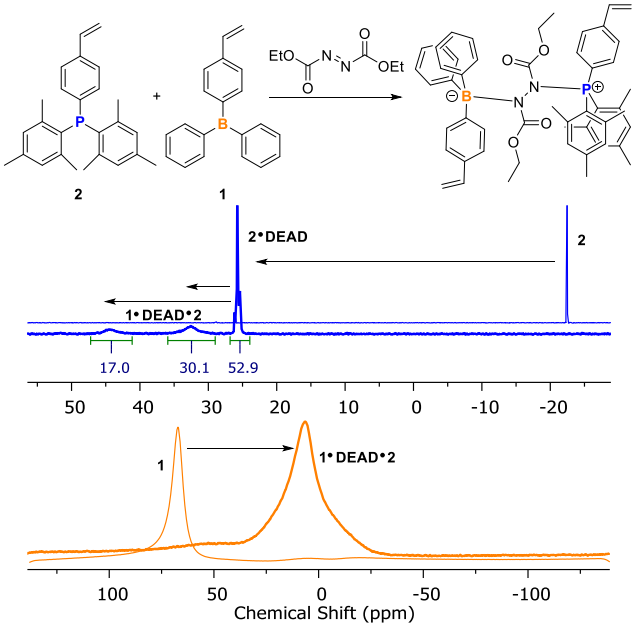


Figure 1. Binding among monomers **1**, **2** and **DEAD** (5 eqv.). Blue line: ^{31}P NMR spectrum of the reaction mixture (bold) and pure monomer (thin); Orange line: ^{11}B NMR spectrum of the reaction mixture (bold) and pure monomer (thin). Broad background peak overlapping with product peak **1•DEAD•2** arises from the borosilicate NMR tube.

As simple free radical polymerizations gave poor yields and uncontrolled properties, we used reversible addition fragmentation chain-transfer (RAFT)[30,31] copolymerization of styrene to produce the target polymers (Scheme 2B). Gradient copolymerization of styrene with a small quantity of either boron or phosphorus containing monomers, using cumyl dithiobenzoate as a chain transfer agent,[30] afforded the desired polymers with excellent yields and product control. Three different feed ratios of monomers (SI Table S1 and S2) gave copolymers B1-# and P1-# containing different amounts of Lewis acid/base centers. While polymerizations in bulk styrene are effective for low loadings of **1** and **2**, the limited solubility of these functional monomers in styrene means that addition of toluene solvent is preferential for copolymer synthesis. Full synthetic protocols are provided in the Supporting Information. Molecular weights were determined by gel-permeation chromatography, with boron-functionalized polymers requiring post-polymerization modification by coordination of trimethylamine or pyridine to allow elution. For all polymerizations, well controlled molecular weights in good agreement with theoretical values coupled with narrow dispersities indicated a "living" polymerization. The boron-containing copolymer's Lewis acidity was examined by Gutmann-Beckett method as well (SI Figure S27 and S28). The acceptor number was determined as 51.9 in CD_2Cl_2 and 58.5 in toluene-d_8, showing a slightly reduced Lewis acidity of the boron post-polymerization due to the random coiled structure of the dissolved chain blocking coordination.

With polymers in hand, network formation experiments began using copolymers **P1** and **B1**. (Figure 2, SI Movie S1) Solutions of **P1** and **B1** polymers in toluene were prepared with an equivalent number of boron and phosphorus atoms. No change in solution morphology or viscosity is observed; the polymers are too bulky to form Lewis acid base adducts. However, addition of **DEAD** (6 eqv.) firstly formed a homogenous solution, transforming into a gel within 2 seconds. Note that the original pink colour arises from the RAFT chain end, while the strong orange color in the gel arises from the orange **DEAD**. Within 10 seconds from **DEAD** addition, gelation was strong enough to maintain its shape upon inversion of the vial, absorbing the toluene solvent. Left to stand in solution, the dynamic gel continues to rearrange, with volume shrinkage expelling some solvent as the network adopted a thermodynamically more favorable configuration.

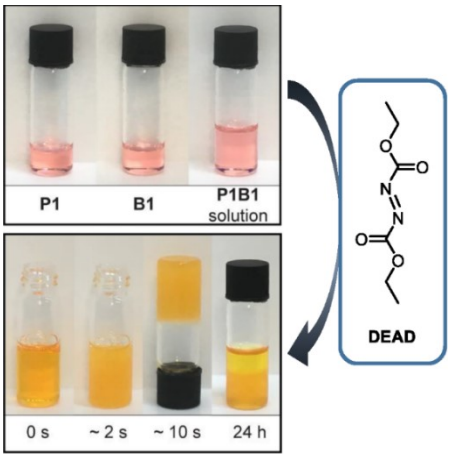


Figure 2. Network formation of copolymer solution **P1B1** by addition of **DEAD**.

The rapid injection of **DEAD** initially reacts with local B and P centers, constraining the system and forming a temporarily set gel. As the exchangeable FLP crosslinks continue to equilibrate, the additional optimized crosslinks will access a more stable gel structure over time. This reorganization can be tracked by measuring the gel volume over time. Gel formation between copolymer **P1** and **B1** (8% boron), **B2** (16% boron) and **B3** (30% boron) was always rapid, with set gels forming in <10s. For **P1B1**, shrinkage starts quickly, with the bulk of reorganization occurring over 240 minutes, to 67% of initial gel volume. **P1B2** shrinking requires over 500 minutes, with this slower reorganization allowing for a smaller end volume (59%). With the higher B concentration, the initial rapid gelation likely has a more constrained configuration, as cross-linking between individual macromolecules is favored over an extended network. **P1B3** extend this concept, with the gels so highly constrained that reorganization is no longer possible. No observable shrinkage is noted over 48 h, and without this reorganization, the strength of the network is compromised and the gel is easier to break. Increasing both B and P loadings also impacts gelation. Addition of **DEAD** to either **P2B2** or **P3B3** solutions gives rapid precipitation of highly cross-linked polymers that do not form gels under standard conditions, (SI Figure S31 and S32) although improved gelation is possible at much higher dilutions. Crosslinking to the FLPs is further confirmed by observation of coordinated DEAD in IR spectroscopy (SI Figure S36-S38).

The dynamic nature of crosslinkings was also observed by rheology analysis. A cross-over between storage (G') and loss (G") moduli was observed (see G'/G" vs. angular frequency plot, Figure S34). Such behavior is observed in vitrimers, suggesting the relaxation of network at long time scales.[32] This result also confirms the fluidity of the gel formed.

After gelation, it is easy to remove the gels from the polymerization vessel. As the FLP interactions are dynamic, the network can be reshaped while swollen with solvent. The best gel stability was with the **P1B1** network. Gels could be dried and reswollen easily, with 329% average swelling ratios after 48 h (SI Figure S30). Weaker **P1B3** gels swell quickly, but break after 2h. (SI Figure S30)

The internal structure also depends upon this crosslink variability, as shown by scanning electron microscopy (SEM) analysis of samples freeze-dried from benzene-swollen gels. (Figure 3) The **P1B1** samples exhibited an irregular, dense structure composed of a network of pores within a continuous polymer mesh. The structure of the **P1B2** gel was significantly different, consisting mainly of a porous and compact continuous structure, with the presence of a secondary network not clear. **P1B3** displayed a clear network-like structure with pores that are 500 – 1000 nm in size, and filament strands about 300 – 600 nm thick. These fine pores and absence of a continuous polymer phase may contribute to the gel being easier to break.

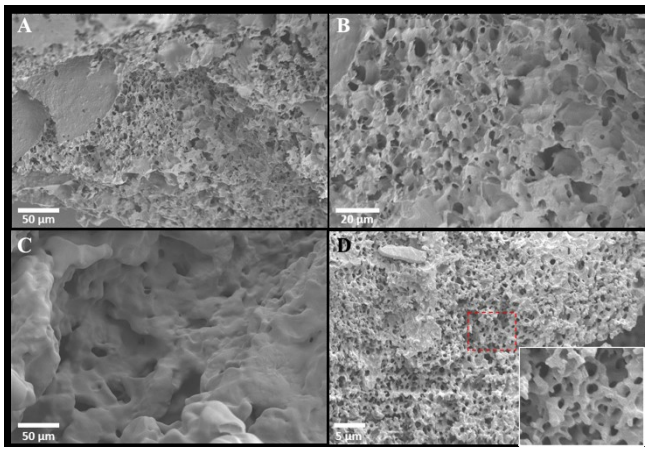


Figure 3. SEM images to show the microstructure of freeze-dried gels of (A) **P1B1** and (B) higher magnification of **P1B1**; (C) **P1B2**; (D) **P1B3**; Inset in (D) higher magnification of the area marked by the dotted square.

The binding between small molecules and FLPs is reversible and can be affected by external stimuli such as temperature and pressure.[2-4] In the case of **DEAD**, higher temperatures may cleave the boron-nitrogen dative bonds. Indeed, external heating of the fully swollen gel to 100 °C leads to rapid (few seconds) gel rupture and dissolution of the polymer chains (Figure 4 and SI Movie S2), with confirmation of cleavage of **DEAD**-boron bonds by NMR spectroscopy. Lower temperatures (i.e. 50 °C) can also break the gel, but much longer heating times are required.

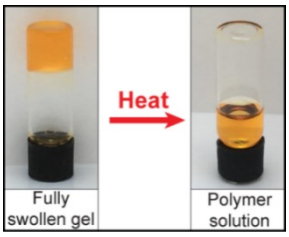


Figure 4. Rupture of FLPs crosslinked polymer network in response to heat.

Of course, if the poly(FLP)s are truly dynamic solvogels, self-healing of the materials should be possible. Both vacuum dried xerogels and swollen gels were explored as potential self-healing materials (Figure 5). For the former, a brittle xerogel was fractured into many pieces and immersed in solvent. The gel absorbed solvent quickly, with individual segments gaining mobility. After 5 h, the gel was swollen and reformed. This initially healed gel was still weak, continuing to rearrange cross-links over 24 hours until no fractures remained and the healed gel was formed. (Figure 5A) The healing of a swollen gel is much more rapid. Cutting a brick-shaped gel into two pieces (Figure 5B), contact of the swollen segments (Figure 5C) and application of toluene to the interface (Figure 5D) promotes fast self-healing, reforming the full gel in only a few minutes (Figure 5E). Self-healing is even faster when immersing the blocks in solvent, with healing occurring in less than 1 min. Note that oscillating rheology was not feasible due to the slow degradation of the broken network in air. While the gels are stable under inert conditions for long periods, slow hydrolysis is observed over 1 week when stored in air.

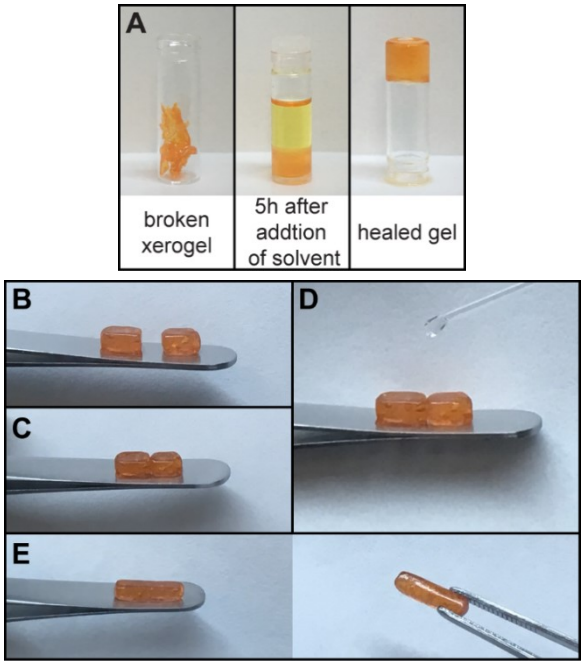


Figure 5. Self-healing of (A) a broken xerogel; (B-E) a cut brick-shaped swollen gel.

We report the development of the first polymeric frustrated Lewis pairs. These poly(FLP)s offer an entirely new type of dynamic crosslinks, allowing for triggered gelation, responsive gel rupture and self-healing. The gels can be tuned by controlling loading of the boron and phosphorus functional monomers, introduced into styrene copolymers through controlled radical polymerization. This initial finding offers a new concept in materials design through altering the macromolecular architecture (blocks, stars, surfaces), monomer reactivity (higher Lewis acidity and basicity) and crosslink nature to tune gel properties and open up applications in small molecule storage (i.e. CO_2 / H_2), stimuli-responsive materials and catalysis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information of detailed experimental synthetic procedures and characterization data is available free of charge on the ACS Publications website.

Experimental details (PDF)

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Notes

The authors declare no competing financial interests.

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