The incorporation of organoborane moieties into polymers is not only of great interest for the development of supported Lewis acid catalysts, but also provides new opportunities for applications in the field of materials chemistry. Our initial synthetic approach for the generation of well-defined boron-containing polymers has relied on the “masking” of styrenic polymers with silyl groups that can then quantitatively be replaced with boron tribromide to give access to the reactive polymer poly(4-dibromoborylstyrene). This unusual functional polymer is highly versatile in that the Lewis acidity of the individual boron sites can readily be fine-tuned through high-yield substitution reactions. We thereby gain access to a family of new boron polymers (PS-BR₂; R = alkyl, aryl, alkoxy, amino groups), including highly Lewis acidic triarylborane polymers that are otherwise very difficult to prepare.

In contrast to most previously reported organoboron polymers, we are able to realize different polymer architectures and place the Lewis acid groups at well-defined positions. Our approach can be directly applied to the synthesis of random copolymers, telechelic (end-functionalized) polymers, and block copolymers containing organoborane moieties at well-defined positions of the polymer chain.

More recently, we have also succeeded in the direct polymerization of functional polymers, thus further expanding the scope of this chemistry. We expect these novel materials to lead us into intriguing new areas including micellar catalysis, nanostructured materials, and even drug delivery applications in the case of B(OH)₂-functionalized polymers. Some recent projects are described in a bit more detail in the following.

### Luminescent Organoboron Polymers for Sensor Systems and Device Applications.

Molecular species such as aluminum tris(8-hydroxyquinolate) (Alq₃) and related diphenylboron-quinolate (Ph₂Bq) are known to possess excellent properties as electron-conduction and light emitting components in organic light emitting diodes (OLEDs) and related devices. The use of polymeric materials is expected to be advantageous due to the improved processability, which facilitates device fabrication. We found that polymer substitution reactions as outlined above provide a straightforward route to suitable organoboron polymers, such as the novel organoboron quinolate polymers shown here. These polymers are highly soluble and luminescent thin films can be cast from solution. Importantly the emission characteristics of these materials are readily tuned by variation of the substituent X on the quinoline moiety, covering almost the entire visible spectrum from blue to red.

We have further extended this work to block copolymers that feature organoboron quinolate chromophores as pendant groups of one of the polyolefin blocks. In this case, direct polymerization techniques can be utilized to successively polymerize each of the constituent blocks. Using this strategy we have prepared fluorescent amphiphilic block copolymers and the first examples of organoboron star polymers by reversible addition-fragmentation chain transfer (RAFT) polymerization of fluorescent styryl-type organoboron monomers.

Well-defined luminescent star polymers can be obtained with a boron quinolate crosslinker and PNIPAM-b-PS in the shell. A combination of dynamic light scattering and TEM imaging was used to confirm the structures. The star polymers further aggregate in water to form strongly green-luminescent superstructures. These polymers could prove useful for biological imaging applications.

Application of our synthetic strategy to tricoordinate organoboron polymers results in interesting sensory materials, which function based on the selective interaction of nucleophiles with the Lewis acidic boron centers. Coordination of the substrate to boron triggers a response in the photophysical characteristics of suitably substituted luminescent organoboron polymers (e.g. bithiophene and mesityl substituents on boron shown here). This response is specific to...
the nature of the nucleophile under investigation and can readily be verified via spectroscopic screening. We discovered that our polymers selectively bind fluoride and cyanide, a process that leads to a distinct change in the absorption and emission color. Intriguingly, amplification effects were observed in the case of fluoride binding, allowing for highly efficient detection in the low micromolar concentration range. The amplification effect, which is more commonly encountered for conjugated polymers (see Project B), is tentatively attributed to through-space energy migration.

II Organoboron Polymers as “Polymeric Lewis Acids”.

We also succeeded in the synthesis of a highly Lewis acidic polymer containing pentafluorophenyl substituents on boron, PS-B(C₆F₅)₂. This unusual polymer represents a supported analog of the industrially important class of fluorinated organoborane Lewis acid catalysts. The key step in the synthesis of PS-B(C₆F₅)₂ relies on the selective exchange of the bromine substituents in PS-BBr₂ with pentafluorophenyl copper, a novel aryl transfer reagent developed in our laboratory (see Project D). These and related polymeric Lewis acids are promising as supported Lewis acid catalysts, as activators for olefin polymerization, and for small molecule activation in combination with bulky Lewis bases (so-called “Frustrated Lewis Pairs”).

Further, we study the coordination of Lewis bases to our polymeric Lewis acids with special emphasis on the aggregation behavior with donor-functionalized polymers. Fine-tuning of the Lewis acidity of the boron centers allows us to control the strength and reversibility of the donor acceptor bonding. For instance, triarylborane polymers PS-BR₂ (R = thienyl, C₆F₅) and borane polymers PS-BH₂ strongly coordinate nucleophiles as exemplified in the formation of soluble, isolable polymeric donor acceptor complexes with pyridines. A temperature-dependent equilibrium between coordinated and non-coordinated sites on the other hand is established with weak donors. The supramolecular assembly of polymeric Lewis acids and Lewis bases is expected to allow reversible formation of complex polymer architectures such as block- and graft-copolymers and of cross-linked materials.

III Boronic-acid Functionalized Block Copolymers.

Polyelectrolytes and amphiphilic block-copolymers are well known for their unique physical properties including the formation of unusual self-assembled structures in solution as well as the bulk material. In an intriguing variation of this theme, we have prepared boronic-acid functionalized block copolymers that are pH sensitive: at high pH they essentially behave like ionic borate-polymers and form spherical micelles in solution as evident from TEM analysis. However, when dissolved at a pH close to 7, (reversible) cross-linking occurs and larger aggregates are observed by TEM analysis. Thanks to their ability to reversibly bind sugars and other biomolecules, they show great potential as stimuli-responsive materials and in delivery applications.

IV Metallopolymers and Supported Catalysts.

We have also successfully converted our organoboron precursor polymers to ionic borate and boronium-based polyelectrolytes and amphiphilic organoboron diblock copolymers. They form very regular micellar structures in solution based on dynamic light scattering and TEM studies. Loading with transition metals (e.g. Rh) leads to catalysts that are encapsulated in the core of the micelles. While the borate moieties are weakly coordinating in the previously described materials, strong metal binding can be achieved with tris(1-pyrazolyl)borate (Tp)-functionalized polymers. Tp complexes are widely applied in catalysis and materials chemistry. Polytopic Tp complexes that are anchored to polystyrene were prepared through a carefully designed synthetic protocol that allows for selective polymer attachment and facile control over the degree of loading with the ligand binding sites. This polymeric ligand scaffold in turn serves as a
versatile precursor to metal-containing polymers. Complexation with CpRu moieties was studied to demonstrate the synthetic utility. In collaboration with the Sheridan group we are extending this concept to other ligand types.

Tris(2-pyridyl)borates represent a new robust and tunable ligand family that combines the desirable complexation behavior of “scorpionate” ligands with the high stability of weakly coordinating arylborate anions. Initial studies on the ligand properties of tris(pyridyl)borates have focused on the ability of the tris(pyridyl)borate to form complexes with M\(^{2+}\) metal ions (M = Mg, Fe, Mn, Cu). As an example, treatment with FeCl\(_2\) in THF/MeOH in the presence of NEt\(_3\) resulted in a red solid that was purified by column chromatography and recrystallized from toluene. Based on the NMR data, the iron complex is diamagnetic in solution at RT, indicating a low spin configuration, which is consistent with solid state data derived from a single crystal X-ray diffraction analysis. UV-vis measurements were performed in CH\(_2\)Cl\(_2\) to further explore this aspect. Absorption maxima at ca. 480 and 430 nm can be assigned to M→L charge transfer (MLCT). Given the high stability, the strongly donating ability toward main group and transition metals, and the possibly for modular synthesis and ligand fine-tuning using different pyridyl derivatives, we anticipate broad applications of this new ligand class in catalysis, bioinorganic chemistry, and in the field of supramolecular polymer chemistry. Current work focuses on polymerizable derivates of the pyridylborates and related charge-neutral pyridylsilane species.

**Relevant Publications:**


