Lewis Acidic Organoboron Polymers

*Yang Qin, Guanglou Cheng, Kshitij Parab, Anand Sundararaman, Frieder Jäkle**

Department of Chemistry, Rutgers University-Newark, 73 Warren Street, Newark, NJ 07102, USA

Summary: We have developed a highly efficient new method for the introduction of Lewis acidic boron centers into the side chains of organic polymers. Our methodology involves three steps: (i) the controlled polymerization of a functional monomer, (ii) the exchange of the functional group for Lewis acidic boron centers, and (iii) the fine-tuning of the Lewis acidity of the individual centers through substituent exchange reactions with nucleophiles. This approach gives access to a family of new well-defined organoboron polymers including moderately Lewis acidic poly(arylboronates) and the first examples of highly Lewis acidic fluorinated triarylborane polymers.

Keywords: ATRP; free radical polymerization; inorganic polymers; Lewis acid; organoborane

Introduction

Inorganic and organometallic polymers have over the past two decades emerged as an important area of research in the field of materials chemistry. New devices have, for example, been developed based on polysiloxanes and polysilanes, new advances in medical research have been triggered by the discovery of polyphosphazenes, and more recently, transition metal containing polymers have been developed for nanoscience applications.[1] The incorporation of electron-deficient boron centers into polymer structures is particularly intriguing as it, for example, provides an opportunity to further manipulate the polymers via donor acceptor bonding.[2] Binding of nucleophiles to organoboron polymers can be exploited for the design of new supported reagents and immobilized catalysts[3] and of highly selective sensor materials[4]. Boron containing polymers also play a major role as intermediates in the synthesis of functionalized polymers with polar side-groups[5-7] and are used as polymeric electrolytes for batteries[8], sophisticated flame retardants[9], and as preceramic[10] and photoluminescent materials[11].

Despite these recent advances, a general straightforward method for the synthesis of Lewis acidic boron polymers of controlled molecular weight and well-defined architecture is currently not

CCC 1022-1360/00/$ 17,50+.50/0

known. Moreover, the boron centers in most of the reported oligomers and polymers are either electronically stabilized by π-interactions with heteroatoms such as oxygen or nitrogen and/or contain highly bulky substituents. The Lewis acidic sites are therefore often not readily available for binding of Lewis bases. Our research program is aimed at the development of well-defined soluble organoboron polymers and copolymers of controlled architecture, molecular weight and degree of functionalization, in which the substituents on boron can be readily exchanged and consequently the strength of the Lewis acid centers can be fine-tuned (Figure 1).

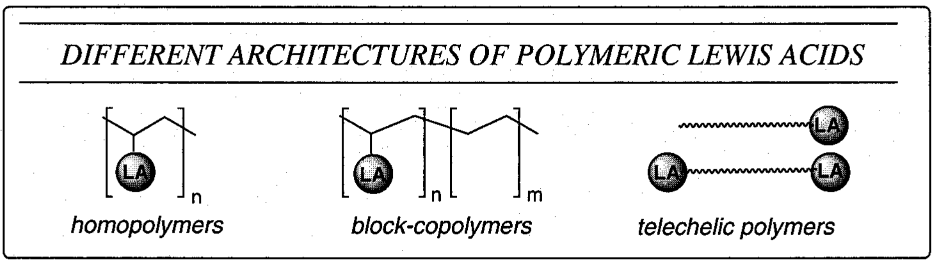
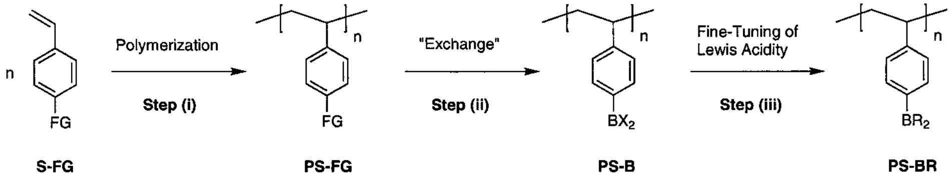


Figure 1. Schematic representation of side-chain boron-based polymeric Lewis acids.

While side-chain organoboron polymers can be prepared from organoboron monomers using a variety of polymerization techniques including standard free radical polymerization[12], metathesis polymerization[13], and Ziegler–Natta polymerization[5], the polymerization of monomers bearing strongly Lewis acidic moieties has been largely restricted to Ziegler-Natta polymerization procedures[5] due to the high reactivity of the monomers. The functionalization of organic polymers or resins in a post-polymerization modification step represents an alternative to the polymerization of borylated monomers. This method has attracted a lot of attention for the development of supported Lewis acid catalyst, in which the Lewis acid centers are attached via multi-step polymer modification reactions with typically moderate degrees of functionalization.[3] The direct borylation of polystyrene has been attempted with boranes X_2BH under forcing conditions, but occurs with low selectivity.[14] In an exciting new development, transition metal catalyzed borylation of polyolefins has been reported by Hartwig and Hillmyer and coworkers to yield boronate-functionalized polymers in one step.[7]

We have developed a new methodology for the synthesis of organoboron polymers that involves three steps: (i) the controlled (co)polymerization of a functional monomer (**S-FG**), (ii) the exchange of the functional group in polymer **PS-FG** for Lewis acidic boron centers to give the borylated polymer **PS-B**, and (iii) the fine-tuning of the Lewis acidity of the individual centers through substituent exchange reactions with nucleophiles, which gives access to a family of new well-defined polymers **PS-BR** bearing Lewis acidic boron centers (Scheme 1).[15]



Scheme 1. General method for the synthesis of organoboron polymers of varying Lewis acidity.

Atom Transfer Radical Polymerization of 4-(Trimethylsilyl)styrene

4-Trimethylsilylstyrene was polymerized in anisole (50%) according to a typical protocol for atom transfer radical polymerization (ATRP)[16] initiated with 1-phenylethyl bromide (PEBr) and catalyzed by CuBr / pentamethyldiethylenetriamine (PMDETA) (68.5% conversion within 5 h at 110 °C). The molecular weight and polydispersity of the resulting polymer were determined by GPC analysis relative to polystyrene standards to M_w = 6,540 and PDI = 1.14.[17] Molecular weight analysis by static light scattering measurements gave a similar result (M_w = 6,810) indicating a close similarity of the MW to elution volume relationship for polystyrene and the silylated polymer **PS-Si**.

Kinetic analysis of the polymerization reaction confirmed the controlled nature of the polymerization. The linearity of $\ln[M]_0/[M]$ vs. time in the pseudo first order kinetic plot (Figure 2) indicates that the number of active species in this system remains constant throughout the reaction and the chain-termination reaction is insignificant, i.e. $K_p[P^*]$ = constant, where K_p stands for the rate constant and $[P^*]$ stands for the concentration of active propagation chains. The molecular weight of the active propagation chains increases linearly with increase in monomer conversion and the polydispersity remains narrow throughout the polymerization (*PDI*<1.2). This demonstrates the applicability of our methodology to the preparation of a wide variety of polymers of different molecular weight and architecture, including *block*-copolymers.

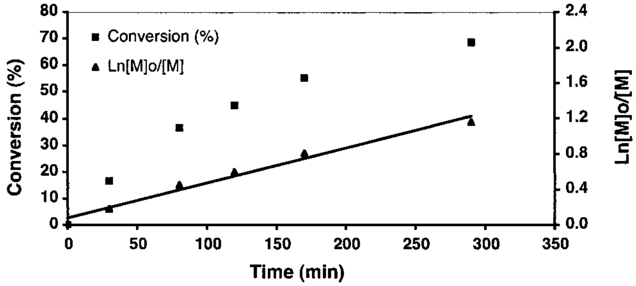


Figure 2. Kinetic data for ATRP of 4-(trimethylsilyl)styrene (50 vol.% in anisole) at 110 °C.

Borylation of Poly(4-trimethylsilyl)styrene

The silylated polymer **PS-Si** was treated with a slight excess of BBr_3, a strong Lewis acid which is known to cleave Si-C(sp^2) bonds under mild conditions with nearly quantitative yields and high selectivity[18]. Selective and quantitative cleavage of the Si-C(sp^2) bonds in **PS-Si** to form **PS-B** was confirmed by multinuclear NMR spectroscopy. Importantly, the signal due to the trimethylsilyl substituents of **PS-Si** in the ^{29}Si NMR spectrum at $\delta = -4.4$ completely disappeared, whereas a new broad resonance developed in the ^{11}B NMR spectrum at $\delta = 54$, in a region typical of arylboron dibromides. The presence of strongly electron-withdrawing substituents on the phenyl rings is reflected in the ^{13}C NMR spectrum (Figure 3). The signal for the carbon atoms in *ortho*-position to the boryl groups at $\delta = 137.9$ is downfield shifted relative to that of **PS-Si** ($\delta = 133.8/133.5$). A broad resonance at $\delta = 136.2$ can be attributed to the carbon atom bearing the boryl substituent and two closely spaced resonances ($\delta = 152.3$, 152.4) are observed for the *ipso*-carbon atom closest to the polymer backbone. Importantly, our data do not show any sign of isomerization reactions at the phenyl rings or of polymer degradation, but rather indicate selective and quantitative borylation of **PS-Si** by BBr_3.

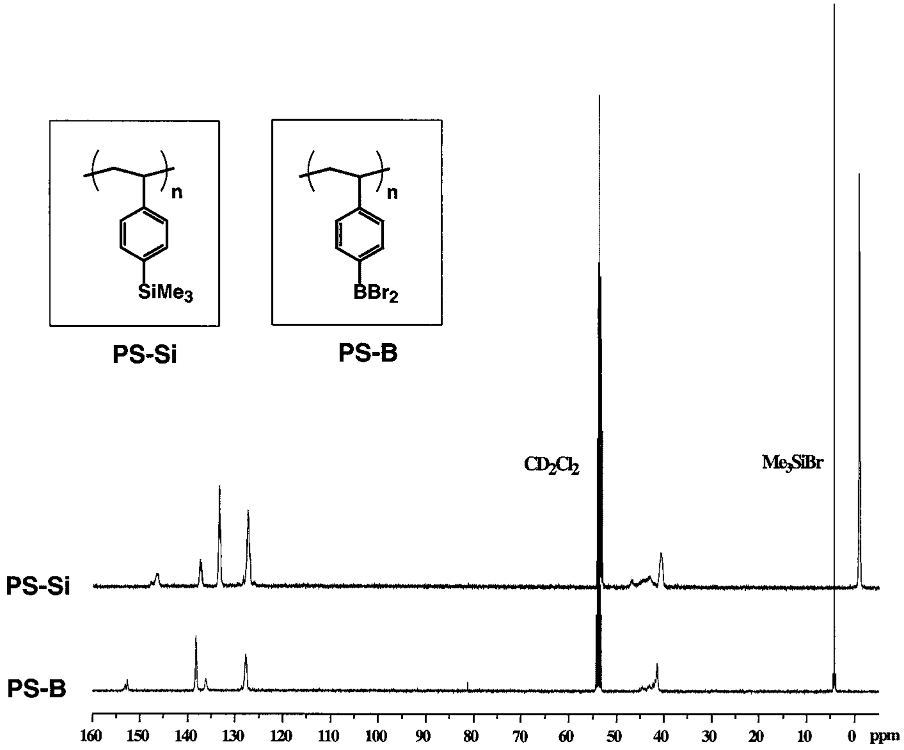


Figure 3. Comparison of the ^{13}C NMR spectra of **PS-Si** and **PS-B**.

Fine-Tuning of Lewis Acidity

The dibromoborylated polymer **PS-B** serves as a precursor to a number of other polymers with boron centers of varying Lewis acidity (Figure 4). When **PS-B** was treated with Me_3SiOEt a weakly Lewis acidic polymeric boronate, **PS-BOEt**, was obtained as a white solid in 90% isolated yield. **PS-BOEt** can readily be converted into the air-stable pinacol derivative **PS-BPin**. Polymers of high Lewis acidity such as **PS-BTh** and **PS-BAr^F** were obtained from **PS-B** with the highly selective aryl transfer reagents trimethylstannylthiophene and pentafluorophenylcopper in 82% and 74% yield, respectively.[19]

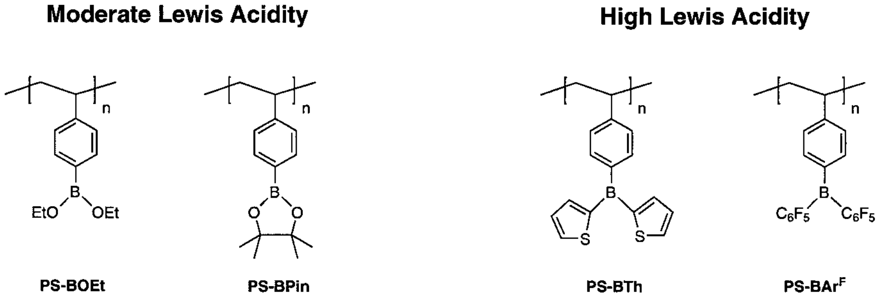


Figure 4. Selected organoboron polymers obtained from reaction of **PS-B** with nucleophiles.

Molecular Weight Determination of Boron-Containing Polymers

The molecular weight of polymer **PS-BPin** was determined by GPC and light scattering analysis. Importantly, both the experimentally determined degree of polymerization and the polydispersity of **PS-BPin** are very close to those of the precursor polymer **PS-Si** (Table 1). This clearly confirms that the borylation and subsequent substituent exchange occur without significant cross-linking or cleavage of the polymer backbone.

Table 1. Comparison of light scattering data for **PS-Si** and **PS-BPin** in THF.

Polymer	*dn/dc* (ml/g)	M_w	*DP*	*PDI*	A_2 (mol·ml/g^2)	R_H (nm)
PS-Si	0.157	10,140	51	1.08	8.774e-4	2.2
PS-BPin	0.138	13,830	53	1.09	4.772e-4	2.4

Estimation of Lewis Acidity via NMR Spectroscopy

***^{11}B NMR Spectroscopy*:** Boron NMR spectroscopy provides a highly useful probe to estimate the

Lewis acidity of organoboron species. An upfield-shifted ^{11}B NMR resonance for the arylboronate polymers **PS-BOR** (R = Et, Pin) at $\delta = 25$ relative to the precursor polymer **PS-B** ($\delta = 54$) is indicative of significant π-overlap between the alkoxy substituents and the boron centers. In contrast, the large chemical shifts of $\delta = 50$ for **PS-BTh** and of $\delta = 56$ for **PS-BAr^F** confirm the expected high Lewis acidity of the triarylborane polymers.

Formation of Crotonaldehyde Adduct (Childs' Method): The relative Lewis acidity of the boron centers can also be estimated by complexation with crotonaldehyde according to Childs' method[20]. On a scale from 0 to 1.0 (BBr_3 = 1.0) a relative Lewis acidity of 0.60 was determined for **PS-BAr^F**. A pronounced Lewis acidity of **PS-BAr^F** was further confirmed by a large chemical shift difference between the *meta-* and *para*-fluorine atoms of $\Delta\delta_{m,p} = 13.0$ for the free acid (Figure 5) that significantly decreases to $\Delta\delta_{m,p} = 6.4$ in the polymeric crotonaldehyde adduct.

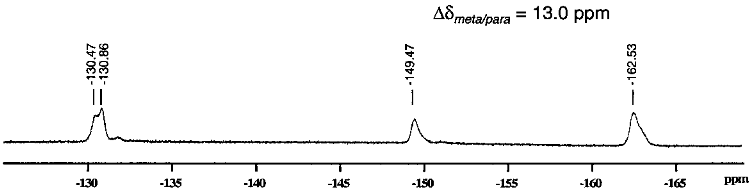


Figure 5. ^{19}F NMR spectrum of poly[4-bis(pentafluorophenyl)borylstyrene] (**PS-BAr^F**).

Conclusions

We have developed a highly efficient new method for the introduction of Lewis acidic boron centers into the side chains of organic polymers. Facile substituent exchange reactions on boron yield a new family of well-defined polymeric Lewis acids including poly(arylboronates) and the first examples of highly Lewis acidic polymeric triarylboranes. Introduction of pentafluorophenyl substituents on boron resulted in formation of **PS-BAr^F**, the first polymeric analog of highly Lewis acidic fluorinated arylboranes, which play a major role as catalyst in organic synthesis[21] and as cocatalysts in olefin polymerization[22-24]. The triarylborane polymers readily coordinate nucleophiles as exemplified in the formation of a soluble polymeric donor acceptor complex with crotonaldehyde. We are currently exploring the potential of these and of related organoboron polymers as supported catalysts and as building blocks in supramolecular polymer chemistry.

Acknowledgements

Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the ACS, and the Rutgers University Research Council for financial support of this research. We also thank the National Science Foundation for GPC and LS instrumentation (NSF-MRI program).

[1] (a) Pomogailo, A. D.; Savost'yanov, V. S.; "Synthesis and polymerization of metal-containing monomers"; CRC Press: Boca Raton, 1994; (b) Interrante, L. V.; Hampden-Smith, M. J.; "Chemistry of advanced materials : an overview"; Wiley-VCH: New York, 1998; (c) Brook, M. A.; "Silicon in organic, organometallic, and polymer chemistry"; Wiley-VCH: New York, 2000; (d) Archer, R. D.; "Inorganic and organometallic polymers"; Wiley-VCH: New York, 2001; (e) Allcock, H. R.; "Chemistry and Applications of Polyphosphazenes"; Wiley-VCH: New York, 2002; (f) Manners, I.; "Synthetic Metal-Containing Polymers"; Wiley-VCH: New York, 2003.

[2] For the coordination of polymeric ligands to transition metals, see for example: (a) Fraser, C. L.; Smith, A. P. *J. Polym. Sci. A: Polym. Chem.* **2000**, *38*, 4704; (b) Lohmeijer, B. G. G.; Schubert, U. S. *Angew. Chem. Int. Ed.* **2002**, *41*, 3825.

[3] (a) De Vos, D. E.; Vankelecom, I. F. J.; Jacobs, P. A.; "Chiral Catalyst Immobilization and Recycling"; Wiley-VCH: New York, 2000; (b) Sherrington, D. C.; Kybett, A. C.; "Supported Catalysts and Their Applications"; Royal Society of Chemistry: Cambridge, 2001.

[4] See, for example: (a) Appleton, B.; Gibson, T. D. *Sensors and Actuators B* **2000**, *65*, 302; (b) Nicolas, M.; Fabre, B.; Simonet, J. *J. Electroanal. Chem.* **2001**, *509*, 73.

[5] Chung, T. C.; Janvikul, W. *J. Organomet. Chem.* **1999**, *581*, 176 and references therein.

[6] Boffa, L. S.; Novak, B. M. *Chem. Rev.* **2000**, *100*, 1479.

[7] Kondo, Y.; Garcia-Cuadrado, D.; Hartwig, J. F.; Boaen, N. K.; Wagner, N. L.; Hillmyer, M. A. *J. Am. Chem. Soc.* **2002**, *124*, 1164.

[8] See, for example: (a) Mehta, M. A.; Fujinami, T.; Inoue, T. *J. Power Sources* **1999**, *81-82*, 724; (b) Sun, X.; Angell, C. A. *Electrochimica Acta* **2001**, *46*, 1467; (c) Xiang, H.-Q.; Fang, S.-B.; Jiang, Y.-Y. *Solid State Ionics* **2002**, *148*, 35; (d) Matsumi, N.; Sugai, K.; Ohno, H. *Macromolecules* **2002**, *35*, 5731.

[9] See, for example: (a) Armitage, P.; Ebdon, J. R.; Hunt, B. J.; Jones, M. S.; Thorpe, F. G. *Polymer Degradation and Stability* **1996**, *54*, 387; (b) Gao, J.; Liu, Y.; Wang, F. *Eur. Polym. J.* **2001**, *37*, 207.

[10] See, for example: (a) Seyferth, D. *Adv. Chem. Ser.* **1995**, *245*, 131; (b) Riedel, R.; Kroke, E.; Greiner, A.; Gabriel, A. O.; Ruwisch, L.; Nicolich, J.; Kroll, P. *Chem. Mater.* **1998**, *10*, 2964; (c) Brunner, A. R.; Bujalski, D. R.; Moyer, E. S.; Su, K.; Sneddon, L. G. *Chem. Mater.* **2000**, *12*, 2770; (d) Weinmann, M.; Kamphowe, T. W.; Schuhmacher, J.; Müller, K.; Aldinger, F. *Chem. Mater.* **2000**, *12*, 2112; (e) Kho, J.-G.; Moon, K.-T.; Nouet, G.; Ruterana, P.; Kim, D.-P. *Thin Solid Films* **2001**, *389*, 78; (f) Keller, T. M. *Carbon* **2002**, *40*, 225.

[11] (a) Matsumi, N.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **1998**, *120*, 3112; (b) Matsumi, N.; Naka, K.; Chujo. Y. *J. Am. Chem. Soc.* **1998**, 10776.

[12] See, for example: (a) Letsinger, R. L.; Hamilton, S. B. *J. Am. Chem. Soc.* **1959**, *81*, 3009; (b) Lennarz, W. J.; Snyder, H. R. *J. Am. Chem. Soc.* **1960**, *82*, 2169; (c) Wulff, G.; Sarhan, A.; Gimpel, J.; Lohmar, E. *Chem. Ber.* **1974**, *107*, 3364; (d) Jackson, L. A.; Allen, C. W. *J. Polym. Sci., A* **1992**, *30*, 577.

[13] (a) Ramakrishnan, S.; Chung, T. C. *Macromolecules* **1989**, *22*, 3181; (b) Wolfe, P. S.; Wagener, K. B. *Macromolecules* **1999**, *32*, 7961.

[14] Paetzold, P.; Hoffmann, J. *Chem. Ber.* **1980**, *113*, 3724.

[15] Qin, Y.; Cheng, G.; Sundararaman, A.; Jäkle, F. *J. Am. Chem. Soc.* **2002**, *124*, 12672.

[16] Matyjaszewski, K.; Xia, J. H. *Chem. Rev.* **2001**, *101*, 2921.

[17] Poly(4-trimethylsilylstyrene) of higher molecular weight (M_w = 90,700) and polydispersity (*PDI* = 1.33) has been synthesized via ATRP with a different ligand system: McQuillan, B. W.; Paguio, S. *Fusion Technology* **2000**, *38*, 108; a kinetic analysis has not been reported.

[18] (a) Haubold, W.; Herdtle, J.; Gollinger, W.; Einholz, W. *J. Organomet. Chem.* **1986**, *315*, 1; (b) Kaufmann, D. *Chem. Ber.* **1987**, *120*, 853.

[19] Sundararaman, A.; Jäkle, F.; manuscript in preparation.

[20] Childs, R. F.; Mulholland, D. L.; Nixon, A. *Can. J. Chem.* **1982**, *60*, 801.

[21] Yamamoto, E. H.; "Lewis Acids in Organic Synthesis"; Wiley-VCH: New York, 2000.

[22] Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391.

[23] For an interesting related dendritic system decorated with up to 12 (perfluoroaryl)borane Lewis acid centers see: Roesler, R.; Har, B. J. N.; Piers, W. E. *Organometallics* **2002**, *21*, 4300.

[24] For the use of polymeric borates as catalyst components see, for example: (a) Roscoe, S. B.; Fréchet, J. M. J.; Walzer, J. F.; Dias, A. J. *Science* **1998**, *280*, 270. (b) Mager, M.; Becke, S.; Windisch, H.; Denninger, U. *Angew. Chem. Int. Ed.* **2001**, *40*, 1898. (c) Turner, H. W.; Patent US 5427991, 1995, Exxon Chemical Patents Inc. (d) Ono, M.; Hinokuma, S.; Miyake, S.; Inazawa, S.; Patent EP 710663, 1996, Japan Polyolefins Co., Ltd. (e) Kanamaru, M.; Okamoto, T.; Okuda, F.; Kamisawa, M.; Patent JP 2000212225, 2000, Idemitsu Petrochemical Co., Ltd.