Self-repairing polymers: poly(dioxaborolane)s containing trigonal planar boron†

Weijun Niu, Caroline O'Sullivan, Brett M. Rambo, Mark D. Smith and John J. Lavigne*

The molecular weight of poly(dioxaborolane)s can be controlled during the polymerization reaction or through post-polymerization processing in such a manner that hydrolytic damage to these materials may be repaired, thereby regenerating the polymer.

Supramolecular polymers represent a novel class of materials that are assembled using non-covalent interactions such as hydrogen bonding or metal–ligand interactions.[1] Unlike conventional covalent polymers, supramolecular polymer assemblies are thermodynamically stable yet kinetically labile allowing the system to repair errors that may occur during the growth process. One limitation of these materials is that the weaker, non-covalent bonds holding these materials together often result in decreased stability compared to their covalent counterparts. It would be preferred to borrow from each situation above in order to offer a covalent alternative that would still exhibit repair capabilities. Polyacetals and polyketals display these criteria, however, the conditions required to generate and repair these materials often require addition of a catalyst and therefore fundamentally constitute a re-synthesis.[2] Boronate ester formation provides another covalent alternative that can be synthesized and repaired under mild conditions without the need for additives (Fig. 1). Herein we present the synthesis, post-polymerization modification to and self-repair of poly(dioxaborolane)s.

Interest in using boronic acids as components in macromolecular assemblies is rapidly increasing and has centered on both hydrogen bonded networks[3] as well as the generation of covalent macromolecular architectures.[4] To this end a number of oligomers,[5] polymers,[6] and macrocycles[7] have been generated using this assembly motif. Our interest in poly(dioxaborolane)s (boronate esters referring specifically to non-aromatic six-membered cyclic esters) lies specifically in the generation of materials linked through trigonal planar boron. It is well known that trigonal boron can form stable esters with the exclusion of water.[8] In anhydrous, non-coordinating organic solvents, the sp^2 hybridized boron of an aryl boronic ester undergoes substitution more readily than tetrahedral boron, allowing for more facile repair from hydrolytic damage.[4a,9]

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, USA.
E-mail: lavigne@mail.chem.sc.edu; Fax: +1-803-777-9521;
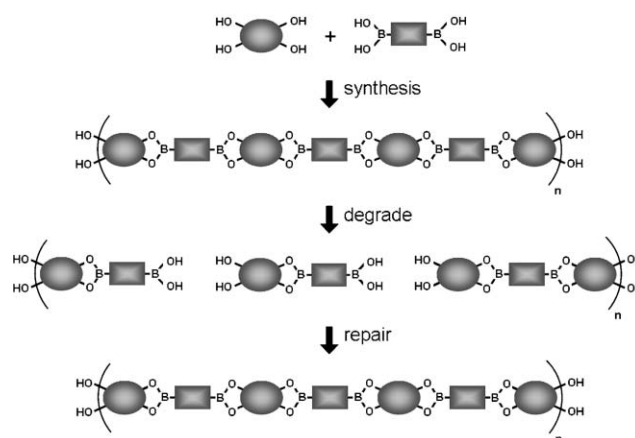*Tel: +1-803-777-2295*

Fig. 1 Schematic of the synthesis, hydrolytic degradation and self-repair of poly(dioxaborolane)s.

The polymers presented herein represent discreet structures that do not exhibit significant inter-chain interactions or borate transesterification (under ambient conditions). Most previously reported poly(boronate)s have used saccharides as the bis-diol building blocks.[6a,b] The excess hydroxyl groups on the sugars often cross-link the polymer main-chains through weak coordinating bonds with the empty p-orbital on the boron resulting in gel formation. The monomers for this study were chosen in order to diminish cross-linking by minimizing unbound hydroxyl groups while maximizing solubility. To this end 9,9-dihexylfluorene-2,7-diboronic acid and pentaerythritol were chosen in order to generate polymer **1**. Compound **2** was synthesized as a structural model using the same fluorene core with the mono-diol, neopentylglycol.
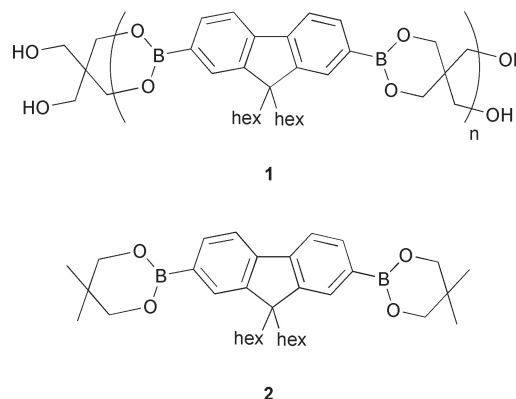
Polymer **1** was readily obtained through the condensation reaction between 9,9-dihexylfluorene-2,7-diboronic acid and pentaerythritol in toluene with azeotropic removal of water. The resulting polymer was soluble in toluene, dichloromethane, chloroform and hexane. Bis-dioxaborolane **2** was obtained in a similar manner in 95% isolated yield. This synthetic method for polymer formation is advantageous given the relative ease and high yields obtained as compared to traditional covalent polymer synthesis. The monomers were simply mixed in a suitable solvent without exhausting regard for exclusion of water or oxygen or need of a catalyst.

Polymer **1** and model compound **2** were characterized using ^{1}H, ^{11}B and ^{13}C NMR such that structural analogies could be drawn between the two. ^{11}B NMR analysis confirmed the trigonal planar geometry of the boron centers in both of these compounds.[10] In chloroform compound **2** has a chemical shift of 25 ppm, while the polymeric structures (**1**) show chemical shifts between 20 and 23 ppm. Furthermore, the solid state structure of **2** was determined through single crystal X-ray diffraction revealing two crystallographically independent conformers that are almost structurally identical, both have C_2 symmetry across the middle of the fluorene core and exhibit the predicted trigonal planar geometry around both boron centers (ESI-5†).

^{1}H NMR end group analysis was used to determine polymer molecular weights. The methylene resonance in the ^{1}H NMR spectrum of **1** was not a simple singlet (Fig. 2a). Further analysis (ESI-4†) confirmed that the two small upfield resonances near 4.0 ppm result from chain terminating residues. When excess pentaerythritol was used in the synthesis to ensure this as the terminal group, molecular weights were available *via* simply comparing the ratio of the integrals for the main peak and either of the smaller peaks.

Gel permeation chromatography (GPC, compared to polystyrene standards) was also used to determine polymer molecular weights. The enhanced stability of the boronate linkage allows for analysis of the resulting materials using GPC, unlike many supramolecular polymers that partially or completely decompose under these conditions. As such, a freshly made and dried polymer has an M_W of 28 000 indicating 58 repeating units with a polydispersity of 2.60 (Fig. 2b). The samples are stable for days in dry chloroform as evidenced by no change in both the GPC and NMR end-group analysis (Fig. 3, diamonds). As expected, longer polymers were generated when equimolar ratios of boronic acid and diol were used as compared to using an excess of one monomer (ESI-1†). Additionally, longer chain lengths could be obtained by longer reaction times, driven by the azeotropic removal of water (ESI-1†).

Interestingly, even when a large excess of one monomer (ten equivalents of pentaerythritol to one equivalent of boronic acid) was used, polymers of appreciable length ($M_W \approx 10\,000$) were still obtained. Traditional condensation polymerizations are quite sensitive to the ratio of starting monomers,[11] however, this synthesis of poly(dioxaborolane)s was not as sensitive. This was due to the limited solubility of pentaerythritol in toluene. As monomer was incorporated into the readily soluble polymer, more pentaerythritol was dissolved maintaining a low, constant concentration of bis-diol monomer. This again offers an advantage over traditional polymer synthesis in that careful attention to monomer ratio is not required in order to obtain high molecular weight polymers.
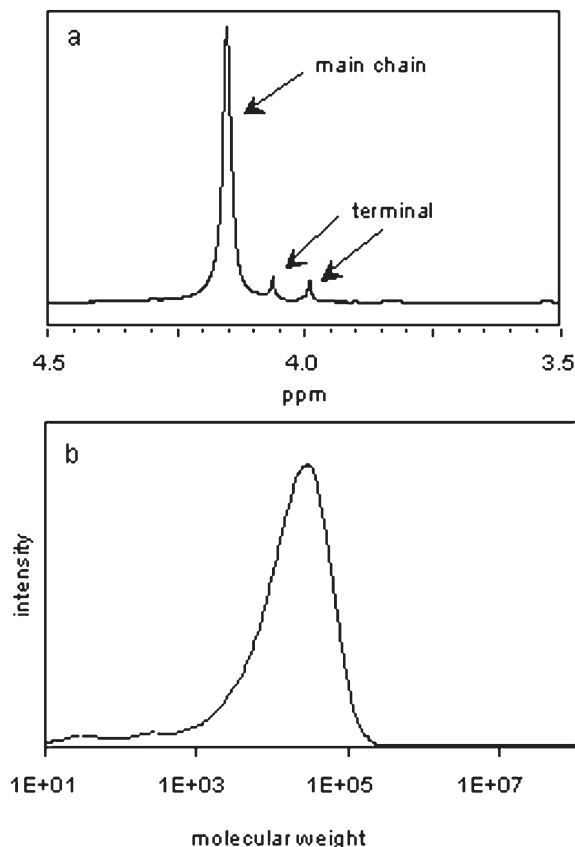

Fig. 2 (a) ^{1}H NMR of a 1 : 10 acid : diol polymer: expansion of the methylene region with the resonances for the main-chain pentaerythritol and terminal residues labeled. (b) Typical GPC trace for a 1 : 10 acid : diol polymer: $M_W = 28\,000$; $M_W/M_N = 2.6$.

The length of the polymer can also be controlled/modified by post-polymerization processing. For example, under reduced pressure ($\sim$3 mmHg) at ambient temperature over seven days, the molecular weight of the stoichiometric polymer increased. In fact, a large amount of insoluble material was formed, suggesting that this solid state growth process can generate higher molecular weight polymers than solution phase processing.[12] GPC data on this material could not be obtained due to low solubility, however, end group analysis was possible on the soluble portion of this material to give a calculated average molecular weight of 76 900.
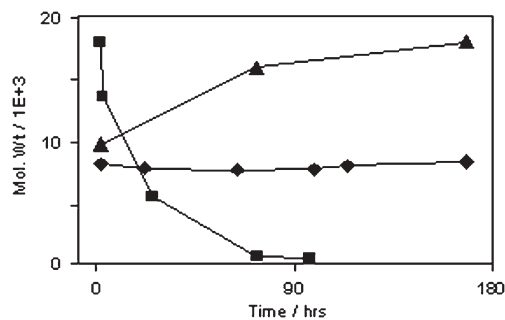

Fig. 3 Molecular weight of a 1 : 10 acid : diol polymer **1** over time in response to reduced pressure (▲), hydrolysis (■) and in dry solvent (◆), depicting the extension, degradation and stability of the polymer respectively.
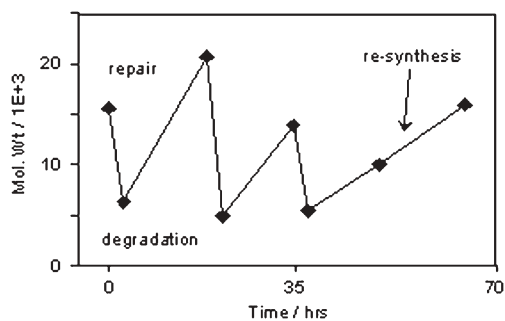
Fig. 4 Molecular weight (by GPC) over time as polymer **1** is degraded and repaired depicting the self-repair capabilities of the polymer.

The actual molecular weight is likely much higher for this sample, however only the shorter, soluble chains could be measured. The increase in molecular weight is likely to result from boronic acid terminal groups reacting with diol termini to link chains together in the solid state.

As can be seen in Fig. 3 (triangles), over the course of a week under reduced pressure, for a 1 : 10 acid : diol polymer the molecular weight increased from 9700 before vacuum, to 15 900 after three days under vacuum, to 18 000 after storage under vacuum for seven days. NMR analysis of the initial 1 : 10 polymer suggests that there are no free boronic acid termini, eliminating the possibility that end groups could combine to extend the polymer chain. Alternatively, the terminal diol moiety could coordinate with main-chain dioxaborolanes effectively cross-linking the polymer chains. However, the solid state ^{11}B NMR chemical shift for the insoluble material is consistent with trigonal planar boron, thereby negating the possibility of coordinative cross-linking. We believe instead, that the polymers are undergoing transesterification in the solid state to release pentaerythritol during the growth process. While ^{1}H NMR analysis of the polymer stored under vacuum for seven days did not show a significant increase in the amount of free pentaerythritol the quantity released would be expected to be quite small and therefore difficult to detect.

Alternatively, the polymer could be effectively shortened under hydrolytic conditions. The molecular weight for a 1 : 10 acid : diol polymer decreases when stored in wet chloroform ($\sim$1% water v/v) Fig. 3 (squares). Analysis of this polymer using GPC showed a decrease in the molecular weight from 18 000 to 13 500 upon dissolution. After storing the polymer in this solvent for 24 h, the molecular weight had decreased to 5400 and after another two days under these conditions, only monomers could be detected.

The self-repair of these hydrolytically damaged materials was accomplished without the addition of catalyst or reintroduction to the original synthetic conditions. These degraded polymers were repaired simply by storage under reduced pressure. Fig. 4 shows the molecular weight over time as a poly(dioxaborolane) was digested and then re-assembled. In order to degrade the polymer it was dissolved in water saturated chloroform. To re-assemble the materials, the solvent was removed under reduced pressure and the resulting residue stored under vacuum ($\sim$1 mmHg). The polymer can be degraded to varying extents and repaired under mild conditions to generate a polymer of comparable length to the original material. Over time the length of the repaired polymer decreases. This slow degradation of the material results from the oxidative cleavage of the boronic acid. However, "re-synthesis" of the material *via* the azeotropic removal of water in toluene regenerated a polymer of comparable molecular weight to the starting polymer.

In conclusion, dioxaborolane formation is a relatively unexplored self-assembly mechanism for the generation of polymeric structures. The length of poly(dioxaborolane)s can be readily defined/modified during the synthesis or post-polymerization. Post-polymerization processing can be used to shorten or lengthen the polymer leading to self-healing materials. Controlling the molecular weight of these polymers will be of importance in further characterizing the properties of this unique class of materials.

Notes and references

1 (*a*) J.-C. Dai, Z.-Y. Fu and X.-T. Wu, Supramolecular Coordination Polymers, in *Encyclopedia of Nanoscience and Nanotechnology*, ed. H. S. Nalwa, American Scientific, Valencia, 2004, vol 10, p. 247; (*b*) J.-M. Lehn, *Polym. Int.*, 2002, **51**, 825; (*c*) L. Brunsveld, B. J. B. Folmer, E. W. Meijer and R. Sijbesma, *Chem. Rev.*, 2001, **101**, 4071.
2 S. Makhseed and N. B. McKeown, *Chem. Commun.*, 1999, 255.
3 (*a*) J.-H. Fournier, T. Maris, J. D. Wuest, W. Guo and E. Galoppini, *J. Am. Chem. Soc.*, 2003, **125**, 1002; (*b*) C. Elschenbroich, M. Wolf, J. Pebler and K. Harms, *Organometallics*, 2004, **23**, 454; (*c*) D. Braga, M. Polito, M. Bracaccini, D. D'Addario, E. Tagliavini, L. Sturba and F. Grepioni, *Organometallics*, 2003, **22**, 2142.
4 (*a*) H. Hopfl, *Struct. Bonding (Berlin)*, 2002, **103**, 1; (*b*) L. G. Sneddon, Boron Polymers and Materials, in *Advances in Boron Chemistry*, ed. W. Siebert, Royal Society of Chemistry, Cambridge, 1997, p. 491.
5 For example see: (*a*) Y. Li, J. Ding, M. Day, Y. Tao, J. Lu and M. D'iorio, *Chem. Mater.*, 2003, **15**, 4936; (*b*) S. Maruyama and Y. Kawanishi, *J. Mater. Chem.*, 2002, **12**, 2245; (*c*) Y. Chujo, I. Tomita and T. Saegusa, *Polym. J.*, 1991, **23**, 743.
6 For example see: (*a*) K. Koumoto, T. Yamashita, T. Kimura, R. Luboradzki and S. Shinkai, *Nanotechnology*, 2001, **12**, 25; (*b*) I. Nakazawa, S. Suda, M. Masuda, M. Asai and T. Shimizu, *Chem. Commun.*, 2000, 881; (*c*) E. I. Musina, I. A. Litvinov, A. S. Balueva and G. N. Nikonov, *Russ. J. Gen. Chem.*, 1999, **69**, 413.
7 For example see: (*a*) E. Barnea, T. Andrea, M. Kapon and M. S. Eisen, *J. Am. Chem. Soc.*, 2004, **126**, 5066; (*b*) V. Barba, H. Hoepfl, N. Farfan, R. Santillan, H. I. Beltran and L. S. Zamudio-Rivera, *Chem. Commun.*, 2004, 2834; (*c*) N. Christinat, R. Scopelliti and K. Severin, *Chem. Commun.*, 2004, 1158–1159.
8 For examples see: (*a*) H. Chaumeil, C. LeDrian and A. Defoin, *Synthesis*, 2002, 757; (*b*) W.-L. Yu, J. Pei, W. Huang and A. J. Heeger, *Chem. Commun.*, 2000, 681.
9 K. L. Bhat, S. Hayik and C. W. Bock, *THEOCHEM*, 2003, 107.
10 (*a*) Tetrahedral boron exhibits a chemical shift of 0 ppm with respect to BF$_3$–OEt$_2$ (defined as 0 ppm), and trigonal boron displays shifts closer to 30 ppm; (*b*) H. Noth and B. Wrackmeyer, *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*, ed. P. Diehl, E. Fluck and R., Kosfeld, Springer-Verlag, Berlin, 1978, vol. 14.
11 D. Braun, H. Cherdron, M. Rehahn, H. Ritter and B. Voit, *Polymer Synthesis: Theory and Practice*, Springer, New York, 4th edn., 2005.
12 Insoluble materials were never generated during the solution-based formation of the poly(dioxaborolane)s.