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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
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Dynamic-Covalent Macromolecular Stars with Boronic Ester Linkages

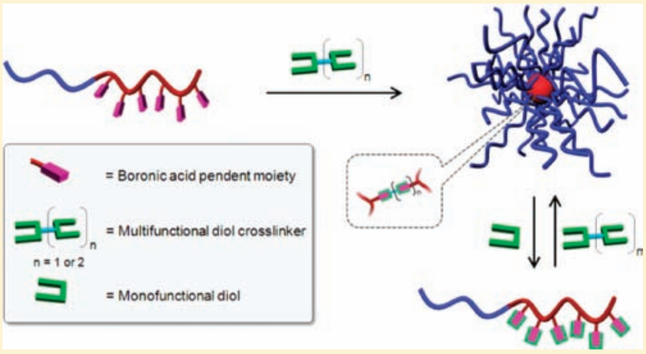
Abhijeet P. Bapat,[†] Debashish Roy,[†] Jacob G. Ray,[§] Daniel A. Savin,[§] and Brent S. Sumerlin*[,†,‡]

[†]Department of Chemistry, and [‡]Center for Drug Discovery, Design, & Delivery, Southern Methodist University, 3215 Daniel Avenue, Dallas, Texas 75275-0314, United States

[§]School of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, Mississippi 39406, United States

S *Supporting Information*

ABSTRACT: Macromolecular stars containing reversible boronic ester linkages were prepared by an arm-first approach by reacting well-defined boronic acid-containing block copolymers with multifunctional 1,2/1,3-diols. Homopolymers of 3-acrylamidophenylboronic acid (APBA) formed macroscopic dynamic-covalent networks when cross-linked with multifunctional diols. On the other hand, adding the diol cross-linkers to block copolymers of poly(*N*,*N*-dimethylacrylamide (PDMA))-*b*-poly(APBA) led to nanosized multiarm stars with boronic ester cores and PDMA coronas. The assembly of the stars under a variety of conditions was considered. The dynamic-covalent nature of the boronic ester cross-links allowed the stars to reconfigure their covalent structure in the presence of monofunctional diols that competed for bonding with the boronic acid component. Therefore, the stars could be induced to dissociate via competitive exchange reactions. The star formation—dissociation process was shown to be repeatable over multiple cycles.



INTRODUCTION

Macromolecular star architectures, with several polymer chains connected to a central core, are interesting due to their well-defined and compact structure, a high density of functional groups, and unique properties in solution and in the melt. Star polymers have been investigated for their potential utility in biomedical and therapeutic applications[1] and as nanoreactors,[2] catalysts,[3,4] photovoltaics,[5] sensors,[6] polymer electrolytes,[7] compatiblizers for polymer blends,[8] and higher order self-assemblies.[9] Controlled radical polymerization techniques (e.g., atom transfer radical polymerization,[10] nitroxide mediated polymerization,[3] and reversible addition—fragmentation chain transfer polymerization[11]) have been extensively utilized for the synthesis of well-defined macromolecular stars.[12] Regardless of the polymerization technique employed, the two general synthetic routes to stars are the "arm-first" and "core-first" methods.

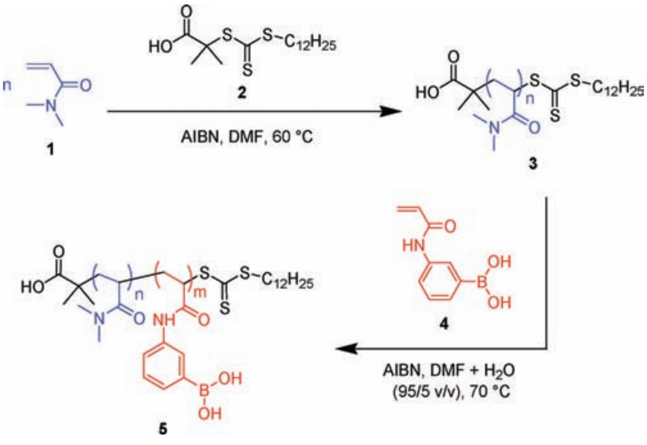
While the majority of macromolecular stars reported in the literature were constructed via robust covalent bonds that link the polymeric arms to the central core, star polymers with degradable/cleavable arms[13] or cores[14] have also been investigated. Adding a characteristic of dynamics (e.g., the potential for controlled degradability) to star polymers is highly desirable in many applications, including drug delivery and biotherapeutics. In this respect, stars linked via supramolecular core interactions have proven particularly promising. Hydrogen-bonding motifs,[15] ion—dipole interactions,[16] and metal—ligand complexes[17] have all been exploited to prepare stars that are capable of controlled dissociation. Indeed, supramolecular motifs are promising as a bottom-up approach for the design of nanomaterials. However, stronger reversible links that respond to specific stimuli while being otherwise stable might also be attractive for the design of adaptive smart materials.

The field of dynamic-covalent chemistry[18] has been applied to the design of reorganizable polymers[19] that are composed of reversible covalent linkages. While retaining the benefits of reversibility, the higher strength of many dynamic-covalent bonds as compared to supramolecular interactions[20] potentially leads to increased structural stability. Not surprisingly, the assembly of dynamic-covalent architectures like macrocycles,[21] dendrimers,[22] and reorganizable polymers[23] is a topic of growing interest. On the basis of this concept, macromolecular stars constructed from alkoxyamines,[24] Diels—Alder[25] adducts, and imines[26] have been investigated.

Boron-containing polymers serve as precursors for nanostructured materials with potential applicability in sensing, electronic devices, catalysis, and biomedical applications.[27] Boronic acid functional polymers have also been used as solid-supported protecting groups and separation agents in organic synthesis.[28] We are exploring the applicability of boronic acid-functionalized polymers for the synthesis of dynamic-covalent macromolecular assemblies. The reversible reaction of boronic acids with 1,2- and

Received: July 26, 2011
Published: November 21, 2011

Scheme 1. Synthesis of Poly(*N,N*-dimethylacrylamide) (PDMA) (3) and Subsequent Chain Extension with 3-Acrylamidophenyl Boronic Acid (APBA) (4) To Give PDMA-*b*-poly(APBA) (5)



1,3-diols to form esters in aqueous and organic media is well-known.[29] The reversible nature of boronic esters has been exploited in the design of “self-repairing” poly- or oligodioxaborolane polymers,[30] blue-emissive materials,[31] covalent organic frameworks,[32] sensors,[33] and RNA mimics.[34] Dehydration of boronic acids[35] has also been used to prepare dynamic-covalent macromolecular assemblies via six-membered boroxine formation.[36,37] We previously reported the successful RAFT polymerization of vinyl monomers containing protected and free boronic acid functionality and their pH- and glucose-responsive behavior.[38,39] Subsequently, we reported the synthesis of a boronic acid functional RAFT chain transfer agent (CTA), which led to well-defined ω-boronic acid functionalized polymers and their subsequent dehydration to yield dynamic-covalent three-arm stars via boroxine formation.[37]

Herein, we demonstrate that well-defined boronic acid-containing block copolymers are highly versatile building blocks for the construction of macromolecular stars via an arm-first approach. The addition of multifunctional 1,2/1,3-diols to block copolymers that contain one segment with pendent boronic acid moieties leads to stars that are composed of covalent, yet readily reversed, boronic ester linkages. The assembly of the stars under a variety of conditions was considered. The dynamic-covalent nature of the boronic ester cross-links allowed the stars to reconfigure their covalent structure in the presence of monofunctional diols that competed for bonding with the boronic acid component. Therefore, the stars could be induced to dissociate via competitive exchange of the multidiol cross-linkers with monodiols.

The stars formed by this approach had a narrow size distribution and many similarities to block copolymer micelles. However, as compared to micelles that are essentially supramolecular assemblies, these boronic ester stars behaved as covalent structures of considerable molecular weight, while maintaining their dynamic and reversible nature.

■ RESULTS AND DISCUSSION

Synthesis of PDMA$_{74}$-*b*-PAPBA$_{18}$ Block Copolymer via RAFT. DMA (**1**) was polymerized at 60 °C in DMF using DMP (**2**) as the chain transfer agent and AIBN as the initiator (Scheme 1). The resulting PDMA macroCTA (**3**) was further chain extended with APBA (**4**) to yield the desired PDMA-*b*-PAPBA block copolymer (**5**). A mixture of DMF/water (95:5 v/v) was used as the polymerization solvent during extension with APBA, with the small amount of water being necessary to avoid gelation due to boroxine formation. NMR spectroscopy indicated good agreement between the experimental and theoretical M_n. Prior to analysis by SEC, the boronic acid units of the block copolymer were protected by esterification with pinacol to prevent column adsorption. SEC traces of the protected block copolymer demonstrated a clean shift toward lower elution volume as compared to the PDMA macroCTA, indicating chain extension was efficient (Figure 1). The final block copolymer had an average composition of PDMA$_{74}$-*b*-PAPBA$_{18}$. Similarly, two additional PDMA-*b*-PAPBA block copolymers with different block compositions were also synthesized (Table 1).

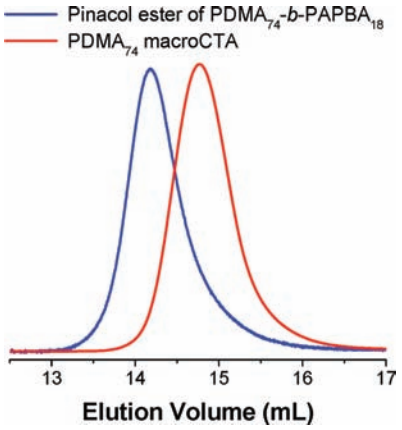


Figure 1. Size exclusion chromatography traces of the poly(*N,N*-dimethylacrylamide) (PDMA) macro-chain transfer agent and the pinacol ester of PDMA-*b*-poly(3-acrylamidophenylboronic acid) (PDMA$_{74}$-*b*-PAPBA$_{18}$) block copolymer.

Table 1. Results for the Synthesis of Poly(*N,N*-dimethylacrylamide) (PDMA) and PDMA-*b*-poly(3-acrylamidophenylboronic acid) (PDMA-*b*-PAPBA)

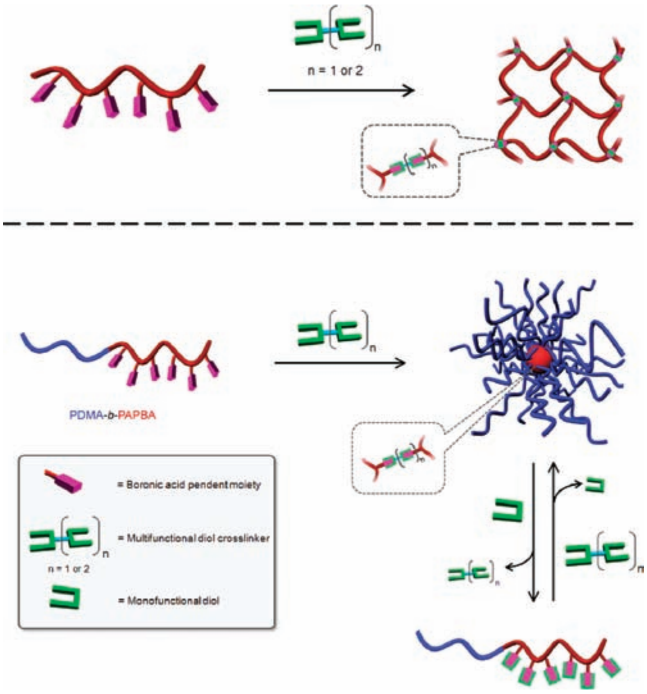
polymer	$M_{n,theo}$^{a} (g/mol)	M_n (g/mol)	M_w/M_n^{b}
PDMA$_{74}$	8700	7700^b	1.11
PDMA$_{74}$-*b*-PAPBA$_{18}$	11 900	11 200^c	1.35
PDMA$_{110}$	11 000	11 300^b	1.10
PDMA$_{110}$-*b*-PAPBA$_{20}$	15 100	15 200^c	1.34
PDMA$_{122}$	11 100	12 500^b	1.16
PDMA$_{122}$-*b*-PAPBA$_{18}$	15 700	15 900^c	1.28

[a] Calculated from stoichiometric ratios and monomer conversion. [b] Determined by SEC. [c] Calculated from ^{1}H NMR spectroscopy.

Formation of Dynamic-Covalent Macromolecular Stars. Boronic acids react with 1,2- and 1,3-diols to form boronic esters in organic media. We hypothesized that addition of a compound with more than one diol functionality (i.e., a multifunctional diol) should lead to cross-linking via boronic ester formation between the pendant boronic acid units of PAPBA homopolymers (Scheme 2).

On the other hand, when cross-linking the boronic acid moieties in a PDMA-*b*-PAPBA block copolymer by addition of multifunctional diols, the passive PDMA segments were

Scheme 2. Formation and Degradation of Dynamic-Covalent Macromolecular Networks and Stars via Boronic Ester Formation and Transesterification



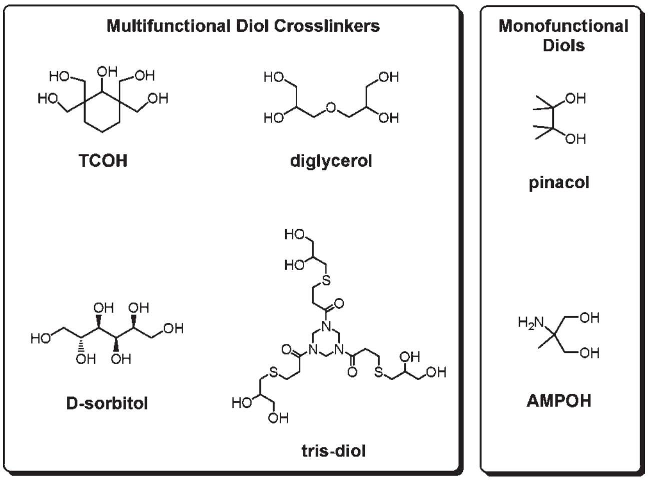


Figure 2. Multifunctional and monofunctional diols used for formation and dissociation of boronic ester macromolecular stars.

expected to prevent macroscopic precipitation, limiting network formation to the nanoscale (Scheme 2). The resulting core-cross-linked structures would therefore be stars formed by an arm-first approach.

Four different multifunctional 1,2- or 1,3-diols, tris-diol, TCOH, diglycerol, and D-sorbitol, were chosen for star formation (Figure 2). Slightly turbid, bluish solutions were observed upon mixing the diols and block copolymer solutions at 50 °C (Figure S2). After the solutions were cooled to room temperature, no change in size was observed over extended times, suggesting the stars were kinetically frozen under the conditions employed. Because accurate SEC analysis of polymers with a fraction of free boronic acid groups can be quite challenging,[39] DLS and TEM were used to investigate star formation. For example, with a 0.5 w/v % solution of $\mathrm{PDMA_{74}}$-*b*-$\mathrm{PAPBA_{18}}$ cross-linked with tris-diol, an increase in D_h from 5 to 9 nm for the unimers to 24 nm was observed after star formation (Figure S3A). Linearity in the correlation function decay rate (Γ) versus q^2 plot for solutions of stars from three PDMA-*b*-PAPBA block copolymers ($\mathrm{PDMA_{74}}$-*b*-$\mathrm{PAPBA_{18}}$, $\mathrm{PDMA_{110}}$-*b*-$\mathrm{PAPBA_{20}}$, and $\mathrm{PDMA_{122}}$-*b*-$\mathrm{PAPBA_{18}}$) (Figure 3) confirmed Brownian diffusion of spherical particles with low polydispersities. Spherical aggregates with average sizes of approximately 20−30 nm were observed by TEM (Figure 3 and Figures S3−5B). Solutions of the stars were colloidally stable, as evidenced by a lack of macroscopic cross-linking or settling over time. In contrast, a control experiment of a bis-diol (diglycerol) being added to a solution of PAPBA homopolymer resulted in gelation and macroscopic precipitation, as expected (Figure S6 in the Supporting Information).

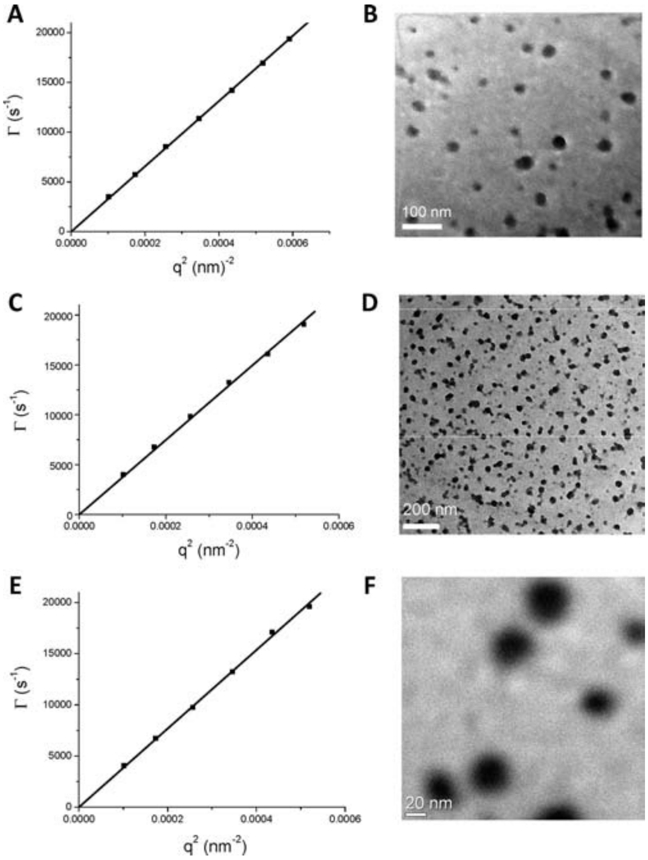


Figure 3. Plots of correlation function decay rate Γ versus q^2 and transmission electron microscopy images of $\mathrm{PDMA_{74}}$-*b*-$\mathrm{PAPBA_{18}}$ (A,B), $\mathrm{PDMA_{110}}$-*b*-$\mathrm{PAPBA_{20}}$ (C,D), and $\mathrm{PDMA_{122}}$-*b*-$\mathrm{PAPBA_{18}}$ (E,F) cross-linked with tris-diol.

Boronic acid-containing polymers may also undergo dehydration to cross-link via boroxine formation at elevated temperatures in anhydrous media. Therefore, to determine if cross-linking of the block copolymers could be attributed to boroxine formation instead of esterification with the multifunctional diols, $\mathrm{PDMA_{74}}$-*b*-$\mathrm{PAPBA_{18}}$ in methanol at two different concentrations (10 and 50 mg/mL) was heated to 50 °C in the absence of diol. No change in turbidity or size (as determined by DLS) was observed over periods of up to 21 h in both cases, suggesting a lack of

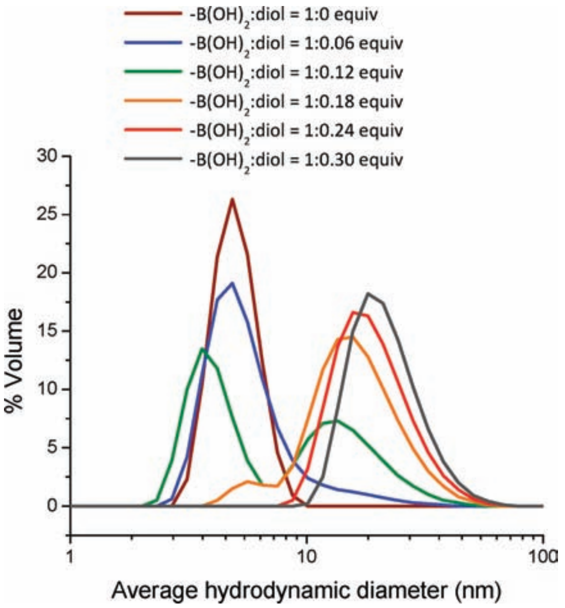


Figure 4. Hydrodynamic size distributions as a function of the ratio of boronic acid [$-$B(OH)$_2$] to diol with 1,1′,1″-(1,3,5-triazinane-1,3,5-triyl)tris(3-(2,3-dihydroxypropylthio)propan-1-one) (tris-diol) as a cross-linker at a concentration of 0.85$-$1 w/v % PDMA$_{74}$-*b*-PAPBA$_{18}$.

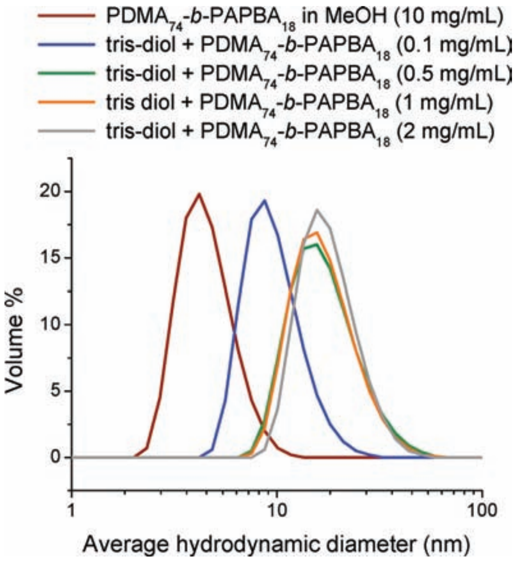


Figure 5. Solution size distributions of PDMA$_{74}$-*b*-PAPBA$_{18}$ in methanol in the presence of tris-diol as a cross-linker at a fixed ratio of boronic acid groups [$-$B(OH)$_2$]:diol = 1:0.3 equiv after 16 h. The distribution of PDMA$_{74}$-*b*-PAPBA$_{18}$ in the absence of cross-linker is shown for comparison.

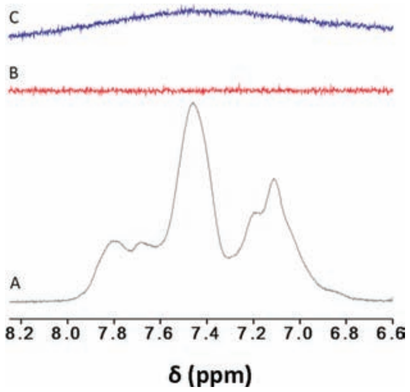


Figure 6. Aromatic region of the ^{1}H NMR spectra of (a) PDMA$_{74}$-*b*-PAPBA$_{18}$, (b) tris-diol, and (c) stars formed by addition of the tris-diol to PDMA$_{74}$-*b*-PAPBA$_{18}$. Attenuation of the APBA repeat unit phenyl signals suggests the star cores are desolvated. Spectra A and B were recorded in methanol-d_4 with [PDMA$_{74}$-*b*-PAPBA$_{18}$] = 50 mg/mL and [tris-diol] = 22 mg/mL respectively, while (C) was recorded for a 1:1 v/v mixture of the PDMA$_{74}$-*b*-PAPBA$_{18}$ and tris-diol solutions. Complete spectra are included in Figure S10 in the Supporting Information.

boroxine formation even at a considerably higher PDMA$_{74}$-*b*-PAPBA$_{18}$ concentration (50 mg/mL) than that used for formation of the stars by addition of multifunctional diol cross-linker (Figure S7). These results suggest a mechanism of star formation by PDMA$_{74}$-*b*-PAPBA$_{18}$ cross-linking via esterification with the multifunctional diols. Therefore, the resulting nanostructures should consist of PDMA shells passivating a cross-linked PAPBA-diol core (Scheme 2). Further insight into the assembly and star formation process was obtained by considering the effects of (i) diol:boronic acid stoichiometry and (ii) overall block copolymer concentration.

A minimum ratio of each diol to boronic acid was required for complete transition from polymeric unimers to stars (Figures 4, and S10A and S11$-$S13A and C in the Supporting Information). It was observed that the concentration of cross-linking diol needed to induce star formation was dependent on the specific diol being considered. At a constant initial concentration of PDMA$_{74}$-*b*-PAPBA$_{18}$ of 1 w/v %, the approximate concentration of diol needed to induce efficient star formation, as determined by DLS, increased in the order tris-diol ≈ 0.3 equiv > TCOH ≈ 0.4 equiv > D-sorbitol ≈ 0.7 equiv > diglycerol ≈ 2.5 equiv. Because the tris-diol was most efficient at inducing star formation, this cross-linker was investigated in greater detail.

Similar to the concept of critical micelle concentration for amphiphilic block copolymers in solution, efficient star formation under the conditions considered also required a minimum concentration of the boronic acid block copolymer. At a temperature of 50 °C and a constant ratio of boronic acid to tris-diol, the concentration of PDMA$_{74}$-*b*-PAPBA$_{18}$ was increased until aggregates were observed by DLS. All DLS measurements were taken at 16 h, well after no further changes were observed during model experiments of star formation (Figure S8). At a constant ratio of boronic acid to tris-diol = 1:0.3 equiv, a slight increase in size was observed by DLS for PDMA$_{74}$-*b*-PAPBA$_{18}$ at a concentration of 0.1 mg/mL (Figures 5 and S9). However, when the concentration of block copolymer was raised to 0.5 mg/mL, stars of 18 nm were observed. Increasing the concentration of block copolymer to 1 and 2 mg/mL did not result in a further increase in size. These results suggest that with the given block copolymer, diol, and solvent combination, steric stabilization provided by the PDMA corona leads to a maximum average star size of approximately 18$-$25 nm.

Additional structural information was obtained by ^{1}H NMR spectroscopy of the aggregates. The spectrum of PDMA$_{74}$-*b*-PAPBA$_{18}$ in methanol-d_4 showed all of the peaks expected for the PDMA and PAPBA blocks. Upon addition of a diol cross-linker, the signals of PAPBA were significantly attenuated, which was most readily observed by the near disappearance of the phenyl

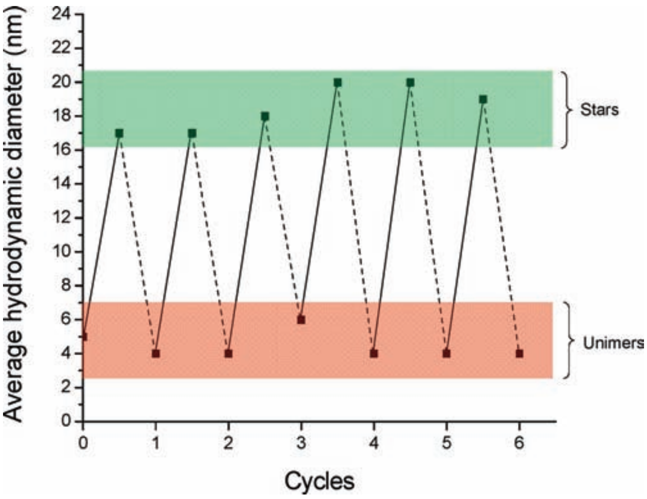


Figure 7. Solution size measured by dynamic light scattering during investigations of the reversibility of dynamic-covalent star formation and dissociation with PDMA$_{74}$-*b*-PAPBA$_{18}$ (original concentration = 20 mg/mL) in methanol. Solid lines indicate the addition of 1,1′,1″-(1,3,5-triazinane-1,3,5-triyl)tris(3-(2,3-dihydroxypropylthio)propan-1-one) (tris-diol) cross-linker, and dashed lines indicate the addition of 2-amino-2-methyl-1,3-propanediol (AMPOH) monodiol cross-link cleaving agent. Specific information for each step of the study is provided in the Supporting Information.

signals at 6.8−8.1 ppm (Figure 6 and Figures S10−13B in the Supporting Information). The reduction in intensity of the PAPBA signals suggested the cores of the stars were significantly desolvated, more closely resembling core-cross-linked micelles than low-density nanogels. This is consistent with the observation of macroscopic precipitation instead of swollen gel formation when PAPBA homopolymer was reacted with a multifunctional diol in methanol, as was previously discussed (Figure S6).

The aggregation number of the stars was estimated by static light scattering during flow injection polymer analysis,[40] a chromatography technique capable of providing M_w when coupled with light scattering instrumentation. For the specific case of PDMA$_{74}$-*b*-PAPBA$_{18}$ cross-linked with tris-diol at a ratio of $-B(OH)_2$:diol = 1:0.57 equiv, the weight average molecular weight (M_w) was determined to be 2.145×10^6 g/mol. Dividing this number by the molecular weight of the PDMA$_{74}$-*b*-PAPBA$_{18}$ arms yielded an estimated 191 arms/star.

Reversibility of Dynamic-Covalent Macromolecular Star Formation. The readily accessible reversibility of boronic esters imparted a dynamic nature to the resulting covalent macromolecular stars. Thus, the stars could be dissociated into individual polymer chains (unimers) after displacement of the multifunctional-diol cross-linker during a competitive reaction with a monodiol (Scheme 2). The ability of a given diol to displace another from a boronic ester (i.e., transesterification) in organic media is well established.[41] In the case of the PDMA$_{74}$-*b*-PAPBA$_{18}$ stars, displacement of the tris-diol cross-linker by addition of a competitive monodiol could lead to cross-link cleavage and a conversion of the stars to unimers with boronic ester pendant groups.

To investigate dynamic-covalent reversibility, the PDMA$_{74}$-*b*-PAPBA$_{18}$ stars formed with tris-diol as the cross-linker were exposed to two monodiols. The DLS results for star dissociation due to cross-link cleavage upon transesterification with AMPOH (see Scheme 2) are shown in Figure 7 (similar data with pinacol as the monodiol are shown in Figure S15). Upon introduction of the AMPOH monodiol and heating at 50 °C for 2 h, stars of approximately 17 nm were dissociated to unimolecular chains of approximately 4 nm (Figure 7). This reduction in size is consistent with dissociation of the stars upon competitive cross-link cleavage by the monodiol. Importantly, after dissociation to unimers, addition of more tris-diol to the same solution led to regeneration of stars with sizes of ∼17 nm. The dissociation/regeneration process was observed to be reversible over at least six cycles for the stars formed with tris-diol as the cross-linker.

The large excess of tris-diol:$-B(OH)_2$ during the sixth cycle did not appear to prevent cross-linking and star formation by saturation of the polymer backbone with diol units. To further confirm this, methanol solutions of PDMA$_{74}$-*b*-PAPBA$_{18}$ and tris diol were directly mixed at a $-B(OH)_2$:diol ratio of 1:24 (corresponding to the final star formation step in Figure 7; see the Supporting Information and Figure S14A for details) and heated for 19 h at 50 °C. DLS measurements confirmed the formation of stars with an average hydrodynamic diameter of 19 nm. Addition of the monodiol AMPOH (5.7 equiv) to the resulting solution and heating at 50 °C for 18 h (analogous to the final star dissociation step in Figure 7; see the Supporting Information and Figure S14A for details) led to dissociation of the stars into unimers of 4 nm. The dissociation of stars to unimers also led to the reappearance of the phenyl proton signals from the PAPBA block in the ^{1}H NMR spectrum (Figure S14B). While stars formed with tris diol as the cross-linker demonstrated repeated dissociation/regeneration, limited success was observed in the case of stars formed with other cross-linking diols. For example, AMPOH readily dissociated the stars formed with TCOH, diglycerol, or D-sorbitol. However, further addition of a large excess of these diol cross-linkers did not lead to star regeneration under the experimental conditions considered. These results suggest that careful selection of the cross-linking and monodiols is necessary to ensure sustained reversibility over many cycles. These results have led to more in-depth investigations regarding the kinetic and thermodynamic factors governing boronic ester formation and transesterification in organic media and will be the subject of a future report.

Preliminary studies indicated stars could also be readily formed in other alcohols that were common solvents to the block copolymer and diol cross-linkers. In both ethanol and isopropanol, star formation was observed upon addition of tris-diol (Figure S16). These results indicate the versatility and scope of this approach to dynamic covalent stars via boronic ester chemistry.

■ CONCLUSIONS

The macromolecular stars described here rely on the self-assembly of diols with boronic acid-containing polymers. While reactions between species with more than one diol functionality lead to macroscopic network formation with boronic acid homopolymers, block copolymers with one boronic acid segment lead to the formation of well-defined stars by the arm-first approach.

A variety of applications can be envisioned for dynamic-covalent stars on the basis of boronic esters. Similar to polymeric micelles that have similar core−shell morphologies, it may be possible to encapsulate cargo (e.g., drugs, dyes, fragrances, catalysts) within the star cores. However, as opposed to supramolecular polymer assemblies that may be susceptible to dissociation upon dilution, the covalently cross-linked stars should be more robust and capable of withstanding significant dilution. Nevertheless, these covalent assemblies can still be induced to dissociate by exposure to an external species that competes for binding with functional groups along the polymer. Macromolecular constructs based on boronic acids are particularly interesting in this respect, given the abundance of potential polyol species encountered in nature (e.g., sugars, polysaccharides, nucleic acids). Further, while the work described here focuses on assemblies in solution, applications in the bulk can also be envisioned, as the dynamic nature of boronic ester-based polymers may have particular utility in the area of rehealable materials.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental details, synthetic schemes, NMR spectra, photographs, DLS data for star formation with various diol cross-linkers, and description of methods for investigation of the dynamics of reversible star formation and dissociation. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

bsumerlin@smu.edu

■ ACKNOWLEDGMENT

This material is based upon work supported by the National Science Foundation (CAREER DMR-0846792) and an Alfred P. Sloan Research Fellowship (B.S.S.). Funding was provided by the NSF DMR MRI-0421406 (USM) for the purchase of the JEOL JEM-2100 electron microscope (D.A.S.).

■ REFERENCES

(1) Dai, F.; Sun, P.; Liu, Y.; Liu, W. *Biomaterials* **2010**, *31*, 559. Navath, R. S.; Wang, B.; Kannan, S.; Romero, R.; Kannan, R. M. *J. Controlled Release* **2010**, *142*, 447. Bilkova, E.; Imramovsky, A.; Buchta, V.; Sedlak, M. *Int. J. Pharm.* **2010**, *386*, 1.

(2) Zhu, L.; Shi, Y.; Tu, C.; Wang, R.; Pang, Y.; Qiu, F.; Zhu, X.; Yan, D.; He, L.; Jin, C.; Zhu, B. *Langmuir* **2010**, *26*, 8875.

(3) Bosman, A. W.; Vestberg, R.; Heumann, A.; Frechet, J. M. J.; Hawker, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 715.

(4) Terashima, T.; Ouchi, M.; Ando, T.; Sawamoto, M. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 373.

(5) Liu, Y.; Guo, X.; Xiang, N.; Zhao, B.; Huang, H.; Li, H.; Shen, P.; Tan, S. *J. Mater. Chem.* **2010**, *20*, 1140.

(6) Payne, S. J.; Fiore, G. L.; Fraser, C. L.; Demas, J. N. *Anal. Chem.* **2010**, *82*, 917.

(7) Marzantowicz, M.; Dygas, J. R.; Krok, F.; Tomaszewska, A.; Florjanczyk, Z.; Zygadlo-Monikowska, E.; Lapienis, G. *J. Power Sources* **2009**, *194*, 51.

(8) Busche, B. J.; Tonelli, A. E.; Balik, C. M. *Polymer* **2010**, *51*, 454.

(9) Xu, J.; Zubarev, E. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 5491.

(10) Matyjaszewski, K.; Miller, P. J.; Pyun, J.; Kickelbick, G.; Diamanti, S. *Macromolecules* **1999**, *32*, 6526. Gao, H.; Matyjaszewski, K. *Macromolecules* **2006**, *39*, 3154.

(11) Mayadunne, R. T. A.; Jeffery, J.; Moad, G.; Rizzardo, E. *Macromolecules* **2003**, *36*, 1505. Chan Justin, W.; Yu, B.; Hoyle Charles, E.; Lowe Andrew, B. *Chem. Commun.* **2008**, 4959.

(12) Gao, H.; Matyjaszewski, K. *Prog. Polym. Sci.* **2009**, *34*, 317. Blencowe, A.; Tan, J. F.; Goh, T. K.; Qiao, G. G. *Polymer* **2009**, *50*, 5.

(13) Setijadi, E.; Tao, L.; Liu, J.; Jia, Z.; Boyer, C.; Davis, T. P. *Biomacromolecules* **2009**, *10*, 2699. Wiltshire, J. T.; Qiao, G. G. *Macromolecules* **2008**, *41*, 623.

(14) Gao, H.; Tsarevsky, N. V.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 5995. Themistou, E.; Patrickios, C. S. *Macromolecules* **2004**, *37*, 6734.

(15) Todd, E. M.; Zimmerman, S. C. *J. Am. Chem. Soc.* **2007**, *129*, 14534.

(16) Huang, F.; Nagvekar, D. S.; Slebodnick, C.; Gibson, H. W. *J. Am. Chem. Soc.* **2005**, *127*, 484.

(17) Munuera, L.; O'Reilly, R. K. *Dalton Trans.* **2010**, *39*, 388.

(18) Rowan, S. J.; Cantrill, S. J.; Cousins, G. R. L.; Sanders, J. K. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2002**, *41*, 899. Corbett, P. T.; Leclaire, J.; Vial, L.; West, K. R.; Wietor, J.-L.; Sanders, J. K. M.; Otto, S. *Chem. Rev.* **2006**, *106*, 3652. Lehn, J.-M. *Chem.-Eur. J.* **1999**, *5*, 2455.

(19) Maeda, T.; Otsuka, H.; Takahara, A. *Prog. Polym. Sci.* **2009**, *34*, 581.

(20) Ciferri, A. *Supramolecular Polymers*, 2nd ed.; CRC Press LLC: New York, 2005.

(21) Ulrich, S.; Buhler, E.; Lehn, J.-M. *New J. Chem.* **2009**, *33*, 271. Galbraith, E.; Kelly, A. M.; Fossey, J. S.; Kociok-Koehn, G.; Davidson, M. G.; Bull, S. D.; James, T. D. *New J. Chem.* **2009**, *33*, 181. Lin, J.-B.; Xu, X.-N.; Jiang, X.-K.; Li, Z.-T. *J. Org. Chem.* **2008**, *73*, 9403. Ulrich, S.; Lehn, J.-M. *Angew. Chem., Int. Ed.* **2008**, *47*, 2240. Yamaguchi, G.; Higaki, Y.; Otsuka, H.; Takahara, A. *Macromolecules* **2005**, *38*, 6316.

(22) Leung, K. C. F.; Arico, F.; Cantrill, S. J.; Stoddart, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 5808.

(23) Otsuka, H.; Aotani, K.; Higaki, Y.; Amamoto, Y.; Takahara, A. *Macromolecules* **2007**, *40*, 1429. Kamplain, J. W.; Bielawski, C. W. *Chem. Commun.* **2006**, 1727. Ono, T.; Nobori, T.; Lehn, J.-M. *Chem. Commun.* **2005**, 1522. Wojtecki, R. J.; Meador, M. A.; Rowan, S. J. *Nat. Mater.* **2011**, *10*, 14. Jean-Marie, L. *Prog. Polym. Sci.* **2005**, *30*, 814. Folmer-Andersen, J. F.; Lehn, J.-M. *J. Am. Chem. Soc.* **2011**, *133*, 10966. De Greef, T. F. A.; Smulders, M. M. J.; Wolffs, M.; Schenning, A. P. H. J.; Sijbesma, R. P.; Meijer, E. W. *Chem. Rev.* **2009**, *109*, 5687. Reutenauer, P.; Buhler, E.; Boul, P. J.; Candau, S. J.; Lehn, J. M. *Chem.-Eur. J.* **2009**, *15*, 1893.

(24) Amamoto, Y.; Higaki, Y.; Matsuda, Y.; Otsuka, H.; Takahara, A. *J. Am. Chem. Soc.* **2007**, *129*, 13298. Amamoto, Y.; Kikuchi, M.; Masunaga, H.; Sasaki, S.; Otsuka, H.; Takahara, A. *Macromolecules* **2010**, *43*, 1785.

(25) Syrett, J. A.; Mantovani, G.; Barton, W. R. S.; Price, D.; Haddleton, D. M. *Polym. Chem.* **2010**, *1*, 102.

(26) Jackson, A. W.; Fulton, D. A. *Chem. Commun.* **2010**, *46*, 6051. Jackson, A. W.; Fulton, D. A. *Chem. Commun.* **2011**, 6807.

(27) (a) Cheng, F.; Jakle, F. *Polym. Chem.* **2011**, *2*, 2122. (b) Cambre, J. N.; Sumerlin, B. S. *Polymer* **2011**, *52*, 4631.

(28) Seymour, E.; Frechet, J. M. J. *Tetrahedron Lett.* **1976**, *17*, 3669. Frechet, J. M. J.; Nuyens, L. J.; Seymour, E. *J. Am. Chem. Soc.* **1979**, *101*, 432.

(29) *Boronic Acids: Preparation, Applications in Organic Synthesis and Medicine*; Hall, D. G., Ed.; Wiley-VCH: Weinheim, 2005. Kim, K. T.; Cornelissen, J. J. L. M.; Nolte, R. J. M.; van Hest, J. C. M. *J. Am. Chem. Soc.* **2009**, *131*, 13908.

(30) Niu, W.; O'Sullivan, C.; Rambo, B. M.; Smith, M. D.; Lavigne, J. J. *Chem. Commun.* **2005**, 4342. Rambo, B. M.; Lavigne, J. J. *Chem. Mater.* **2007**, *19*, 3732.

(31) Niu, W.; Smith, M. D.; Lavigne, J. J. *J. Am. Chem. Soc.* **2006**, *128*, 16466.

(32) Côté, A. P.; Benin, A. I.; Ockwig, N. W.; O'Keeffe, M.; Matzger, A. J.; Yaghi, O. M. *Science* **2005**, *310*, 1166. Tilford, R. W.; Gemmill, W. R.; zur Loye, H.-C.; Lavigne, J. J. *Chem. Mater.* **2006**, *18*, 5296.

(33) Fossey, J. S.; James, T. D. *Rev. Fluoresc.* **2009**, *4*, 103.

(34) Kobayashi, H.; Amaike, M.; Koumoto, K.; Shinkai, S. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1311.

(35) Perttu, E. K.; Arnold, M.; Iovine, P. M. *Tetrahedron Lett.* **2005**, *46*, 8753. Kua, J.; Iovine, P. M. *J. Phys. Chem. A* **2005**, *109*, 8938.

(36) Qin, Y.; Cui, C.; Jäkle, F. *Macromolecules* **2007**, *40*, 1413. Iovine, P. M.; Fletcher, M. N.; Lin, S. *Macromolecules* **2006**, *39*, 6324. Korich, A. L.; Walker, A. R.; Hincke, C.; Stevens, C.; Iovine, P. M. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 5767.

(37) De, P.; Gondi, S. R.; Roy, D.; Sumerlin, B. S. *Macromolecules* **2009**, *42*, 5614.

(38) Cambre, J. N.; Roy, D.; Gondi, S. R.; Sumerlin, B. S. *J. Am. Chem. Soc.* **2007**, *129*, 10348. Roy, D.; Cambre, J. N.; Sumerlin, B. S. *Chem. Commun.* **2009**, 2106.

(39) Roy, D.; Cambre, J. N.; Sumerlin, B. S. *Chem. Commun.* **2008**, 2477.

(40) Lyons, J. W.; Poche, D.; Wang, F. C. Y.; Smith, P. B. *Adv. Mater.* **2000**, *12*, 1847.

(41) Roy, C. D.; Brown, H. C. *J. Organomet. Chem.* **2007**, *692*, 784.