

Supramolecular Star Polymers. Increased Molecular Weight with Decreased Polydispersity through Self-Assembly

Eric M. Todd and Steven C. Zimmerman*

Department of Chemistry, University of Illinois at Urbana—Champaign, 600 South Mathews Avenue, Urbana, Illinois 61801

Received July 21, 2007; E-mail: sczimmer@uiuc.edu

The increasing interest in polymer architectures with defined structures and low polydispersities arises from their applications in drug delivery, catalysis, and advanced materials.^{1,2} In this regard, major advances have been made in preparing a wide range of polymers by living/controlled polymerization methods. The programmed self-assembly of hydrogen-bonding modules provides an alternative, bottom-up approach to complex polymeric structures but has received much less attention.³

A recent example of the bottom-up approach involved the ditopic hydrogen-bonding module, Bis-DeAP, which is capable of forming cyclic assemblies, including the hexamer shown (Figure 1). An analogue of **1** and related modules were reported to assemble dendrimers,^{4–6} but they could also serve as self-assembled cores for supramolecular star polymers. The unique combination of reversibility with thermodynamically stable discrete assemblies suggests this organic approach might uniquely complement self-assembled star polymers with cores based on strong metal–ligand bonding.⁷ Here we report the use of Bis-DeAP **1** as an initiator for polymerization and its ability to convert low molecular weight polymers into significantly higher molecular weight structures while at the same time narrowing the overall molecular weight distribution through the assembly process.

Bis-DeAP **1** was prepared using an approach reported for an unfunctionalized analogue.^{4b,8} The alcohol group can be further manipulated, and aryl groups provide increased solubility in nonpolar organic solvents. Figure 2 shows data from a DMAP-catalyzed ring opening polymerization of D,L-lactide⁹ using **1** as the initiator. Although NMR analysis indicated an M_n of only 3100 and MALDI showed a bimodal molecular weight distribution with the majority of material below 4 kDa, the SEC revealed a single peak with a narrow molecular weight distribution. The M_n was determined to be ca. 16 kDa with a polydispersity index (PDI) of 1.23. The difference in polymer characteristics from the NMR and MALDI, where self-assembly does not affect the measurements, and by SEC, where the assembled structure is observed, demonstrates the ditopic hydrogen-bonding module's ability to increase molecular weight, while decreasing the polydispersity through self-assembly.

To further investigate the nature of the assembly and expand the utility of the ditopic hydrogen-bonding module, **1** was reacted with 2-bromo-2-methylpropanoyl bromide to yield the atom transfer radical polymerization (ATRP) initiator **2**.^{1d} Reaction with styrene was carried out neat at 90 °C with **2**, CuBr, and PMDETA. The molecular weight grew linearly with time, indicating a living polymerization (Figure 3). The intercept of the upper line in Figure 3 corresponds closely to the molecular weight of the hexameric assembly of **2**.¹⁰ The SEC molecular weights, in toluene, of all of the polymers generated from **2** did not change appreciably over a 10-fold change in concentration, indicating the formation of discrete aggregates, which had a PDI generally between 1.3 and 1.5.

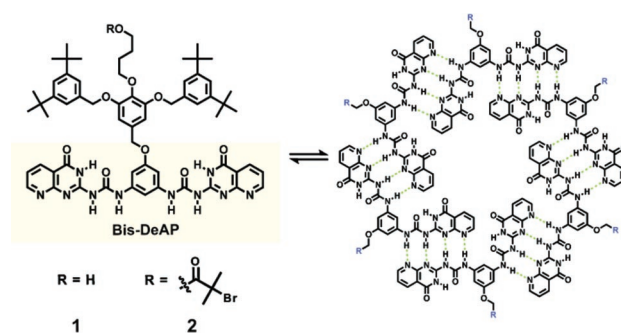


Figure 1. Ditopic hydrogen-bonding modules **1** and **2** and hexamer they form. Pentamers and heptamers may also form.

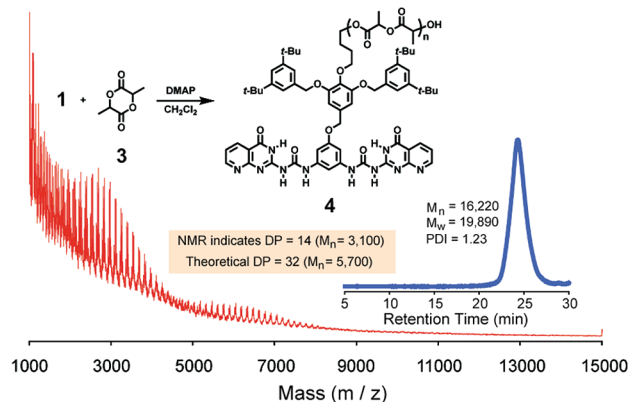


Figure 2. Organocatalytic polymerization of D,L-lactide using **1** as initiator. MALDI and NMR indicate low MW material with a bimodal distribution. Assembly of the ditopic hydrogen-bonding module in THF leads to higher MW star polymers with monomodal distribution and low PDI. SEC in THF using RI detector and PS calibration.

Polystyrene polymers, **6**, were prepared from a model initiator, under the same polymerization conditions as **2**, to obtain an estimate of the molecular weight of the polymer chains in the absence of assembly. The model polymerization also displayed a linear increase in molecular weight with conversion, and the slope of the best fit line to the polymerization of the model initiator had a slope 1/6 that of the polymerization from **2**, supporting the formation of hexameric assemblies.

Direct analysis of the MW and PDI of the arms of a star polymer by cleavage is a common technique in polymer science.¹¹ The PS polymer in **5** is connected to the ditopic hydrogen-bonding module through an ester bond that is susceptible to cleavage, and control experiments indicated that the PS backbone would be unaffected by basic hydrolysis conditions. Cleavage of the core was carried out as indicated in Figure 4. The heterocyclic portion of **5** absorbs at 310 nm, and the SEC data in Figure 4 show its presence in the star polymer but not in the cleaved polymer arms. ¹H NMR analysis

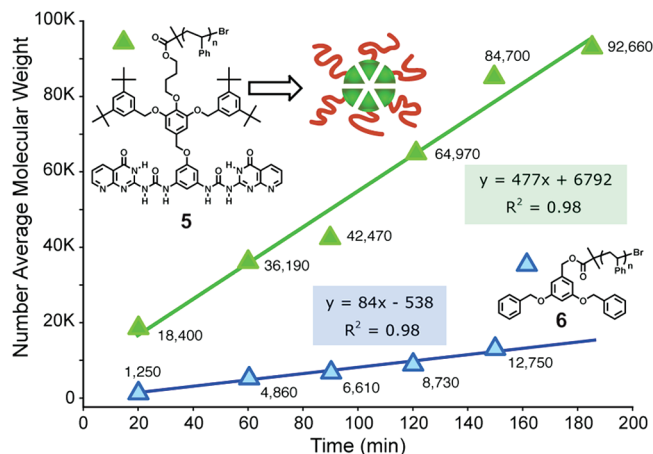


Figure 3. M_n of polymers from ATRP of **2** and of a model initiator versus time. MWs determined from the average of 3–4 runs on a toluene SEC using RI detection and PS calibration. Polymerization conditions: $[2] = [\text{CuBr}] = [\text{PMDETA}] = 21 \text{ mM}$ in styrene, 90°C .

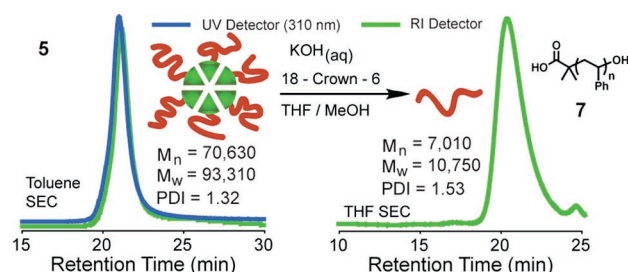


Figure 4. Toluene SEC of self-assembled star polymer and THF SEC of PS arms from basic hydrolysis. UV detector $\lambda_{\text{max}} = 310 \text{ nm}$. Molecular weight determined from RI signal using PS calibration.

confirms that the hydrolysis product is PS. The SEC shows that the star polymer with $M_n \sim 70 \text{ kDa}$ was formed by linear PS fragments having an $M_n \sim 7 \text{ kDa}$. The cleaved PS was analyzed in THF because of its tendency to absorb to the SEC column (acid group). In toluene, the molecular weight of the PS arms was greatly underestimated, although the PDI of the cleaved arms was approximately the same in both toluene and THF.

The cleavage experiment indicates that the apparent MW of the assembly is about 10 times that of the PS MW, whereas the comparisons in Figure 3 indicate an average 8.5-fold increase. Of course, the comparatively large Bis-DeAP core will contribute to the molecular weight of the assembly. Given this contribution, the uncertainty in the MW measurements,⁸ and the previous studies of self-assembling dendrimers,^{4b} a hexamer model is favored.

Whatever the exact structure of the assembly, it produces a dramatic increase in molecular weight, with a narrowing of the molecular weight distribution as indicated by the decrease in PDI from 1.53 for the linear PS arms to 1.32 for the self-assembled star polymer. Application of statistical models to the assembly of the star polymers indicates that even more dramatic decreases in the PDI should be achievable.¹² In the present case, it appears that the smaller polymeric material is assembling before the larger material, leading to a structure at least partially controlled by the kinetics of assembly.¹³

Preliminary mixing studies of large and small supramolecular star polymers are consistent with slow kinetics, significant mixing requiring days to weeks at room temperature. Thermodynamically,

the polymer coils should want to alternate between large and small to minimize steric interactions in the system. This behavior has already been observed in the hydrogen-bonded self-assembly of large and small dendrimers.^{4c} Current efforts are directed toward finding conditions that favor the thermodynamic assembly and investigating the properties of materials that incorporate the Bis-DeAP motif.

In conclusion, we have reported the ability of the Bis-DeAP motif to assemble low molecular weight materials into high molecular weight supramolecular star polymers while narrowing the overall PDI. The ability to assemble large, discrete structures from smaller components is essential to the bottom-up approach to nanoscale materials, and it is anticipated that the reversible nature of the hydrogen-bonded core will yield new and interesting properties.

Acknowledgment. Funding of this work by the NSF (CHE-0212772) and by ICI National Starch and Chemical Company (SRF 2209 R2AB3287) is gratefully acknowledged.

References

- (1) Selected reviews: (a) Bielawski, C. W.; Grubbs, R. H. *Prog. Polym. Sci.* **2007**, *32*, 1–29. (b) Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H. *Chem. Rev.* **2001**, *101*, 3747–3792. (c) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661–3688. (d) Matyjaszewski, K.; Xia, J. H. *Chem. Rev.* **2001**, *101*, 2921–2990.
- (2) Recent examples involving star polymers: (a) Gao, H.; Matyjaszewski, K. *Macromolecules* **2007**, *40*, 399–401. (b) Gao, H.; Ohno, S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2006**, *128*, 15111–15113.
- (3) (a) Lehn, J.-M. *Makromol. Chem., Macromol. Symp.* **1993**, *69*, 1–17. (b) Zimmerman, N.; Moore, J. S.; Zimmerman, S. C. *Chem. Ind.* **1998**, 604. (c) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071–4097. (d) Ciferri, A., Ed. *Supramolecular Polymers*, 2nd ed.; CRC Press LLC: Boca Raton, FL, 2005.
- (4) Cyclic, hydrogen-bonded self-assembled dendrimers: (a) Zimmerman, S. C.; Zeng, F.; Reichert, D. E. C.; Kolotuchin, S. V. *Science* **1996**, *271*, 1095–1098. (b) Corbin, P. S.; Lawless, L. J.; Li, Z. T.; Ma, Y. G.; Witmer, M. J.; Zimmerman, S. C. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 5099–5104. (c) Ma, Y.; Kolotuchin, S. V.; Zimmerman, S. C. *J. Am. Chem. Soc.* **2002**, *124*, 13757–13769.
- (5) Selected examples of heterocycles that form cyclic assemblies: (a) Zerkowski, J. A.; Seto, C. T.; Whitesides, G. M. *J. Am. Chem. Soc.* **1992**, *114*, 5473–5475. (b) Vreekamp, R. H.; van Duynhoven, J. P. M.; Hubert, M.; Verboom, W.; Reinhoudt, D. N. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1215–1218. (c) Marsh, A.; Silvestri, M.; Lehn, J.-M. *Chem. Commun.* **1996**, 1527–1528. (d) Mascari, M.; Hext, N. M.; Warmuth, R.; Moore, M. H.; Turkenburg, J. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2204–2206. (e) Fenniri, H.; Mathivanan, P.; Vidale, K. L.; Sherman, D. M.; Hallenga, K.; Wood, K. V.; Stowell, J. G. *J. Am. Chem. Soc.* **2001**, *123*, 3854–3855. (f) Keizer, H. M.; Gonzalez, J. J.; Segura, M.; Prados, P.; Sijbesma, R. P.; Meijer, E. W.; de Mendoza, J. *Chem.-Eur. J.* **2005**, *11*, 4602–4608.
- (6) Selected reviews: (a) Jeffery, T. D. *Angew. Chem., Int. Ed.* **2004**, *43*, 668–698. (b) Prins, L. J.; Reinhoudt, D. N.; Timmerman, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 2382–2426.
- (7) (a) Viau, L.; Even, M.; Maury, O.; Haddleton, D. M.; Le Bozec, H. C. R. *Chimie* **2005**, *8*, 1298–1307. (b) Schubert, U. S.; Eschbaumer, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 2892–2926 and references therein. (c) Lamba, J. J. S.; Fraser, C. L. *J. Am. Chem. Soc.* **1997**, *119*, 1801–1802.
- (8) Synthesis and detailed characterization will be presented in a future paper.
- (9) Nederberg, F.; Connor, E. F.; Moller, M.; Glauser, T.; Hedrick, J. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 2712–2715.
- (10) The exact structure of **2** in styrene has not been determined; however, the nature of the assembly during the polymerization is irrelevant to the post-polymerization properties described here.
- (11) Selected examples where the cleaved arms have a higher PDI: (a) Plamper, F. A.; Becker, H.; Lanzendorfer, M.; Patel, M.; Wittmann, A.; Ballauff, M.; Muller, A. H. E. *Macromol. Chem. Phys.* **2005**, *206*, 1813–1825. (b) Ueda, J.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1998**, *31*, 6762–6768. (c) Jacob, S.; Majoros, L.; Kennedy, J. P. *Macromolecules* **1996**, *29*, 8631–8641.
- (12) (a) Shiao, L.-D. *Macromol. Theory Simul.* **2004**, *13*, 783–789. (b) Zhu, S.; Li, D.; Yu, Q.; Hunkeler, D. *J. Macromol. Sci., Pure Appl. Chem.* **1998**, *35*, 33–56.
- (13) Annealing the sample did not significantly change the observed PDI. Likewise, the PDI and MW did not noticeably change over several months in solution.

JA075453J