

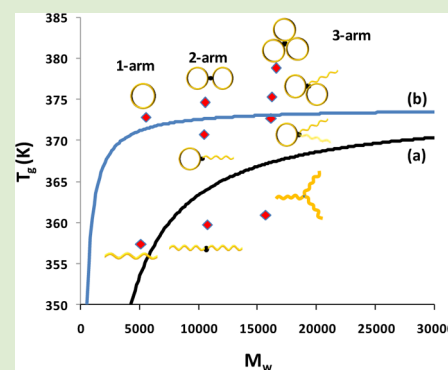
Glass Transition Temperature of Cyclic Stars

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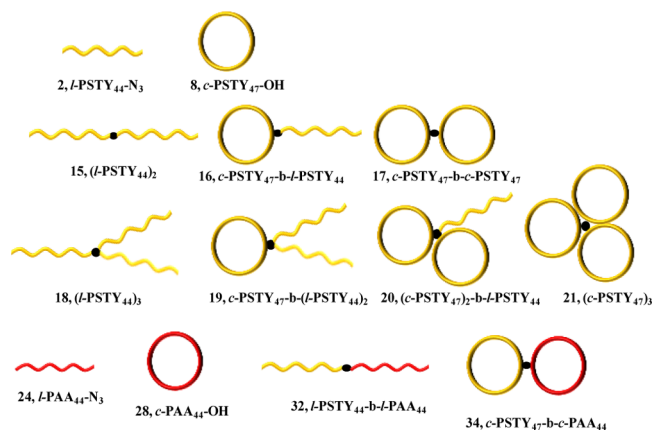
Supporting Information

ABSTRACT: Cyclic homo- and diblock copolymers with different topologies were synthesized using a combination of “living” radical polymerization and “click” coupling reactions. The topologies included 2- and 3-arm stars, with the arms consisting of either cyclic or linear polystyrene. In addition, a diblock consisting of a cyclic polystyrene and a cyclic poly(acrylic acid) was also made. The topologies by imposing topological constraints due to the presence of cyclic polymers and branch points had a marked influence on the glass transition temperature (T_g). It was found that for the polystyrene topology series, the T_g increased above the glass transition temperature at infinite molecular weight for a linear chain (i.e., T_g^∞) and correlated to the more compact nature of cyclic polymers. For the cyclic diblock of polystyrene and poly(acrylic acid), the T_g increased significantly due to separation of the blocks into their pure phases. This resulted in significant stretching of the chains and thus loss of conformation entropy.



Cyclic polymers have attracted great interest in the polymer field both from a synthetic and, more particularly, from a property point of view.¹ Linear polymers obey the well-known reptation model, in which a polymer chain can diffuse through a matrix constrained within a “tube” defined by the interactions of the neighboring chains.² The chain-ends play an important role in the motion of the polymer chain and also allow relaxation of the tube constraints. Cyclic (i.e., ring) topologies have no chain-ends, and thus cannot be modeled using “reptation”.³ Complicating matters further is that cyclic polymers have a more compact structure compared to an analogous linear polymer with the same molecular weight due to the cyclic’s fewer degrees of freedom as observed by the lower hydrodynamic volume (by a factor of ~ 0.71 for polystyrene) by size exclusion chromatography (SEC).⁴ These effects imply that cyclic polymers have very different physical properties to their linear analogues. A large body of work has examined the effect of molecular weight of homopolymer cyclic polymers on the glass transition temperature (T_g) and relaxation properties.^{5–7} Here, we synthesized a range of polystyrene (PSTY) and poly(acrylic acid) (PAA) architectures built by coupling cyclic polymers to either linear or other cyclics (see Scheme 1). The effect of the topologies on T_g was determined, and the data provided some insight into the effect of imposing topological constraints due to the cyclic nature of the polymer and branch points on the resulting physical properties of the polymer.

The ring closure method is straightforward, allowing the production of cyclic polymers consisting of different types of polymers and topologies.⁸ Our laboratory has detailed an efficient ring-closure method to produce cyclic polymers from “living” radical polymerization (LRP) and “click”-type coupling reactions to produce a wide range of complex polymer architectures.^{9,10} In this work, we used the combination of

Scheme 1. Cyclic Topologies Synthesized Using a Combination of “Living” Radical Polymerization (LRP) and CuAAC “Click” Coupling Reaction^a

^aYellow and red chains indicate polystyrene and poly(acrylic acid), respectively.

atom transfer radical polymerization (ATRP) and the copper catalyzed azide–alkyne cycloaddition (CuAAC) coupling “click” reaction. The cyclization of a monodisperse linear PSTY ($\equiv(\text{OH})-l\text{-PSTY}_{47}-\text{N}_3$, 7) under feed conditions produced cyclic structure $c\text{-PSTY}_{47}-\text{OH}$ (8) in 3 h at 25 °C with a cyclic purity of 82% (see Table S1 in SI). Purification of the crude $c\text{-PSTY}_{47}-\text{OH}$ by preparative SEC increased the purity to 99% as determined by using the log-normal

Received: October 26, 2014

Accepted: November 20, 2014

Published: November 24, 2014

distribution (LND) model¹¹ based on fitting multiple Gaussian functions for all possible polymer species.^{10,12} Table S1 in SI also provided the change in hydrodynamic volume used in the LND simulations for all polymer products. The OH group on *c*-PSTY₄₇-OH was converted to an azide via a two-step process (see Scheme S1 in SI) to produce *c*-PSTY₄₇-N₃ (**10**). Cyclic **10** was used as the main building blocks to construct all the other cyclic topologies. The cyclic poly(*tert*-butyl acrylate) (*c*-PBA-N₃, **30**) building block was constructed using a similar procedure, and then after coupling to cyclic polystyrene it was hydrolyzed to PAA. All products made were produced with high “click” efficiency and after fractionation through the preparative SEC gave purities greater than 95% as determined by the LND simulations (see Table S1 in SI). The molecular weight distributions for all products were narrow with polydispersity index (PDI) values all less than 1.07 based on RI detection. It should be noted that PDI values obtained by light scattering (i.e., triple detection) are always lower than that found by RI due to the lower scattering intensity for the lower molecular weight polymers.

The glass temperature for linear polymers was found to be dependent upon the molecular weight of the polymer according to the Kanig-Ueberreiter equation.¹³

$$T_g = \left[\frac{1}{T_g^\infty} + \frac{K}{M_w} \right]^{-1} \quad (1)$$

where K is a constant ($K = 7.8 \times 10^{-4}$ mol/kg for PSTY⁷), $T_g^\infty = 374$ K, and M_w is the molecular weight of the polymer. This equation provides an excellent fit to the experimental data of Gan et al.⁶ The equation accounts for linear polymer chains and cannot be used to predict the T_g of a cyclic polymer. The glass temperature of a cyclic polymer should be equal to T_g^∞ at molecular weights much lower than for linear polymer chains. In theory, Di Marzio and co-workers¹⁴ showed that the glass temperature for very low molecular weight cyclic polymers should in theory be higher than T_g^∞ . The molecular weight dependence on T_g for cyclic polymers found experimentally by Gan et al.⁶ showed that, at lower molecular weights, less than 4000, the T_g was lower than T_g^∞ (see solid lines in Figure 1A).

We have included the molecular weight dependence on T_g for all our homopolymer PSTY linear and cyclic polymer topologies in Figure 1A, and all T_g values are given in Table 1. There was good agreement for *l*-PSTY₄₄-N₃ (**2**) and *c*-PSTY₄₇-OH (**8**) compared with the data from Gan et al. (curves a and b in Figure 1A). The T_g values at a molecular weight of approximately 10 k for the linear (**15**), diblock *c*-PSTY₄₇-*b*-*l*-PSTY₄₄ (**16**) and *c*-PSTY₄₇-*b*-*c*-PSTY₄₇ (**17**) increased from 359.8 to 374.7 K with a decrease in the number of chain ends from 2 to 0. There are two opposing factors that contribute to the T_g based on the free volume theory: the first, chain-ends increase the free volume and thus lower the T_g ; and second, branch points (or cross-links) reduce the free volume leading to an increase in the T_g .^{15,16} With the addition of a branch point in **16** (i.e., with three chains branching from the core branch point), the T_g increased, and when there were no chain-ends (i.e., **17**), the T_g increased further. An increase in the molecular weight to ~15.5 k for the range of cyclic/linear topology combinations further supported the topology dependence on T_g . A 3-arm star (*l*-PSTY₄₄)₃ (**18**) with three free chain-ends gave a T_g of 361.0 K that was much less than that expected for a linear chain with two chain-ends (~366.8 K). This data suggested that the free chain-ends play a

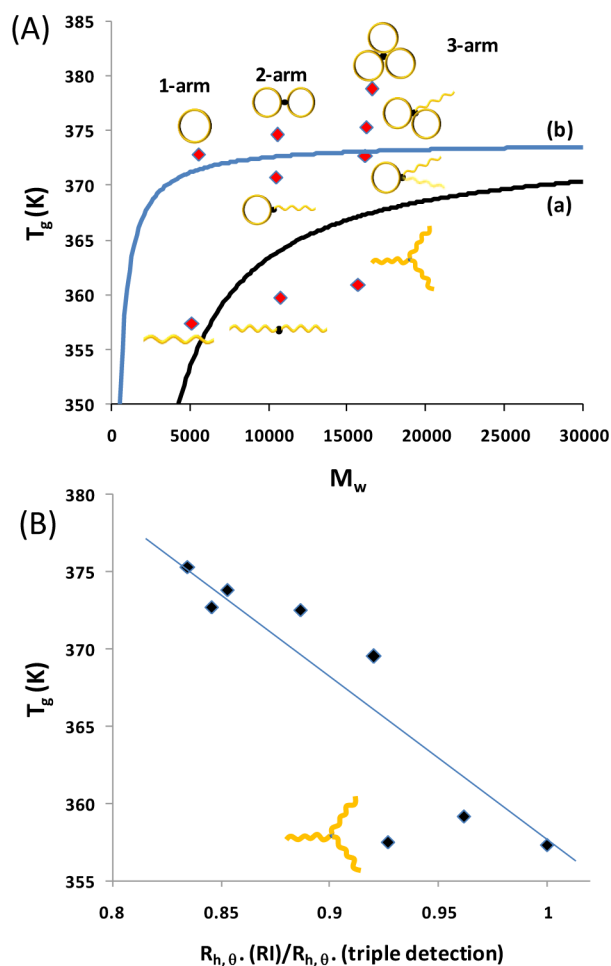















Figure 1. Influence of molecular weight (M_w) and coil size in a θ -solvent on the glass temperature (T_g). (A) Curve a, T_g as a function of M_w determined from eq 1 ($K = 7.8 \times 10^{-4}$ mol/kg for PSTY⁷), $T_g^\infty = 374$ K; curve b, experimental data from Gan et al.⁶ for cyclic T_g vs M_w . (B) Coil compactness under θ -conditions; ratio of coil radius under θ -conditions determined by RI (i.e., relative to PSTY standards) and triple detection SEC; Mark–Houwink parameters used were $K = 0.0141$ and $a = 0.7$.

greater role in reducing the T_g compared to the incorporation of a single branch point (i.e., with 3 branches). Decreasing the number of chain-ends to 2 (i.e., *c*-PSTY₄₇-*b*-(*l*-PSTY₄₄)₂, **19**, with four branches) increased the T_g by 11.8 to 372.7 K, which was also greater than that for a linear chain with the same molecular weight (solid black line in Figure 1A). A further decrease in the number of chain-ends to 1 for **20** ((*c*-PSTY₄₇)₂-*b*-*l*-PSTY₄₄) with five branches) and 0 for **21** ((*c*-PSTY₄₇)₃) with six branches) led to T_g values of 375.4 and 378.9 K, respectively, that were greater than for the corresponding linear analogue. Taken together, the data suggested that the chain-ends have a much greater influence on T_g than having a single branch point even with greater crowding of chains at that branch for the various topologies. This postulate was supported by previous work.¹⁶

A qualitative method to obtain the polymer’s random coil conformation in the bulk is to determine the coil size in a good solvent, and convert this size to what would be expected in a Flory θ -solvent.¹⁷ Excluded volume effects are canceled under θ -solvent conditions, resulting in an approximate coil size in the bulk assuming the polymer does not have entanglements.¹⁸ The

Table 1. Glass Transition Temperature (T_g) for Cyclic Homopolystyrene and Amphiphilic Block Copolymers

No	Code	Structure	T_g (K)		Coil radius (SEC) ^a	
			PSTY	PAA	$R_{h,\theta}$ (RI) (nm)	$R_{h,\theta}$ (TD) (nm)
2	<i>l</i> -PSTY ₄₄ -N ₃		358.55	--	0.94	0.94
8	<i>c</i> -PSTY ₄₇ -OH		372.95	--	0.82	0.97
15	(<i>l</i> -PSTY ₄₄) ₂		359.75	--	1.30	1.36
16	<i>c</i> -PSTY ₄₇ - <i>b</i> - <i>l</i> -PSTY ₄₄		370.75	--	1.23	1.34
17	(<i>c</i> -PSTY ₄₇) ₂		374.65	--	1.14	1.34
18	(<i>l</i> -PSTY ₄₄) ₃		360.95	--	1.52	1.64
19	<i>c</i> -PSTY ₄₇ - <i>b</i> -(<i>l</i> -PSTY ₄₄) ₂		372.75	--	1.47	1.66
20	(<i>c</i> -PSTY ₄₇) ₂ - <i>b</i> - <i>l</i> -PSTY ₄₄		375.35	--	1.39	1.66
21	(<i>c</i> -PSTY ₄₇) ₃		378.85	--	1.33	1.68
24	<i>l</i> -PAA ₄₄ -N ₃			386.45		
28	<i>c</i> -PAA ₄₄ -OH			388.25		
32	<i>l</i> -PSTY ₄₄ - <i>b</i> - <i>l</i> -PAA ₄₄		368.65	391.85		
34	<i>c</i> -PSTY ₄₇ - <i>b</i> - <i>c</i> -PAA ₄₄		381.65	394.05		

^aCoil radius under θ -conditions using the hydrodynamic radius (i.e., M_n) determined from SEC using RI (relative to PSTY standards) and triple detection (i.e., absolute molecular weight). The M-H parameters used were $K = 0.0141$ and $a = 0.7$ in THF, and $a = 0.5$ for a θ -solvent.

molecular weights used in our work are well below the critical entanglement molecular weight for PSTY. We determined the coil size from the hydrodynamic volume (V_h) obtained from SEC based on the Mark–Houwink relationship between the molecular weight and the intrinsic viscosity¹⁹

$$[\eta] = KM^a = KM^{0.5}\alpha^3 \quad (2)$$

$$\alpha = M^{(a-0.5)/3} \quad (3)$$

where K and a are constants for a particular polymer–solvent pair, M is the molecular weight of the polymer, and α is the expansion coefficient of the hydrodynamic radius, R_h , from a θ to a good solvent (i.e., $\alpha = R_{h,\theta}/R_{h,\theta}$). The value of a in a θ -solvent is 0.5, and in a good solvent can range between 0.7 and 0.85. R_h is related to the intrinsic viscosity by the following equation

$$R_h^3 = \frac{3[\eta]M}{10\pi N_A} \quad (4)$$

where N_A is Avogadro's number. Therefore, one can determine R_h from K and a values according to the following relationship

$$R_h^3 = \frac{3KM^{a+1}}{10\pi N_A} \quad (5)$$

Producing stars or cyclic polymers or combinations of both resulted in producing coils that were more compact compared to their linear molecular weight analogues, resulting in a lower molecular weight by RI compared to triple detection (see Table S1 in SI). Therefore, the hydrodynamic volume for each polymer topology can be determined based on PSTY standards (i.e., using the RI calibration curve) or via triple detection, and together with α from eq 3 one can calculate $R_{h,\theta}$ (see Table 1). It can be seen from Figure 1B that the T_g decreased linearly as the ratio of $R_{h,\theta}$ from RI to $R_{h,\theta}$, determined by triple detection, increased, suggesting that a more compact coil and, thus, lower free volume increased the glass temperature. The one outlier was the three-arm star ((*l*-PSTY₄₄)₃, **18**), which showed a much

lower T_g than the other topologies, most probably due to the three free chain end-groups. Although free volume was a good predictor for most of the structures, it seems to be limited to systems where the number of free chain-ends was small. The glass transition temperatures of diblock topologies consisting of *l*-PSTY₄₄-*b*-*l*-PAA₄₄ (**32**), as shown in Scheme 1, were determined (Table 1). The T_g of *l*-PAA₄₄-N₃ (**24**) was 386.5 K, and after cyclization (*c*-PAA₄₄-OH, **28**), the T_g increased by only 1.8 K compared to the increase of 14.4 K found after cyclization of PSTY. This suggested that the PAA linear chains have a coil conformation extended well beyond that of a Gaussian coil. The diblock *l*-PSTY₄₄-*b*-*l*-PAA₄₄ (**32**) showed two glass transitions indicative of the blocks separating into pure phases. The first T_g (368.7 K) corresponding to PSTY was 10 K higher than *l*-PSTY₄₄ (**2**), and the second T_g at 391.85 K corresponding to PAA was only 3.6 K higher than *l*-PAA₄₄ (Table 1). A theoretical calculation of the Flory interaction parameter gave a χN value of approximately 77 (where N equals the number of monomer units in the polymer chain). This value was well within the ordered-state composition in which the blocks should be well-separated with defined interfaces and highly stretched chains.²⁰ Such a loss of entropy in the chains will result in an increase in the T_g of each block. The coupling of two cyclics to form a diblock copolymer (i.e., *c*-PSTY₄₇-*b*-*c*-PAA₄₄, **34**) resulted in a marked increase in the PSTY T_g by 23 K to that of the linear *l*-PSTY₄₄, **2**, while the T_g of the PAA block increased by 7.6 K. The diblocks **32** and **34** were spin-coated from a 2 wt % polymer solution in THF onto a silicon wafer substrate and annealed overnight at 130 °C. The morphology of the resulting films was then characterized by atomic force microscopy (AFM). It can clearly be seen that the blocks phase separated into distinct lamella domains (Figure 2). The average domain spacing for **32** and the cyclic analogue (**34**) was 23.0 and 12.2 nm, respectively. This suggested that the linear chains from **32** were highly stretched, extending well beyond what would be expected for coil dimensions in the bulk state (see $R_{h,\theta}$ values for **2** in Table 1). The data also suggested that the cyclic chains from **34** were also

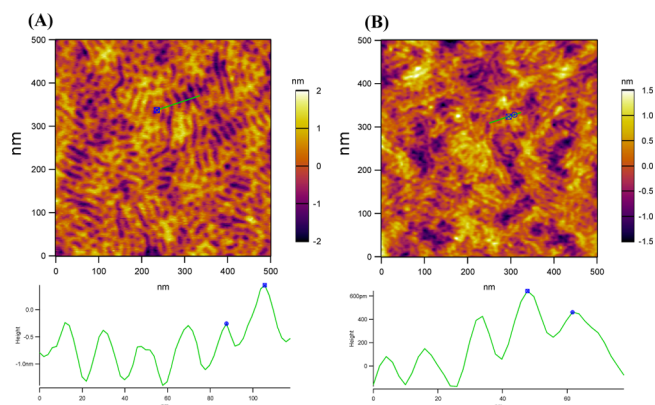


Figure 2. Atomic force microscopy (AFM) height images for (A) *l*-PSTY₄₄-*b*-*l*-PAA₄₄, **32**, and (B) *c*-PSTY₄₇-*b*-*c*-PAA₄₄, **34**, diblock copolymers.

highly stretched with the expected half the domain spacing as its linear analogue **32**.

In summary, the effect of different cyclic topologies on the glass temperature were evaluated. The cyclic blocks with no chain-ends showed an increase in the T_g above T_g^∞ . Coupling of linear chains to a cyclic to make two- or three-arm stars reduced the T_g , well below that for two- and three-arm cyclic stars, and played a greater influence than the inclusion of a branch point. It was found there was a good correlation between the compact nature of the coil in a θ -solvent and the glass temperature when the number of chain ends was less than 3. For the diblock consisting of two linear chains (i.e., *l*-PSTY₄₄-*b*-*l*-PAA₄₄) and two cyclic chains (i.e., *c*-PSTY₄₇-*b*-*c*-PAA₄₄) there was a large influence on the glass temperature by ~ 10 K. This was due to the separation of the blocks into their pure phases, resulting in the stretching of the chains and loss of conformational entropy.

■ ASSOCIATED CONTENT

📄 Supporting Information

Synthesis and characterizations of all polymers, including ¹H NMR spectra, SEC traces, and MALDI-ToF spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

M.J.M. acknowledges financial support from the ARC Discovery Grant (DP140103497).

■ REFERENCES

- (1) McLeish, T. *Science* **2002**, *297* (5589), 2005–2006.
- (2) de Gennes, P.-G. *J. Chem. Phys.* **1971**, *55*, 572–579.
- (3) McKenna, G. B.; Hostetter, B. J.; Hadjichristidis, N.; Fetters, L. J.; Plazek, D. J. *Macromolecules* **1989**, *22* (4), 1834–52.
- (4) (a) Geiser, D.; Hoecker, H. *Macromolecules* **1980**, *13* (3), 653–6.
- (b) Roovers, J.; Toporowski, P. M. *Macromolecules* **1983**, *16* (6), 843–849.
- (5) Santangelo, P. G.; Roland, C. M. *Macromolecules* **1998**, *31* (14), 4581–4585.

(6) Gan, Y. D.; Dong, D. H.; Hogenesch, T. E. *Macromolecules* **1995**, *28* (1), 383–385.

(7) Santangelo, P. G.; Roland, C. M.; Chang, T.; Cho, D.; Roovers, J. *Macromolecules* **2001**, *34* (26), 9002–9005.

(8) (a) Jia, Z.; Fu, Q.; Huang, J. *Macromolecules* **2006**, *39* (16), 5190–5193. (b) Endo, K. *Synthesis and Properties of Cyclic Polymers*. In *New Frontiers in Polymer Synthesis*; Kobayashi, S., Ed.; Springer: New York, 2008; Vol. 217, pp 121–183. (c) Laurent, B. A.; Grayson, S. M. *Chem. Soc. Rev.* **2009**, *38* (8), 2202–2213. (d) Kricheldorf, H. R. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48* (2), 251–284. (e) Yamamoto, T.; Tezuka, Y. *Polym. Chem.* **2011**, *2* (9), 1930–1941. (f) Laurent, B. A.; Grayson, S. M. *J. Am. Chem. Soc.* **2006**, *128* (13), 4238–4239. (g) Dong, Y.-Q.; Tong, Y.-Y.; Dong, B.-T.; Du, F.-S.; Li, Z.-C. *Macromolecules* **2009**, *42* (8), 2940–2948. (h) Shi, G.-Y.; Pan, C.-Y. *Macromol. Rapid Commun.* **2008**, *29* (20), 1672–1678. (i) Eugene, D. M.; Grayson, S. M. *Macromolecules* **2008**, *41* (14), 5082–5084.

(9) (a) Lonsdale, D. E.; Bell, C. A.; Monteiro, M. J. *Macromolecules* **2010**, *43* (7), 3331–3339. (b) Lonsdale, D. E.; Monteiro, M. J. *Chem. Commun.* **2010**, *46* (42), 7945–7947. (c) Lonsdale, D. E.; Monteiro, M. J. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49* (21), 4603–4612. (d) Kulis, J.; Jia, Z. F.; Monteiro, M. J. *Macromolecules* **2012**, *45* (15), 5956–5966. (e) Hossain, M. D.; Jia, Z. F.; Monteiro, M. J. *Macromolecules* **2014**, *47* (15), 4955–4970.

(10) Jia, Z. F.; Lonsdale, D. E.; Kulis, J.; Monteiro, M. J. *ACS Macro Lett.* **2012**, *1* (6), 780–783.

(11) Cabaniss, S. E.; Zhou, Q. H.; Maurice, P. A.; Chin, Y. P.; Aiken, G. R. *Environ. Sci. Technol.* **2000**, *34* (6), 1103–1109.

(12) Hossain, M. D.; Valade, D.; Jia, Z. F.; Monteiro, M. J. *Polym. Chem.* **2012**, *3* (10), 2986–2995.

(13) Ueberreiter, K.; Kanig, G. *J. Colloid Sci.* **1952**, *7* (6), 569–583.

(14) Di Marzio, E. A.; Guttman, C. M. *Macromolecules* **1987**, *20* (6), 1403–7.

(15) Wooley, K. L.; Hawker, C. J.; Pochan, J. M.; Frechet, J. M. J. *Macromolecules* **1993**, *26* (7), 1514–1519.

(16) Farrington, P. J.; Hawker, C. J.; Frechet, J. M. J.; Mackay, M. E. *Macromolecules* **1998**, *31* (15), 5043–5050.

(17) Flory, P. J. *Principles of Polymer Chemistry*; Cornell Univ. Press: New York, 1953.

(18) Daoud, M.; Cotton, J. P. *J. Phys.* **1982**, *43* (3), 531–538.

(19) Sperling, L. H. *Introduction to Physical and Polymer Science*; John Wiley & Sons, Inc: New York, 1992.

(20) Fredrickson, G. H.; Bates, F. S. *Annu. Rev. Mater. Sci.* **1996**, *26*, 501–550.