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Synthesis of Nanosized "Cored" Star Polymers

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ABSTRACT: A synthetic approach to nanosized "cored" star polymers is reported. A 5,10,15,20-tetrakis-(4-carboxyphenyl)porphyrin core was functionalized with four 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) initiating groups. Four-armed star copolymers of styrene and 4-hydroxystyrene were synthesized and functionalized with 3,5-di(3-buten-1-oxy) benzyl bromide groups but exhibited poor solubility. As an alternative, 5,10,15,20-tetrakis(3′,5′-dihydroxyphenyl)porphyrin was functionalized with 2-bromo-2-methyl-propionyl groups capable of initiating atom transfer radical polymerization (ATRP). Copolymerization of the core initiator with 1-but-3-enyl-4-vinylbenzene and styrene at low conversion produced soluble eight-armed star block copolymers. Through the ring-closing metathesis (RCM) reaction, the alkene groups of the polymer were intramolecularly cross-linked. The ester groups linking the cross-linked polymer arms to the porphyrin core were hydrolyzed, producing a "cored" star polymer with a molecular weight of approximately 20 kDa and a polydispersity index (PDI) of 1.5.

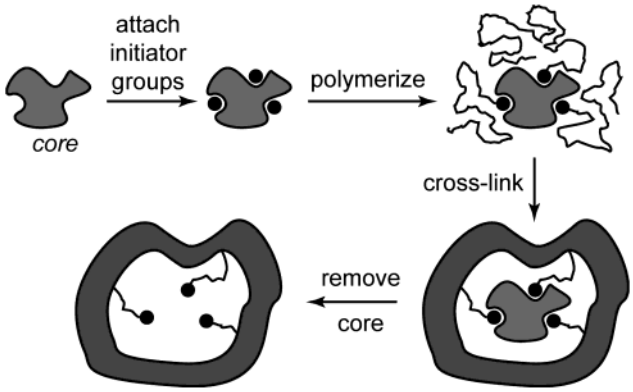
Introduction

Recently, there has been growing interest in hollow nanospheres and nanocapsules that are formed by the self-assembly of linear polymers.[1−12] Such structures are of particular interest as a result of their potential applications in drug delivery,[1−7] catalysis,[1,3,4] and encapsulation[1,5,8] and as nanoreactors[1,3,5,7] and bioremediation agents.[1,3] Vesicles formed from traditional lipids may also function in many of these capacities, but their instability often limits their applications.[1,5] As a result, functionally analogous but more stable nanostructures are desired. In this regard, synthetic nanosized compounds that are covalently linked provide certain advantages over noncovalently assembled systems and have recently attracted considerable attention.

One approach to hollow nanospherical macromolecules is to cross-link vesicular structures that have been assembled from lipids or block copolymers.[1,3−5,7,11] Another approach is that pioneered by Wooley and co-workers.[2,12] These investigators synthesized block copolymers that self-assembled into micellar structures, which were cross-linked to form unimolecular core−shell nanoparticles (filled spheres). The cross-linked nanoparticles were subsequently "cored", forming hollow nanospherical structures. Similarly, Liu and co-workers synthesized triblock polymers, which were also shown to self-assemble into micellar structures.[7] The outer shell of these structures was photo-cross-linked, and the interior was removed, generating a "cored" structure capable of encapsulating rhodamine B in water.[7]

We recently disclosed an approach to "cored" dendrimers[13−16] and dendrimer assemblies.[17] Thus, dendrimers or their assemblies were cross-linked via the RCM reaction, and the core was removed hydrolytically. In cases where the core is a molecular template, such "cored" dendrimers can selectively bind small molecules; the overall process is a type of "monomolecular imprinting".[14] The cored dendrimer approach allows for a high degree of control over the dimensions, core functionality, and overall properties of these unique structures. However, the preparation of dendrimers generally requires multistep syntheses with their attendant purifications. Alternatively, star polymers can be prepared in far fewer steps but, nonetheless, share some structural similarities with dendrimers, in particular having multiple arms attached to a core.[18−23] Herein we report the synthesis of cross-linked and cored star polymers using a core-first approach.[24]

Scheme 1. Design of a "Cored" Star Polymer



Results and Discussion

The synthesis of "cored" star polymers involves four key steps (Scheme 1): (i) an appropriate core molecule is functionalized with initiator groups, (ii) polymerization is carried out to form the arms of the star, (iii) the polymer arms are intramolecularly cross-linked with a minimum of $n - 1$ cross-links between the arms (n = number of arms), and (iv) the core is removed.

Using a procedure reported by Hawker and co-workers, benzoyl peroxide, styrene, and TEMPO were heated to 80 °C to form **1**.[25] Hydrolysis of **1** resulted in the formation of alcohol **2**,[25] which was reacted with the tetra-acid chloride of porphyrin core **3** forming macroinitiator **4** in 34% yield (Scheme 2). To synthesize a monomer capable of post-polymerization cross-linking, analogous to the synthesis of cored dendrimers, the

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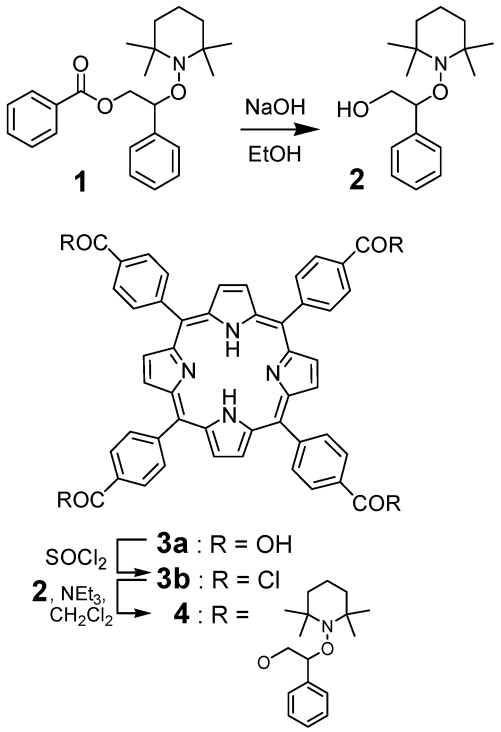
Scheme 2. Synthesis of Porphyrin–TEMPO Macroinitiator 4

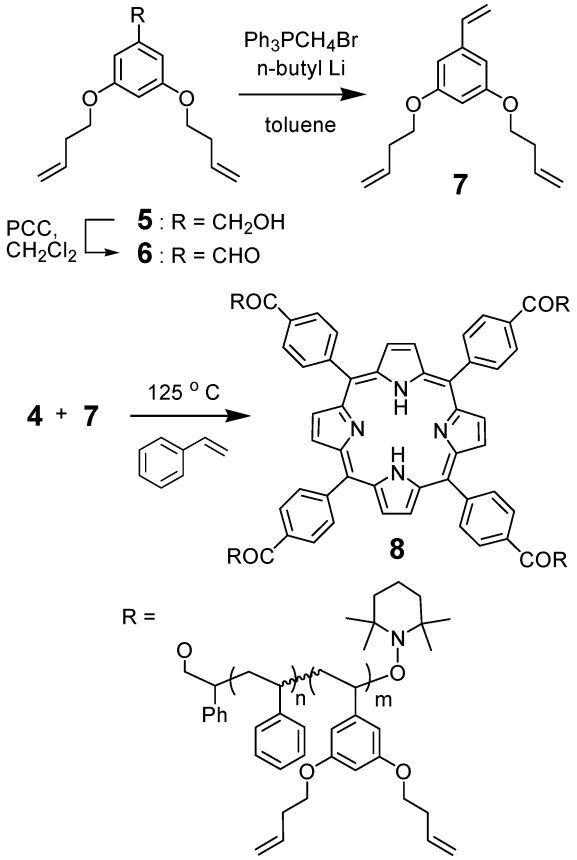


previously reported alcohol **5**[13] underwent PCC oxidation to produce aldehyde **6** in 74% yield. Aldehyde **6** was subsequently treated with triphenylphosphonium bromide to produce the desired styryl monomer **7** in 84% yield. The target random star copolymer **8** was subsequently formed by heating a mixture of macroinitiator **4** and monomer **7** to 125 °C. Upon formation, **8** precipitated and could not be dissolved in a range of organic solvents, possibly due to the formation of a cross-linked polymer network.

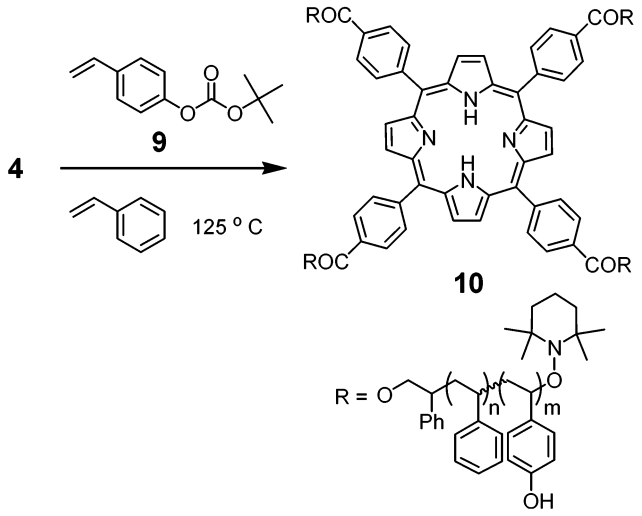
A second approach was investigated wherein the alkene groups to be cross-linked were attached to the polymer arms in a post-polymerization, functionalization step. Thus, macroinitiator **4** was reacted with a mixture of styrene and *tert*-butyl carbonate monomer **9**, resulting in the formation of hydroxyl-functionalized random star copolymer **10** (Scheme 4), which was characterized by ^{1}H NMR and analytical size exclusion chromatography (SEC). A representative ^{1}H NMR of **10** in acetone-d_6 shows broadened peaks at 8.0 and 7.1–6.6 ppm (Figure 1). These peaks correspond to the phenolic hydroxyl proton and aromatic protons, respectively, whereas the broadened peaks at 1.9 and 1.5 ppm correspond to the aliphatic protons in the backbone of the polymer chain. The appearance of the peak at approximately 8.0 ppm in the ^{1}H NMR and the absence of a peak representing the *tert*-butyl group at approximately 1.4 ppm support the conclusion that the carbonate group was removed thermally during the polymerization.

Polymerization reactions were performed under a wide range of conditions, using analytical SEC data to determine the average molecular weight and PDI of **10**. Typical results of these experiments are shown in Table 1 and Figure 2. The low molecular weights measured for $\mathbf{10}_{32}$–$\mathbf{10}_{34}$ indicated that more than 6 h of reaction time was needed to achieve molecular weights approaching the theoretical values. Broad molecular

Scheme 3. Synthesis of Target Polymer 8, Star(polystyrene-*ran*-poly-7)



Scheme 4. Synthesis of Hydroxyl-Functionalized Star Polymer 10, Star(polystyrene-*ran*-poly-4-hydroxystyrene)



weights and multimodal distributions (illustrated in Figure 2) were observed for most of the polymers that were formed, and the PDI values for **10** ranged from 1.1 to 276. Most of the SEC chromatograms exhibited major peaks in the region of the theoretical molecular weight but also significant peaks corresponding to polymers with much higher molecular weight, indicating that poor control over the polymerization of **10** was achieved in a number of runs. Interestingly, the solubility of **10** in common organic solvents changed over time with initially prepared samples fully dissolved in both THF and acetone, but after sitting for extended periods,

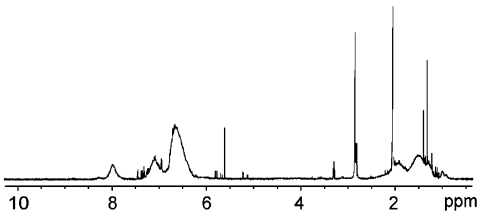


Figure 1. Representative ^{1}H NMR for **10** in acetone-d_6 showing broadened peaks corresponding to the polymer protons and some organic solvent impurities. The top of the spectrum was cropped to better illustrate the important peaks.

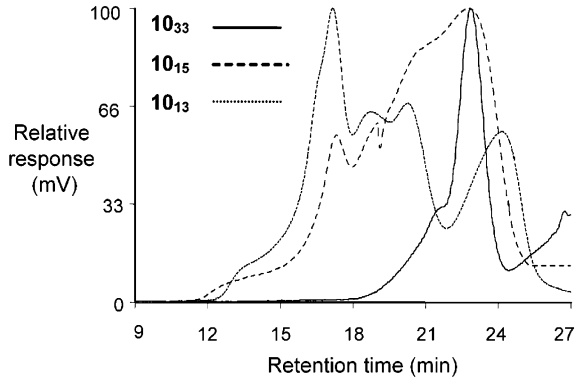


Figure 2. Representative analytical SEC chromatograms (THF) for polymers of type $\mathbf{10}_{33}$, $\mathbf{10}_{15}$, and $\mathbf{10}_{13}$.

Table 1. Representative Data for Polymers of Type 10

polymer	styrene:**9**[a]	theoretical MW (kDa)	M_n (kDa)	M_w (kDa)	PDI	major SEC peaks (kDa)
$\mathbf{10}_2$	52:48	26	1.5	8	5.4	2, 13, 24
$\mathbf{10}_3$	23:77	30	2.3	7.3	3.1	2, 13
$\mathbf{10}_4$	73:23	33	2.6	445	170	2.5, 48, 160
$\mathbf{10}_7$	82:18	15	2.0	10.8	5.2	2, 7, 16, 25
$\mathbf{10}_B$	56:44	40	8	27	3.5	8, 62
$\mathbf{10}_{12}$	53:47	48	32	49	1.5	15, 40, 75
$\mathbf{10}_{13}$	56:44	40	8.8	192	22	2, 25, 76, 191
$\mathbf{10}_{15}$	53:47	48	9.3	34	3.7	6, 18, 34, 111
$\mathbf{10}_{22}$	48:52	17	176	336	1.9	100, 300, 600
$\mathbf{10}_{23}$	57:43	13	44	49	1.1	34, 67
$\mathbf{10}_{32}$[b]	23:77	22	1.2	15	63	5
$\mathbf{10}_{33}$[c]	23:77	21	0.03	8	276	8
$\mathbf{10}_{34}$[d]	19:81	24	0.6	16	25	10, 190

[a] Comonomer feed ratio. [b] Polymerization time was 2 h. [c] Polymerization time was 4 h. [d] Polymerization time was 6 h.

most batches precipitated with a significant loss of solubility.

To explain the formation of the higher molecular weight polymers in the multimodal distributions, it could be hypothesized that some polymer stars have been covalently linked during the polymerization reaction. Such a process would lead to the formation of single star polymers as well as star dimers, trimers, etc., which is consistent with some of the SEC chromatograms observed. For example**,** the major peaks in the SEC of polymer $\mathbf{10}_{12}$ correspond to molecular weights of 15, 40, and 75 kDa, the approximate values expected for mono-, di-, and tristar polymers. On the other hand, many more of the SEC chromatograms for **10** do not exhibit a pattern consistent with oligomeric stars. For example, polymer $\mathbf{10}_B$ has major molecular weight peaks of 8 and 62 kDa, representing mono- and octastar polymers; however, no peaks corresponding to the intermediate oligomers (i.e., dimer through heptamer) are observed. On the basis of these observations, it appears that the multimodal molecular weight distribution found for **10** may not be arising from the covalent linking of stars during polymerization.

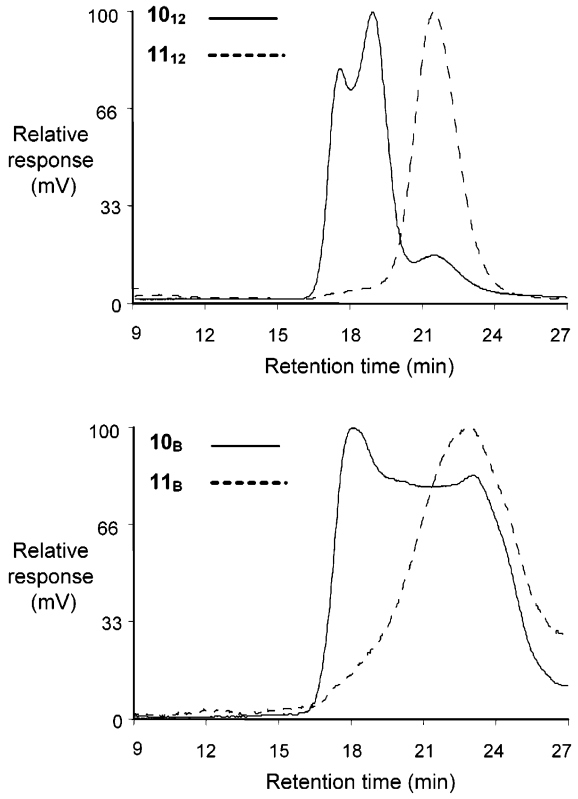


Figure 3. Analytical SEC chromatograms (THF) for polymers $\mathbf{10}_{12}$, $\mathbf{10}_B$, $\mathbf{11}_{12}$, and $\mathbf{11}_B$.

Scheme 5. Hydrolysis of Four-Armed Star Polymer 10 To Give Polystyrene-*ran*-poly-4-hydroxystyrene (11)

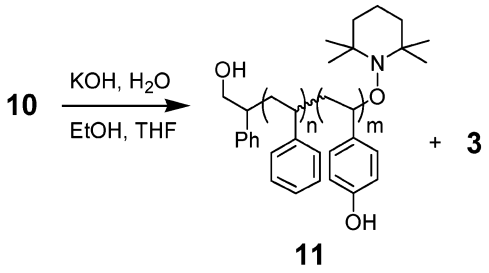
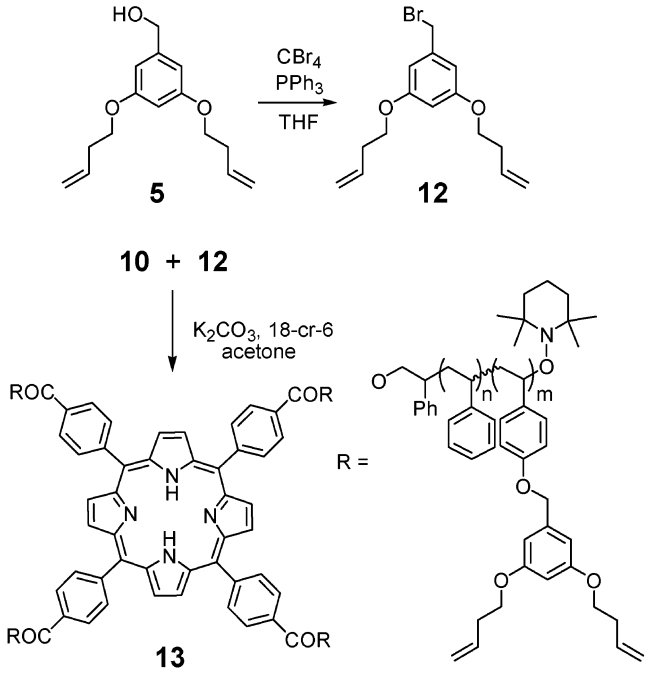


Table 2. Polymers $\mathbf{10}_{12}$ and $\mathbf{10}_B$ and Their Hydrolysis Products, $\mathbf{11}_{12}$ and $\mathbf{11}_B$

polymer	M_n (kDa)	M_w (kDa)	PDI	major SEC peak (kDa)
$\mathbf{10}_B$	9	40	6	8, 62
$\mathbf{10}_{12}$	32	49	1.5	15, 44, 75
$\mathbf{11}_B$	8	11	1.5	10
$\mathbf{11}_{12}$	14	16	1.1	15

To further investigate the structure of polymer **10** and the nature of its multimodal distribution, hydrolysis of both $\mathbf{10}_{12}$ and $\mathbf{10}_B$ was carried out (Scheme 5), and the resulting linear polymers $\mathbf{11}_{12}$ and $\mathbf{11}_B$ were characterized (Figure 3, Table 2). Polymers $\mathbf{11}_{12}$ and $\mathbf{11}_B$ both exhibited monomodal distributions with PDI values that are significantly lower than that of their corresponding star polymer precursors, $\mathbf{10}_{12}$ and $\mathbf{10}_B$. These observations tend to further argue against the possibility that star oligomerization is occurring during the polymerization reaction. It is possible that the multimodal distribution observed for **10** is the result of noncovalent star polymer aggregation. Finally, through the star

Scheme 6. Synthesis of Alkylating Group 12 and Alkene-Functionalized Polymer 13, Star(polystyrene-*ran*-poly-4-(bis(3,5-butenoxy)benzyloxy)styrene



hydrolysis reaction it was possible to calculate the average number of arms grown during the polymerization. Thus, on the basis of the observed decrease of 29 and 33 kDa in the M_w values for the hydrolysis products $\mathbf{11}_{12}$ and $\mathbf{11}_B$, respectively, it could be estimated that star polymers $\mathbf{10}_{12}$ and $\mathbf{10}_B$ contain an average number of arms of 3.1 and 3.6, respectively.

By analogy to the synthesis of cored dendrimers,[13−16] bromide **12** was considered to be a suitable compound for the post-polymerization functionalization of **10** in preparation for its cross-linking. By treating the previously described benzylic alcohol **5** with carbon tetrabromide and triphenylphosphine, bromide **12** was synthesized in 90% yield (Scheme 6). Alkylation of soluble samples of star polymer **10** with **12** resulted in the formation of alkene-functionalized, random star copolymer **13** (Scheme 6). A representative ^{1}H NMR spectrum for star polymer **13** in THF-d_8 (Figure 4) shows broadened peaks at the positions expected for the protons of both the styrene and the bis(homoallyl ether)phenyl moieties. Also, the disappearance of the phenolic hydroxyl peak at 8.0 ppm indicated that the starting polymer **10** had completely reacted. Star **13** was soluble in THF, so this solvent was also used for analytical SEC characterization. In comparison to precursor **10**, **13** is approximately 16 kDa larger. As with **10**, prolonged storage of **13** resulted in a reduction in its solubility in common organic solvents such as THF. For this reason, intramolecular cross-linking of **13** was not attempted.

The above approach illustrates a new way of forming alkene-functionalized star polymers. The process of post-polymerization functionalization has the advantage that the alkene density could be varied readily by changing the alkene density of the alkylating agent or the degree of alkylation. At the same time, this approach has the disadvantage that it incorporates an additional step into the synthetic scheme, which would not be necessary if alkene-functionalized star polymers could be synthesized directly from a corresponding alkene-functionalized monomer. The core-first method was chosen in the

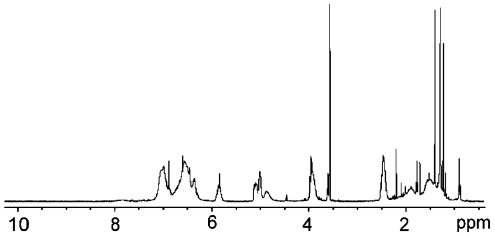
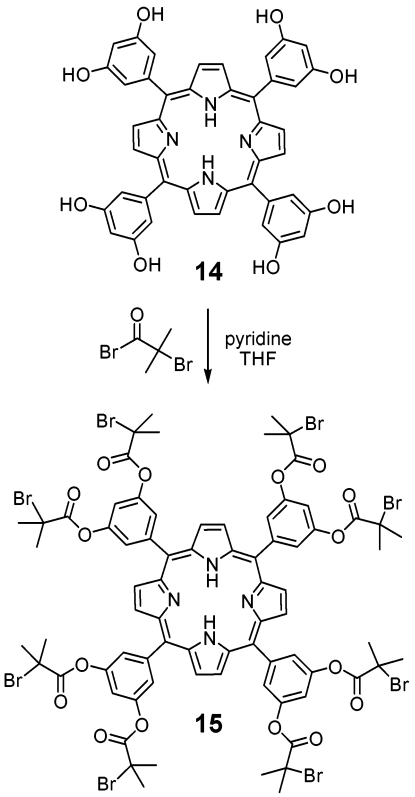


Figure 4. Representative ^{1}H NMR for **13** in THF-d_8 showing broadened peaks corresponding to the polymer protons as well as some organic solvent impurities. The top of the spectrum was cropped to better illustrate the important peaks.

Scheme 7. Synthesis of Porphyrin Octa-Initiator 15



above approach because it usually produces star polymers with few defects and a low PDI. However, the molecular weight and polydispersity of star polymers **8**, **10**, and **13** could not be controlled by using initiator **3** at high conversion. The greatest control over core-first star polymerizations may be obtained when reactions are run to conversions well below 100%, including some below 30%.[23] This is accomplished by using a large excess of monomer, with monomer-to-initiator ratios ranging from approximately 100 to 20 000.[23]

The new star polymer system described below has the key advantages that the alkene-functionalized star polymer is formed directly from alkene-functionalized monomer, and the monomer can be formed in one step from commercially available materials. In addition, the ATRP[26] process was employed on a more readily available core with eight initiator sites. Carrying out the polymerization at low conversion allowed for a high degree of control over polymer molecular weight and PDI.

Thus, treatment of an octahydroxylporphyrin **14** with 2-bromo-2-methylpropionyl bromide resulted in the formation of porphyrin **15** in 21% yield (Scheme 7). Initiator **15** features eight α-bromo ester groups, which

Scheme 8. Synthesis of Eight-Armed Alkene-Functionalized Star Polymer 17, Star(poly-4-butenylstyrene)

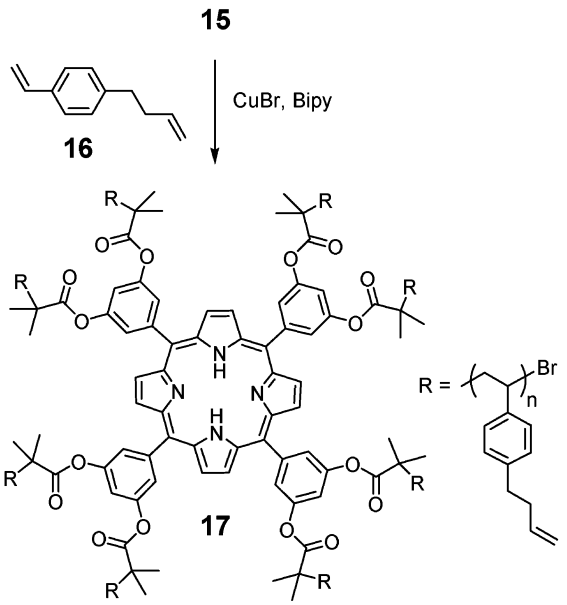


Table 3. Representative Data for Star Polymers of Type 17, Formed at Low Conversion

polymer	theoretical MW (kDa)	M_n (kDa)	M_w (kDa)	PDI	major SEC peak (kDa)	% conversion
17$_1$	338	13	20	1.56	21	6.2
17$_2$	306	19	24	1.23	24	14
17$_3$	526	20	27	1.34	29	n.d.

have been shown to initiate polymerization under ATRP conditions.[26] In addition, the initiating sites of **15** are connected to the porphyrin core through ester linkages, which should be readily cleavable during the core removal step.

Following a known procedure, monomer **16** was synthesized by reacting allylmagnesium chloride with 4-vinylbenzyl chloride.[27] Monomer **16** features both a styryl alkene group capable of polymerization under radical conditions and a pendant alkene moiety that was expected to be significantly less reactive under radical polymerization conditions (i.e., nonbenzylic radical formation) but participate in the RCM cross-linking reaction. Pendant alkene groups are not expected to be reactive toward radical attack because of the relative instability of the resulting secondary carbon radical species. Bulk polymerization of initiator **15** and monomer **16** was performed under ATRP conditions to form 8-armed, star polymer **17** (Scheme 8). When the percent conversion remained low, **17** was prepared with monomodal mass distributions (SEC), low PDI, and excellent solubility in organic solvents including toluene, dichloromethane, and THF (Table 3 and Figure 5).

Recently, we demonstrated that when alkene groups are placed on the interior of a dendrimer, intramolecular cross-linking of the dendrimer can be achieved at higher concentrations.[15] To allow for the possibility of cross-linking the star polymers at higher concentrations and also to demonstrate the degree of control that can be gained over the size and chemical structure of such polymer nanostructures, star block copolymer **18** was synthesized (Scheme 9). Polymer **17**$_3$ was reacted with styrene under ATRP conditions to afford the eight-armed block copolymer, star **18**. Upon formation of the

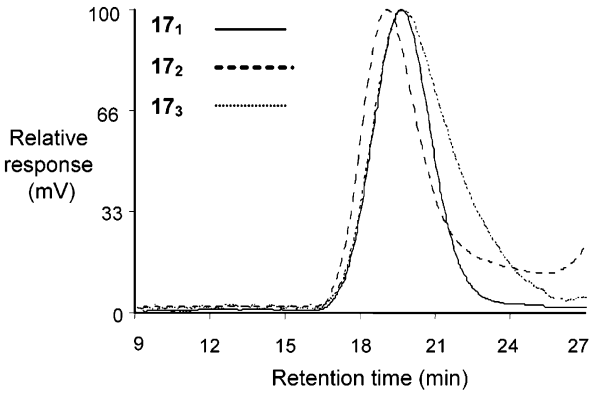
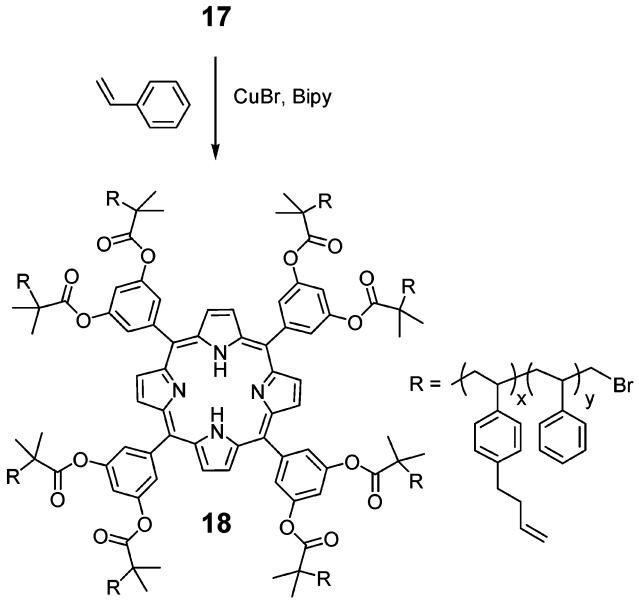


Figure 5. Representative analytical SEC chromatograms (THF) for polymer **17**, formed at low conversion.

Scheme 9. Synthesis of Eight-Armed Star 18, Star(poly-4-butenylstyrene-*block*-polystyrene)



outer polystyrene block, the average molecular weight of **18** increased by approximately 7 kDa. The PDI of **18** was 1.34. For polymer **18**, the comonomer ratio, **16**/styrene = 2/1, was determined by ^{1}H NMR (Figure 6).

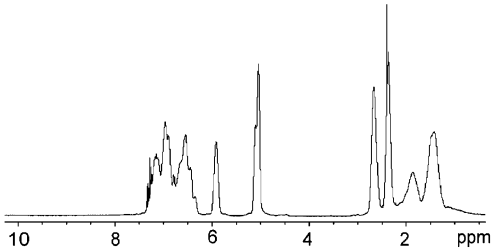
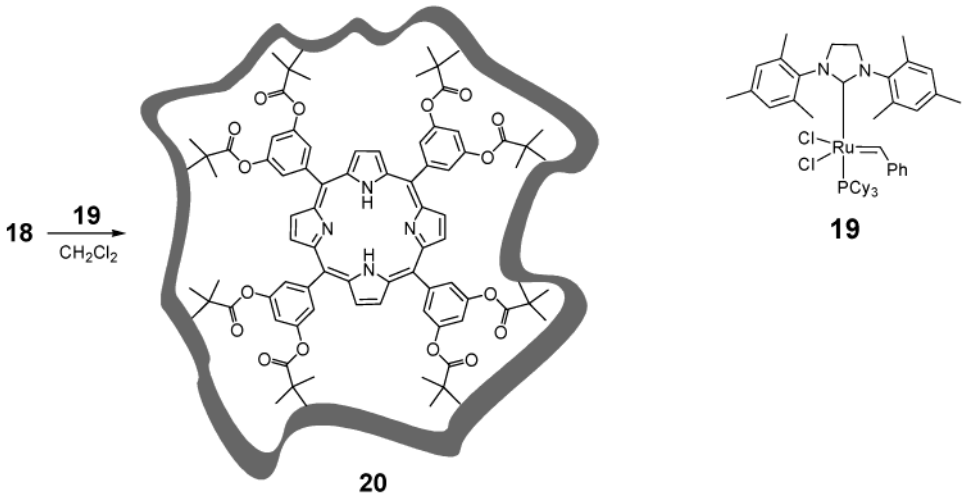


Figure 6. ^{1}H NMR for **18** in chloroform-*d* showing broadened peaks corresponding to the polymer protons.

The weight-average molecular weight of one sample of **18** was measured by dynamic light scattering (DLS) to be approximately 68 kDa. Hydrolysis of the same sample of **18** was carried out to remove the linear arms from the porphyrin core and characterize them independently. The arms were too small to characterize by DLS, but SEC generally provides an appropriate estimate for linear polymers of this type. Thus, the weight-average molecular weight of the arms was determined

Scheme 10. Synthesis of Cross-Linked Star Polymer 20



to be 9 kDa with SEC using PS standards. On the basis of these measurements, star polymer **18** was calculated to have an average of about 7.6 arms.

Intramolecular cross-linking of the alkene groups of **18** was performed by reacting **18** with olefin metathesis catalyst **19**,[28] resulting in the formation of cross-linked star copolymer **20** (Scheme 10). Evidence for extensive RCM of the alkenes came from both SEC and ^{1}H NMR analysis. Thus, upon formation of **20**, ^{1}H NMR peaks between 5 and 6 ppm disappear, indicating that nearly all of the pendant alkene groups have been reacted in the cross-linking process (Figure 7). With respect to the starting polymer **18**, polymer **20** exhibited a significant increase in the SEC retention time corresponding to a decrease in polystyrene-based SEC molecular weight of approximately 13 kDa (Figure 8). This is expected due to the loss of one ethylene unit for each RCM reaction. Also, because molecular weight values are measured

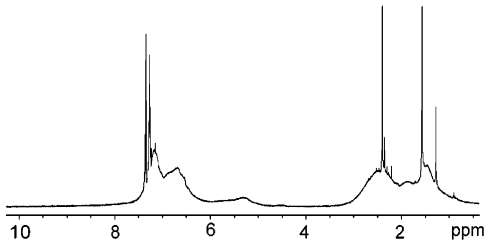


Figure 7. ^{1}H NMR for **19** in chloroform-*d* showing broadened peaks corresponding to the cross-linked polymer protons. The top of the spectrum was cropped to better illustrate the important peaks.

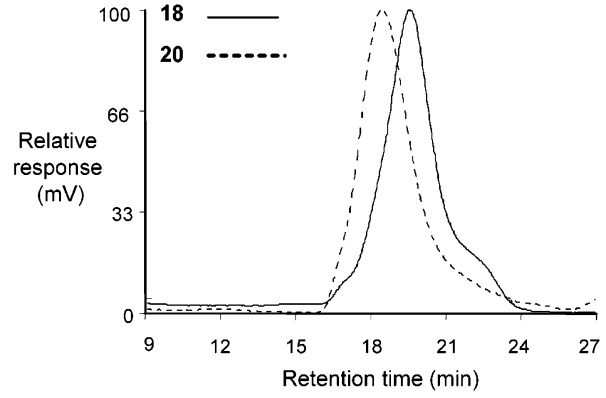
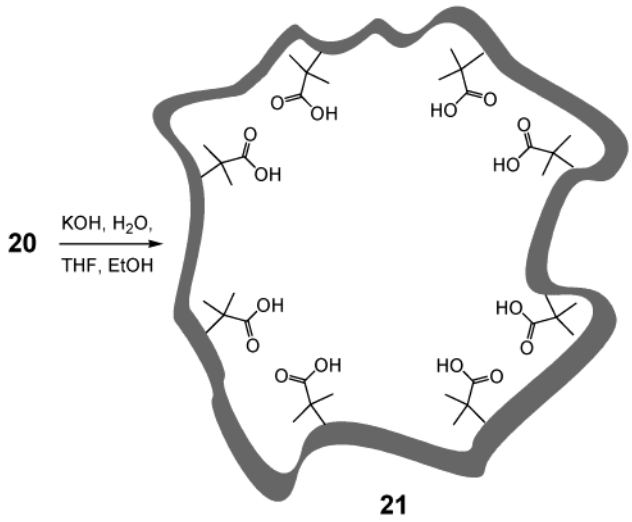


Figure 8. Analytical SEC chromatograms for **18** and **20**.

Scheme 11. Coring of Cross-Linked Star Block Copolymer 20



with an analytical SEC instrument that is calibrated with linear polystyrene standards, a change in size to a more compact structure upon cross-linking also yields an apparent decrease in molecular weight. Unexpectedly, upon complete removal of solvent from **20**, it became insoluble in common organic solvents. Even after extended sonication and mild heating, once dried **20** could not be redissolved in methylene chloride or THF. Because of this property, **20** must be stored in solution.

Once the cross-linking reaction was performed, the porphyrin core of **20** was removed through base hydrolysis of the ester linkages (Scheme 11). This produced **21**, a "cored," nanosized polymeric structure with approximately eight carboxylic acid functional groups per macromolecule. Taking advantage of the very high absorption at the Soret band of the porphyrin ($\lambda \approx 420$ nm), spectrophotometric measurements were used to show that >99% of the porphyrin was removed. SEC analysis of **21** indicated an overall size that is similar to **20**, suggesting that no large conformational changes occurred upon "coring" (Table 4, Figure 9). Because the porphyrin unit constitutes only approximately 5% of the overall mass of polymer **20** and resides at the core of the macromolecule, the size and globular shape of "cored" product **21** were expected to be similar to those

Table 4. Molecular Weight Data for Single Runs of Polymers 20 and 21

polymer	M_n (kDa)	M_w (kDa)	PDI
20	17.2	23.3	1.36
21	15.4	22.7	1.47

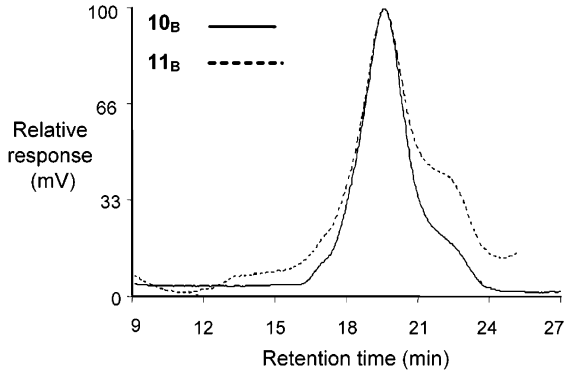


Figure 9. Analytical SEC chromatograms for **20** and **21**.

of **20**. A slight decrease in molecular weight for **21** was observed, along with a slight increase in PDI. Additionally, a small shoulder was observed in the analytical SEC chromatogram of **21** at approximately 7 kDa. This shoulder likely arises from a small amount of fragmentation caused by the cleavage of polymer arms that are incompletely cross-linked or, more likely, lacking cross-links to other arms of the star.

One sample of **21** that had an average MW of approximately 27 kDa by SEC was measured by DLS to have an average molecular weight of 65 kDa. To determine the average number of carboxylic acid groups per molecule of **21**, the sample was titrated with KOH to a phenolphthalein end point. To a solution of **21**, phenolphthalein, and toluene were added aliquots of a 0.01 M solution of KOH and methanol. The appearance of phenolphthalein was observed by UV−vis after 7.2 equiv of KOH had been added, indicating that **21** contains an average of greater than 7.2 carboxylic acid groups per molecule. This value compares well with the estimate of 7.6 arms in star polymer **18** obtained by measuring the mass of its arms following hydrolysis (vide supra).

A molecular model of **20** was built with a molecular weight of approximately 36 kDa and an overall **16**/styrene comonomer ratio of 4/1. Using the Cerius[2] molecular modeling package, a linear homopolymer of **16** (DP = 24) was constructed with a small polystyrene block (DP = 8) at one end. The resulting linear block copolymer was minimized, and then eight copies were attached to the porphyrin core through ester linkages. The star polymer **20** was minimized by the following procedure: (i) Three annealing cycles, simulating an increase in temperature from 300 to 800 °C and then cooling back down to 300 °C, were performed, and after each cooling step, the molecule underwent 500 steps of global minimization using the DREIDING 2.21 force field. (ii) Alkene groups that were near to one another were connected manually (olefin metathesis). (iii) Steps 1 and 2 were performed three more times. A total of 93 out of 96 possible cross-links were made The porphyrin core (black-CPK) of the resulting structure is shown near the surface of the polymer, indicating that in this particular cross-linked star the cavity holding it is not deep within the polymer (Figure 9). Finally, many of the cross-links throughout the polymeric structure are

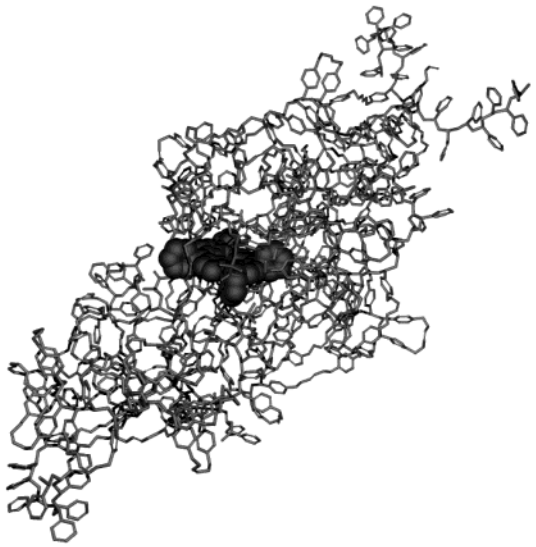


Figure 10. Molecular model of star polymer **20** (hydrogen atoms omitted) with porphyrin highlighted (see text for details).

intra-arm connections, and it is hypothesized that if a high degree of inter-arm cross-linking is not achieved, this may lead to a very flexible structure that does not retain its shape or carboxylic acid functionality placement after the porphyrin core is removed.

Conclusions

In the experiments described above, star polymers were synthesized, cross-linked, and cored. The facile synthesis of cored star polymer **21** was accomplished in six steps from commercially available materials. Its precursor, star polymer **18**, was synthesized at low percent conversion, which led to a compound exhibiting good solubility in common organic solvents and a low PDI. This novel strategy to produce such cored nanostructures is currently being adapted to our monomolecular imprinting approach[14,16] as well as other applications wherein small molecules are encapsulated in polymeric matrices. Finally, it is expected that the novel physical properties of star polymers can be further modulated through the type of architectural control offered by the intramolecular cross-linking approach described herein.

Experimental Section

All reactions were performed in an atmosphere of dry nitrogen, and all solvents and reagents were of reagent grade quality purchased commercially, unless noted otherwise. THF was distilled over sodium and benzophenone. Methylene chloride, styrene, triethylamine, and toluene were distilled over CaH_2. Methanol was distilled over magnesium. Acetone, DMF, and ethanol were stored over 4 Å molecular sieves.

Thin-layer chromatography was performed on 0.2 mm silica 60-coated plastic or aluminum sheets (EM Science). Column chromatography was performed on Merck 40−63 μm silica following the procedure reported by Still.[29] NMR spectra were acquired at the Varian-Oxford Inova Center for Excellence in NMR Spectroscopy (VOICE) lab at UIUC. ^{1}H and ^{13}C spectra were recorded on a Varian Unity 500 or 400 MHz spectrometer. Coupling constants are reported in hertz (Hz). The ^{1}H NMR chemical shifts are referenced to residual protio-solvent peak at 7.26 ppm in chloroform-*d*, 2.05 ppm in acetone-d_6, and 3.58 and 1.73 ppm in THF-d_8. The ^{13}C NMR chemical shifts were referenced to the solvent peak at 77.0 ppm in chloroform-*d*. Unless stated otherwise, the ^{1}H and ^{13}C NMR spectra were acquired in $CDCl_3$.

Mass spectra were obtained in the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois, Urbana−Champaign. Preparative SEC was carried out on Bio-Beads S-X1 Beads gel permeation gel 200−400 mesh (Bio-Rad Laboratories). SEC was performed on a Waters Styragel HR3 double column (molecular weight range 0.5−30 kDa) connected to a HR4E single column (molecular weight range 5−100 kDa) coupled with Viscotek TDA model 300 triple detector array (conventional calibration) using a Hitachi L-6000 pump. Unless otherwise stated, molecular weights (M_w and M_n) and PDI values were calculated from SEC data using polystyrene standards. DLS measurements were made using a DynaPro MS/X from Protein Solutions.

The following compounds were obtained from the sources indicated and used without additional purification. 5,10,15,20-Tetrakis(4-carboxyphenyl)porphyrin (**3**), *tert*-butyl-4-vinylphenyl carbonate (**9**), 4-vinylbenzyl chloride, and vinylmagnesium chloride were purchased from Sigma-Aldrich Co. Benzylidene(1,3-dimesitylimidazolidin-2-ylidene)(tricyclohexylphosphine)ruthenium dichloride (Grubbs' Ru−dihydroimidazolylidene catalyst) (**19**) was purchased from Strem Chemicals. 1-Benzoyloxy-2-phenyl-2-(2′,2′,6′,6′-tetramethyl-1-piperidinyloxy)ethane (**1**),[25] 1-hydroxy-2-phenyl-2-(2′,2′,6′,6′-tetramethyl-1-piperidinyloxy)ethane (**2**),[25] 3,5-bis(3-buten-1-oxy)benzyl alcohol (**5**),[13] 5,10,15,20-tetrakis(3′,5′-dihydroxyphenyl)porphyrin (**14**),[30] and 1-but-3-enyl-4-vinylbenzene (**16**)[27] were prepared using published procedures.

5,10,15,20-Tetrakis[4′-[1-benzoyloxy-2-phenyl-2-(2′,2′,6′,6′-tetramethyl-1-piperidinyloxy)ethane]phenyl]-porphyrin (4). A mixture of 176 mg (0.223 mmol) of 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (**3**) and 4.3 mL (59 mmol) of thionyl chloride was heated to reflux for 3.5 h. Excess thionyl chloride was removed at reduced pressure. To the mixture was added a solution of 683 mg (2.47 mmol) of 1-hydroxy-2-phenyl-2-(2′,2′,6′,6′-tetramethyl-1-piperidinyloxy)ethane (**2**), 2.8 mL (20 mmol) of triethylamine, and 12 mL of dichloromethane. The reaction mixture was refluxed for 20 h. The reaction mixture was added to 50 mL of water and extracted three times with 50 mL portions of dichloromethane. The organic layers were combined, and the solvent was evaporated at reduced pressure. A solution of the product in methylene chloride (2 mL) was added to 500 mL of petroleum ether, and the resulting solid was filtered to give 207.5 mg (34%) of product as a purple solid. The purity of the product was estimated to be 96% by elemental analysis, and it was used in the next step without further purification. ^{1}H NMR δ: 8.85 (8H, s), 8.29 (16H, m), 7.44 (20H, m), 5.22 (4H, t, J = 5.8), 5.03 (4H, dd, J = 11.2, 5.0), 4.73 (4H, dd, J = 11.2, 6.8), 1.20−1.70 (48H, m), 1.14 (12H, s), 0.83 (12H, s), −2.85 (2H, s).

3,5-Di(3-buten-1-oxy)benzaldehyde (6). To a suspension of 3.5 g (16 mmol) of pyridinium chlorochromate (PCC) and 25 mL of dichloromethane was added a solution of 2.67 g (10.75 mmol) of 3,5-di(3-buten-1-oxy)benzyl alcohol (**5**) and 20 mL of dichloromethane. The reaction mixture was stirred at room temperature for 2 h, and 20 mL of diethyl ether was added. The supernatant solution was decanted from the black gum. The resulting black gum was washed three times with 50 mL portions of diethyl ether. The washings were combined and passed through florisil. Purification using column chromatography afforded 1.9 g (74%) of product as colorless oil. ^{1}H NMR δ: 9.88 (1H,s), 6.99 (2H, d, J = 2.3), 6.70 (1H, t, J = 2.3), 5.89 (2H, ddt, J = 16.8, 11.7, 6.7), 5.17 (2H, dq, J = 16.5, 1.3), 5.11 (2H, dq, J = 9.8, 1.3), 4.04 (4H, t, J = 6.7), 2.54 (4H, qt, J = 6.5, 1.3).

3,5-Di(3-buten-1-oxy)styrene (7). To a suspension of 1.8 g (5.0 mmol) of methyltriphenylphosphonium bromide in 15 mL of toluene was added 4.2 mL (5.2 mmol) of butyllithium. The mixture was allowed to stir at room temperature for 2 h. A solution of 970 mg (4.0 mmol) of 3,5-di(3-buten-1-oxy)-benzaldehyde (**6**) and 10 mL of toluene was added, and the reaction mixture was stirred at 45−50 °C for 17 h. The reaction mixture was combined with 100 mL of water and extracted three times with 100 mL portions of dichloromethane. The extracts were combined, and the organic layer was evaporated under reduced pressure. Purification using column chromatography with an elutant of 9:1 petroleum ether:ethyl acetate afforded 0.82 g (84%) of product as colorless oil. ^{1}H NMR δ: 6.63 (1H, dd, J = 17.5, 9.8), 6.56 (2H, d, J = 2.3), 6.39 (1H, t, J = 2.3), 5.90 (2H, ddt, J = 15.5, 10.9, 6.7), 5.71 (1H, dd, J = 17.9, 0.7), 5.23 (1H, dd, J = 9.8, 0.7), 5.17 (2H, dq, J = 16, 1.6), 5.11 (2H, dq, J = 10.3, 1.6), 4.01 (4H, t, J = 6.7) 2.54 (4H, qt, J = 6.7, 1.3). ^{13}C NMR (125 MHz $CDCl_3$) δ: 160.40, 139.8, 137.1, 134.7, 117.3, 114.5, 105.3, 101.3, 67.6, 33.8. Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.47. Found: C, 78.31; H, 8.25.

Typical Procedure for TEMPO-Mediated Free Radical Polymerization. *Used for Compounds **8** and **10**. General Procedure.* To a sealable test tube with a narrowed neck were placed 15 mg (0.008 mmol) of 5,10,15,20-tetrakis[4′-[1-benzoyloxy-2-phenyl-2-(2′,2′,6′,6′-tetramethyl-1-piperidinyloxy)-ethane]phenyl]porphyrin (**4**) and 2.8 mmol of monomer(s). The test tube was placed in ice, and the solution was evacuated and flushed with argon twice. The tube was evacuated again and left under reduced pressure for 5 min. The test tube was sealed with a flame, while under reduced pressure, and placed in an oil bath at 125 °C. After 20 h, the solution had solidified, and the seal was broken. Resulting solid polymers were purified by both precipitation in methanol and preparative SEC. Polymerizations were generally run to approximately 75% conversion.

Poly(styrene-*ran*-4-hydroxystyrene) (11). To a mixture of 240 mg (0.02 mmol) of 5,10,15,20-tetrakis[4′-(polystyrene-*co*-poly4-hydroxystyrene)phenyl]porphyrin (**10**), 1.6 mL of ethanol, and 4 mL of THF was added 0.3 mL (1 M) of a sodium hydroxide solution in water. The solution was refluxed for 24 h. The organic layer was evaporated under reduced pressure. The resulting solid was filtered and washed three times with 5 mL portions of water. The product was then dried under reduced pressure, affording a slightly yellowish solid. ^{1}H NMR performed in acetone-d_6 δ: 8.0, 7.1, 6.6, 1.9, 1.5.

3,5-Di(3-buten-1-oxy)benzyl Bromide (12). To a solution of 3.0 g (12.1 mmol) of 3,5-di(3-buten-1-oxy)benzyl alcohol (**5**), 5.04 g (15.2 mmol) of carbon tetrabromide, and 5 mL of THF was added slowly over a period of 20 min 3.96 g (15.1 mmol) of triphyenylphosphine. The reaction mixture turned cloudy and was stirred at room temperature for 25 min. The reaction mixture was added to 25 mL of water and extracted three times with 50 mL portions of dichloromethane. The extracts were combined, and the organic layer was evaporated at reduced pressure. Purification by column chromatography eluted in a stepped solvent gradient of 9:1 petroleum ether: ethyl acetate to 7:3 petroleum ether:ethyl acetate afforded 3.37 g (90%) of product as colorless oil. ^{1}H NMR δ: 6.55 (2H, d, J = 2.2), 6.41 (1H, t, J = 2.2), 5.91 (2H, ddt, J = 16.5, 10.7, 6.7), 5.19 (2H, dq, J = 16.5, 1.6), 5.13 (2H, dq, J = 10.7, 1.6), 4.43 (2H, s), 4.01 (4H, t, J = 6.8), 2.55 (4H, dtt, J = 6.8, 6.7, 1.6). FDMS m/z 310.1 $(M-H)^+$.

5,10,15,20-Tetrakis[4′-[polystyrene-*co*-poly[1,3-bis(but-3-enyloxy)-5-(4-vinylphenoxymethyl)benzene]phenyl]-porphyrin (13). To a mixture of 320 mg (1.03 mmol) of 3,5-di(3-buten-1-oxy)benzyl bromide (**12**), 14 mg (0.053 mmol) of 18-crown-6, 176.1 mg (1.27 mmol) of potassium carbonate, and 400 mg (0.016 mmol) of 5,10,15,20-tetrakis[4′-(polystyrene-*co*-poly4-hydroxystyrene)phenyl]porphyrin (**10**) was added 75 mL of acetone. The solution was refluxed for 72 h and cooled to room temperature. The organic layer was evaporated under reduced pressure. The resulting solid was added to 75 mL of water and extracted twice with 75 mL portions of diethyl ether. The organic extracts were combined, washed with 75 mL of water and a mixture of water:brine (50 mL:50 mL), and dried with sodium sulfate. The resulting organic layers were evaporated under reduced pressure, affording a purple solid product. ^{1}H NMR performed in THF-d_8 δ: 7.0, 6.6, 6.4, 5.8, 5.12, 5.1, 4.9, 3.9, 2.5, 1.9, 1.5.

5,10,15,20-Tetrakis[3′,5′-di(2-bromo-2-methylpropionyloxyester)phenyl]porphyrin (15). To a mixture of 53.9 mg (0.0726 mmol) of 5,10,15,20-tetrakis(3′,5′-dihydroxyphenyl)-porphyrin (**14**) and 1 mL of THF were added sequentially 90 μL (1.11 mmol) of pyridine and 120 μL (0.971 mmol) of 2-bromo-2-methylpropionyl bromide. The mixture was stirred

at room temperature for 20 h. To the reaction were added sequentially 1 mL of THF, 90 μL (1.11 mmol) of pyridine, and 120 μL (0.971 mmol) of 2-bromo-2-methylpropionyl bromide. The mixture was allowed to stir at room temperature for 6 h. The reaction mixture was added to 50 mL of water and extracted three times with 50 mL portions of dichloromethane. The extracts were combined, dried with magnesium sulfate, and filtered, and the solvent was evacuated under reduced pressure. Purification by column chromatography eluted with 4/1 petroleum ether/ethyl acetate afforded 29.2 mg (21%) of product as purple solid. The purity of the product was estimated to be 94% by elemental analysis, and it was used in the next step without further purification. ^{1}H NMR δ: 9.10 (8H, s, H_{11}), 7.97 (8H, d, J = 2.44, H_7), 7.53 (4H, t, J = 2.02 H_5), 2.15 (48H, s H_1). MS (MALDI−TOF): 1935.7 ($M + H^+$).

5,10,15,20-Tetrakis[3′,5′-di(poly-1-but-3-enyl-4-vinylbenzene)phenyl]porphyrin (17). *Typical Polymerization Procedure.* To a mixture of 19.1 mg (9.87 μmol) of 5,10,15,20-tetrakis[3′,5′-di(2-bromo-2-methylpropionyloxyester)phenyl]-porphyrin (**15**), 14.4 mg (0.10 mmol) of copper(I) bromide, and 30.3 mg (0.194 mmol) of 2,2′-bipyridine was added 1.5 g (9.5 mmol) of 1-but-3-enyl-4-vinylbenzene (**16**) via syringe. The reaction mixture was heated to 100 °C. Aliquots of the reaction mixture were removed every 2 h and analyzed by SEC. When the desired molecular weight was reached, the reaction mixture was added to 0.5 mL of dichloromethane and precipitated into 200 mL of methanol. The resulting suspension was filtered and washed with another 200 mL of methanol. ^{1}H NMR δ: 6.25−7.1 (4H, m, broad), 5.75−6.0 (1H, s, broad), 4.95−5.1 (2H, m, broad), 2.5−2.8 (2H, s broad), 2.25−2.5 (2H, s, broad), 1.55−2.25 (3H, m, broad).

5,10,15,20-Tetrakis[3′,5′-di(poly-1-but-3-enyl-4-vinylbenzene-*block*-polystyrene)phenyl]porphyrin (18). The same procedure used for compound **17** was followed. ^{1}H NMR δ: 6.3−7.4 (6.44H, m, broad), 5.8−6.0 (1H, s, broad), 4.9−5.2 (2H, m,), 2.5−2.8 (2H, s, broad), 2.2−2.5 (2H, s, broad), 1.7−2.1 (1.5H, s, broad), 1.2−1.7 (3H, s, broad).

5,10,15,20-Tetrakis[3′,5′-di(poly-1-but-3-enyl-4-vinylbenzene-*block*-polystyrene)phenyl]porphyrin-cross-linked (20). *Typical RCM (Cross-Linking) Conditions.* To a mixture of 155.6 mg (4.8 μmol) of 5,10,15,20-tetrakis[3′,5′-di-(poly-1-but-3-enyl-4-vinylbenzene-*block*-polystyrene)phenyl]-porphyrin (**18**) and 1.5 L of dichloromethane was added 36 mg (0.043 mmol) of ruthenium catalyst **19**. The reaction mixture was stirred at reflux for 12 h, at which time another 36 mg (0.043 mmol) of **19** was added. The reaction mixture was stirred at room temperature for 12 h, at which time solvent was removed and 200 mL of methanol was added. The solid was filtered and washed with 200 mL of methanol. Purification by preparative SEC afforded 149 mg (96%) of a purple solid. ^{1}H NMR δ: 6.35−7.5 (m, very broad), 5.0−5.5 (s, very broad), 2.0−3.0 (s, very broad), 1.0−2.0 (m, very broad).

Cored Star Polymer (21). To a mixture of 30 mg (1 μmol) of 5,10,15,20-tetrakis[3′,5′-di(poly-1-but-3-enyl-4-vinylbenzene-*block*-polystyrene)phenyl]porphyrin-cross-linked (**20**) and 4 mL of THF was added a solution of 123.9 mg (2.2 mmol) of KOH, 0.5 mL of EtOH, and 0.5 mL of water. The mixture was heated to reflux for 60.5 h, at which time it was cooled to 0 °C, and 4 mL of 1 M HCl was added. The mixture was allowed to stir at room temperature for 20 h. The reaction mixture was added to a mixture of 150 mL of dichloromethane and 50 mL of water. The aqueous layer was extracted three times with 150 mL portions of dichloromethane. 4 mL of 12 M HCl was added to the aqueous layer, and it was extracted three times with 150 mL portions of dichloromethane. The organic portions were combined, and the solvent was removed. The resulting solid was dissolved in 0.5 mL of dichloromethane and added to 200 mL of methanol and sonicated for 5 min. The suspension was filtered, and the resulting solid (55 mg, 1 μmol) was added to a mixture of 5 mL of THF, 0.9 mL of EtOH, 56.1 mg (1.7 mmol) of KOH, and 0.9 mL of water. The reaction mixture was heated to reflux for 57 h, at which time it was cooled to 0 °C, and 4 mL of 1 M HCl was added. The mixture was allowed to stir at room temperature for 20 h. The reaction mixture was added to a mixture of 150 mL of dichloromethane and 50 mL of water. The aqueous layer was extracted three times with 150 mL portions of dichloromethane. 4 mL of 12 M HCl was added to the aqueous layer, and it was extracted three times with 150 mL portions of dichloromethane. The organic portions were combined, and the solvent was removed. The resulting solid was dissolved in 0.5 mL of dichloromethane and added to 200 mL of methanol. The resulting suspension was filtered and afforded 24.9 mg (20%) of a slightly yellowish solid. ^{1}H NMR δ: 6.25−7.5 (m, very broad), 4.5−6.0 (s, very broad), 1.0−3.0 (m, very broad).

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