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Reversible Switching between Linear and Ring Polystyrenes Bearing Porphyrin End Groups

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Supporting Information

ABSTRACT: A route to macrocyclic polymers based on a new unimolecular ring-closure process has been investigated. It involves the direct end-to-end coupling of an α,ω-bis[chloroiron(III) *meso*-tetraphenylporphyrin] telechelic linear polystyrene synthesized by living polymerization followed by chain-end functionalization. The corresponding macrocyclic polystyrene was obtained readily and selectively by intramolecular condensation of the α,ω-bis[chloroiron(III) *meso*-tetraphenylporphyrin] polymer ends in the presence of a base to yield a diiron(III)-μ-oxobis(porphyrin) dimer as ring-closing unit. Addition of dilute HCl was shown to rapidly reconvert the diiron(III)-μ-oxobis(porphyrin) unit into the initial bis[chloroiron(III) porphyrin], demonstrating the selectivity and complete reversibility of the cyclization process. The synthesis and detailed structural characterization of the α,ω-homodifunctional precursor and the corresponding macrocyclic polystyrene along with an analysis of the porphyrin dimerization reaction using NMR spectroscopy and size-exclusion chromatography coupled with a diode array detector are presented.

The synthesis of cyclic polymers with controlled molar masses and low molar-mass dispersity and the study of their physical properties have attracted considerable interest in the last 50 years.[1−5] The methods of preparation of cyclic polymers can be classified into three main categories: (a) ring/linear chain equilibrations,[6−8] (b) ring-expansion polymerizations,[9,10] and (c) end-to-end cyclization reactions.[11−15]

The last category is one of the most explored and versatile routes. It relies on the ring closure of an α,ω-difunctional linear polymer precursor generally prepared by living/controlled polymerization techniques.[16] Cyclization was first achieved by the bimolecular coupling, under high dilution, of an α,ω-homodifunctional linear polymer, typically an anionically prepared polystyrene or polydiene in which a difunctional electrophilic molecule had been introduced in perfectly stoichiometric proportion.[11−13] Other bimolecular coupling reactions, such as interfacial condensation[17−19] and radical coupling,[20] have also been used. One original approach proposed by Tezuka[21,22] consists of a dipolar precyclization step before formation of a covalent linkage. A second ring-closing approach involves the intramolecular coupling of α,ω-heterodifunctional precursors bearing two complementary reactive end groups, for instance, acetal/styrenyl,[11,23,24] carboxy/amino,[25,26] acetal/hydroxyl,[27] and azide/alkyne (i.e., click chemistry).[16,28−31]

The bimolecular approach is generally more prone to byproduct formation, while the unimolecular route, with sufficiently high-yielding end-group transformations and couplings, offers the potential to yield high-purity cyclic polymers by using high dilution. To extend the scope of unimolecular cyclization reactions, it remains necessary to find new high-yielding end-group transformations and efficient end-to-end coupling reactions, resulting the desire to explore alternative approaches.

The present study reports a new selective and reversible cyclization method based on the coupling of iron(III) porphyrin moieties into a bis[iron(III) μ-oxoporphyrin] dimer.[32−35] One of the very few examples of reversible cyclization that we found in the literature as the most pertinent precedent is the ring closing/reopening of thiol-end-capped polystyrene reported by Whittaker.[36] Our approach consists of the end-to-end ring closure of an α,ω-homodifunctional polystyrene chain bearing an iron(III) porphyrin group at each end. Macrocyclization is achieved under high dilution by coupling of the two iron(III) porphyrin ends under slightly basic conditions, yielding a polystyrene ring with a stable bis[iron(III) μ-oxoporphyrin] dimer as closing unit (Scheme 1). This unimolecular macrocyclization reaction, which has been shown to be very fast, is fully reversible by switching the "basicity"/"acidity" of the organic polymer solution. Here the strategy of synthesis, the structure of the functional linear and cyclic polystyrenes, and the characteristics of the cyclization reaction are presented and discussed.

Iron(III) chloride *meso*-tetraphenylporphyrin telechelic polystyrene (**5**) was prepared by the procedure described in Scheme 2. Linear bis(hydroxymethyl) telechelic polystyrene precursors (**3**) were synthesized by living anionic polymerization of styrene using isopropylidene-2,2-bis(hydroxymethyl)-1-(2-lithiobutyl)butane as an initiator, yielding (**1**) and isopropylidene-2,2-bis(hydroxymethyl)-1-(2-chlorobutyl)butane as a functional chain-terminating agent to form the bisacetal-ended polystyrene (**2**). The latter was converted into (**3**) by acidic hydrolysis of the acetal ends and then trans-acetalized in presence of diethylacetal-functionalized tetraphenylporphyrin in an acidic medium to yield (**4**). Finally, the iron(III) chloride *meso*-tetraphenylporphyrin telechelic polystyrene (**5**) was obtained by metalation of (**4**) using $FeCl_2$. The experimental degree of polymerization (DPn) of 65 for the polystyrene chain (**2**) determined from SEC data was found to agree well with

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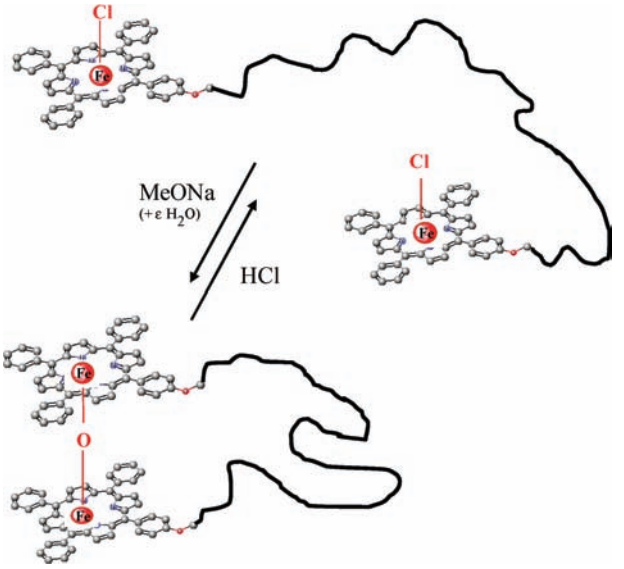
Scheme 1. Reversible Switching between Linear and Macrocyclic Polystyrenes Induced by Iron(III) *meso*-Tetraphenylporphyrin Coupling (εH_2O Denotes a Trace of H_2O)



theoretical values calculated on the basis of complete initiation of styrene polymerization by the lithioacetal derivative, whereas the polymer molar-mass dispersity (MWD) was very low (1.05).

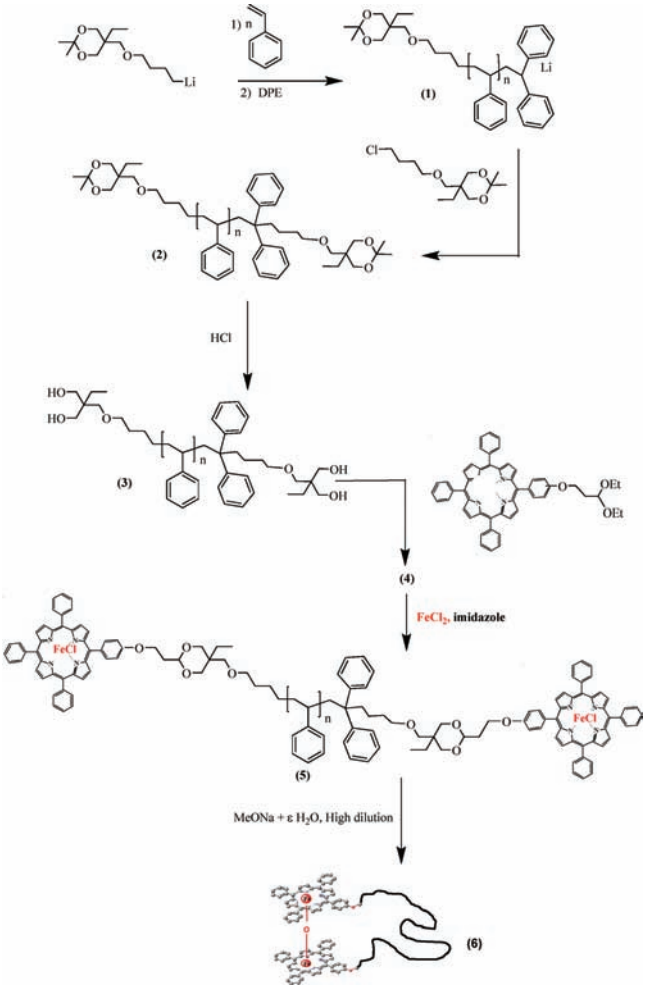
The relative number of *meso*-tetraphenylporphyrin end groups per polystyrene chain (**4**) was determined from their relative ^{1}H NMR peak areas on the basis of the polystyrene DPn of 65. The chain-end functionality was found to be very close to 2. Experimental reaction conditions, characterization data, and proton NMR spectra are given in the Supporting Information.

Cyclization of (**5**) was performed in dichloromethane under high dilution by slow addition of a small amount of sodium methanolate/methanol solution as ring-closing catalyst. The crude size-exclusion chromatography (SEC) chromatograms of both the linear precursor (**5**) and the cyclized polystyrene (**6**) are presented in Figure 1.

As expected, the cyclized polymer (apparent number-average molecular weight $M_{n,app}$ = 4700 as determined by SEC) eluted at a higher volume than the linear precursor (M_n = 6800 as determined by SEC). This corresponds to a ratio of the two SEC signals (M_{pc}/M_{pl}) of $\langle G \rangle$ = 0.7, which agrees well with $\langle G_{exp} \rangle$ values previously reported for macrocyclic polystyrenes.[37−39] The cyclization appeared to be almost quantitative. The formation of high-molar-mass polycondensates was not detected, and only a small SEC peak attributed to polystyrene cyclic dimer (see below) was observed. As confirmed by UV−vis spectroscopy (Figure 2), the cyclization mechanism (see Scheme 1) involves the intramolecular coupling of the two iron(III) *meso*-tetraphenylporphyrin polystyrene ends to yield a diiron(III)-μ-oxobis(porphyrin) dimer as ring-closing unit. This reaction is triggered under basic conditions by methanolate anions or more likely by hydroxide ions present in the methanolate/methanol solution.[33] According to the literature, the coupling proceeds in two steps: (1) substitution of the two Cl ligands by attack of OH^- from the basic medium,

$$\mathrm{TPPFeCl} + \mathrm{OH^-} \rightarrow \mathrm{TPPFeOH} + \mathrm{Cl^-} \qquad (1)$$

Scheme 2. Strategy of Synthesis of Telechelic Polystyrene with Iron(III) *meso*-Tetraphenylporphyrin Chloride Ends (εH_2O Denotes a Trace of H_2O)



and (2) ring closing via condensation of the two OH ligands to form a μ-oxo bridge with liberation of one molecule of water,

$$2\mathrm{TPPFeOH} \rightarrow (\mathrm{TPPFe})_2\mathrm{O} + \mathrm{H_2O} \qquad (2)$$

which corresponds to an unimolecular cyclization process.

In tetrahydrofuran, the red-brown-colored iron(III) *meso*-tetraphenylporphyrin chloride-functionalized linear polystyrene precursor exhibits characteristic metal-to-porphyrin absorption bands at 370.1 nm, 419.4 nm (charge-transfer band), and 507.7 nm (Q band). After addition of sodium methanolate, the polymer solution turns green and exhibits new absorbance bands at 320.2 nm, 409.7 nm (Soret band), and 572.1 and 613.6 nm (Q bands), characteristic of the $(FeTPP)_2O$ dimer[35,40,41] (see Figure 2).

Because of the different UV−vis absorbance spectra of the monomeric and dimeric iron(III) *meso*-tetraphenylporphyrin species, the cyclization reaction could be analyzed for polymer fractions eluting at different volumes using a UV−vis diode-array detector coupled to the SEC instrument. The rapid and almost complete disappearance of the initial iron(III) bands for all of the cyclized polymer fractions indicated that conversion into the diiron(III)-μ-oxobis(porphyrin) is very fast and close to quantitative (see Figure 3).

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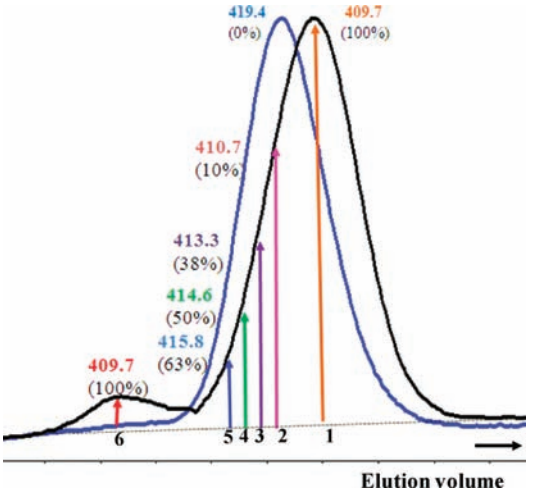

Figure 1. SEC chromatograms of linear (blue trace) and cyclized (black trace) polystyrene obtained using a using a refractive index detector. Characterization data: (linear) M_n = 6800, MWD = 1.05; (cyclic) $M_{n,app}$ = 4700, MWD = 1.08. Arrows 1−6 refer to cyclized polymer fractions analyzed using a UV−vis diode-array detector. The indicated data refer to the observed λ_{max} position and the calculated percentage of linear contaminant (see Figure 3).

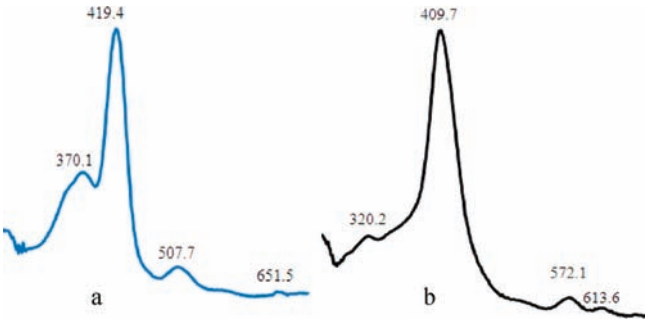

Figure 2. Characteristic wavelengths (in nm) of main metal-to-porphyrin absorption bands of (a) α,ω-terminated iron(III) *meso*-tetraphenylporphyrin chloride polystyrene (blue spectrum) and (b) the corresponding cyclic polystyrene with a diiron(III)-μ-oxobis(porphyrin) dimer as a ring-closing unit (black spectrum).

Although not observable using refractive-index detection (Figure 1), the presence of traces of uncyclized linear precursor could be deduced from the shift of the Soret band to higher wavelength, characteristic of Fe(III)ClTPP or Fe(III)OHTPP (which have Soret bands at 419.4 and 415.0 nm, respectively).[42] The fractions eluting at the peak maximum of the cyclic polymer (arrows 1 and 2 in Figure 1) and the one centered on polystyrene dimers (arrow 6) show a Soret band position in agreement with the almost unique presence of diiron(III)-μ-oxobis(porphyrin) species and the quantitative formation of cyclic polystyrene and cyclic polystyrene dimer. In contrast, in the peak tail corresponding to polymer fractions 3−5, the amount of linear contaminant is significant.

From the estimated percentage of linear polystyrene in the different polymer fractions and their relative weights, the total amount of linear contaminant, mostly in the SEC peak tail, was estimated to be ~9% (see Figure 4). Incomplete cyclization likely results from the presence of some nonfunctionalized chains.

As described in the literature, in presence of a Brønsted acid (HCl, for instance), the μ-oxo-Fe(III)TPP dimer readily breaks,

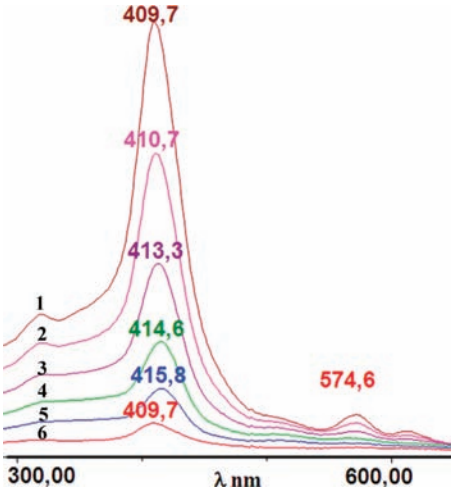

Figure 3. Soret bands of cyclized polystyrene fractions taken at different SEC elution volumes (see Figure 1) using a UV−vis diode-array detector.

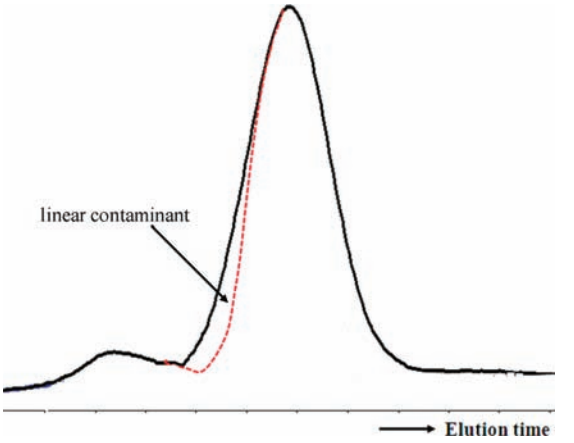

Figure 4. SEC chromatogram of cyclized polystyrene showing the relative amount and location of the linear polystyrene contaminant.

regenerating the chloroiron(III) tetraphenylporphyrin molecule:[35,40]

$$(TPPFe)_2O + 2HCl \rightarrow 2TPPFeCl + H_2O$$

Under similar acidic conditions, the polystyrene macrocycles readily "re-open", giving back the linear telechelic polystyrene with identical M_n and MWD. For instance, addition of few drops of HCl/CH_2Cl_2 to the green cyclic polystyrene solution yielded a rapid color change of the solution to red-brown. The selective reformation of linear polystyrene (**5**) with iron(III) *meso*-tetraphenylporphyrin chloride end groups was confirmed by the shift of the SEC peak to higher elution volume and the location of the Soret band at 419.4 nm.

Reversible commutation between linear and macrocyclic polystyrene was checked by switching the solution from acidic to basic over several cycles. The color change from red-brown to green and from green to red-brown observed upon alternative addition of a few drops of methanolate and of 1 M HCl to the solution as well as the corresponding shifts in the Soret band strongly support the reversibility of the process.

In conclusion, we have described a new approach for the synthesis of macrocyclic polymers based on the rapid intramolecular

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conversion of the iron(III) *meso*-tetraphenylporphyrin chloride chain ends of a linear polymer precursor into a diiron(III)-μ-oxobis(porphyrin) dimer as a ring-closing unit. This process, which is readily catalyzed by the addition of a base, involves a unimolecular chain-end coupling reaction that shows very little dependence on the dilution conditions and is very efficient for the end-to-end cyclization of polymers. The reversibility of the cyclization is another important and original feature of this process.

■ ASSOCIATED CONTENT

Supporting Information. Experimental conditions for the synthesis of *meso*-tetraphenylporphyrin derivatives, preparation of end-functionalized linear polystyrene and of polystyrene macrocycles, and their characterization by ^{1}H NMR and UV−vis spectroscopy. This material is available free of charge via the Internet at http://pubs.acs.org.

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