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Characterization and Fluorescence of Macrocyclic Polystyrene by Anionic End to End Coupling. Role of Coupling Reagents

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ABSTRACT: Macrocyclic polystyrene (PS) was synthesized by initiation of styrene by naphthalide anion or benzylic dianions in the presence of Li or K ions followed by reaction of the resulting PS dianions with dibromomethane (DBM) or 1,4-bis(bromomethylbenzene) (DBX) in THF at −78 °C under high dilution conditions. MALDI and NMR studies of the DBM cycles showed the presence of 1,2-diphenyl linkages. Fluorescence studies on the DBM cycles show strongly enhanced and anomalous structured emission bands between 300 and 320 nm attributable to linear chains containing styrenic chain end impurities. This indicates rapid metal bromine exchange to give chain end benzyl bromides that eliminate with polystyryl anion to give small (<1.0%) fractions of styrene type chain end structures. In comparison, the cycles obtained with DBX show only the PS monomer and excimer bands at 285 and 330 nm, respectively, and appear to be substantially free of such side reactions. These DBX coupled cycles show up to a 2-fold enhancement in the monomer fluorescence at low MW compared with matching linear polystyrenes that show essentially no MW dependence. This may be due to the increased rigidity of the cycles as molecular weights decrease and appears to be a general feature for cyclic vinyl aromatic polymers.

Introduction

The synthesis and properties of macrocyclic vinyl aromatic polymers have been the subject of increased interest in recent years.[1−19] We have recently reported that macrocyclic polystyrene (PS) is formed conveniently and in high yield by the lithium naphthalide initiated polymerization of styrene in THF at −78 °C, followed by high dilution end to end coupling of the resulting PS dianion with 1,4-bis(bromomethyl)benzene (DBX) or dibromomethane (DBM) (Scheme 1).[17] Low MW macrocyclic PS coupled with DBM showed what appeared to be increased PS excimer emissions between 300 and 320 nm that were absent in the matching linear PS samples.[18] As increased emissions due to macrocyclic architectures may be exploited for the design of new macromolecular light harvesting structures, it is important to fully characterize such macrocycles. Thus, as shown by the much higher glass transition temperatures compared with the matching linear polymers, the changed topology, i.e., the absence of chain ends, of macrocyclic polystyrene (PS) appears to increasingly constrain the ring as the degree of polymerization (DP) decreases below a DP of 50.[1] This may influence energy transfer and other photophysical processes involving the pendent chromophoric groups.

An exhaustive set of studies to investigate the nature of the coupling mechanism is described, and we show that the increased emissions between 300 and 320 nm for DBM-mediated PS cycles are due to the presence of extremely small amounts (as low as 0.1 mol %) of strongly emitting linear chains containing chain end styrenic impurities. However, *low molecular weight* PS cycles formed by end to end coupling with DBX are essentially free of side reactions and instead show enhanced emission in the *monomer* band compared to the matching linear polymers and a corresponding greater emission quantum yield.

Experimental Section

Reagents and Solvents. All polymerizations and coupling reactions were carried out in THF at −78 °C under high-vacuum conditions (10^{-5}−10^{-6} Torr) using break-seal techniques as reported elsewhere.[20,21] THF was purified by distillation from Na/K alloy onto fresh Na/K alloy, from which it was vacuum-distilled onto a carbanion THF solution such as 1,1-diphenylhexyllithium. It was finally distilled in vacuo into ampules that were stored at −15 °C. Hexane was purified in a similar manner. Cyclohexane used in emission measurements (EM Science spectrophotometric grade) was purified by fractional distillation in order to remove small amounts of residual benzene that gave rise to an appreciable baseline. Styrene (99%, Aldrich) was stirred over freshly crushed sodium hydride for 24 h and then vacuum-distilled onto dibutylmagnesium, from which it was distilled into ampules and diluted with solvent (THF or hexane) to about 1 M solutions and stored at −15 °C. The synthesis and dimerization of 3-methyl-2-phenyl-1-butene (MPB) were carried out as reported elsewhere.[20−22] MPB was purified by vacuum distillation from CaH_2 followed by vacuum distillation from 1-lithio-3,3-dimethyl-1,1-diphenylbutane formed by reaction of *n*-BuLi and MPB in THF.[22] Naphthalene (99+%, Fisher) was recrystallized three times from methanol (mp 78−80 °C). 1,4-Bis(bromomethyl)benzene (DBX 98%, Aldrich) was recrystallized three times from chloroform (mp 146−147 °C), dried under high vacuum for 5 h, and then dissolved in highly purified THF (10^{-2}−10^{-3} M) and stored in ampules.

Dibromomethane (99+%) or dibromomethane-d_2 (99%, Aldrich) was distilled under high vacuum twice from freshly

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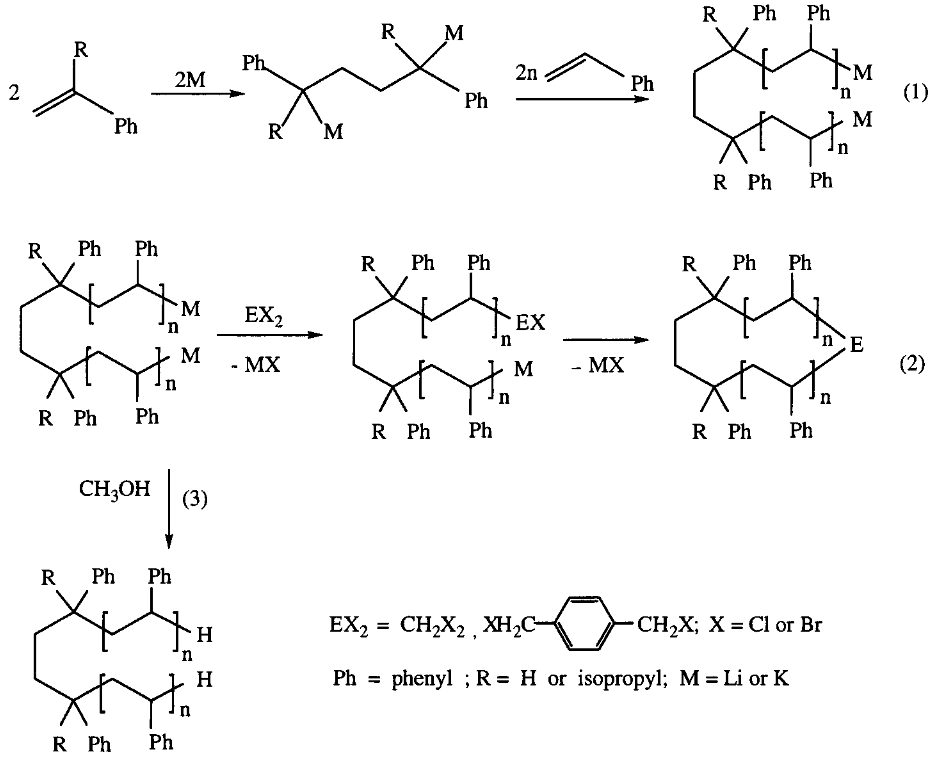
Scheme 1. Synthesis of Matching Cyclic and Linear Polystyrene



EX_2 = CH_2X_2 , XH_2C–⟨ring⟩–CH_2X; X = Cl or Br

Ph = phenyl ; R = H or isopropyl; M = Li or K

crushed calcium hydride and stored neat or as 1:1 v/v THF solutions. *tert*-Buytllithium (1.7 M, Aldrich) was diluted with purified hexanes to between 0.1 and 0.5 M, divided into ampules, and stored at −15 °C. Lithium or potassium naphthalide was prepared by reaction of naphthalene with lithium or potassium metal in THF at ambient temperature for about 15 min and used immediately after preparation. For the hydrogenation of PS samples, approximately 1−2 mg of palladium, 5% on activated carbon (Aldrich), and 70 mg of a PS sample dissolved in toluene were reacted at 25 °C for 1 h under hydrogen. The product was then filtered to remove catalyst and precipitated in cold methanol.

Polymerization/Cyclizations. Method 1. About 100 mL total of THF was distilled through the vacuum line into flask "A" (Figure 1). A triphenylmethyllithium or similar carbanion solution (10^{-5} mol) was then added via ampule "V" into flask "A" to remove residual protic impurities in the THF and after rinsing the entire apparatus the anion solution was collected into flask "D". All flasks were rinsed until colorless by distillation of THF from D into all accessible parts of the apparatus utilizing a cold dauber. After collection into D the THF was then distilled into flask "C" for later use and stopcocks 4 and 5 were closed.

Lithium naphthalide (5.6×10^{-4} mol) dissolved in 25 mL of THF was then added to "A" via ampule "W" and cooled to −78 °C, and 1.0 g of styrene dissolved in 10 mL of THF (ampule "X"), kept at −78 °C, was slowly added to flask "A" through stopcock 2 with vigorous stirring. After 15 min about 60−70% of the orange PSLi precursor was transferred into flask "B", precooled to −78 °C, and stopcock 3 is now closed. The remainder was stored in "A" and was reacted with degassed methanol at −78 °C after the completion of the cyclization reaction. A few drops of the PS dianion solution (cooled to −78 °C) were added to 100−150 mL of THF in flask "C", yielding a faint yellow-orange color. After this the coupling agent (EX_2) (7×10^{-4} mol in 100 mL of THF) solution, also cooled to −78 °C, was added slowly from ampule "Y" to flask "C" under rapid stirring over a period of about 30 min. The rates of addition of EX_2 and the PS dianion were adjusted so that a faint yellow-orange color from the PS dianion (corresponding to an anion concentration of 10^{-4}−10^{-6} M) was maintained, and this was continued until all of the PS dianion solution had reacted.

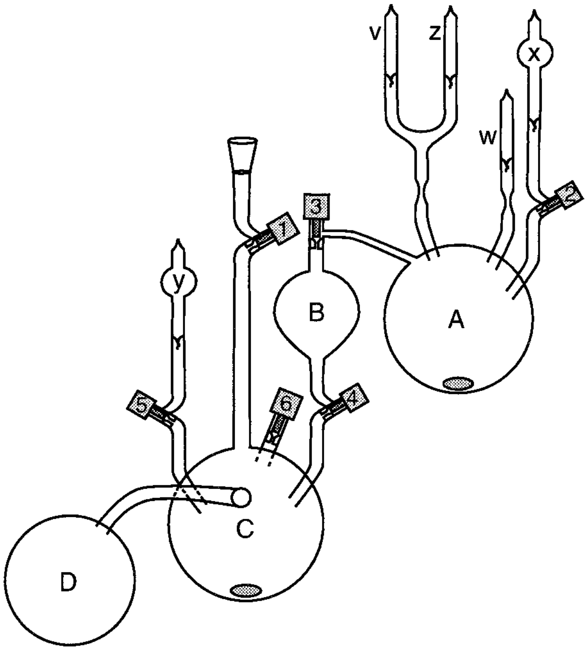


Figure 1. Apparatus for the synthesis of cyclic polystyrene (method 1).

Cyclization Method 2. In this case MPB (300 mg) was reacted with 1−4 g of lithium or potassium in THF at −100 °C or potassium in 25 mL of THF at −78 °C for times varying from 2 to 4 h to form the 2,7-dimethyl-3,6-diphenyloctane dianion (DDO^{2-}) initiator (see Scheme 1). The apparatus is nearly identical to method 1, except that ampule "W" was replaced with two ampules, one of which contained carefully cleaned Li (or K) chunks. After the metal was introduced into "A", the apparatus was allowed to evacuate. After distillation and washing as outlined above, the entire apparatus (including the metal) was washed with a carbanion solution as in method 1. The break-seal to the second ampule containing MPB (0.7 mmol) in 2 mL of hexane was then broken, and the contents were added to flask "A". After distillation of about 20 mL of

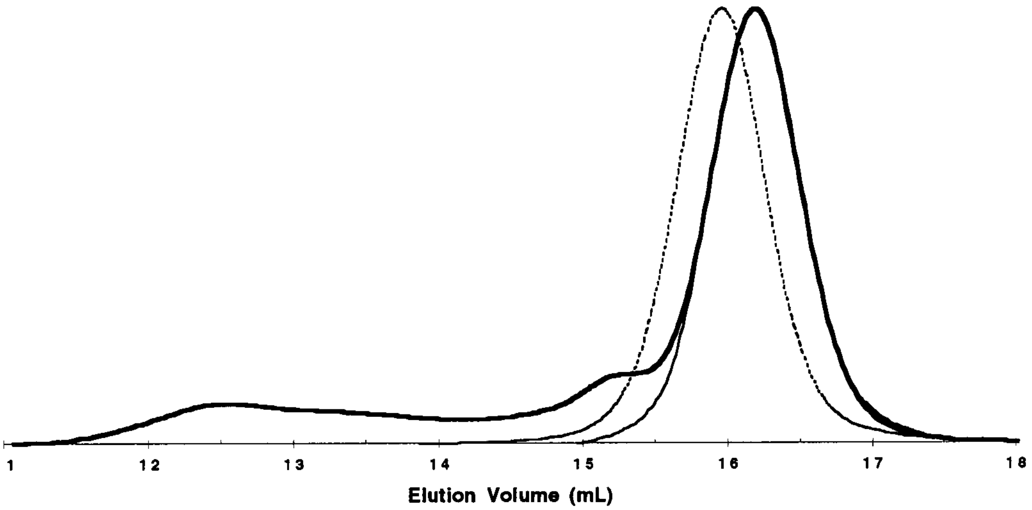


Figure 2. SEC chromatogram of unfractionated cyclic PS (Table 1, sample no. 10, solid line), fractionated cyclic PS (Table 1, no. 10 xf-thin solid line), and matching linear PS (Table 1, no. 10m, dotted line).

THF from "C" into "A", the MPB solution was now allowed to react for 2−4 h at −100 °C (for Li metal) or −78 °C (for K metal) with vigorous stirring. The styrene (9.0 mmol in 7 mL of THF) was then added dropwise to the deep red DDO^{2-} solution, instantly giving the orange $PSLi_2$ or red PSK_2 dianions. Cyclizations and protonations were carried out at −78 °C as described above.

Syntheses of polystyryllithium were carried out by dropwise addition of 400 mg of styrene dissolved in about 4 mL of THF to between 1.5×10^{-3} and 1.5×10^{-5} mol of *t*-BuLi dissolved in 10−15 mL of THF at −78 °C. A portion of the resulting PSLi was protonated, and the remainder was coupled with DBM or DBX by slow addition of their THF solutions to the PSLi kept at −78 °C (Scheme 1). The stoichiometry was controlled by monitoring the fading of the reddish PSLi solutions. Alternatively, the PSLi was added to solutions of an excess of DBM or DBX.

The PS cycles were purified by quantitative precipitation in methanol, followed by dissolution in toluene and incremental addition of aliquots of methanol leading to partial precipitation. After each addition of methanol the SEC chromatograms of the *supernatant* solution were analyzed by SEC, and this continued until the desired cyclic PS was obtained with a SEC peak maximum that is identical to that of the cyclic polymer in the unfractionated polymer. The PS cycles that were fractionated in this way typically have molecular weight (MW) distributions that are nearly identical to that of the linear precursor, consistent with the virtual absence of significant fractions of isobaric linear PS or dimer cycles (Figure 2). Polymers were isolated by precipitation into excess methanol and dried in a vacuum oven at 50 °C for 24 h.

In the case of low MW oligomers (DP <10), the oligomer solutions were first evaporated and after dissolution in methylene chloride and washing with water were then evaporated under high vacuum.

Characterization. SEC measurements were done in THF at 25 °C at a flow rate of 1 mL/min, using a LC system consisting of a Waters 510 HPLC pump, Waters 410 refractive index detector, and a U6K injector. Size exclusion chromatography (SEC) was carried out at room temperature with THF as the carrier solvent at a flow rate of 1 mL/min using a Waters model 510 pump, a model 410 differential refractometer, and two "Ultrastyragel" 500 and 10^4 Å 10 μm particle size columns connected in series and calibrated with polystyrene (PS) standards (Polysciences) in the range of 600−100 000 Da. The linear and macrocyclic polymers were analyzed by SEC prior to precipitation and in the case of the cycles after fractionation as well. After precipitation of the polymers, NMR analysis was carried out in $CDCl_3$ using a Bruker AC-250 FT-NMR spectrometer. Deuterium NMR measurements were carried out on CH_2Cl_2 solutions using a Bruker 500 FT NMR spectrometer and naphthalene-d_8 as internal standard. Emission at concentrations of 0.100 g/L were recorded in cyclohexane on a PTI QuantaMaster model C-60SE spectrofluorimeter with a 1527 PMT detector using a 3.0 nm slit width. Excitation of polymers is carried out at 240 nm to avoid solvent Raman scattering peaks interfering with the measured monomer band profile.

Mass spectra were recorded on a Kratos MALDI IV instrument operated in linear mode using a nitrogen laser (337 nm) and an accelerating voltage of 20 kV. Samples were prepared by mixing 10 μL of a polystyrene solution (2 mg mL^{-1} in THF) with 50 μL of the matrix solution (dithranol, 10 mg mL^{-1} in THF) and 10 μL of a silver trifluoroacetate solution (2 mg mL^{-1} in THF). A 1 μL aliquot of the resulting mixture was deposited onto the sample slide and allowed to dry. The spectra were calibrated against an external poly(ethylene oxide) standard, with M_p at 960 Da, and all data averaged over 200 laser shots.

Results and Discussion

Ring Formation. Matching linear and cyclic PS initiated by the Li or K naphthalides or the corresponding salts of 2,7-dimethyl-3,6-diphenyloctane dianion (DDO^2) were synthesized by the simultaneous addition of 10^{-2}−10^{-3} M solutions of the lithium or potassium PS dianion and more dilute (10^{-3}−10^{-4} M) solutions of DBM or DBX (EX_2, see Experimental Section) at −78 °C (Scheme 1).[1,3−6,17,23] The stoichiometry of the coupling reaction was maintained by making sure that a small excess of the reddish PS dianion was always present. As the coupling reactions occur where the EX_2 droplets hit the surface of the reaction solution this solution must be dilute and was added slowly. A local excess of EX_2 would give rise to the formation of the bis-alkylated polymer (XE−PS−EX), which reacts further to give higher MW cycles and /or linear polymers by a combination of intra- and intermolecular reactions.[24] To explore the coupling yields, a series of reactions were performed by addition of EX_2 to relatively *concentrated* PS dianion solutions (about 10^{-2} M). This should lead to a "step polymerization" of the PS precursor dianion and EX_2 by intermolecular rather than intramolecular coupling. Following the simplified Carothers expression[25] (1a) for the number-average degree of polymerization (DP_n) of a step polymerization

$$DP_n = 2/(2 - pf_{av}) = 2/(2 - f_{av}) \tag{1a}$$

$$f_{av} = \sum n_i f_i / \sum n_i = (n_1 f_1 + n_2 f_2)/(n_1 + n_2) \tag{1b}$$

where p and f_{av} denote the extent of reaction and the number-average functionality of the PS dianion and the EX_2 as defined by eq 1b, where n_i and f_i are the moles and functionalities of the PS dianion and EX_2 reagents. The value of f_{av} should be slightly less than two because of reagent, solvent, or monomer impurities and side reactions that may partially terminate the PS dianion, especially in the highly dilute solutions used here.[25] For instance, at lower anion concentrations the participation of free anions is plausible, and this is known to lead to faster anion termination reactions.[26]

Although the relative importance of all of these factors is not precisely known, their overall effect on the *apparent* f_{av} value may be determined by comparing the number-average degree of polymerization (DP_n) of the high MW fraction formed in this step polymerization with that of the protonated precursor. For instance, the peak MW of the broad band ("polycondensate") between 11.5 and 15.0 mL of the crude cyclic polymer (Figure 2) is about 67 000, indicating a high degree of intermolecular coupling and thus a high average functionality of the reagents. This band appears to represent a mixture of linear and cyclic polymers. For instance, the shoulder at 15.2 mL corresponding to an apparent MW of about 6000 appears to be a mostly cyclic dimer as the linear polymer dimer would have a peak molecular weight at 7600 (twice that of the linear precursor with a mass of 3800). As the high MW polymers require multiple coupling reactions and as each inadvertent anion termination during coupling will make the formation of cycles impossible, the fraction of the linear polymers in the coupled polymer product will increase with increasing degrees of coupling.[24]

The overall degree of anion termination calculated from the SEC yield of the target cycles (about 75%) following earlier simulations of end to end coupling is about 10%.[24] A similar value is calculated from the number-average MW of the polycondensate fraction (between 11.5 and 15 mL in Figure 2) that is assumed to be linear using eq 1a. Thus, the fraction of the precursor linear PS deactivated at *both* ends should be very small (about 1%). This is important, as the separation of the cycle from the matching linear polymer is difficult.

Attempts to couple the PSLi dianion at ambient temperatures gave much wider MW distributions, presumably due to spontaneous protonation of the DDO and or PS dianions during preparation or coupling especially at anion concentrations below 10^{-3} M.[26−28]

The availability of matching samples of linear and macrocyclic polystyrene facilitates analysis in several ways. First, the MW distribution of the linear precursor allows detection of problems in the synthesis of the PS dianion, for instance the occasional inadvertent presence of high or low MW shoulders due to solvent or monomer impurities or other experimental difficulties. Second, the MW distributions of the fractionated cycles may be compared to those of the linear precursor so that the presence of linear and other impurities may be detected more readily. The use of M_p rather than number-average-molecular weights (M_n) has the advantage that it is obtained directly from the SEC chromatograms of the *unfractionated* cycles (see below).

The predominant formation of cycles is confirmed by the consistently lower apparent molecular weights of the PS cycles compared to that of the matching linear polymers and by the virtually identical widths of the MW distributions of the linear and cyclic polymers (Table 1). Furthermore, the ratios of the hydrodynamic volumes $\langle G \rangle$, defined as the apparent peak MW's (M_p) of the polymer cycles divided by that of the matching linear polymers, systematically varied between 0.71 at the highest MW (Table 1, no. 28) to 0.97 for the case of the lowest MW (Table 1, no. 12).The increase of $\langle G \rangle$ with decreasing MW has been documented.[14−18,27]

Table 1. Synthesis and Characterization of Linear and Macrocyclic Polystyrene[a]

sample	initiator	terminator or coupler	MW_{calc}	M_p[b]	M_n[b]	M_w/M_n	$\langle G \rangle$[c]
1a	LiNaph	MeOH	4000		4200	1.53	
1b[d]	LiNaph	DBM			1400	<1.40	
1c[d]	LiNaph	DBM			3800	<1.40	
1d[d]	LiNaph	DBM			6700	1.47	
3a	DDO^{2-}	MeOH	1040	1020	1030	1.35	
3b	DDO^{2-}	DBM		930	1200	1.80	0.91
10m	DDO^{2-}	MeOH	3210	3800	3700	1.07	
10xf[d]	DDO^{2-}	DBX		2800	2800	1.06	0.78
12m	DDO^{2-}	MeOH	700	680	720	1.13	
12x	DDO^{2-}	DBX		660	1140	3.60[e]	0.97
28m	DDO^{2-}	MeOH	(f)	32200	29700	1.07	
28xf[d]	DDO^{2-}	DBX		23400	22200	1.15	0.71
32m	DDO^{2-}	MeOH	3440	3000	2900	1.20	
32xf[d]	DDO^{2-}	DBX		2300	2300	1.16	0.80
33m	DDO^{2-}	MeOH	7580	6800	6900	1.18	
33xf[d]	DDO^{2-}	DBX		4900	5000	1.15	0.74

[a] Polymers from the same PS dianion precursor have same sample number. [b] SEC peak MW (M_p) or number-average MW (M_n) using PS standards. [c] Ratio of apparent M_p's of unfractionated cyclic and linear PS. [d] Fractionated cycles. [e] Unfractionated sample. [f] Initiator formation was incomplete due to deactivated lithium metal surface.

Mechanisms of Ring Formation. MALDI−TOF spectra of the DBM-mediated PS cycles initiated with lithium naphthalide and coupled with DBM (Table 1, no. 1c) showed two sets of peaks in the approximate ratio of 2:1 (Figure 3). Each set has the expected peak-to-peak separations of 104 Da. Only the *minor* series agreed well with that of the calculated molecular weights of the expected cycle (**3**) by two consecutive substitutions (eqs 4 and 5, Scheme 2).

As shown in Table 2, the masses of the major series are about 3 Da less than that of the protonated linear PS precursor dianions that could have been formed by reactions with solvent or DBM (Scheme 2, eq 10). As indicated above, the formation of linear chains by inadvertent protonation of *both* chain end anions is unlikely (Scheme 2, eqs 6, 9, and 10). Furthermore, the assignment of the predominant cycles to the fully protonated PS does not agree with the SEC data that show the nearly exclusive formation of cycles. However, the observed masses for the major series are much closer to the calculated values of macrocycles, **6**, formed by a direct lithium−halogen exchange or through radical intermediates[29−38] followed by intramolecular coupling to give cycles with a 1,2-diphenyl linkage (Scheme 2, eqs 7 and 8). The competing intramolecular elimination (eq 9) should result in the formation of linear β-substituted styrenic chain end structure, **7**, having the same mass as **6**. The formation of the cycles, **3**, through reaction 5 should be accompanied by elimination (eq 6), giving a linear polymer, **4**, with an α-styrenic end group.

MALDI data do not distinguish between **3** and **4** (or **6** and **7**), which have the same mass. From the predominant formation of cycles **6** rather than **3** we conclude that reaction 7 occurs faster than reaction 4

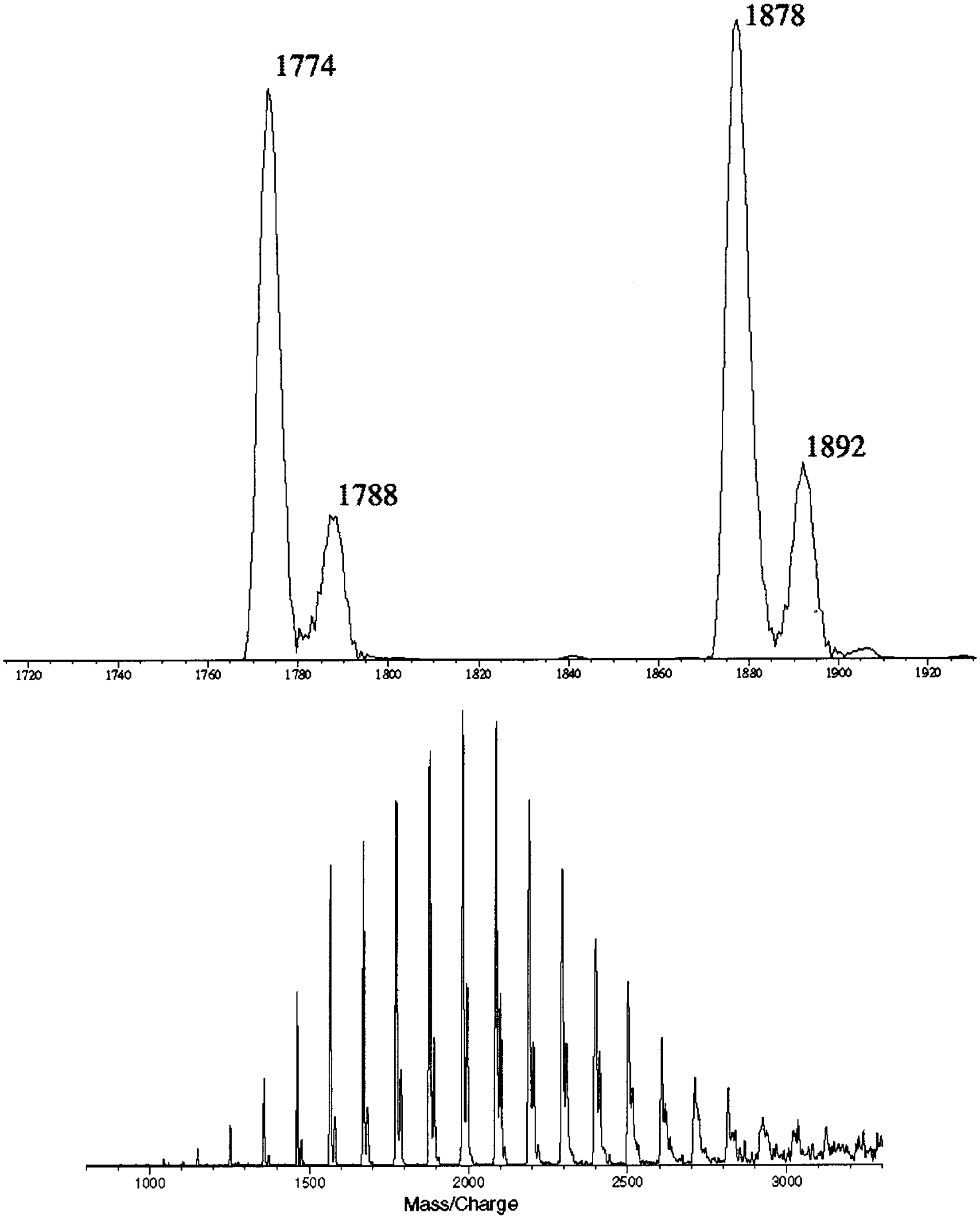


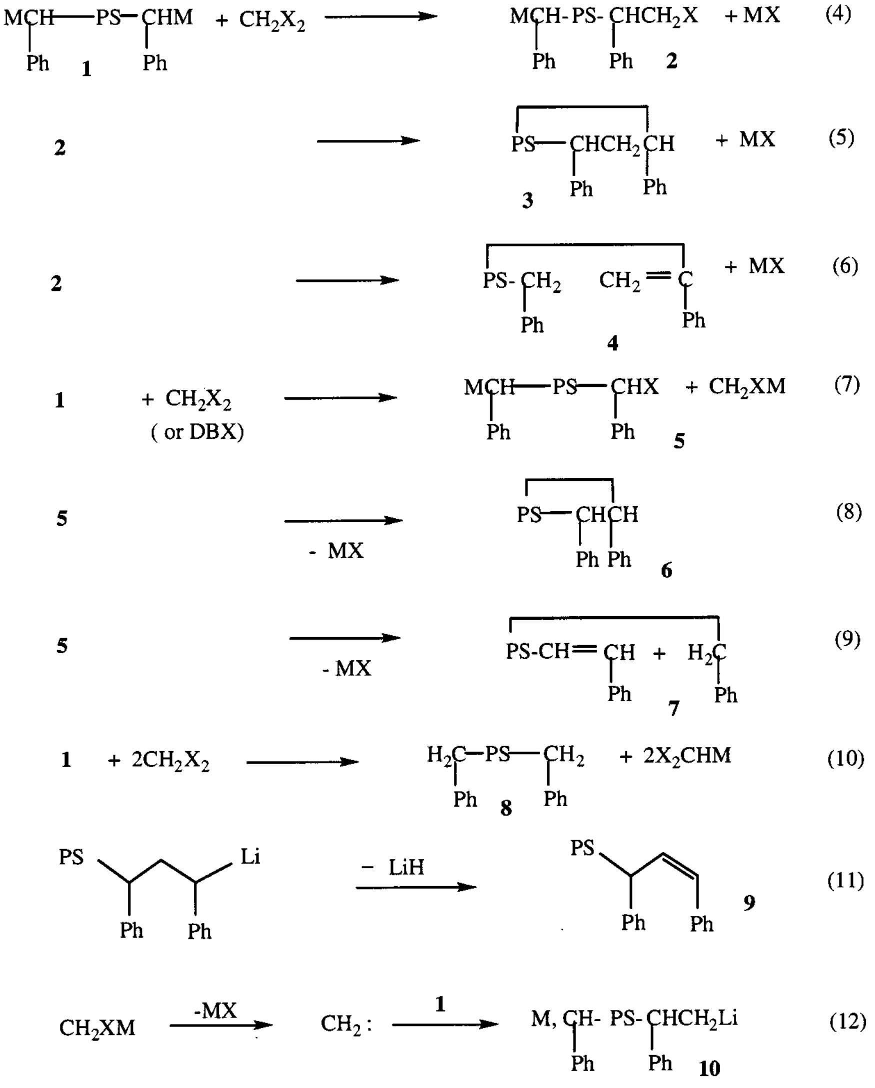
Figure 3. MALDI−TOF spectrum of DBM-coupled PS (Table 1, no. 1b): (a, top) magnified view showing major and minor series; (b, bottom) full spectrum. Sample masses include Ag^+ from the matrix added.

(see below). To gain more insight into the above coupling reactions, we studied the reactions of one-ended PSLi (*t*-BuLi-initiated polymerization of styrene in THF at −78 °C) with DBM. In this case, it is easier to distinguish the coupled PS from its precursor as the doubling of MW is more readily detected and quantified by SEC. The reaction rate is fast enough to ensure reaction stoichiometry by following the fading of the yellow-orange color of the PSLi upon addition of coupling agents.

Table 3 shows the results of coupling reactions between PSLi and DBM at PSLi concentrations between 1×10^{-2} and 3×10^{-2} M. The degree of PS dimer formation observed by SEC increased from 15 to more than 90% with a decreasing rate of DBM addition (Table 3, no. 1−4, 11). When the PSLi solution was added dropwise into an excess of DBM/THF solution, no coupling was observed. As illustrated in Table 3, the MW of the polystyryllithium does not appear to affect the extent of coupling.

Proton NMR analysis of low MW bromomethylated PS synthesized by slow addition of PSLi to an excess of DBM (Table 3, no. 15 and 16) shows the presence of both bromobenzyl (4.7 ppm) and bromomethyl end groups between 3.4 and 3.6 ppm (data not shown). The presence of the bromobenzyl group is consistent with the MALDI results, indicating the formation of coupled polymers containing 1,2-diphenyl linkages (Scheme 2, eqs 7 and 8). No vinyl resonances were observed due the occurrence of elimination reactions (eqs 6 or 9) (see

Scheme 2. Reactions of Polystyryldilithium with Dihalomethanes in THF at −78 °C



PS = polystyrene; Ph = Phenyl; X = Cl, Br ; M = Li, K.

below). A partially coupled product formed by addition of DBM to PSLi (Table 3, no. 4) was fractionated into coupled and uncoupled PS fractions. Proton NMR analysis of the uncoupled product clearly shows the presence of CH_2Br end groups.[39] The corresponding coupled product isolated by fractional precipitation shows no such resonances and looks identical to PS prepared by anionic polymerization and terminated by protonation.

To gain further insight into the nature of the coupling reactions, we examined the reaction products of a low MW PSLi and CD_2Br_2 by slow distillation of a CD_2Br_2/THF (1:7 v/v) solution into PSLi oligomer solution (Table 3, no. 10). Although SEC revealed a high degree of coupling (95%), deuterium NMR showed only an approximately 50% overall incorporation of the CD_2 moiety into the coupled polymer, in agreement with the MALDI and ^1H NMR data and consistent with the formation of the 1,2-diphenyl coupling linkages (data not shown). A broad CD_2 resonance was observed at 1−2 ppm (45%) and a group of smaller resonances (5%) between 3.4 and 3.6 ppm of the CD_2Br end group.[39] For the case where the CD_2Br_2 was in excess over the course of the reaction (Table 3, no. 15) a small benzylic deuterium resonance (about 5%) was visible at about 2.6 ppm consistent with some deuteration by DBM (eq 10).

Carbon-13 NMR of this sample (Table 3, no. 10) shows the expected methylene and methine carbon resonances at 40−48 and 38−40 ppm. The 39.8 ppm resonance is attributable to the methine carbon adjacent to the *tert*-butyl initiator group (Figure 4).[40−42] The CH_2Br group should display a resonance at 45−47 ppm.[39] The resonances between 48 and 52 ppm are assigned to the benzylic carbons of the 1,2-diphenyl linkage, in agreement with the above MALDI and deuterium NMR.

Fluorescence Measurements. As reported previously, the cyclic polystyrenes coupled with DBM have emissions that are dramatically enhanced and blue-shifted compared to those of linear materials; these effects increase with decreasing MW.[18] As shown in Figure 5a, the emission spectra of more recently prepared and fractionated cycles prepared with DBM as the coupling agent (M_n's of 1400, 3800, and 6700) show distinct bands at about 295, 305, 320, and 335 nm. This seems to be inconsistent with polystyrene excimers as the sole emitters.[43−45] The emission bands at 320 and 335 nm are consistent with the presence of naphthalene (Figure 5b). Comparison of the absorption and fluores-

Table 2. Calculated and Observed Molecular Weights of Sample 2b from Table 1 by MALDI−TOF

DP_n	calcd linear PS[a]	calcd cyclic PS[b]	sample 2b minor series	calcd cyclic PS (exchange product)[c]	sample 2b major series
10	1151.4	1163.4		1149.4	
11	1255.6	1267.6		1253.6	1252.8
12	1359.7	1371.7		1357.7	1357.3
13	1463.9	1475.9	1475.4	1461.9	1461.2
14	1568.0	1580.0	1579.7	1566.0	1565.6
15	1672.2	1684.2	1683.9	1670.2	1669.5
16	1776.3	1788.3	1788.2	1774.3	1773.8
17	1880.5	1892.5	1892.3	1878.5	1877.7
18	1984.6	1996.7	1996.0	1982.6	1981.7
19	2088.8	2100.8	2100.2	2086.8	2085.7
20	2192.9	2205.0	2204.7	2190.9	2189.9
21	2297.1	2309.1	2307.8	2295.1	2293.6
22	2401.3	2413.3	2412.1	2399.2	2398.0
23	2505.4	2517.4	2516.4	2503.4	2501.9
24	2609.6	2621.6	2619.8	2607.5	2605.8
25	2713.7	2725.7		2711.7	2709.8
26	2817.9	2829.9		2815.8	2814.2
27	2922.0	2934.0		2920.0	

[a] Calculated mass of linear PS precursor terminated by two protons plus silver matrix: $MW = (DP_n)(104.15) + (2)(1.008) + 107.87$. [b] Calculated mass of cyclic PS with methylene coupling moiety plus silver matrix: $MW = (DP_n)(104.15) + 14.027 + 107.87$. [c] Calculated mass of cyclic PS without coupling moiety plus silver matrix: $MW = (DP_n)(104.15) + 107.87$.

Table 3. DBM-Mediated Coupling of PSLi in THF at −78 °C[a]

run	M_n (precursor)	M_w/M_n (precursor)	M_n (dimer)	% dimer	DBM addn time[e]
1	12500	1.07	14500	15	<1
2	5860	1.04	7400	33	3
3	4780		6900	45	5
4	27350	1.03	43000	70	10
10	250	1.32	500	>95	25
11[b]	900	1.19	1750	>90	20
12[b]	650	1.17	1300	∼85	15
13	450	1.30	900	>95	25
14	350	1.35	625	>95	25
15[c]	440	1.34	440	<5	
16[c]	950	1.10	1000	<5	
17[d]	1500	1.09			

[a] *t*-BuLi ($(0.50-2.0) \times 10^{-4}$ mol) initiated polymerizations of styrene in 5−10 mL of THF at −78 °C (see Experimental Section). A portion (about 30%) of the resulting PSLi was protonated. The remainder was reacted with DBM ($(0.50-2.0) \times 10^{-4}$ mol) by addition of a (20% v/v) THF solutions over varying periods. Stoichiometry controlled by the fading of the red PSLi solutions. [b] *n*-BuLi initiator. [c] PSLi added dropwise to DBM. [d] Was not coupled. [e] Minutes of addition of DBM.

cence excitation spectra as well as emission experiments under deoxygenated conditions confirms the assignment of residual naphthalene that is generated as a result of electron transfer to styrene. Being a much better fluorophore than the pendent phenyls, its contribution to the emission spectrum is amplified especially for the low MW cycles. We found it difficult to completely remove this naphthalene by repeated precipitation into methanol or by sublimation of the PS cycles by heating under high vacuum.

Thus, an alternative initiator, dianion (DDO^{2-} Scheme 1), formed by the reaction of 3-methyl-2-phenyl-1-butene (MPB) with Li or K metals at −78 to −100 °C, was used to form the PS dianion and the corresponding PS cycles using DBM as the coupler (Table 1, no. 3a and 3b). The polystyrene cycles generated from this initiator still showed significant emission enhancements when compared to the excimer band of their linear analogues, including the presence of bands at 295, 305, and 320 nm (Figure 6a) that are not present in the protonated linear precursors. These emission increases were greater at the lower MW's and appear to correspond closely to that of styrene, α-methylstyrene (AMS), *β*-methylstyrene (BMS), or similar olefins that have emissions at around 290, 305, and 315 nm (Figure 6b).[46]

The linear PS dimers (Table 3, no. 14) generated by DBM-mediated coupling of very low MW one-ended PS oligomer anions gave similar emission spectra. In this case also, the fluorescence increased compared with the linear precursors with the low PS oligomers being the largest. These emissions are not due to the 1,2-diphenyl linkages given the fact that the corresponding model compounds show no such behavior.[47−49] Although the fractions of styrene type structures in the above linear and cyclic polymers were too small for detection by NMR (<5%), their effects on the emission spectra could be considerable given their much higher absorptivities and quantum efficiencies compared to those of alkylbenzene derivatives.[46]

As pointed out earlier, the emissions of the linear and cyclic DBM-mediated coupling products resemble those of AMS or BMS, particularly the latter (Figure 6a,b). Although the AMS and BMS emissions are slightly shifted compared to that of the PS coupling products, the overall shape is similar and the bands are spaced equally. The resemblance of the emission of BMS which has a 35% greater absorption and a 5 times greater emission than AMS, with the low MW sample (Table 1, no. 3b) is particularly striking. Such a structure is consistent with the PS anion mediated elimination of the predominant (see above) chain end benzyl bromide, **5**.

The fraction of BMS or AMS structures at the chain end was estimated by simulation of the spectrum of sample no. 3b (Table 1) by superposition of the spectra of a linear PS standard and small amounts of BMS or AMS. The corresponding fractions (compared to styrene units) of BMS- or AMS-like chain end structures are about 0.1 and 0.6 mol %, respectively. Although small changes are seen in the UV absorption spectrum of the DBM coupled or cyclized PS samples, these are much less clear and do not allow unambiguous identification of the chain end structures. In further support of the presence of chain end styrenic structures, the hydrogenation product of the coupled polymer dimer (Table 3, no. 14) gave a reduced 325 nm emission and a red shift to the emission of the PS excimer (330 nm) (see below).

The presence of inadvertent amounts of styrenic impurities in the PS cycles and coupled dimers could also give rise to the anomalous emissions. However, TLC analysis of the coupled PS dimer showed a single component whereas a mixture of linear PS and 1 mol % AMS showed two spots. This indicates that the postulated styrenic structures are part of the coupled polymer and are not monomeric. This is not surprising given the rapid anionic polymerization of styrene under our conditions.[26] Initiator effects were explored by comparing the fluorescence of the coupled dimer polymers obtained by initiation with *n*-butyllithium and *tert*-butyllithium and subsequent coupling of PSLi with DBM (Table 3, no. 11 and 17). However, no differences in emission were observed.

Olefinic chain end structures may have formed by hydride loss from the PS anion (Scheme 2, eq 11).[25] However, the linear polymers show no evidence for the presence of this structure (Figure 6c) which is hardly

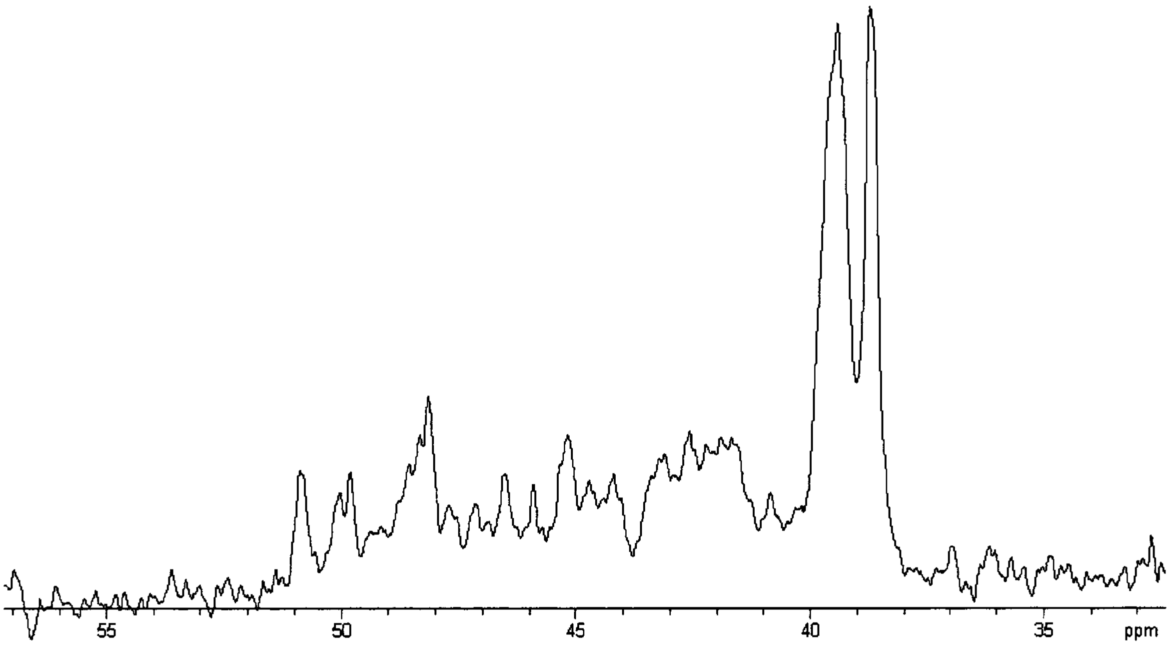


Figure 4. Carbon-13 NMR of the 1,2-diphenyl linkages in coupled PS dimer (Table 3, no. 10).

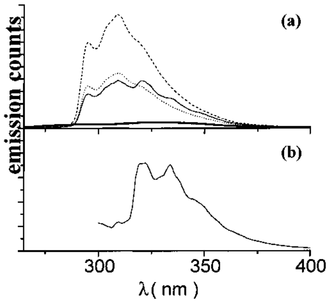


Figure 5. (a) Emission spectra ($\lambda_{ex} = 240$ nm), from bottom to top, of linear PS (thick line, Table 1 no. 1a), and of DBM coupled and fractionated cyclic polystyrenes, no. 1b (solid line), no. 1d (dotted), and no. 1c (dashed). All solutions are 100 mg/L in cyclohexane. (b) Emission spectrum of naphthalene ($\lambda_{ex} = 270$ nm).

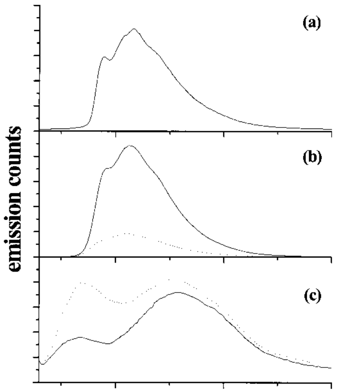


Figure 6. Emission spectra in cyclohexane ($\lambda_{ex} = 240$ nm): (a) DDO-initiated PS cycle with DBM coupler at 100 mg/ L (Table 1, no. 3b); (b) emission from AMS at 1.0 mg/L (dashed trace) and BMS (1.0 mg/L) (solid trace); (c) DDO-initiated linear PS (Table 1, no. 32m-thick line) and DBX-coupled PS cycles after hydrogenation (no. 32xf-dashed) at 100 mg/L.

surprising given the polymerization conditions. Although other structures formed in the course of carbenoid type reactions through the loss of bromide from bromomethyl anions and reaction with PS anion (Scheme 2, eq 12)[50,51] are possible, no experimental evidence for these reactions could be found.

The PS cycles or dimers (Table 3) coupled with DBX are largely free from styrenic chain end structures. Thus, no large anomalous fluorescence increases seen for the DBM cycles were observed upon benzylation of PSLi with benzyl bromide or DBX. The fluorescence bands of the benzylated and protonated PS are virtually identical in both shape and intensity, verifying the absence of styrenic structures or other chromophores. Furthermore, in this case no dimerization was observed resulting from lithium bromide exchange, and proton NMR shows complete benzylation (by integration against the *tert*-butyl end group).

The virtual absence of anomalous emissions is confirmed by the identical absorption spectra of the linear and cyclic polymers (see Figure 7) and by the absence of peaks above 270 nm in the fluorescence excitation spectra. For one case of a very low MW DBX cycle (Table 1, 32xf, $DP_n = 29$) a slightly blue-shifted and enhanced emission at around 320 nm is observed (Table 1, no. 32xf). This emission appeared to be due in part to linear BMS type structures (**7**) (Scheme 2, eqs 7 and 9). Significantly, the Pd/carbon-catalyzed hydrogenation of this cycle gave a product that does not have an emission at 320 nm (Figure 6c), consistent with the removal of the very small fraction of styrenic end groups. Corresponding decreases were observed in the fluorescence excitation and absorption spectra particularly between 270 and 290 nm that were almost identical with that of the matching linear polymer (Table 1, no. 32m). This is consistent with the presence of an extremely low (<0.02 mol % for) overall content of β-styrenic end groups.

Given the presence in the cycles of extremely small quantities of linear polymer with styrenic end groups, it is not surprising that detection by NMR, SEC, and MALDI was not possible. Thus, emission and its accompanying excitation spectra provide exquisitely sensitive means of observing the presence of tiny fractions of olefinic impurities.

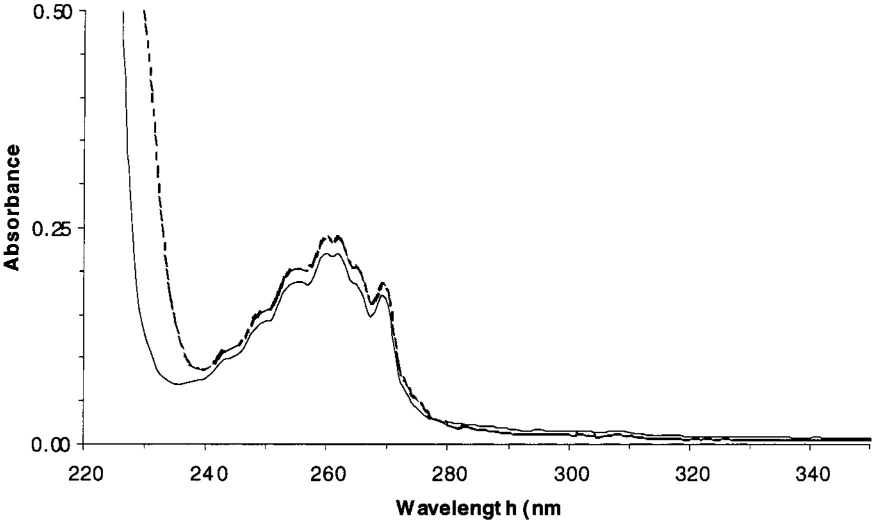


Figure 7. Absorption spectra of linear (solid line) and DBX cyclized PS (dashed line) at 100 mg/L in cyclohexane (samples 32m and 32xf, respectively).

Monomer Fluorescence Enhancements. As shown in Figure 6c, the cycles formed with DBX gave the expected emissions at about 285 and 330 nm corresponding to the PS monomer and excimer emission, respectively. However, the emission of these PS cycles consistently increase in the *monomer* band with decreasing MW, while excimer emission is essentially unchanged. Interestingly, the intensity of monomer emission from these cycles, recorded at equal phenyl group concentrations and thus almost equivalent absorbances (see Figure 7), increase with decreasing MW while the shape of the monomer band is unchanged for all linear and macrocyclic PS. As the excimer band intensity changes little with molecular weight, the monomer to excimer intensity ratio shows a corresponding increase. In contrast, the intensity of the matching linear polymers show little MW dependence. For example, the cycles for samples 10 and 32 have monomer emission enhancements of factors of 1.7 and 2.1, respectively, once normalized for the slight change in absorbance. After correction for the increasing fractions of the xylenic (DBX) coupling linkage (*p*-xylene has ~2−3 times higher quantum yield compared to isopropylbenzene),[46] this enhancement is still significant (increase of at least 50%) for the lowest MW cycle (no. 32xf) and must be due to other causes.

This assessment is backed up by observation of similar enhancements for other vinyl aromatic macrocycles with 2-naphthyl and 2-fluorenyl pendent groups.[52] For instance, for the case of macrocyclic poly(2-vinylnaphthalene), the monomer emission intensity of a P2VN cycle of a degree of polymerization of about 12 is enhanced about 2-fold compared to that of the matching linear polymer. Similar emission enhancements in quantum yield are observed for macrocyclic poly(9,9-dimethyl-2-vinylfluorene).[52]

Although the reason(s) for these emission enhancements are not fully elucidated, we can speculate as to possible causes. The formation of excimer sites on a macrocycle is likely hindered at low MW due to increasing conformational strain on the backbone. Therefore, we would expect a greater fraction of emission from monomer sites. However, a greater *total* quantum yield for emission is observed. There is very little variation in the absorption spectrum and oscillator strength of the PS $S_0 \rightarrow S_1$ band in any of the polymers. Therefore, to explain both observations, a decrease in the phenyl group radiationless decay rate as well as a greater proportion of the emission coming from monomeric chromophore sites is required for the small cycles. Radiationless deactivation of the excited state of alkyl-substituted benzenes is a well-studied and complex problem occurring both by internal conversion and intersystem crossing.[53−55] It is known that a “loose bolt” substituent can dramatically decrease the fluorescence quantum yield by enhancing radiationless decay.[55] In the smaller cycles, the conformational strain along the polymer backbone may well diminish the ability of certain vibrational modes to promote the relevant radiationless process. As indicated earlier, the increased rigidity of the smaller cycles is demonstrated by the increase in the glass transition temperature of macrocyclic vinyl polymers compared to that of linear vinyl polymers.[28] Extensive photophysical studies of the fluorescent lifetimes for these macrocyclic vinyl polymers are in progress to interrogate this idea.

Conclusions

The dibromomethane-mediated coupling of polystyryldilithium in THF at −78 °C, besides the expected displacement of bromide ion, gives extensive lithium−bromine exchange, giving a benzyl bromide end group that couples with the PS anion giving rings with 1,2-diphenyl linkages. This is revealed by MALDI mass spectrometry and by carbon and deuterium NMR. The presence of benzyl bromide end groups in turn gives rise to the formation of small amounts of styrene end groups that greatly contribute to the PS emissions, which can be used as a diagnostic tool for these side reactions that are substantially diminished when dibromoxylene (DBX) is used as coupling agent.

The DBX coupled PS macrocycles, however, show characteristic polystyrene emission spectra but with significantly enhanced monomer emission compared with the matching linear polymers. The excimer emission intensity is virtually unchanged. The monomer band enhancements in macrocyclic polystyrene increase with decreasing MW. The overall increase in emission quantum yield for the macrocycles, which may be due to the slower radiationless decay rate for the more rigid vinyl aromatic cyclic polymers, is being investigated further.

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Supporting Information Available: Deuterium and carbon-13 NMR spectra of PS dimer. This material is available free of charge via the Internet at http://pubs.acs.org.

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