

# FORMATION OF CYCLIC POLYSTYRENE BY ANIONIC POLYMERIZATION: FLUORESCENCE STUDIES

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## Introduction

The synthesis and properties of macrocyclic vinylaromatic polymers has been the subject of increased interest in recent years.<sup>1-10</sup> The low molecular weight macrocyclic polymers (MW<5,000) appear to have severely constrained chain conformation as indicated by the much higher glass transition temperatures compared to the matching linear polymers and this may be expected to influence energy transfer and other photophysical processes involving pendent chromophoric groups.<sup>11</sup> Initially, the synthesis of macrocyclic polystyrene was carried out by lithium naphthalide initiated polymerizations of styrene in THF at -78°C to give the PS dianion followed by high dilution end-to-end coupling with bis-1,4-(bromomethyl)benzene (DBX) or dibromomethane (DBM).<sup>10</sup> The macrocycles coupled with DBM showed emission increases up to a factor of ten over their linear counterparts as well as a blue shift of around 20 nm.<sup>10</sup> This work reports on the cause of these observations.

## Experimental

All polymerizations and cyclizations were carried out in THF at -78°C under high vacuum conditions (10<sup>-5</sup>-10<sup>-6</sup> Torr) using breakseal techniques as reported elsewhere.<sup>12</sup> Polymerizations, and purifications of solvents, monomers etc. were carried out as reported.<sup>13,14</sup> 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. DBX (98%, Aldrich) was recrystallized three times in chloroform (m.p. 146-147°C), and was dried under high vacuum. Dibromomethane (99+%, Aldrich) was distilled under high vacuum twice from freshly crushed calcium hydride and stored neat or as 1:1 v/v THF solutions.

**Characterization.** Linear and macrocyclic polymers were analyzed by SEC prior to and during precipitation in methanol and in the case of the cycles after and during fractionation as well.<sup>13,14</sup> NMR analysis was carried out in CDCl<sub>3</sub> after precipitation using a Bruker AC-250 FT-NMR. 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 bandpass. Excitation is at 240 nm, except where indicated.

## Results and Discussion

The synthesis of matching linear and cyclic PS initiated by the Li or K salts of naphthalene or DDO<sup>2-</sup> was carried out under high dilution conditions by the simultaneous addition of (10<sup>-2</sup>-10<sup>-3</sup>M) solutions of the lithium or potassium PS dianion and solutions of the coupling agent EX<sub>2</sub> to a reactor at -78°C as reported elsewhere.<sup>1,6,8</sup>

Coupling reactions were also carried out at high concentrations of dianion and coupling agent (10<sup>-2</sup> M) and gave Mn values of the coupled polymers that were at least ten times that of the precursor indicating that the coupling yields were high.

For the case where lithium naphthalide was used as the initiator and DBM as coupler the emission spectra showed clear evidence of naphthalene contamination that was difficult to remove completely. An alternative polymerization/DBM coupling using the dimer of the Li or K radical anion of 3-methyl-2-phenyl-1-butene (MPB) at -78°C to -100°C gave PS cycles that still showed significant emission enhancements over the matching linear polymers including the presence of bands at 295, 305, and 320 nm that are not present in the protonated linear precursors. This emission pattern appears to resemble that of styrene, alpha- (AMS), beta-methylstyrene (BMS) and similar olefins that have emissions at around 290, 305 and 315 nm (Figure 1).<sup>15</sup> Although slightly shifted compared to the PS coupling products, the

overall shape is similar and the bands are spaced equally. The absorption of BMS that is a much stronger emitter (about 100-fold) than the polymer styrene units whereas the emission of AMS is about 25 times stronger (Figure 1). The resemblance of the emission of BMS with that shown in Figure 1a (Table 1, #3b) is particularly striking.

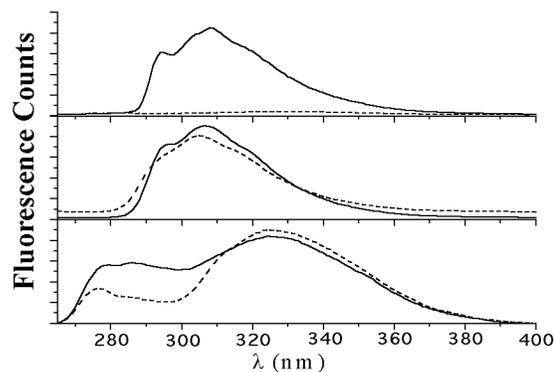
**Table 1. Synthesis and Characterization of Linear and Macrocyclic Polystyrene.<sup>a</sup>**

Sample	Initiator	Terminator or Coupler	Mp <sup>b</sup>	Mn <sup>c</sup>	Mw/Mn	<G> <sup>d</sup>
3a	DDO <sup>2-</sup>	MeOH	1020	1030	1.35	
3b	DDO <sup>2-</sup>	DBM	930	1200	1.80	0.91
4a	DDO <sup>2-</sup>	MeOH	3600	3440	1.09	
4b	DDO <sup>2-</sup>	DBX	2810	3420	3.49	0.78
4c <sup>e</sup>	DDO <sup>2-</sup>	DBX	2850	2720	1.07	

(a) Numbers refer to polymers with the same PS dianion precursor (b) Peak molecular weights by SEC using PS standards. (c) SEC number average MW's of unfractionated cyclization product, fractionated cycles, or linear precursor (d) Ratio of apparent Mp's of unfractionated cyclic and linear PS. (e) Fractionated cycles.

As shown in Figure 1c the use of DBX as coupling agent did not show any of the shifted and enhanced emissions observed with DBM but gave the expected emissions at about 290 and 330 nm corresponding to the PS monomer and excimer emissions respectively. The protonated PS samples likewise do not show any evidence for anomalous emissions.

Thus the coupling reactions with DBM appear to be related to side reactions involving halide intermediates. One of these may involve elimination from the bromomethyl chain end formed in the course of the bromomethylation (Figure 2 eqn. 3) thus giving an AMS type chain end.



**Figure 1.** Emission spectra in cyclohexane ( $\lambda_{\text{ex}}=240$  nm) except where noted. (a) DDO-initiated linear PS. (#3a-dashed) and DBM-coupled PS cycles (#3b-solid). (b) AMS at 1.0 mg/L (dashed) emission multiplied by factor of 4.5, and BMS (1.0 mg/L) (solid). (c) DDO-initiated linear PS. (#4a-dashed) and DBX-coupled PS cycles (#4c-solid). Excitation at 253 nm for better signal-to-noise ratio.

A second and well-documented reaction involves lithium bromine exchange (Figure 2, eqn 4).<sup>16</sup> The resulting benzyl bromide chain end could undergo an elimination with available PS anion to give a BMS type chain end. Because of the very high emission yields of the AMS and especially the BMS chain ends the emissions in the DBM mediated cycles are accounted for by the presence of very small amounts (<1% by weight) of olefinic chain ends.

The above is consistent with MALDI-TOF analysis showing a minor and a major series of peaks each separated by 104 Daltons and corresponding to cycles **3** and **6** respectively.<sup>14</sup> The masses of the major series closely match the calculated masses of the products that would result from the lithium-bromine exchange (Figure 2, eqns. 4-6). As the extent of bromide lithium exchange exceeds fifty percent the BMS type emissions are expected to predominate. However the fluorescence data do not allow determination of the relative amounts of AMS and BMS structures.

